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BIBLIOGRAPHY

OF

ACETO ACETIC ESTER

AND ITS DERIVATIVES

BY

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LETTER OF TRANSMITTAL.

NEW YORK, August 22, 1892.

The Committee of the American Association for the Advancement of Science having charge of Indexing Chemical Literature has voted to recommend to the Smithsonian Institution for publication the following Index :—

Bibliography of Aceto Acetic Ester and its Derivatives, by P. H. Seymour, M. S., Assistant in General Chemistry, University of Michigan.

This work was compiled under the direction of Prof. Albert B. Prescott, Ph. D., a member of this Committee.

H. CARRINGTON BOLTON,
Chairman.

TO THE SECRETARY OF THE
SMITHSONIAN INSTITUTION.

PREFACE.

It is the purpose of this brief contribution to point out the existing literature upon acetoacetic ester, rather than to make an addition to this literature. The outlines of memoirs are given, not to enable the reader to do without the originals, but to help him to find just the ones he may require. To this end it has been undertaken to furnish a description, without the detail of a condensation, of so much literary material as has been cited. The subject is one so far interwoven with research upon organic oxygen derivatives in general that its boundaries have been often drawn at a venture. In questions upon the subject-matter Mr. Seymour has had the benefit of consultation with Professor Paul C. Freer, of this University, who has carried on investigations of acetoacetic ester for some years. For the plan of the bibliography, whatever defects the plan may have, the undersigned acknowledges himself responsible. In the execution of the task Mr. Seymour has devoted studious care, with clear critical inquiry on his own part, from first to last. And his work is offered with confidence by the undersigned, to the Committee on Indexing Chemical Literature, for issue under the beneficent provisions of THE SMITHSONIAN INSTITUTION, to whose time-saving publications chemists are so greatly indebted.

ALBERT B. PRESCOTT.

UNIVERSITY OF MICHIGAN,
August, 1892.

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INTRODUCTION.

In the following work the articles were abstracted with reference to the subject of the bibliography, consequently some articles were abstracted only in part; that is, omitting what had no relation to acetoacetic ester. The word "ester" has been used to mean an acid in which the carboxylic hydrogen has been replaced by an alkyl radical, and where the alkyl radical is not specified, ethyl is understood.

The bibliography is arranged in chronological order, with author and subject indices appended.

All references given were verified, except where otherwise stated.

The reference given first in each case is the original publication, the others are reprints or abstracts.

The literature on the subject begins in 1840.

I wish to express my gratitude to Professors Prescott and Freer for direction and aid in the work.

PAUL H. SEYMOUR.

UNIVERSITY OF MICHIGAN,
June 11, 1892.

LIST OF PERIODICALS CONSULTED.

The following periodicals were examined carefully for articles upon the subject of the bibliography from the first volume in each case to the end of 1891 :

Annalen der Chemie und Pharmacie (*Vol. I., 1832*).
Berichte der deutschen Chemischen Gesellschaft (*Vol. I., 1868*).
**Jahresbericht über die Fortschritte der Chemie* (*Vol. I., 1847*).
Journal of the Chemical Society (*Vol. I., 1849*).
Bulletin de la Société chimique de Paris (*Vol. I., 1864*).

The following were consulted upon references :

Comptes rendus de l'Académie des Sciences.
Annalen der Physik und Chemie, **Poggendorff.**
Journal of the American Chemical Society.
Journal für praktische Chemie.
Archiv der Pharmacie.
Jahresbericht über die Fortschritte der Chemie, **Berzelius.**
Chemical News.
American Chemical Journal.
Annales de Chimie et de Physique.

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*Of this 1887 was the last volume published.

BIBLIOGRAPHY

OF

ACETO ACETIC ESTER.

LÖWIG, CARL AND SAL. WEIDEMANN, 1840.

Ann. der Phys. Pogg. **50**, 95-125 ; Ann. Chem. **36**, 297-304 ; Berzelius' Jsb. **21**, 425.

Action of Potassium and Sodium on Some Ethers.

Potassium attacks acetic ester at once and is dissolved. No gas is given off ; the mass solidifies and is found to be composed of potassium ethoxid and a compound of acetyl and oxygen, having less oxygen than acetic ester ; in other words the potassium abstracts oxygen from acetic ester. The product obtained, treated with sulfuric acid, gives acetic acid. The author decides that it is probably "Hypoacetous acid" (unteracetylig-saure) $C_4\,H_6\,O_{1\frac{1}{2}}$.

GEUTHER, A., 1863.

Arch. der Pharm. **116,** 97-110 ; Jsb. Chem. 1863, 323.

Researches Upon Monobasic Acids.

Acetic ester was boiled with sodium and a stream of hydrogen passed through. Sodium acetate and a compound *$C_{12}\,H_9\,Na\,O_6$ were formed. This compound was named dimethylen-carbonethylen ether sodium, as the author supposed it to be formed thus :—

$$2\ {}^*C_2\,H_2,\ C_2\,O_2\left.\begin{matrix}\\ \\\end{matrix}\right\}\begin{matrix}OH\\OH,C_4\,H_4\end{matrix} + 2\ Na = \left.\begin{matrix}{}^*C_2\,H_2,\ C_2\,O_2\\C_2\,H_2,\ C_2\,O_2\end{matrix}\right\}\begin{matrix}Na\ O\\H\ O,\ C_4\,H_4\end{matrix} + C_4\,H_5\,Na\,O_2 + H_2.$$

By treating this compound with ethyl iodid he formed dimethylen-carbonethylen ether * $C_{16}\,H_{14}\,O_6,$ boiling at 198° with a specific gravity of .998 at 12°. By using methyl iodid dimethylen-carbonmethylen ether *$C_{14}\,H_{12}\,O_6$ boiling at 186.8° was produced. By the action of ammonia on the former, two bodies were formed ;—* $C_{16}\,H_{15}\,NO_4,$ insoluble in water, melting at 59.5°, and $C_{12}\,H_{11}$ * $NO_4,$ soluble in water, melting at 90° and subliming at 100°. By passing carbon dioxid through * $C_{12}\,H_9\,Na\,O_6,$ $C_{12}\,H_{10}\,O_6$ was produced. It colors ferric chlorid, a dark violet.

*C = 6 ; O = 8.

WANKLYN, A., 1864.

J. Chem. Soc. **17**, 371-377 ; Chem. News. **10**, 195 ; Jsb. Chem. 1864, 461.

Some Actions of Sodium and Sodethoxid.

The difference is shown between treating sodethoxid with an alkyl iodid and an alkyl acetate.

In the first case sodium iodid is produced thus :

$$\left.\begin{matrix} Na \\ C_2H_5 \end{matrix}\right\} O + \left.\begin{matrix} I \\ C_2H_5 \end{matrix}\right\} = \left.\begin{matrix} Na \\ I \end{matrix}\right\} + \left.\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\right\} O$$

In the second case the sodium replaces the acetyl group and not the ethyl. This could not be shown in acetic ester, therefore valeric ester was worked with. It was treated with metallic sodium, reaction took place and no gas was given off.

The reaction was $2 \left.\begin{matrix} C_5H_9O \\ C_2H_5 \end{matrix}\right\} O + 2\ Na = 2 \left.\begin{matrix} Na \\ C_2H_5 \end{matrix}\right\} O + \left.\begin{matrix} C_5H_9O \\ C_5H_9O \end{matrix}\right\}$

GEUTHER, A., 1866.

Arch. der Pharm. **125**, 29-50, and **201**, 223 ; J. Prakt. Chem. **99** 113-125 ; Jsb. Chem. 1865. 302 ; Bull. Soc. chim. **6**, 222.

Acetic Acid.

Acetic ester was treated with sodium and $C_6H_9NaO_3$ was produced. By boiling with water it was decomposed into acetone, alcohol, carbon dioxid and sodium carbonate. $C_6H_{10}O_3$ was produced from its sodium compound by treating with hydrochloric acid, carbon dioxid or acetic acid, when it was called by the author ethyl-diacetic acid ; it has a specific gravity of 1.03 at 5°, boils at 180.8° and reddens litmus only when water is added. In obtaining it some dehydracetic acid was always formed. It has the composition $C_8H_8O_4$ and melts at 108.5° and boils at 269.6°. The barium and copper compounds of ethyl-diacetic acid and the barium, sodium and calcium salts of dehydracetic acid were described. Ethyl-diacetic ethyl $C_8H_{14}O_3$ produced by ethyl iodid boils at 198° and colors ferric chlorid blue. Ethyl-diacetic methyl $C_7H_{12}O_3$ boils at 186.8° has a specific gravity of 1.009 at 6° and colors ferric chlorid a deep blue.

FRANKLAND, E., AND B. F. DUPPA, 1866.

J. Chem. Soc. **19**, 395-434 ; Ann. Chem. **138**, 204-225 and 328-360 ; Phil. Trans. Lond. **156**, 37 ; Jsb. Chem. 1865, 304.

Synthetical Researches on Esters. Part I.

Acetic ester was made from sodium acetate, alcohol and sulfuric acid. It was treated with sodium when an action took place and hydrogen was given off. The product was treated with ethyl iodid and the result was a small amount of $C_6 H_9 (C_2 H_5) O_3$ and a larger amount of $C_6 H_8 (C_2 H_5)_2 O_3$. The latter is colorless, insoluble in water, miscible with alcohol and ether, boils at 137.5°–139° and has a specific gravity of .8171 at 22°.

Ethylic ethacetone carbonate $C_6 H_9 (C_2 H_5) O_3$ is colorless, almost insoluble in water, miscible with alcohol and ether, boils at 195° and distils unchanged, it has a specific gravity of .9834 at 16°. When saponified with a water solution of potassium hydroxid, ethyl acetone, $CH_3 CO C (C_2 H_5) H_2$, is produced which boils at 101° and has a specific gravity of .8046 at 22°. Both of these acetones have the smell and the taste of camphor. The di-methylderivative of acetoacetic ester (as it is now known) was prepared, the reactions given were $2 CH_3 CO_2 C_2 H_5 + 2 Na = CH_3 CO C Na_2 CO_2 C_2 H_5 + C_2 H_5 OH + H_2$ and $CH_3 CO CNa^2 CO_2 C_2 H_5 + 2CH_3 I = CH_3 CO C (CH_3)_2 CO_2 C_2 H_5 + 2 Na I$. Some of the mono methyl derivative was also formed but was decomposed by a water solution of potassium hydroxid. Methyl acetone, $CH_3 CO C H_2 (CH_3)$, boils at 81° and has a specific gravity of .8125 at 13°. Dimethyl acetone, $CH_3 CO C H (CH_3)_2$, boils at 93° and has a specific gravity of .8099 at 13°.

Ethylic dimethyl acetone carbonate, $CH_3 CO C (CH_3)_2 CO_2 C_2 H_5$, boils at 184° and has a specific gravity of .9913 at 16°.

BRANDES, R., 1866.

Arch. der Pharm. [2] **129**, 193-212 ; Jsb. Chem. 1866, 305; Bull. Soc. chim. **7**, 501.

Acetic Acid.

Methylen-dimethylen carboxylic acid, $C_5 H_8 O_3$ (acetoacetic methyl ester), is produced from acetic methyl ester and sodium, sodmethoxid and hydrogen being formed in the reaction. It is supposed to be an acid, and to be acetic acid in which two hydrogen atoms of the methyl group are replaced, one by methyl and the other by acetyl. It is colorless, boils at 169° 170°, and has a specific gravity of 1.037 at 9°. Blue litmus is scarcely changed by it until water is added. Alkalis and acids decompose it into acetone, carbon dioxid and methyl alcohol. The copper salt was made and described. Methylen-dimethylen carboxylic acid ethylen (ethyl-acetoacetic methyl ester), prepared from the former by treating with sodium and then with ethyl iodid, is colorless, boils at 189.7° and has a specific gravity of .995 at 14°. It is isomeric with Geuther's ethyl-dimethylen carboxylic acid methylen (methyl aceto acetic ester). By using methyl iodid methylen-dimethylen carboxylic acid methylen (methyl acetoacetic methyl ester), was produced, it boils at 177.4° and has a specific gravity of 1.020 at 9°. Methylen-dimethylen carboxylic acid ethylen treated with ammonia gives two compounds; $C_7 H_{13} NO_2$, which is insoluble in water, and $C_5 H_9 NO_2$, which is soluble in water. When the above esters are distilled some dehydracetic acid $C_8 H_8 O_4$ is formed as a solid in the flask.

Geuther appends a note to this article in which he gives his opinion as to the constitution of dehydracetic acid. He supposes it to be acetic acid in which two hydrogen atoms have been replaced by acryl, $C_3 H_3 O$, thus: $C H (C_3 H_3 O)_2 CO_2 H$.

FRANKLAND, E., AND B. F. DUPPA, 1867.

J. Chem. Soc. **20**, 102-116; Ann. Chem. **145**, 78-93; Jsb. Chem. 1867, 394.

Synthetical Researches on Esters. Part II.

By the action of sodium and then isopropyl iodid on acetic ester, monoisopropyl acetoacetic ester was produced, it is insoluble in water, miscible with ether and alcohol. has a specific gravity of .9804, boils at 201° with 758.4 m. m. pressure and distils unchanged. When saponified isopropyl acetone, $CH_3 CO CH_2 CH (CH_3)_2$, is produced, it is sparingly soluble in water, miscible with alcohol and ether, boils at 114° with 758.4 m. m. pressure and has a specific gravity of .8189 at 0°.

The difference is shown between it and two isomers, methyl valeral and ethyl butyral.

GEUTHER, A., 1869.

Ztschr. *Chem. **5**, 27; Bull. Soc. chim. **12**, 377.

Changing Acetoacetic Ester into Ethylacetic Ester.

Acetoacetic ester heated to 120° with sodethoxid and acetic ester is changed into ethyl acetic acid, $CH_2 C_2 H_5 CO_2 H$.

*Original article not consulted.

WANKLYN, A., 1869.

Ann. Chem. **149**, 43-49; Jsb. Chem. 1868, 509.

Research upon Esters.

The action of sodium in sealed tubes upon a number of esters was investigated and in no case was hydrogen evolved. The esters thus worked with were acetic ester; acetic allyl ester; butyric ester; valeric ester and benzoic ester. The equation for sodium and acetic ester was given as follows:

$3 C_2 H_3 O_2 C_2 H_5 + 4 Na = 3 Na OC_2 H_5 + Na (C_2 H_3 O)_3$. The author looks upon sodacetoacetic ester as a triacetyl derivative of sodium and upon acetoacetic ester as a triacetyl derivative of hydrogen ; making sodium and hydrogen trivalent.

WISLICENUS, J., 1869

Ann. Chem. **149**, 205-215.

β-Oxybutyric Acid.

The source of obtaining β-oxybutyric acid is acetoacetic ester which is treated with sodium amalgam and must be kept cool during the reaction for other-wise enough heat is generated by the reaction to decompose the substances into carbonates, acetone and alcohol.

WANKLYN, A., 1869.

Ber. **2**, 64-65 ; Ann. Chem. **150**, 206-208.

Action of Sodium on Alcohol.

By the action of sodium on alcohol, sodethoxid was formed, from which the author concludes that sodium is trivalent $[Na'''(C_2 H_4)'']'OH$. This gives rise to a new set of compounds by replacing the hydroxyl hydrogen by radicals.

WANKLYN, A., 1869.

Ber. **2**, 425-427.

Product of the action of Sodium and then Ethyl Iodid on Acetoacetic Ester.

No hydrogen is evolved in the first part of this reaction, the chief products of which are sodethoxid and sodacetoacetic ester. Then sodethoxid reacts with acetic ester to form ethyl acetate of sodium, $CH_2 (C_2 H_5) CO_2 Na$. This reacts with ethyl iodid thus : $2 CH_2 (C_2 H_5) CO_2 Na + 2 C_2 H_5 I = 2 Na I + C_2 H_5 OH + C_6 H_8 (C_2 H_5)_2 O_3$ and finally $C_6 H_8 (C_2 H_5)_2 O_3$ reacts with sodethoxid to form $CH_2 (C_2 H_5) CO_2 Na$ and butyric ester, $C_6 H_{12} O_2$.

LADENBURG, A., 1870.

Ber. 3, 305-306.

Action of Sodium on Acetic Ester.

By experimenting on this reaction the author concludes that no hydrogen is given off, and that with perfectly dry acetic ester no action will take place below 100°.

GEUTHER, A., 1871.

Ztschr. *Chem. **7**, 237 ; Bull. Soc. chim. **16**, 107.

Acetoacetic Ester and Some of its Derivatives.

When acetoacetic ester is treated with phosphorus pentachlorid, two metameric acids of the formula $C_4 H_6 O_2$ are formed, quartenylic and tetracrylic. Chlortetracrylic acid $C_4 H_5 Cl O_2$ and its salts are described. Tetrolic acid, $C_4 H_4 O_2$, is formed from chlortetracrylic ester by an excess of alcoholic potash. Ammonia in the cold acts on acetoacetic ester to form a soluble amid, $C_6 H_{11} NO_2$, and an insoluble amid, $C_8 H_{15} NO_2$.

*Original article not consulted.

MIXTER, WM. G., 1874.

Ber. **7**, 499-504 ; Bull. Soc. chim. **22**, 279.

Knowledge of Derivatives of Sodacetic Esters.

Sodacetoacetic ester was treated with isobutyl iodid and $C_6 H_8 (C_4 H_9)_2 O_3$ was obtained together with some of the mono-butyl derivative, $C_6 H_9 (C_4 H_9) O_3$. The dibutyl derivative is colorless, insoluble in water, miscible with alcohol and ether and boils at 250° to 253°. $C_6 H_9 (C_4 H_9) O_3$ treated with barium hydroxid is saponified to iso-butyl acetone, $CH_3 CO CH_2 (C_4 H_9)$.

WISLICENUS, J., 1874.

Ber. **7**, 683-692 ; J. Chem. Soc. **27**, 883 ; Bull. Soc. chim. **22**, 457.

Researches on Derivatives of Acetoacetic Ester.

In regard to the disputed action of sodium on acetic ester the author agrees with Geuther that as final products only sodethoxid and sodacetoacetic ester are produced. By the action of sodium on acetoacetic ester only one hydrogen atom can be replaced, but by replacing that sodium atom by an alkyl group the other hydrogen of the methylene group is rendered replaceable by sodium and then by an alkyl group. The ethyl and diethyl substituted esters were produced and described.

WISLICENUS, J., RUEGHEIMER, CONRAD, EHRLICH AND ZEIDLER, 1874.

Ber. **7**, 892-893 ; J. Chem. Soc. **29**, 367 ; Bull. Soc. chim. **23**, 72.

Derivatives of Acetoacetic Ester.

Sodacetoacetic ester treated with iodin forms diacetosuccinic ester which melts with decomposition at 77°. Sodacetoacetic ester treated with monochloracetic ester forms acetosuccinic ester which boils at 260° to 263° with partial decomposition, its specific gravity is 1.079 at 21°.

Sodacetoacetic ester treated with chlorcarbonic ester, $Cl\ CO_2\ C_2\ H_5$, forms aceto-malonic ester which boils at 238° to 240° and has a specific gravity of 1.080 at 23°.

Sodacetoacetic ester treated with allyl iodid forms allylacetoacetic ester an oil with a specific gravity of .982 at 20°.

WISLICENUS, J., ZEIDLER, EHRLICH, ROHRBECK, WALDSCHMIDT, SAUR AND CONRAD, 1875.

Ber. **8**, 1034-1040; J. Chem. Soc. **29**, 368; Bull. Soc. chim. **25**, 299.

Derivatives of Acetoacetic Ester.

Allylacetoacetic ester is saponified to allylacetone, $CH_3\ CO\ CH_2\ CH_2\ CH\ CH_2$, which boils at 130°. Allylacetoacetic ester when treated with sodethoxid gives allylacetic ester, $CH_2\ (C_3\ H_5)\ CO_2\ C_2\ H_5$ boiling at 142° to 144°, from which comes allylacetic acid boiling at 182°. Benzylacetoacetic ester $CH_3\ CO\ CH\ (CH_2\ C_6\ H_5)\ CO_2\ C_2\ H_5$ and the dibenzyl derivative are prepared. Methylacetoacetic ester is converted into α-methyl β-oxybutyric acid and α-methyl crotonic acid, α-ethyl β-oxybutyric acid and α-ethyl crotonic acid are obtained similarly. Ethyl-methyl acetoacetic ester boiling at 198° is prepared and from it ethyl-methyl acetic ester boiling at 132° and its acid (valeric) boiling at 137°.

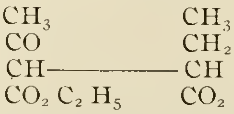
Dichlor-acetoacetic ester boiling at 205°-207° is prepared and from it dichloracetone. Ethyl acetoacetic ester will form but a mono chlor derivative therefore it is $CH_3\ CO\ C\ Cl\ (C_2\ H_5)\ CO_2\ R$ not $CH_2\ Cl\ CO\ CH\ (C_2\ H_5)\ CO_2\ R$.

WISLICENUS, J., F. CLOWES AND C. HUGGENBERG, 1875.

Ber. **8**, 1206-1209; J. Chem. Soc. **29**, 565; Bull. Soc. chim. **25**, 460.

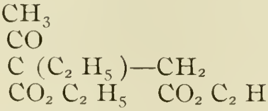
Ethyl-aceto Succinic Esters.

β-Ethyl-acetosuccinic ester was obtained from sodaceto acetic ester and α-brombutyric ester. Its formula is



$$\begin{array}{lcl} CH_3 & & CH_3 \\ CO & & CH_2 \\ CH & \text{———} & CH \\ CO_2\ C_2\ H_5 & & CO_2\ C_2\ H_5 \end{array}$$

, it is a colorless oil, boils at 262 and dissolves sodium at ordinary temperatures, giving off hydrogen. α-ethyl-acetosuccinic ester was obtained by treating aceto succinic ester with sodium, and the product with ethyl iodid. Its formula is



$$\begin{array}{l} CH_3 \\ CO \\ C\ (C_2H_5)—CH_2 \\ CO_2C_2H_5 \quad CO_2C_2H_5 \end{array}$$

it boils at 263° to 265°, and does not dissolve sodium at ordinary temperatures nor when gently heated.

OPPENHEIM, A., AND H. PRECHT, 1876.

Ber. **9**, 318-323; J. Chem. Soc. **30**, 69; Jsb. Chem. 1876, 604; Bull. Soc. chim. **26**, 355.

Formation of Acetoacetic Ester and Oxyuvitic Acid.

After studying the action of sodium on acetic ester the authors conclude that no hydrogen is given off, and that the reaction is as follows: $3\ CH_3CO_2C_2H_5 + 4\ Na = CH_3COCH\ Na\ CO_2C_2H_5 + 3\ C_2H_5ONa$.

In reference to oxyuvitic acid, they conclude that it cannot be formed directly from sodacetoacetic ester and chloroform but that the presence of sodium ethoxid is necessary.

OPPENHEIM, A., AND H. PRECHT, 1876.

Ber. **9**, 323-325; J. Chem. Soc. **30**, 69; Jsb. Chem. 1876, 572.

Production and Properties of Dehydracetic Acid.

Dehydracetic acid was made by passing the vapor of aceto acetic ester through an iron tube heated to dull redness. It is a crystalline substance of the formula $C_8H_8O_4$ which melts at 108 and boils at 269°. Acids do not affect it but alkalis decompose it into acetone and acetic acid.

DEMARCAY, E., 1876.

Compt. rend. **82**, 1337-1339; J. Chem. Soc. **30**, 403; Ber. **9**, 962; Jsb. Chem. 1876, 551; Bull. Soc. chim. **27**, 120.

Oxypyrotartaric Acid—A Derivative of Acetoacetic Ester.

Acetoacetic ester treated with hydrocyanic acid forms an addition product, $CH_3COH\ (CN)\ CH_2CO_2C_2H_5$, which is decomposed by water, forming oxypyrotartaric acid, $CH_3C\ OH\ (CO_2H)\ CH_2CO_2H$, ammonia, and alcohol.

DEMARCAY, E., 1876.

Compt. rend **83**, 449-451; J. Chem. Soc. **30**, 506; Jsb. Chem. 1876, 569.

Research upon the Derivatives of Acetovaleric Ester.

Sodacetoacetic ester and isopropyl iodid, $CH\ I\ (C\ H_3)_2$, react to form isopropyl acetoacetic ester, $CH_3CO\ CH\ (C_3H_7)\ CO_2C_2H_5$, which is acetovaleric ester. It boils at 200 to 202°, colors ferric chlorid rose violet, when treated with bromin and then alcoholic potash and then hydrochloric acid, two acids are formed according to the amount of bromin used. The acids resemble angelic and oxy-angelic acids.

EMMERLING, O. AND A. OPPENHEIM, 1876.

Ber. **9**, 1096-1097 ; Bull. Soc. chim. **27**, 298.

A New Ester of Acetoacetic Acid.

Isobutyl-acetoacetic ester was formed which boils at 202° to 206° with some decomposition ; its specific gravity is .979 at 0° The ester dissolves sodium, and oxyuvitic acid can be made from it.

OPPENHEIM, A. AND H. PRECHT, 1876.

Ber. **9**, 1098 ; Bull. Soc. chim. **27**, 299.

Action of Anilin on Acetoacetic Ester.

Acetoacetic ester was treated with anilin in hopes of producing an anilid but diphenyl carbamid $CO\left\{\begin{matrix}NH\ C_6\ H_5\\ NH\ C_6\ H_5\end{matrix}\right.$ melting at 235°, was produced instead.

EMMERLING, O. AND A. OPPENHEIM, 1876.

Ber. **9**, 1098 ; Bull. Soc. chim. **27**, 299.

Oxidization of Acetoacetic Ester.

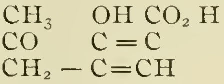
When acetoacetic ester is oxidized by potassium permanganate, potassium acetate, potassium oxalate, alcohol and water are formed.

OPPENHEIM, A. AND H. PRECHT, 1876.

Ber. **9**, 1099-1102 ; Bull. Soc. chim. **27**, 299.

Dehydracetic Acid.

Dehydracetic acid boiled with phosphorus trichlorid gives no reaction but when treated with phosphorus oxychlorid and phosphorus pentachlorid a compound, $C_8H_6Cl_2O_2$, melting at 101° is formed, which proves the presence of the hydroxyl and carboxyl groups, and also that the fourth oxygen atom is united to carbon. Dehydracetic ester, $C_8H_7(C_2H_5)O_4$, melts at 91.6°, dehydracetanilid, $C_8H_7(NHC_6H_5)O_3$, fuses at 115, and chlor-dehydracetic acid, $C_8H_7ClO_4$, fuses at 93°, brom-dehydracetic acid, $C_8H_7BrO_4$, was also described. The formula assigned to dehydracetic acid is



$$\begin{array}{ll} CH_3 & OH\ CO_2H \\ CO & C=C \\ CH_2 - & C=CH \end{array}$$

WISLICENUS, J., 1877.

Ann. Chem. **186,** 161-228; J. Chem. Soc. **32,** 432.

Acetoacetic Ester.

A short review is given of the work done by different chemists on the reaction between sodium and acetoacetic ester. The methylene hydrogen atoms of acetoacetic ester can be replaced by alkyl groups *only* by passing through the mono-sodium, mono-alkyl, and sodium-alkyl compounds, in that order. Diethyl acetoacetic ester boils at 218° and is not attacked by sodium even at 100°. In the reaction between sodium and acetic ester, sodium acetoacetic ester and sodethoxid are formed, and if ethyl iodid be added now, ethyl-acetoacetic ester is formed, upon some of which sodethoxid will instantly act and form sodethylacetoacetic ester, which, in contact with ethyl iodid now gives diethylacetoacetic ester. Frankland and Duppa wrongly attribute the last named body to the first action of sodium on acetic ester. These complications are due to not removing sodethoxid before adding ethyl iodid. The saponification of acetoacetic ester derivatives yields either substituted ketones and a carbonate, or substituted acetates and alcohol.

CONRAD, M., 1877.

Ann. Chem. **186,** 228-232; J. Chem. Soc. **32,** 435; Jsb. Chem. 1877, 689.

Acetoacetic Amyl Ester

Amyl acetate treated with sodium produces acetoacetic amyl ester, $CH_3COCH_2CO_2C_5H_{11}$, with no evolution of hydrogen if cold, and only slight evolution in a warm reaction. Amyl alcohol is also produced. Acetoacetic amyl ester is colorless, boils at 223°, has a specific gravity of .954 at 10°, and colors ferric chlorid red. Ethylacetoacetic amyl ester, $CH_3\ CO\ CH\ (C_2H_5)\ CO_2C_5H_{11}$, was also produced, it boils at 233° to 236°, has a specific gravity of .937 at 26° and gives no color with ferric chlorid.

CONRAD, M., 1877.

Ann. Chem. **186**, 232-244; J. Chem. Soc. **32**, 435; Jsb. Chem. 1877, 690.

Halogen Substitution Products of Acetoacetic Ester.

When acetoacetic ester is treated with bromin it takes it up and hydrobromic acid is given off, forming the compound $C_6H_8Br_4O_3$. Its specific gravity is 2.32 at 21° and it is decomposed upon distillation. Chlorin passed through acetoacetic ester is absorbed, hydrochloric acid is given off, and $C_6H_8Cl_2O_3$ is formed, This boils at 205° to 207° and its specific gravity is 1.293 at 16°. To prove the constitution of the last compound it was treated with hydrochloric acid at 180°, when dichloracetone, $CH_3\ CO\ CH\ Cl_2$, was formed, and with caustic potash when dichloracetic ester, $CH\ Cl_2\ CO_2\ C_2H_5$, was separated. Ethylacetoacetic ester was treated with chlorin and $CH_3\ CO\ C\ Cl\ (C_2H_5)\ CO_2\ C_2H_5$ was obtained. The author decides that the dichloracetoacetic ester is $CH_3\ CO\ C\ Cl_2\ CO_2\ C_2H_5$. Amyl ester of acetoacetic acid and the amyl ester of ethylacetoacetic acid were treated with chlorin, and dichloracetoacetic amyl ester and ethyl-monochloracetoacetic amyl ester were produced.

BONNÉ, JULIUS, 1877.

Ann. Chem. **187**, 1-11; J. Chem. Soc. **32**, 437

Benzoylacetoacetic Ester.

When benzoyl chlorid acts upon sodacetoacetic ester the two substances combine and sodium chlorid is formed. The compound, benzoylacetoacetic ester, $CH_3\ CO\ CH\ (CO\ C_6H_5)\ CO_2\ C_2H_5$, decomposes, upon being distilled, into carbon monoxid, carbon dioxid, benzoic ester and benzoic acid. When treated with caustic potash methyl phenyl ketone, $CH_3\ CO\ C_6H_5$, and a little benzoic acid are produced.

EHRLICH, FRANZ LOUIS, 1877.

Ann. Chem. **187**, 11-30; J. Chem. Soc. **32**, 438; Jsb. Chem. 1877, 689.

Benzylacetoacetic Ester.

Benzylacetoacetic ester was made by treating sodacetoacetic ester with benzyl chlorid, it is $CH_3\ CO\ CH\ (CH_2\ C_6\ H_5)\ CO_2\ C_2\ H_5$, it has a specific gravity of 1.083 at 18.4° and cannot be distilled. When saponified methyl-phenylethyl ketone, $CH_3\ CO\ CH_2\ (CH_2\ C_6\ H_5)$, is obtained, it boils at 235°-236° and has a specific gravity of .989 at 23.5°. When this ketone is oxidized acetic and benzoic acids, carbon dioxid and water are produced. Dibenzylacetoacetic ester was also produced. The action of nascent hydrogen on benzylacetoacetic ester was found to be analogous to that on acetoacetic ester, that is, α-benzyl β-oxybutyric ester was produced.

ZEIDLER, FRANZ, 1877.

Ann. Chem. **187**, 30-47; J. Chem. Soc. **32**, 437.

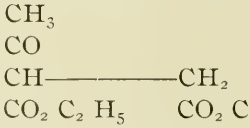
Allyl-acetoacetic Ester.

Allyl-acetoacetic ester boils at 206° and gives a carmine color with ferric chlorid, its specific gravity is .982 at 20°. When saponified it yields allyl-acetone, $CH_3\ CO\ CH_2\ C_3\ H_5$, which boils at 128° to 130° and has a specific gravity of .834 at 27°. It is isomeric with mesityl oxid, boiling point 131°-132°; with dumasin boiling point 120°-125°, and with metacetone boiling point 84°-86°. Allyl acetic acid, $CH_2\ (C_3\ H_5)\ CO_2\ H$, also obtained from the saponification, when oxidized becomes succinic acid. Nascent hydrogen converts allyl acetoacetic ester into α-allyl β-oxybutyric acid.

CONRAD, M., 1877.

Ann. Chem. **188**, 217-226; J. Chem. Soc. **34**, 137.

Acetsuccinic Esters and Derivatives.

Acetsuccinic ester 

$$\begin{array}{ll} CH_3 & \\ CO & \\ CH\text{———————} & CH_2 \\ CO_2\ C_2\ H_5 & CO_2\ C_2\ H_5 \end{array}$$

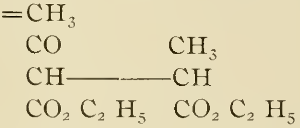
was obtained from sodacetoacetic ester and monochlor-acetic ester, it is insoluble in water, soluble in alcohol, ether and benzene, and boils at 254° to 256°. When saponified with alcoholic potash, acetic and succinic acids are produced. Barium hydroxid produces β-aceto-propionic acid CH_3 CO CH_2 CH_2 CO_2 H, a crystalline substance which melts at 31°. This is probably the same as the levolinic acid of Grote and Tollens (Ann. Chem. **175**, 181) The ethyl ester was also produced.

CONRAD, M, 1877.

Ann. Chem. **188**, 226-228 ; J. Chem. Soc. **34**. 137.

Synthesis of Pyrotartaric Acid from Acetoacetic Ester.

When sodacetoacetic ester is treated with α-brom-propionic ester, β-methyl-aceto-succinic ester is formed, thus:— CH_3 CO C H Na CO_2 C_2 H_5 + CH_3 C H Br CO_2 C_2 H_5 =



$$\begin{array}{lcl} CH_3 & & \\ CO & & CH_3 \\ CH & \text{———} & CH \\ CO_2\,C_2\,H_5 & & CO_2\,C_2\,H_5 \end{array}$$

β-Methyl aceto-succinic ester is acted upon by barium hydroxid and the barium salt of pyrotartaric acid is formed.

ROHRBECK, HERMANN, 1877.

Ann. Chem. **188**, 229-239 ; J. Chem. Soc. **34**, 136.

α=Methyl β=Oxybutyric Acid and α=Methyl Crotonic Acid.

α-Methyl β-oxybutyric acid was obtained from methyl-acetoacetic ester by the action of sodium amalgam and when heated this α-methyl β-oxybutyric acid was changed into α-methyl crotonic acid, CH_3 CH : C CH_3 CO_2 H. The properties and salts of each acid were described.

WALDSCHMIDT, ERNST, 1877.

Ann. Chem. **188**, 240-248 ; J. Chem. Soc. **34**, 136.

Reactions of Acetoacetic Ester.

α-Ethyl β-oxybutyric acid and α-ethyl-crotonic acid were produced from acetoacetic ester, the reactions being similar to those of Rohrbeck* which proves that they are general. The salts of these two acids were studied and described.

*See pages 7 and 13.

SAUR, RICHARD, 1877.

Ann. Chem. **188**, 257-269.

Methyl-ethyl-acetoacetic Ester, Methyl-ethyl-acetic Acid and α-Methyl-ethyl-β-oxybutyric Acid.

Methyl-ethyl-acetoacetic ester, $CH_3\ CO\ C(CH_3)(C_2\ H_5)CO_2\ C_2\ H_5$, is colorless, boils at 198° and its specific gravity is .974 at 22°. It produces a violet color with ferric chlorid. When treated with sodium ethoxid it gives methyl-ethyl acetic ester, $CH\ (CH_3)(C_2\ H_5)\ CO_2\ C_2\ H_5$, while sodium amalgam acting on it produces α-methyl-ethyl-β-oxybutyric ester.

CONRAD, M., 1877.

Ann. Chem. **188**, 269-274.

Metal Acetoacetic Esters.

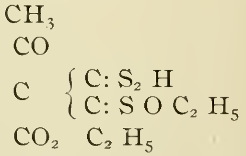
The copper, nickel, cobalt, magnesium, and aluminum salts of acetoacetic ester were produced and described. In each case but one hydrogen atom of the methylene group in acetoacetic ester can be replaced. This can be replaced by either a metal or a non-metal because its position between two carbonyl groups weakens its positive character.

NORTON, TH. AND A. OPPENHEIM, 1877.

Ber. **10**, 701-704; Jsb. Chem. 1877, 685.

Action of Carbon Bisulfid on Acetoacetic Ester.

By this action a monobasic acid of the formula



$$\begin{array}{l} CH_3 \\ CO \\ C \left\{ \begin{array}{l} C{:}\ S_2\ H \\ C{:}\ S\ O\ C_2\ H_5 \end{array}\right. \\ CO_2\ \ C_2\ H_5 \end{array}$$

was formed which was named by the authors thiorufic acid. A metallic oxid and carbon bisulfid acting on acetoacetic ester produce a compound $CH_3\ CO\ C\ (:C{:}\ S)\ CO_2\ C_2\ H_5$ which the authors consider as the acetyl derivative of $CH\ (:C{:}\ S)\ CO_2\ H$, which they name thio-carbacetic acid.

DEMARCAY, E., 1877.

Ber. **10**, 1177-1178.

Acetoacetic Ester.

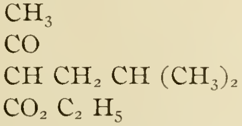
The author has worked on the chlorcrotonic acids. The methyl,—ethyl,—and propyl-acetoacetic esters were converted into the corresponding chlorcrotonic acids and described.

ROHN, WILHELM, 1877.

Ann. Chem. **190**, 305-322; Ber. **11**, 252; Jsb. Chem. 1877, 688.

Isobutyl-acetoacetic Ester......... and Isobutyl-acetic Acid.

Acetoacetic ester treated with isobutyl iodid gives isobutyl acetoacetic ester



$$\begin{array}{l} CH_3 \\ CO \\ CH\ CH_2\ CH\ (CH_3)_2 \\ CO_2\ C_2\ H_5 \end{array}$$

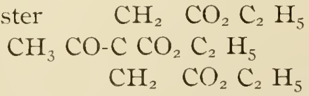
which boils at 217°-218° and has a specific gravity of .951 at 17.5°. When saponified it yields isobutyl acetone, $CH_3\ CO\ CH_2\ [CH_2\ CH\ (CH_3)_2]$, which boils at 142° to 144° and has a specific gravity of .817 at 17° and isobutyl acetic acid, $CH_2\ [CH_2\ CH\ (CH_3)_2]\ CO_2\ H$.

MIEHLE, GUSTAV., 1877.

Ann. Chem. **190**, 322-327; J. Chem. Soc. **34**, 490; Jsb. Chem. 1877, 688.

Synthesis of Tricarballylic Acid.

Acetosuccinic ester, made from sodacetoacetic ester and monochloracetic ester, was treated with sodium and then with monochlor-acetic ester and aceto-tricarballylic ester



$$\begin{array}{l} \qquad\qquad\ \ CH_2\ \ CO_2\ C_2\ H_5 \\ CH_3\ CO\text{-}C\ CO_2\ C_2\ H_5 \\ \qquad\qquad\ \ CH_2\ \ CO_2\ C_2\ H_5 \end{array}$$

was produced.

It boils, with decomposition at 280° to 300°. When treated with hot potassium hydroxid it gives potassium tricarballylate from which can be obtained tricarballylic acid $C_3\ H_5\ (CO_2\ H)_3$.

DEMARCAY, E., 1877.

Compt. rend. **84**, 554-556 and 1087-1089; J. Chem. Soc. **32**, 590; Ber. **10**, 732; Jsb. Chem. 1877, 690.

Simple Method of Preparing Certain Mono, Di, and Trichlor Acids.

Phosphoric pentachlorid, acting on a compound of the formula CH_3 CO $CH \times CO_2$ C_2 H_5, forms a substituted monochlor crotonic ester of the formula CH_2 : C Cl $CH \times CO_2$ C_2 H_5. In this manner the methyl, ethyl, propyl, isopropyl and allyl crotonic monochlor esters were prepared. Also some di-radical monochlor crotonic esters of the formula CH_2 : C Cl C X Y CO_2 C_2 H_5 both where X and Y were alkyl radicals and where they were acid radicals. The ethyl-monochlor crotonic ester and its isomer dimethyl-monochlor crotonic ester were prepared and the differences between them noted.

DEMARCAY, E., 1877.

Compt. rend. **84**, 1032–1033; J. Chem. Soc. **32**, 594.

Some Derivatives of Acetoacetic Ester.

By treating ethyl- and methyl-acetoacetic esters each with a quantity of bromin representing one molecule and saponifying the products, two compounds of the composition $3\ C_5\ H_6\ O_2 + H_2\ O$ and $3\ C_4\ H_4\ O_2 + H_2\ O$ were obtained, which were named *pentic* and *tetric* acids respectively. Just double the amount of bromin being used, two acids were formed each containing one atom of oxygen more. These were named *pentenic* and *tetrenic*. Mono- and di-brom-isopropyl acetoacetic esters also gave rise to two acids, *hexic*, $3\ C_6\ H_8\ O_2 + H_2\ O$, and *hexenic*, $3\ C_6,\ H_8\ O_3 + H_2\ O$.

SCHNAPP, HEINR., 1877.

Ber. **10**, 1953–1954 and 2227; Ann. Chem. **201**, 62–73; Jsb. Chem. 1877, 718.

Di-ethyl-β-oxybutyric Acid.

Di-ethyl-acetoacetic ester when treated with sodium amalgam gives diethyl-β-oxybutyric acid $CH_3\ CH\ (OH)\ C\ (C_2\ H_5)_2\ CO_2\ H$. By heating instead of forming the crotonic acid by splitting off water, it forms acetic aldehyde and di-ethyl-acetic acid. The latter boils at 195° to 197° and has a specific gravity of .945.

RÜCKER, AUG., 1877.

Ber. **10**, 1954; Ann. Chem. **201**, 54; J. Chem. Soc. **34**, 292; Jsb. Chem. 1880, 810.

Methyl Crotonic Acid.

Methyl-acetoacetic ester, $CH_3\ CO\ CH\ (CH_3)\ CO_2\ C_2\ H_5$, treated with phosphorus pentachlorid gives only one compound *α*-methyl *β*-chlor crotonic acid CH_2
$C\text{-}Cl$
$CH\ (CH_3)$
$CO_2\ H$ which melts at 69.5° The barium, sodium and silver salts and the ethyl ester were described.

WOLFF, CARL, 1877.

Ber. **10**, 1956-1958; Ann. Chem. **201**, 45; Jsb. Chem. 1877, 687.

Diallyl-acetoacetic Ester and its Derivatives.

Diallylacetoacetic Ester, $CH_3\ CO\ C\ (C_3\ H_5)_2\ CO_2\ C_2\ H_5$, boils at 239° to 241° and has a specific gravity of .948 at 25° It is decomposed by alkalis in two ways forming (1) diallylacetone which boils at 174°-175° and (2) into diallylacetic acid which boils at 221°-222° and has a specific gravity of .949 at 25° To obtain the first product the alkali is added cold and the substance is shaken out with ether. To obtain the second add sulfuric acid to the dry mixture and the acid separates as an oil. The barium, calcium and silver salts are described. Possibly this diallylacetic acid $C\ H\ (C_3\ H_5)_2\ CO_2\ H$ when oxidized will give tricarballylic acid $C_3\ H_5\ (CO_2\ H)_3$ since allylacetic acid gives succinic acid.

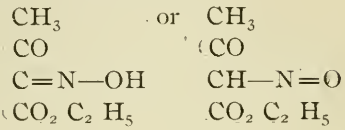
MEYER, VICTOR, 1877.

Ber. **10**, 2075-2078; Jsb. Chem. 1877, 518 and 770.

Azophenylacetoacetic Acid.

When azobenzene nitrate $C_6\ H_5\ N_2\ NO_3$ is treated with potassium acetoacetic ester, azophenylacetoacetic acid $CH_3\ CO\ CH\ (N_2\ C_6\ H_5)$

CO_2 H is formed, it melts at 154° 155°. A new acid, $C_6 H_9 NO_4$, was produced by treating acetoacetic ester with nitrous acid, it is so unstable that it cannot be distilled. Its constitution is either



$$\begin{array}{lcl} CH_3 & \text{or} & CH_3 \\ CO & & CO \\ C{=}N{-}OH & & CH{-}N{=}O \\ CO_2\,C_2\,H_5 & & CO_2\,C_2\,H_5 \end{array}$$

WISLICENUS, J., 1877.

Ber. **10**, 2226-2227.

The Saponification of Acetoacetic Esters.

The author calls attention to the double saponification of acetoacetic esters. Substituted acetic esters or acids are obtained as well as substituted ketones.

WISLICENUS, J., 1878.

Ann. Chem. **190**, 257-281 ; J. Chem. Soc. **34**, 402 ; Ber. **11**, 251.

Decomposition of Acetoacetic Ester by Alkalis.

A large number of experiments have been performed and tables are given showing the proportions of the different products of saponification under different conditions. It was found that the more concentrated the alkali and the more it was in excess the larger was the proportion of acetic acid and substituted acetic acids and the smaller was the proportion of carbonate and ketones.

CONRAD, M., 1878.

Ber. **11**, 58-60 ; J. Chem. Soc. **34**, 403 ; Jsb. Chem. 1878, 687.

Action of Sodium on Ethoxyacetic Ester.

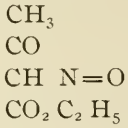
By the action of sodium and then acetic acid on ethoxyacetic ester, $CH_2\ (O\ C_2\ H_5)\ CO_2\ C_2\ H_5$, a compound $C_{10}\ H_{18}\ O_5$ is formed which boils at 245° and is believed to be ethoxyacetyl-ethoxyacetic ester, $CH_2\ (OC_2\ H_5)\ CO\ CH\ (O\ C_2\ H_5)\ CO_2\ C_2\ H_5$. It colors ferric chlorid violet, dissolves sodium and forms a barium compound. Heated with an alkali it gives ethoxyacetic ester.

MEYER, VICTOR AND J. ZÜBLIN, 1878.

Ber. **11**, 320-324 ; J. Chem. Soc. 34, 487 ; Jsb. Chem. 1878, 426.

Nitroso Compounds of Fatty Series. Part I.

By the action of nitrous acid on acetoacetic ester a compound $C_6 H_9 NO_4$ was produced. It was liquid even at 25° below zero but after standing some months some of it crystallized. Acetyl chlorid has no action on it which is one proof of the formula



$$\begin{array}{l} CH_3 \\ CO \\ CH\ N{=}O \\ CO_2\,C_2\,H_5 \end{array}$$

Methyl acetoacetic ester treated with nitrous acid gives nitroso-methyl acetone, $CH_3\ CO\ CH\ (CH_3)\ NO$, which forms white crystals soluble in alcohol, ether and chloroform ; it melts at 74°, and boils at 185° 186° undecomposed. It is the first nitroso compound whose vapor density has been determined. Ethyl-acetoacetic ester treated with nitrous acid gives nitroso-ethyl-acetone, $CH_3\ CO\ CH\ (C_2\ H_5)\ NO$, crystals which are soluble in alcohol, ether and chloroform and slightly soluble in water, it melts at 53°-55°.

ALLIHN, F., 1878.

Ber. **11**, 567-570 ; J. Chem. Soc. 34, 566 ; Jsb. Chem. 1878, 707.

Action of Sulfuryl Chlorid on Acetoacetic Ester.

This action produces two compounds according to the proportions of the chlorid used. If an excess of sulfuryl chlorid act upon acetoacetic ester, $CH_3\ CO\ C\ Cl_2\ CO_2\ C_2\ H_5$, is formed. If molecular quantities of the two substances are taken, $CH_3\ CO\ C\ HCl\ CO_2\ C_2\ H_5$, is formed which is a colorless liquid boiling at 193° to 195°. Its specific gravity is 1.19 at 14°. When saponified mono-chlor-acetic ester is produced.

MEYER, VICTOR AND J. ZÜBLIN, 1878.

Ber. **11**, 692-697 ; J. Chem. Soc. 34, 659 ; Jsb. Chem. 1878, 726.

Nitroso Compounds of the Fatty Series. Part II.

By different manipulations of nitrous acid and methyl-acetoacetic ester three bodies were obtained :—

1) Nitroso-methyl acetone CH_3 CO CH (CH_3) (NO),
2) Nitroso-propionic ester CH_3 CH (NO) CO_2 C_2 H_5.
3) Nitroso-propionic acid CH_3 CH (NO) CO_2 H.

Each one was described, as was nitroso acetone, CH_3 CO CH_2 (NO), also.

CONRAD, M., 1878.

Ber. **11**, 1055-1058; J. Chem. Soc. **34**, 732; Jsb. Chem. 1878, 743.

Synthesis of Phenylated Fatty Acids.

Benzylacetoacetic ester, CH_3 CO CH (C_7 H_7) CO_2 C_2 H_5, made from acetoacetic ester, sodium ethoxid and benzyl chlorid is a colorless liquid with boiling point 276° and specific gravity 1.036 at 15.5°. When this is treated with sodium and then with methyl iodid CH_3 CO C (CH_3) (C_7 H_7) CO_2 C_2 H_5 is produced. It is colorless, its boiling point is 287° and its specific gravity 1.046 at 23°; when saponified it yields methyl benzyl acetic acid, CH (CH_3) (C_7 H_7) CO_2 H. Methyl benzyl acetic benzyl ester or methyl-hydrocinnameïn, ethyl benzyl acetoacetic ester, CH_3 CO C (C_2 H_5) (C_7 H_7). CO_2 C_2 H_5; and benzyl acetosuccinic ester CH_3
CO
C (C_7 H_7)——CH_2
CO_2 C_2 H_5 CO_2 C_2 H_5 were prepared and described.

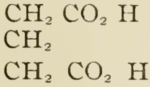
WISLICENUS, J. AND L. LIMPACH, 1878.

Ann. Chem. **192**, 128-135; J. Chem. Soc. **34**, 783; Ber. **11**, 1245;
Jsb. Chem. 1878, 720.

Synthesis of Glutaric (Pyrotartaric) and α-Methyl Glutaric Acids.

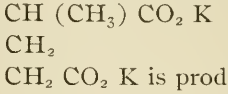
When sodacetoacetic ester is treated with β-iodio-propionic ester, CH_2 I CH_2 CO_2 C_2 H_5, aceto-glutaric ester, CH_3
CO
CH—CH_2 CH_2 CO_2 C_2 H_5,
CO_2 C_2 H_5 is produced.

It is a colorless oil boiling at 271°-272°, it has a specific gravity of 1.0505 at 14.1°. Treating this with alcoholic potash and then sulfuric acid, glutaric acid,



$\begin{array}{l} CH_2\ CO_2\ H \\ CH_2 \\ CH_2\ CO_2\ H \end{array}$

is produced. Methyl-aceto-glutaric ester, formed similarly from sodmethylacetoacetic ester boils at 280°-281° and has a specific gravity of 1.043 at 20°. When this is saponified potassium methyl-glutarate



$\begin{array}{l} CH\ (CH_3)\ CO_2\ K \\ CH_2 \\ CH_2\ CO_2\ K \end{array}$

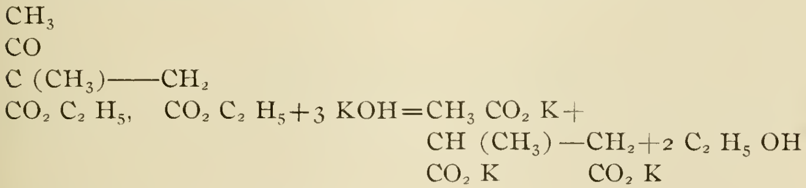
is produced which is a crystalline substance melting at 76°. The zinc and silver salts were described.

KRESSNER, G., 1878.

Ann. Chem. **192**, 135-141; J. Chem. Soc, **24**, 783; Ber. **11**, 1245; Jsb. Chem. 1878, 721.

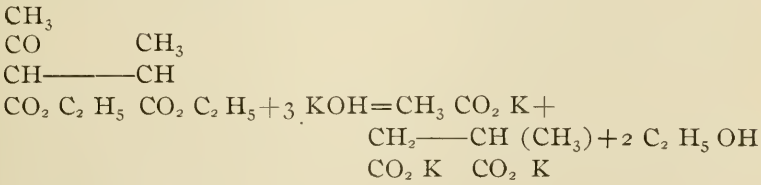
Synthesis of Pyrotartaric Acid from α-Methyl-aceto-succinic Ester.

α-Methyl-aceto-succinic ester saponified yields pyrotartaric acid identical with that produced by Conrad, (Ann. Chem. **188**, 226,) from β-methyl-aceto-succinic ester. The two equations are (1) α



$$\begin{array}{l} CH_3 \\ CO \\ C\ (CH_3)\text{——}CH_2 \\ CO_2\ C_2\ H_5,\quad CO_2\ C_2\ H_5 + 3\ KOH = CH_3\ CO_2\ K + \end{array} \begin{array}{l} \\ \\ \\ \\ CH\ (CH_3)\text{—}CH_2 + 2\ C_2\ H_5\ OH \\ CO_2\ K \qquad\quad CO_2\ K \end{array}$$

(2) β



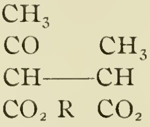
$$\begin{array}{l} CH_3 \\ CO \qquad\quad CH_3 \\ CH\text{———}CH \\ CO_2\ C_2\ H_5\ \ CO_2\ C_2\ H_5 + 3\ KOH = CH_3\ CO_2\ K + \end{array} \begin{array}{l} \\ \\ \\ \\ CH_2\text{——}CH\ (CH_3) + 2\ C_2\ H_5\ OH \\ CO_2\ K \quad CO_2\ K \end{array}$$

HARDTMUTH, F, 1878.

Ann. Chem. **192**, 142-146; J. Chem. Soc. **34**, 782; Ber. **11**, 1245; Jsb. Chem. 1878, 726.

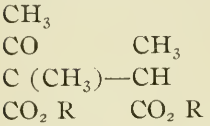
α-β-Dimethyl-acetosuccinic Ester and Symmetrical Dimethylsuccinic Acid.

β-Methyl-acetosuccinic ester



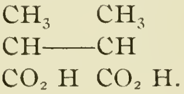
$$\begin{array}{ll} CH_3 & \\ CO & CH_3 \\ CH- & -CH \\ CO_2\,R & CO_2\,R \end{array}$$

is treated with sodium and then with methyl iodid and thus *α-β*-dimethyl-acetosuccinic ester



$$\begin{array}{ll} CH_3 & \\ CO & CH_3 \\ C\,(CH_3)- & -CH \\ CO_2\,R & CO_2\,R \end{array}$$

was produced. It boils at 270° to 272° and its specific gravity is 1 057 at 27° When saponified it gives symmetrical dimethyl succinic acid.



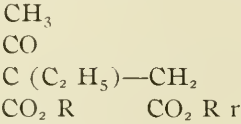
$$\begin{array}{ll} CH_3 & CH_3 \\ CH- & -CH \\ CO_2\,H & CO_2\,H. \end{array}$$

HUGGENBERG, CARL, 1878.

Ann. Chem. **192**, 146-152; J. Chem. Soc. **34**, 782; Ber. **11**, 1246; Jsb. Chem. 1878, 725.

α-Ethyl-aceto-succinic Ester and Ethyl-succinic Acid.

When sodacetosuccinic ester is treated with ethyl iodid *α*-ethyl-acetosuccinic ester



$$\begin{array}{ll} CH_3 & \\ CO & \\ C\,(C_2\,H_5)- & -CH_2 \\ CO_2\,R & CO_2\,R \end{array}$$

results. It boils at 263° to 265° and sodium will not act upon it. When this is saponified ethylsuccinic acid is produced which melts at 98° The barium, calcium and silver salts and ethyl ester of this acid were described.

CONRAD, M. AND LEONARD LIMPACH, 1878.

Ann. Chem. **192**, 153-160; Ber. **11**, 1246; J. Chem. Soc. **34**, 781; Jsb. Chem. 1878, 706.

Improved Method of Production of Mono- and Di-organic Substituted Acetoacetic Esters.

Add the ester to a solution of sodium ethoxid made by dissolving sodium in absolute alcohol and then add the alkyl iodid. The products are obtained very free from the byproducts which are formed in the usual methods.

PRECHT, H., 1878.

Ber. **11**, 1193-1195; J. Chem. Soc. **34**, 970; Jsb. Chem. 1878, 706.

Action of Ammonia on Acetoacetic Ester.

By this action the compound $C_6 H_{11} NO_2$ is formed. It is insoluble in water, soluble in alcohol and ether, and is decomposed by heating. It is probably an amid and is isomeric, not identical with the substance which Geuther obtained and called ammonium ethylene-dimethylene carbonate.*

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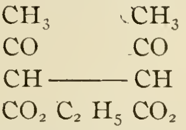
*See pages 1 and 6.

HARROW, GEO. H. U., 1878.

J. Chem. Soc. **33**, 425-438; Ann. Chem. **201**, 141; Jsb. Chem. 1878, 731.

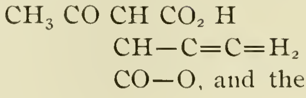
Pyrotritartaric and Carbopyrotritartaric Acids.

Diacetosuccinic ester



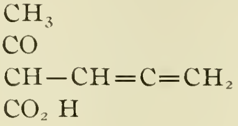
$$\begin{array}{ll} CH_3 & CH_3 \\ CO & CO \\ CH & \!\!\!\text{———}\; CH \\ CO_2\,C_2\,H_5 & CO_2\,C_2\,H_5 \end{array}$$

made from sodacetoacetic ester and iodin, is crystalline and melts at 78°-79°. This treated with dilute sulfuric acid yields the two acids, pyrotritartaric or uvic $C_7 H_8 O_3$ melting at 135°-136° and carbopyrotritartaric, $C_8 H_8 O_5$ which melts at 230°-231°. Carbopyrotritartaric acid heated gives pyrotritartaric acid and carbon dioxid. Carbopyrotritartaric acid fused with potassium hydroxid gives succinic and acetic acids. The formula assigned to carbopyrotritartaric acid is



$$\begin{array}{l} CH_3\ CO\ CH\ CO_2\ H \\ \qquad\qquad\quad CH{-}C{=}C{=}H_2 \\ \qquad\qquad\quad CO{-}O \end{array}$$

, and the one assigned to pyrotritartaric acid is



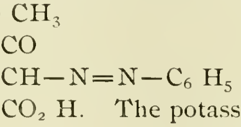
$$\begin{array}{l} CH_3 \\ CO \\ CH{-}CH{=}C{=}CH_2 \\ CO_2\ H \end{array}$$

ZÜBLIN, J., 1878.

Ber. **11**, 1417-1420; J. Chem. Soc. **34**, 879; Jsb. Chem. 1878, 811.

Azobenzene-acetoacetic Acid.

This name is proposed for what V. Meyer calls Azo-phenylacetoacetic acid* (Ber. **10**, 2075.)



$$\begin{array}{l} CH_3 \\ CO \\ CH{-}N{=}N{-}C_6\ H_5 \\ CO_2\ H. \end{array}$$

The potassium, barium, lead, silver and copper salts and ethyl ester are described and also paraazotoluol-acetoacetic acid, $CH_3\ CO\ CH\ (N_2\ C_6\ H_4\ CH_3)\ CO_2\ H$, and its ethyl ester.

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*See page 17.

BANDROWSKI, E., 1879.

Ber. **12**, 344-346; J. Chem. Soc. **36**, 523; Jsb. Chem. 1879, 628.

Behavior of Dibromsuccinic Acid with Water.

At high temperatures water decomposes dibromsuccinic acid by abstracting hydrobromic acid. Two acids are left, one with a boiling point between 129° and 130° which is bromomaleic acid, the other one boils at 172°.

HILGER, A., 1879.

Ann. Chem. **195**, 314-317; Ber. **12**, 664; J. Chem. Soc. **36**, 560; Jsb. Chem. 1879, 1081.

Detection of Acetoacetic Ester in Urine.

Acetoacetic ester was found in the urine of diabetic patients to the amount of .0399 to .1909 in 100 parts.

KÖNIG, HEINR., 1879.

Ber. **12,** 768-770; J. Chem. Soc. **36,** 706; Jsb. Chem. 1879, 662.

Action of Hydrocyanic and Hydrochloric Acids on Methyl-aceto-acetic Ester.

Just as these acids act on acetoacetic ester to produce oxypyrotartaric acid so they act on methyl-acetoacetic ester and produce the next higher homologue, oxyadipic acid thus: $CH_3\ CO\ CH\ (CH_3)\ CO_2\ C_2\ H_5 + HCN = CH_3\ COH\ (CN)\ CH\ (CH_3)\ CO_2\ C_2\ H_5$ and then $CH_3\ C\ OH\ (CN)\ CH\ (CH_3)\ CO_2\ C_2\ H_5 + 2\ HCl + 2\ H_2\ O = CH_3\ COH\ (CO_2\ H)\ CH\ (CH_3)\ CO_2\ H + N\ H_4\ Cl + C_2\ H_5\ Cl$.

LADENBURG, A. AND L. RÜGHEIMER, 1879.

Ber. **12,** 953-954; J. Chem. Soc. **36,** 715; Jsb. Chem. 1879, 435.

Acetoacetic Ester Derivatives of Ortho-tolylendiamin.

Ortho-tolylendiamin $C_6\ H_3\ CH_3\ (NH_2)_2$ reacts with acetoacetic ester to form $C_6\ H_3\ CH_3{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}\ C\ {<}\genfrac{}{}{0pt}{}{CH_3}{CH_2}CO_2\ C_2\ H_5$, a solid, melting at 82°. It is insoluble in water, soluble in alcohol and such solvents; when heated it decomposes into ethenyl-tolylendiamin $C_6\ H_3\ CH_3{<}\genfrac{}{}{0pt}{}{N=}{NH\diagup}C\ C\ H_3$, a solid which melts at 198°-199°.

ALLIHN, F., 1879.

Ber. **12,** 1298-1300; J. Chem. Soc. **36,** 915; Jsb. Chem. 1879, 627.

Chlorinated Metal Derivatives of Acetoacetic Ester.

The chlorinated metal derivatives, corresponding to the formula $(CH_3\ CO\ CCl\ CO_2\ C_2\ H_5)_x\ M$, may be produced by shaking the monochlor-acetoacetic ester with an ammoniacal solution of the salt. The copper, magnesium, nickel, and cobalt salts were described. The dichlor-acetoacetic ester will give no metal derivatives.

JOURDAN, FRIEDRICH, 1879.

Ann. Chem. **200**, 101-119; J. Chem. Soc. **38**, 313; Jsb. Chem. 1879, 668.

Mono- and Di-heptyl-acetoacetic Esters.

Acetoacetic ester treated with heptyl iodid, $C_7 H_{15} I$, and sodium ethoxid forms heptyl-acetoacetic ester, $CH_3 CO CH C_7 H_{15} CO_2 C_2 H_5$, a colorless oil which boils at 271° to 273° and has a specific gravity of .9324 at 17.1°. This was saponified and heptyl acetone, $CH_3 CO CH_2 C_7 H_{15}$, boiling at 214°-215°, with a specific gravity of .829 at 17.7°, and heptyl-acetic acid, identical with nonyl acid, were produced. Di-heptyl-acetoacetic ester was made in the similar way, and from this methyl diheptyl carbin ketone (diheptyl acetone), $CH_3 CO CH (C_7 H_{15})_2$, and diheptyl acetic acid, $CH (C_7 H_{15})_2 CO_2 H$, were produced.

VENABLE, F. P., 1880.

Ber. **13**, 1649-1652 ; Jsb. Chem. 1880, 438.

Derivatives of Heptanes.

Heptyl-acetoacetic ester was produced by the Conrad and Limpach method, it boils at 250° to 260°. When saponified it yielded methyl octyl ketone, $CH_3 CO CH_2 CH CH_3$

$C_5 H_{11}$, which boils at 196° to 198°. This formula was assigned to it because the heptyl bromide, $C_5 H_{11} CH Br CH_3$, was used to start with.

MORRIS, GEO. H., 1880.

J. Chem. Soc. **37**, 6–14 ; Ber. **13**, 427 ; Jsb. Chem. 1880, 813.

α-Methyl-hydroxy-succinic Acid.

Acetoacetic ester treated with hydrocyanic acid and then with hydrochloric acid gives, $CH_3 C (OH) CH_2 CO_2 H$,

$CO_2 H$ a crystalline substance, soluble in water, alcohol and ether which melts at 108°. It is the same acid as Demarçay's oxy-pyrotartaric described in *Compt. rend. 82*, 1337. The barium, calcium, potassium, silver, lead and copper salts were described. The three isomeric acids of this formula were shortly discussed.

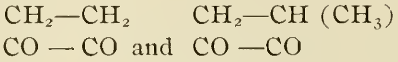
DEMARCAY, E., 1880.

Bull. Soc. chim. **33**, 516–525 and 575–580 and **34**, 31–37 ; J. Chem. Soc. 38, 625.

Tetric and Oxytetric Acids and their Homologues.

Methyl-acetoacetic ester when treated with bromin forms two compounds, $CH_3\ CO\ C\ (CH_3)\ Br\ CO_2\ C_2\ H_5$ and $CH_2\ Br\ CO\ C\ (CH_3)\ Br\ CO_2\ C_2\ H_5$. If these are allowed to stand they form $CH_3\ CO\ C\ (CH_3)\ Br\ H$ and $CH_2\ Br\ CO\ C\ (CH_3)\ Br\ H$, but if treated with alcoholic potash they form tetric, $3\ C_4\ H_4\ O_2 + H_2\ O$, and oxytetric acids, $3\ C_4\ H_4\ O_3 + H_2\ O$. Three sets of salts of tetric acid are formed. (1) $Cu\ O,\ C_4\ H_4\ O_2$; (2) $Ba\ O,\ 2\ C_4\ H_4\ O_2$; (3) $2\ M_2\ O,\ 5\ C_4\ H_4\ O_2$. Phosphoric pentachlorid with tetric acid forms $C_4\ H_4\ OCl_2$ which when treated with chlorin gives $C_4\ H_4\ Cl_4\ O$.

In the above manner, from the alkyl substituted acetoacetic esters, the following acids and many of their salts were produced ; pentic, $3\ C_5\ H_6\ O_2 + H_2\ O$; hexic, $3\ C_6\ H_8\ O_2 + H_2\ O$; heptic, $3\ C_7\ H_{10}\ O_2 + H_2\ O$; oxypentic, $3\ C_5\ H_6\ O_3 + H_2\ O$; oxyhexic, $3\ C_6\ H_8\ O_3 + H_2\ O$; oxyheptic, $3\ C_7\ H_{10}\ O_3 + H_2\ O$, and isohexic and isoxyhexic. The constitution of these was worked out to be ;



$$\begin{array}{l} CH_2\text{—}CH_2 \\ CO\text{ — }CO \end{array} \text{ and } \begin{array}{l} CH_2\text{—}CH\ (CH_3) \\ CO\text{ —}CO \end{array} \quad \text{etc.}$$

HOFMANN, OTTO, 1880.

Ann. Chem. **201**, 73–89 ; Ber. **13**, 431.

Action of Zinc and Allyl Iodid on Acetoacetic and Diethyl-aceto-acetic Esters.

The action is the same as with sodium and an alkyl halogen, that is, with acetoacetic ester the mono- and the di-alkyl acetoacetic esters are produced ; $C_6\ H_9\ (C_3\ H_5)\ O_3$ and $C_6\ H_8\ (C_3\ H_5)_2\ O_3$, when allyl iodid is used. When the diallyl acetoacetic ester is treated with zinc and allyl iodid, diallyl acetic ester, $CH\ (C_3\ H_5)_2\ CO_2\ C_2\ H_5$ is produced.

GUTHZEIT, MAX, 1880.

Ann. Chem. **204,** 1-14; Ber. **13,** 1983; J. Chem. Soc. **38,** 871; Jsb. Chem. 1880, 827.

Octylic-acetoacetic Ester and its Derivatives.

Sodacetoacetic ester treated with octylic iodid, $C_8 H_{17} I$, gives octylicacetoacetic ester, $CH_3 CO CH (C_8 H_{17}) CO_2 C_2 H_5$, which boils at 280° to 282° and has a specific gravity of .9354 at 18.5° It yields the two usual saponification products, methyl nonyl ketone $CH_3 CO C H_2 (C_8 H_{17})$, which boils at 224° to 226°, and octylacetic acid $CH_2 (C_8 H_{17}) CO_2 H$ which is capric acid which boils at 265° to 267° The barium and calcium salts and ethyl ester of this acid were described. Di-octyl-acetoacetic ester is formed by further treatment of the monoctyl derivative with sodium and octyl iodid, it boils at 340° to 342° This upon saponification gives dioctylacetone, boiling at 325° to 330° and dioctylacetic or isostearic acid which melts at 37°-38° and boils at 270° to 275° under 100 m. m. pressure. The barium and silver salts and ethyl ester were described.

BÖCKING, EDUARD, 1880.

Ann. Chem. **204,** 14-26; Ber. **13,** 1983; J. Chem. Soc. **38,** 872. Jsb. Chem. 1880, 812.

Two New Syntheses of Ethyl-methyl-oxy-acetic Acid.

(1) From ethyl-methyl ketone, $C_2 H_5 CO CH_3$, by treating it with hydrocyanic acid and then with hydrochloric acid, $C (C_2 H_5) (CH_3) (OH) CO_2 H$, is produced.

(2) From ethyl-methyl-acetic acid (active valeric) which was obtained from ethyl-methyl-acetoacetic ester by saponification. $CH (CH_3) (C_2 H_5) CO_2 H$ boils at 170° to 175°, when treated with bromin, α brom-ethyl-methyl-acetic acid is produced and this with water gives ethyl-methyl-oxy-acetic acid, $C (C_2 H_5) (CH_3) (OH) CO_2 H$.

WISLICENUS, J., 1880.

Ann. Chem. **206**, 308-313; J. Chem. Soc. **40**, 409; Ber. **14**, 843; Jsb. Chem. 1881, 502; Bull. Soc. chim. **36**, 657.

Decomposition of Polybasic Acetoacetic Esters by Alkalis.

By a great number of experiments it was found that the proportion of ketone or ketonic acid and carbonate increased with the dilution of the alkali and the proportion of acetates or substituted acetates increased with the concentration of the alkali; also that isomers do not give the same proportions of like products.

BISCHOFF, CARL, 1880.

Ann. Chem. **206**, 313-337; J. Chem. Soc. **40**, 412; Jsb. Chem. 1881, 744; Ber. **14**, 844.

Two Homologues of Aceto-propionic Acid.

β-Aceto-isobutyric or α-methyl-aceto-propionic acid, CH_3 CO CH_2 CH (CH_3) CO_2 H, and β-aceto-butyric acid, CH_3 CH ($COCH_3$) CH_2 CO_2 H, were described together with their production and their salts.

CLAISEN, L., 1881.

Ber. **14**, 345-349; J. Chem. Soc. **40**, 405; Jsb. Chem. 1881, 580; Bull. Soc. chim. **36**, 357.

Condensation of Aldehyde with Acetoacetic Ester.

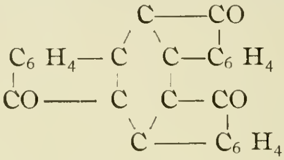
The condensation is effected by passing hydrochloric acid gas through a mixture of the substances. With acetaldehyde, acetethylidenacetic ester, CH_3 CO C (CH CH_3) CO_2 C_2 H_5, is produced. It boils at 210° to 212° and will take up two molecules of bromin. Acetobenzylidenacetic ester, CH_3 CO C (CH C_6 H_5) CO_2 C_2 H_5, produced similarly from benzaldehyde boils at 295° to 297°. This also will take up two molecules of bromin.

GABRIEL, S., 1881.

Ber. **14**, 919-927 ; J. Chem. Soc. **40**, 733 ; Jsb. Chem. 1881, 798; Bull. Soc. chim. **36**, 598.

Condensation Products of Phthalic Anhydrid.

Acetoacetic ester, phthalic anhydrid, $C_6 H_4 (CO)_2 O$, and sodium acetate react together to form ortho-tri-benzoyl-benzene, $C_{27} H_{12} O_3$, and a compound, $C_{12} H_8 O_2$, the composition of which is unknown which boils at 209 to 211 Ortho-tribenzoyl-benzene has the constitution :—



HANTZSCH, A., 1881.

Ber. **14**, 1637-1638 ; J. Chem. Soc. **40**, 1028 ; Jsb. Chem. 1881, 586 ; Bull. Soc. chim. **36**, 569.

Condensation Product of Aldehyde-ammonia and Acetoacetic Ester.

Acetoacetic ester treated with aldehyde-ammonia in presence of zinc chlorid gives $C_{14} H_{21} NO_4$ which melts at 131° and boils at 310°. Boiled with hydrochloric acid it is entirely decomposed, treated with dry hydrochloric acid gas it gives two bases, $C_{11} H_{17} NO_2$, and $C_8 H_{13} N$. It combines with bromin to form $C_{14} H_{19} Br_4 NO_4$, and this treated with nitric acid gives $C_{14} H_{15} Br_4 NO_4$, which melts at 102°. $C_{14} H_{21} NO_4$ can be oxidized to the base, $C_{14} H_{19} NO_4$, which is the ester of collidine-dicarboxylic acid and has the formula $C_5 N (C H_3)_3 (CO_2 C_2 H_5)_2$.

DEICHMÜLLER, A., 1881.

Ann. Chem. **209**, 22-30 ; J. Chem. Soc. **40**, 1162 ; Jsb. Chem. 1881, 1054.

Diabetic Urine.

The author decides that the substance in diabetic urine which produces a red color with ferric chlorid is acetoacetic acid, not the ester of that acid because by acidification and distillation acetone but no alcohol is obtained.

TOLLENS, B., 1881.

Ann. Chem. **209**, 30-38 ; J. Chem. Soc. **40**, 1162 ; Jsb. Chem. 1881, 1054.

Diabetic Urine.

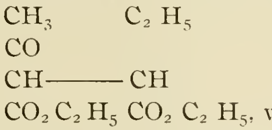
The author decides that the substance in urine of diabetic patients which gives a red color with ferric chlorid is not acetoacetic ester as is claimed, but the free acid of that ester.

THORNE, L. T., 1881.

J. Chem. Soc. **39**, 336-344 ; Ber. **14**, 2238, Jsb. Chem. 1881, 759.

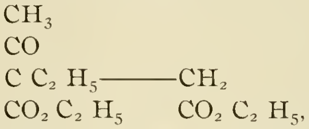
Products of the Action of Alkalis on β-Ethylaceto-succinic Ester.

Acetoacetic ester treated with α-brom-butyric ester gives β-ethyl-aceto-succinic ester,



$$\begin{array}{ll} CH_3 & C_2H_5 \\ CO & \\ CH - & CH \\ CO_2C_2H_5 & CO_2C_2H_5 \end{array}$$

, which boils at 263° and has a specific gravity of 1,064 at 16°. When this is treated with an alkali ethyl-succinic acid is formed which is identical with that produced from α-ethyl-aceto-succinic ester,



$$\begin{array}{ll} CH_3 & \\ CO & \\ C\,C_2H_5 - & CH_2 \\ CO_2C_2H_5 & CO_2C_2H_5 \end{array}$$

, by Huggenberg (Ann. Chem. **192**, 146.) and also α-ethyl-β-aceto-propionic acid, $(CH_3CO)\,CH_2\,CH\,(C_2H_5)\,CO_2H$.

BURTON, BEVERLY S., 1881.

Am. Chem. J. **3**, 385-395 ; J. Chem. Soc. **42**, 599 ; Ber. **15**, 949 ; Jsb. Chem. 1882, 653.

On the Propyl Derivatives and Decomposition Products of Acetoacetic Ester.

Propyl-acetoacetic ester is a liquid which boils at 208° to 209° and has a specific gravity of .981 at 0°.

Di-propyl-acetoacetic ester boils at 235° to 236° and has a specific gravity of .958 at 0°. Quantitive experiments were made in the saponification of these esters and results were obtained, similar to those of

Wislicenus,* which are given in a table. Di-propyl-acetic acid boils at 219.5° and has a specific gravity of .9215 at 0°. Di-propyl-acetone boils at 173° to 174°. Sodium amalgam acting upon di-propyl-aceto-acetic ester failed to produce di-propyl-β-oxy-butyric acid as was expected but decomposition resulted.

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*Ann. Chem. **186**, 161. See pages 10 and 29.

WISLICENUS, J., 1882.

Ann. Chem. **212**, 239-250; J. Chem. Soc. **42**, 934;
Jsb. Chem. 1882, 370.

Comparisons of the Combining Energies of the Halogens and Sodium with Different Organic Residues.

Many experiments were performed with acetoacetic esters and the following results formulated :

1) Towards similar organic residues the combining energy of chlorin is greatest and of iodin is the least.

2) Among compounds of the same halogen with isomeric radicals, the primary show the least and the tertiary the greatest combining energy.

3) The combining energy of iodin for alcohol radicals of the same category (primary or secondary) increases with the molecular weight (addition of CH_2) this increase being the reciprocal of the increase of the molecular weight.

4) The combining energy of the halogen is considerably less when the residue is an unsaturated primary alcohol radical (allyl for example) but is considerably increased when the halogen is united to a primary but unsaturated carbon atom (vinyl iodid for example.)

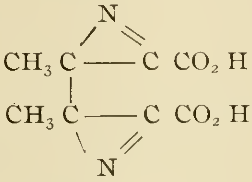
5) A diminution of combining energy is produced by linking of CH_2 group united with the halogen to carboxyl. The author also shows that the combining energy of the sodium in the sodium-acetoacetic esters is greater than that of the sodium in the sodium-alkyl-acetoacetic esters.

WLEÜGEL, S., 1882.

Ber. **15**, 1050–1056; J. Chem. Soc. **42**, 949; Jsb. Chem. 1882, 839; Bull. Soc. chim. **38**, 389.

Upon the Knowledge of Nitroso-acetoacetic Esters.

Since of the three compounds formed by the treatment of acetoacetic ester with nitrous acid, namely: (1) the nitroso-acetoacetic ester; (2) nitroso–propionic acid and (3) nitroso-acetone, only the second can be reduced to an amid, while the third forms a ketine, the author investigates the action of nascent hydrogen on the first, nitroso-acetoacetic ester, and obtained a dibasic acid which he calls ketindicarboxylic acid, $C_8H_8N_2O_4$. The barium, silver, potassium, ammonium and lead salts were described. The author advances the structural formula



PROPPER, MAX, 1882.

Ber. **15**, 1154; J. Chem. Soc. **42**, 1193.

Action of Fuming Nitric Acid on Acetoacetic and on Mono-chlor-acetoacetic Esters.

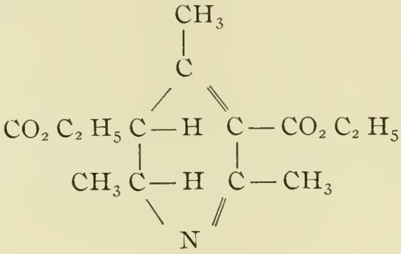
A preliminary notice stating that the author has obtained nitroso-acetic and mono-chlor nitrosoacetic esters by these reactions.

HANTZSCH, A., 1882.

Ann. Chem, **215**, 1–82 ; J. Chem. Soc. **44**, 82 ; Ber. **15**, 2912 ; Jsb. Chem. 1882, 491.

Synthesis of Pyridin Derivatives from Acetoacetic Ester and Aldehyde-Ammonia.

The condensation product of acetoacetic ester and aldehyde-ammonia is dihydrocollidin-dicarboxylic ester,



The author describes this and many of its derivatives.

CERESOLE, M., 1882.

Ber. **15**, 1326–1328 ; J. Chem. Soc. **42**, 1052 ; Jsb. Chem. 1882, 758 ; Bull. Soc. chim. **38**, 390.

Nitrosoacetone and Acetoacetic Acid.

By allowing a mixture of acetoacetic ester and potassium hydroxid to stand a day and then treating it with an acid, acetoacetic acid is produced. This is the first production of it. It is a colorless liquid, mixes with water and is strongly acid. It is very unstable, decomposing at less than 100°.

DUISBERG, C., 1882.

Ber. **15**, 1378-1388 ; Ann. Chem. **213**, 133-181 ; J. Chem. Soc. **42**, 1192 ; Jsb. Chem. 1882, 841 ; Bull. Soc. chim. **38**, 391.

Contribution to the Knowledge of Acetoacetic Ester.

By treating acetoacetic ester with bromin the author cannot get Lippmann's dibrom addition product or Conrad's dibrom addition dibrom substitution product but gets the five successive substitution products and describes each one. The monobrom product treated with ammonia gives $C_6 H_8 O_3$, the ethyl ester of an acid which the author names oxytetrolic. This ester is also produced if sodium act in place of ammonia, and the acid can be obtained by treating the ester with sodium hydroxid. Oxytetrolic acid has just half the molecular formula of Herrmann's succinosuccinic ester (Ann. Chem. **211**, 306). Passing ammonia through acetoacetic ester gives a substance which melts at 20° to 21° which the author calls paramidoacetoacetic ester. Passing hydrochloric acid gas through acetoacetic ester gives a substance $C_8 H_{10} O_3$, which boils at 290° to 295° and the author calls it carbacetoacetic ester.

GOTTSTEIN, L., 1882.

Ann. Chem. **216**, 29–38; J. Chem. Soc. **44**, 454; Ber. **16**, 403; Jsb. Chem. 1882, 869.

Two New Caprolactones.

When acetoacetic ester is treated with *α* brom propionic ester; *β* acetoisobutyric acid can be obtained, and when sodium amalgam acts upon this, *α* methyl valero-lactone, $CH_3CH{<}\substack{CH_2\\CO_2}{>}CHCH_3$ is formed. *β* Methyl valero-lactone, $CH_2{<}\substack{CHCH_3\\CO_2}{>}CH\,CH_3$, can be formed in an impure state by the action of sodium amalgam on *β* acetobutyric acid, $CH_3CH(C_2H_3O)CH_2CO_2H$, which is formed from acetosuccinic ester.

JAKSCH, R. v., 1882.

Ber. **15**, 1496; J. Chem. Soc. **42**, 1120; Jsb. Chem. 1882, 1219.

Occurrence of Acetoacetic Acid in Urine.

The substance occurring in diseased urine, which gives a red color with ferric chlorid, is proven to be acetoacetic acid.

HALLER, A. AND A. HELD, 1882.

Compt. rend. **95**, 235-237; J. Chem. Soc. **42**, 1280; Jsb. Chem. 1882, 845.

Cyanacetoacetic Ester and its Derivatives.

Cyanacetoacetic ester, $CH_3\,CO\,CH\,(CN)\,CO_2\,C_2\,H_5$, was produced by passing cyanogen chlorid into sodacetoacetic ester. It is a solid, melts at 26° and remains in a superfused condition even at—15°; the liquid has a specific gravity of 1.102 at 19° Potassium hydroxid decomposes it. The sodium and calcium derivatives were described.

SCHMID, WILHELM, 1882.

J. prakt. Chem. **133**, 81–83.

New Method of Producing Resocyanin.

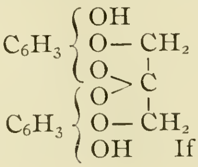
Acetoacetic ester and resorcin react in the presence of zinc chlorid to form resocyanin, which is: $C_6H_3(OH)_2C(CH_3):CHCO_2H$ [C : OH : OH = 1 : 2 : 4].

WITTENBERG, MAX, 1882.

J. prakt. Chem. **134**, 66–78; J. Chem. Soc. **42**, 1289; Ber. **15**, 2908; Jsb. Chem. 1882, 716; Bull. Soc. chim. **39**, 72.

Resocyanin and the Action of Acetoacetic Ester on Phenols in Presence of Dehydrating Agents.

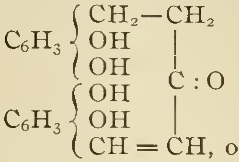
Pyrogallol, $C_6H_3(OH)_3$, and acetoacetic ester react in the presence of sulfuric acid to form allylene-digallein, $C_{15}H_{12}O_6$, which melts at 235° and has the constitution:



$$\begin{array}{l} C_6H_3\left\{\begin{array}{l}OH\\ O-CH_2\\ O\end{array}\right. \\ \qquad\qquad\qquad >C \\ C_6H_3\left\{\begin{array}{l}O\\ O-CH_2\\ OH\end{array}\right. \end{array}$$

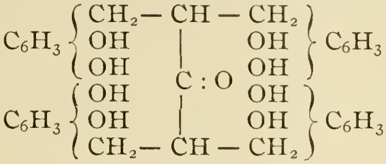
If orcinol, $C_6H_3(CH_3)(OH)_2$,

be used, a substance is produced which answers either to the formula $C_{17}H_{16}O_5$, which would be



$$\begin{array}{l}C_6H_3\left\{\begin{array}{l}CH_2-CH_2\\OH\qquad|\\OH\qquad|\end{array}\right.\\ \qquad\qquad\quad C:O\\ C_6H_3\left\{\begin{array}{l}OH\qquad|\\OH\qquad|\\CH=CH\end{array}\right.\end{array}$$

, or to the formula $C_{31}H_{30}O_9$, which is



$$\begin{array}{l}C_6H_3\left\{\begin{array}{lcl}CH_2- & CH & -CH_2\\OH & | & OH\\OH & | & OH\end{array}\right\}C_6H_3\\ \qquad\qquad\qquad C:O\\ C_6H_3\left\{\begin{array}{lcl}OH & | & OH\\OH & | & OH\\CH_2- & CH & -CH_2\end{array}\right\}C_6H_3\end{array}$$

CERESOLE, M., 1882.

Ber. **15**, 1871-1878 ; J. Chem. Soc. **44**, 41 ; Jsb. Chem. 1882, 860 ; Bull. Soc. chim. **39**, 35.

Acetoacetic Acids.

Acetoacetic acid, methyl-, dimethyl- and benzyl-acetoacetic acids were prepared by treating their esters with an alkali in the cold, proving this to be an intermediate action in the ordinary saponification of these esters. The ease with which these compounds decompose, as they do below 100°, is attributed to the position of the carbonyl and carboxyl groups separated by only one methylene or alkyl substituted methylene group.

CONRAD, M., 1882.

Ber. **15**, 2133–2134 ; J. Chem. Soc. **44**, 177 ; Jsb. Chem. 1882, 845.

Halogen Substituted Acetoacetic Esters.

The author admits that his formerly described dibrom-acetoacetic dibromid * is probably only Duisberg's tetrabrom-acetoacetic ester.†

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* See page 11.
† See page 34.

LIPPMANN, E., 1882.

Ber. **15**, 2142—2144. Jsb. Chem. 1882, 845.

The Position of Bromin in Acetoacetic Ester.

The author insists upon the correctness of his former statement, which Duisberg denies, that a dibrom-addition dibrom-substitution product of acetoacetic ester, $C_6H_8Br_2O_3Br_2$, exists.

MATTHEWS, A. E. AND W. R. HODKINSON, 1882.

Ber. **15**, 2679 ; J. Chem. Soc. **44**, 311 ; Jsb. Chem. 1882, 839.

Production of Acetoacetic Ester.

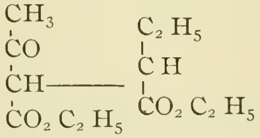
Monochlor acetone, CH_3COCH_2Cl, was treated with potassium cyanid and the cyanid of acetone, $CH_3COCH_2(CN)$, was obtained. This, when treated with hydrochloric acid, gave acetoacetic ester.

YOUNG, SIDNEY, 1882.

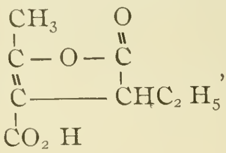
Ann. Chem. **216**, 45–52 ; J. Chem. Soc. **44**, 456 ; Ber. **16**, 405 ; Jsb. Chem. 1882, 883.

Peculiar Decomposition of Substituted Acetoacetic Esters.

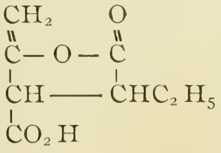
When β-ethyl-aceto-succinic ester, , is heated it breaks down into ketolactonic ester which can be changed into keto-lactonic acid, , or



$$\begin{array}{ll} CH_3 & \\ | & C_2H_5 \\ CO & | \\ | & CH \\ CH \text{———} & | \\ | & CO_2C_2H_5 \\ CO_2C_2H_5 & \end{array}$$



$$\begin{array}{lll} CH_3 & & O \\ | & & \| \\ C & -O- & C \\ \| & & | \\ C & \text{———} & CHC_2H_5 \\ | & & \\ CO_2H & & \end{array}$$



$$\begin{array}{lll} CH_2 & & O \\ \| & & \| \\ C & -O- & C \\ | & & | \\ CH & \text{———} & CHC_2H_5 \\ | & & \\ CO_2H & & \end{array}$$

JANNY, ALOIS, 1882.

Ber. **15**, 2778–2783.

Acetoxim.

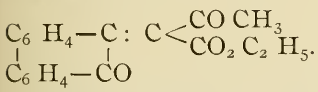
Near the close of this article the author records having treated acetoacetic ester with hydroxylamin and obtaining a very stable, nitrogenous acid body.

JAPP, FRANCIS R. AND F. W. STREATFEILD, 1883.

J. Chem. Soc. **43**, 27–34.

Condensation Product of Phenanthraquinone with Acetoacetic Ester.

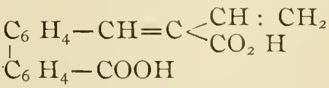
These substances will condense in presence of either ammonia or an alkali, preferably the latter, to form phenanthroxylene-acetoacetic ester which is:—



$$\begin{array}{l} C_6H_4-C:C<\begin{matrix}CO\,CH_3\\ CO_2\,C_2H_5.\end{matrix} \\ \ \ |\qquad\ \ | \\ C_6H_4-CO \end{array}$$

It decomposes at 184.5 –185.5

It was reduced by hydriodic acid by which the acetyl oxygen was removed giving phenanthroxylene-isocrotonic ester. This was dissolved in an alkali and by adding an acid another substance was produced which was:—



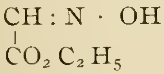
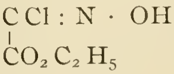
$$\begin{array}{l} C_6H_4-CH=C<\begin{matrix}CH:CH_2\\ CO_2\,H\end{matrix} \\ \ \ | \\ C_6H_4-COOH \end{array}$$

The investigation is being continued.

PROPPER, MAX, 1883.

Ber. **16**, 67 ; Ann. Chem. **222**, 46 ; J. Chem. Soc. **44**, 573 ; Ber. **17**, 14 (c).

Action of Fuming Nitric Acid on Acetoacetic and on Mono-chlor-acetoacetic Esters.

The author has decided after further study that the two compounds, $C_4H_7O_3N$ and $C_4H_6ClO_3N$, obtained by these reactions are oximido bodies,  $\begin{array}{l}CH:N\cdot OH\\ |\\ CO_2\,C_2H_5\end{array}$, and  $\begin{array}{l}C\,Cl:N\cdot OH\\ |\\ CO_2\,C_2H_5\end{array}$, not nitroso bodies, as he thought at first. His principal reason for this belief is that no corresponding body can be formed from the dichlor-acetoacetic ester as should be the case if it were the monad nitroso group which was introduced.

CLAISEN, L. AND F. E. MATTHEWS, 1883.

Ann. Chem. **218**, 170–185; J. Chem. Soc. **46**, 443; Jsb. Chem. 1883, 963; Bull. Soc. chim. **40**, 473.

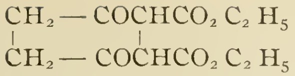
Condensation of Acetoacetic Ester with Aldehydes.

By treating acetoacetic ester with aldehydes, the following two compounds are formed, the first one much more easily than the second, $CH_3 CO C : (: CHR) CO_2 C_2 H_5$ and $CH : (: CHR) COCH_2 CO_2 C_2 H_5$. Acet-ethylidenacetic ester, $CH_3 COC : (: CHCH_3) CO_2 C_2 H_5$, made by passing hydrochloric acid gas through a mixture of acetoacetic ester and aldehyde is a colorless liquid which boils at 210° to 212°. Its specific gravity is 1.022 at 15°. It easily changes back into aldehyde and acetoacetic ester. The following were prepared and described. Acetisobutylidenacetic ester, $C_6 H_8 (C_4 H_8) O_3$; acetisamylidenacetic ester, $C_6 H_8 (C_5 H_{10}) O_3$; acet-trichlor-ethyliden acetic ester, $C_6 H_8 (C_2 HCl_3) O_3$, which is *α* aceto-trichlor-crotonic ester; aceto-furfural acetic ester, $C_6 H_8 (C_5 H_4 O) O_3$, which is *α* acet–furfuracrylic ester; aceto benzal acetic ester $C_6 H_8 (CHC_6 H_5) O_3$, which is *α* acet-cinnamic ester; benzal-acetoethylacetic ester, $C_6 H_5 CH : CHCOCH (C_2 H_5) CO_2 C_2 H_5$; and benzalacetodiethylacetic ester, $C_6 H_5 CH : CHCOC (C_2 H_5)_2 CO_2 C_2 H_5$.

DUISBERG, C., 1883.

Ber. **16**, 133–139; Jsb. Chem. 1883, 1112.

Converting Acetoacetic Ester into Succinosuccinic Ester which is Convertable into Hydroquinone.

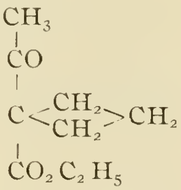
Succinic ester, made from acetoacetic ester, was treated with sodium and sodium succinosuccinic ester, $C_{12}H_{14}O_6Na_2$, prepared. As in dry acetic ester, the sodium caused no reaction even at 100° until some sodium ethoxid was added. Sodium succinosuccinic ester which has the formula  $\begin{array}{l} CH_2 - COCHCO_2C_2H_5 \\ | \qquad\quad | \\ CH_2 - COCHCO_2C_2H_5 \end{array}$ melts at 127° and was found to be identical with the substance produced from brom-acetoacetic ester and sodium. This can be changed into hydroquinone, $C_6H_4(OH)_2$, so that these reactions show a case of changing an acid of the fatty series (acetic) into a benzene ring.

PERKIN, Jr., W. H., 1883.

Ber. **16**, 208-210; Jsb. Chem. 1883, 1015; Bull. Soc. chim. **40**, 46.

Action of Trimethylene Bromid on Sod-acetoacetic Ester.

This reaction gives acetotetramethylene carboxylic ester,



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ C < \begin{array}{c} CH_2 \\ CH_2 \end{array} > CH_2 \\ | \\ CO_2C_2H_5 \end{array}$$

which boils at 223° to 225°. From this the acid and the silver salt of the acid can be obtained.

DUISBERG, C., 1883.

Ber. **16**, 295-297; J. Chem. Soc. **44**, 656.

Addition of Bromin to Acetoacetic Ester.

This article is a reply to Lippmann and Conrad on this subject. The author declares that acetoacetic ester is saturated and cannot form an addition product.

CHANCEL, G., 1883.

Compt. rend. **96**, 1466-1470; J. Chem. Soc. **44**, 914; Jsb. Chem. 1883, 1078; Ber. **16**, 1495.

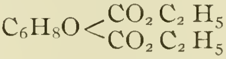
New Method of Synthesis of Alkylnitrous Acids.

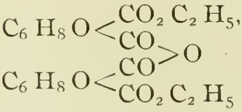
Acetoacetic ester and its alkyl derivatives are treated with nitric acid and then with alcoholic potash when the nitrites are formed. Treated in this manner acetomethyl-acetic ester yields potassium ethyl nitrite, $CH_3C(NO_2)_2K$. Ethyl-acetoacetic ester gives potassium propyl nitrite, $CH_3CH_2C(NO_2)_2K$. Propyl-acetoacetic ester boils at 212° at 750 m.m. pressure and has a specific gravity of .979 at 0.° When treated with nitric acid it gives potassium butyl nitrite, $CH_3CH_2CH_2C(NO_2)_2K$. By acidifying the latter butyl nitrous acid is obtained, which boils with some decomposition at 197° and has a specific gravity of 1.205 at 15.°

HANTZSCH, A., 1883.

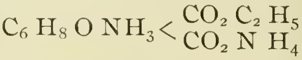
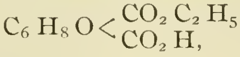
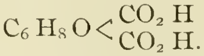
Ber. **16**, 740-742 ; J. Chem. Soc. **44**, 1083.

Condensation Products of Acetoacetic Esters.

Strong sulfuric acid acting on acetoacetic ester produces (1) mesityl-oxid-di-carboxylic ester,  $C_6H_8O<\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}$ (2) mesityl-oxid-anhydro-dicarboxylic ester,



$$\begin{matrix}C_6H_8O<\begin{matrix}CO_2C_2H_5,\text{ and}\\CO\end{matrix}\\ \qquad >O\\ C_6H_8O<\begin{matrix}CO\\CO_2C_2H_5\end{matrix}\end{matrix}$$

(3) a crystalline body, polymeric with dehydracetic acid which is a dibasic acid, the formula for which is probably $C_{14}H_{14}O_7$; the name metadehydracetic acid is proposed for it. Ammonia acts on mesityl-oxid-anhydrodicarboxylic ester to form a salt  $C_6H_8ONH_3<\begin{matrix}CO_2C_2H_5\\CO_2NH_4\end{matrix}$ which with hydrochloric acid gives  $C_6H_8O<\begin{matrix}CO_2C_2H_5\\CO_2H,\end{matrix}$ which in turn can be saponified to  $C_6H_8O<\begin{matrix}CO_2H\\CO_2H.\end{matrix}$

CERESOLE, M., 1883.

Ber. **16**, 830-832.

Diethyl-acetoacetic Acid.

Diethyl-acetoacetic ester is allowed to stand several weeks with a 10% solution of potassium hydroxid, the salt produced is treated with hydrochloric acid and diethyl-acetoacetic acid, $CH_3CO\,C(C_2H_5)_2CO_2H$, is thus produced. It is very unstable, decomposing at 60 into diethyl-acetone, $CH_3\,CO\,CH\,(C_2H_5)_2$, which boils at 135° to 137°. Diethyl-acetoacetate of sodium was produced.

ELION, H., 1883.

Rec.* trav. chim. **2**, 33-34 and 202-204 ; Ber. **16**, 1368 and 2762.

Diacetyl-acetic Ester.

By treating ethyl-acetoacetic ester with water-free, sodium hydroxid and the product with acetyl chlorid, ethyl-diacetyl-acetic ester was produced, it boils at 235°. Acetoacetic ester treated thus gives diacetyl-acetic ester which boils at 210° to 213° with some decomposition, its specific gravity is 1.1 at 15°. It is decomposed by boiling with water.

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* Original article not consulted.

MATTHEWS, F. E., 1883.

J. Chem. Soc. **43**, 200-207 ; Ber. **16**, 1372.

Condensation Products of Aldehydes with Acetoacetic Ester and some Substituted Acetoacetic Esters.

This article is almost the same as the one by Claisen and Matthews in †Ann. Chem. **218**, 170. The author concludes that all aldehyde condensations with acetoacetic ester take place with the methylene group and are easily accomplished because of the position of the methylene group between the carbonyl and carboxyl groups, but that such condensations with mono-or di-substitution acetoacetic ester take place in the methyl group and consequently are more difficult to accomplish.

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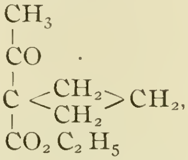
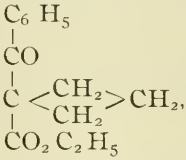
† See page 40.

PERKIN, Jr., W. H., 1883.

Ber. **16**, 1787-1789; J. Chem. Soc. **44**, 1083; Jsb. Chem. 1883, 1015.

Action of Trimethylene Bromid on Acetoacetic, Benzoylacetic and Malonic Esters.

By the action of trimethylene bromid on acetoacetic ester, aceto-tetramethylene carboxylic ester,  $\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ C<{}^{CH_2}_{CH_2}>CH_2 \\ | \\ CO_2\,C_2\,H_5 \end{array}$, is formed which is isomeric but not identical with allyl-acetoacetic ester. From this is obtained aceto-tetramethylene, $CH_3\,CO\,CH\ (CH_2)_3$, which boils at 109°-110°.

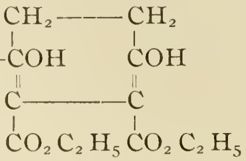
Benzoyl-tetra-methylene carboxylic ester,  $\begin{array}{l} C_6\,H_5 \\ | \\ CO \\ | \\ C<{}^{CH_2}_{CH_2}>CH_2 \\ | \\ CO_2\,C_2\,H_5 \end{array}$, was formed from tri-methylene-bromid and benzoyl-acetic ester and from it the acid, the silver salt and benzoyl-tetra-methylene, $C_6\,H_5\,CO\,CH\ (CH_2)_3$, were obtained.

WEDEL, WILHELM, 1883.

Ann. Chem. **219**, 71-119; J. Chem. Soc. **46**, 834; Jsb. Chem. 1883, 1060; Bull. Soc. chim. **41**, 181; Ber. **16**, 2288.

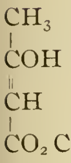
Derivatives of Acetoacetic Ester.

By treating dibrom-acetoacetic ester with sodium, an ester, $C_6\,H_7\,O_3$, is produced and from this its acid, $C_4\,H_3\,O_3$. These resemble in properties Duisberg's oxytetrolic acid and ester, but the author decides that the ester is identical with Herrmann's quinon-hydrodicarboxylic ester of the formula $C_{12}\,H_{14}\,O_6$. By the action of acetyl chlorid on this ester, a diacetyl compound is formed which the author takes as proof of the existance of the hydroxyl group in both quinon-hydrodicarboxylic ester and acetoacetic ester thus:—



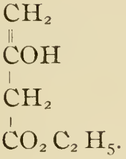
$$\begin{array}{lcl} CH_2 & \text{———} & CH_2 \\ | & & | \\ COH & & COH \\ \| & & \| \\ C & \text{———} & C \\ | & & | \\ CO_2C_2H_5 & & CO_2C_2H_5 \end{array}$$

and



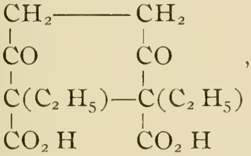
$$\begin{array}{l} CH_3 \\ | \\ COH \\ \| \\ CH \\ | \\ CO_2C_2H_5 \end{array}$$

or



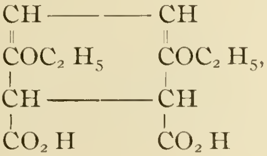
$$\begin{array}{l} CH_2 \\ \| \\ COH \\ | \\ CH_2 \\ | \\ CO_2C_2H_5 \end{array}$$

. By the action of bromin on acetoacetic ester the mono-, di-, and tri-derivatives only could be formed, therefore it was decided that all compounds seeming to have more than three atoms of bromin are mixtures containing some per-brom-acetoacetic ester, $C_6Br_{10}O_3$, which was formed and which melts at 79°-80°. By heating mono-brom-ethyl-acetoacetic ester ethyl-succino-succinic acid is produced, which is



$$\begin{array}{lcl} CH_2 & \text{———} & CH_2 \\ | & & | \\ CO & & CO \\ | & & | \\ C(C_2H_5) & \text{—} & C(C_2H_5) \\ | & & | \\ CO_2H & & CO_2H \end{array}$$

, according to the common formula for acetoacetic ester or



$$\begin{array}{lcl} CH & \text{———} & CH \\ \| & & \| \\ COC_2H_5 & & COC_2H_5 \\ | & & | \\ CH & \text{———} & CH \\ | & & | \\ CO_2H & & CO_2H \end{array}$$

, according to the author's formula. Acetoacetic ester is decomposed by being heated to 140° with acetic acid. Acetyl chlorid decomposes acetoacetic ester and some carbacetoacetic ester is formed, which shows the presence of hydroxyl in acetoacetic ester with which the acetyl chlorid formed hydrochloric acid which produced the carbacetoacetic ester. Glycolic, oxalic and succinic acids decompose acetoacetic ester into carbon dioxid and acetone.

HANTZSCH, A., 1883.

Ber. **16,** 1946-1948 ; J. Chem. Soc. **44,** 1082 ; Jsb. Chem. 1883, 1068.

Condensation of Acetoacetic Methyl Ester with Aldehyde-ammonia.

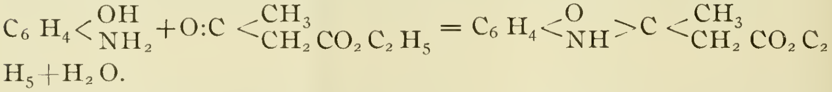
This condensation is entirely similar to that with the ethyl ester, a dihydro-collidin-dicarboxylic methyl ester, $C_5NH_2(CH_3)_3(CO_2CH_3)_2$, being formed. From this were formed dihydro-collidin-monocarboxylic methyl ester, $C_5NH_2(CH_3)_3H(CO_2CH_3)$, and collidin-dicarboxylic methyl ester, $C_5N(CH_3)_3(CO_2CH_3)_2$.

HANTZSCH, A., 1883.

Ber. **16,** 1948-1952 ; J. Chem. Soc. **44,** 1111 ; Jsb. Chem. 1883, 1069 ; Bull. Soc. chim. **42,** 182.

Condensation of Acetoacetic Ester and Ortho-amidophenol.

These substances condense as follows :



$$C_6H_4<\begin{matrix}OH\\NH_2\end{matrix}+O{:}C<\begin{matrix}CH_3\\CH_2CO_2C_2H_5\end{matrix}=C_6H_4<\begin{matrix}O\\NH\end{matrix}>C<\begin{matrix}CH_3\\CH_2CO_2C_2H_5\end{matrix}+H_2O.$$

The product, very unstable, being easily decomposed into its components, melts at 107°-108°. A potassium salt, $C_{24}H_{29}KO_6N_2$, was formed ; one hydrogen atom of the amid group of every two molecules apparently being replaceable.

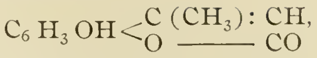
PECHMANN, H. v. AND C. DUISBERG, 1883.

Ber. **16,** 2119-2128 ; J. Chem. Soc. **46,** 66 ; Jsb. Chem. 1883, 1065; Bull. Soc. chim. **42,** 587.

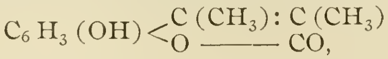
Compounds of Phenols and Acetoacetic Ester.

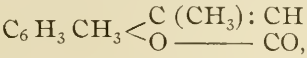
In the presence of a dehydrating agent phenols and acetoacetic ester react to form substituted coumarins.

If resorcin, $C_6H_4(OH)_2$, is used β-methyl-umbelliferone,


$$C_6H_3OH<\begin{array}{l}C(CH_3):CH,\\ O\text{———}CO\end{array}$$

is formed which when treated with potassium hydroxid gives resacetophenon, $C_6H_3(OH)_2COCH_3$. The methyl ester and the carboxylic acid of β-methyl-umbelliferone were formed. α-β-Di-methyl-umbelliferone,

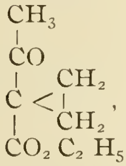

$$C_6H_3(OH)<\begin{array}{l}C(CH_3):C(CH_3)\\ O\text{———}CO,\end{array}$$

was formed from resorcin and dimethyl-acetoactic ester. Metatoluene-β-methyl-coumarin,  $C_6H_3CH_3<\begin{array}{l}C(CH_3):CH\\ O\text{———}CO,\end{array}$ was formed from para-cresol, $C_6H_4OHCH_3$, and acetoacetic ester.

PERKIN, Jr., W. H., 1883.

Ber. **16**, 2136-2140 ; J. Chem. Soc. **46**, 64.

Action of Ethylene Bromid on Acetoacetic and Benzoyl=acetic Esters.

From acetoacetic ester, ethylene bromid and sodium, aceto-trimethylene carboxylic ester,  $\begin{array}{l}CH_3\\ \,|\\ CO\\ \,|\quad CH_2\\ C<|\\ \,|\quad CH_2\\ CO_2C_2H_5\end{array}$, is formed, which boils at 193° to 195°. The acid and the silver salt were obtained. Benzoyl-trimethylene carboxylic ester and acid and benzoyl-trimethylene were also produced.

GEUTHER, A., 1883.

Ann. Chem. **219**, 119-128 ; J. Chem. Soc. **46**, 836 ; Ber. **16**, 2290 ;
Jsb. Chem. 1883, 1065.

Constitution of Acetoacetic Esters and of Benzene.

The formation of tri-brom-acetoacetic ester by Wedel and the formation of acetoacetic ester from acetic ester are cited as proof of the formula $CH_3COH:CHCO_2C_2H_5$ and against $CH_2:COHCH_2CO_2$

C_2H_5. Attention is called to the colors produced by acetoacetic compounds and phenol compounds with ferric chlorid as indicating by their similarity that these bodies are similarly constituted. Comment is made upon changing the fatty acid into the benzene ring as pointed out by Wedel, that is, acetic ester into acetoacetic ester and this into quinonehydrodicarboxylic ester and this finally into hydroquinone.

JAKSCH, R. v., 1883.

*Ztschr. physiol. Chem. **7**, 487-490, Ber. **16**, 2314.

Acetoacetic Acid in Urine.

The author states that he published a paper in 1880 identifying acetoacetic acid in urine, he therefore claims priority to Tollens † (Ber. **14**, 2594).

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* Original article not consulted.

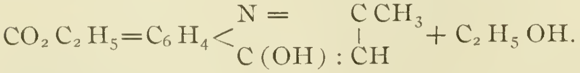
† See page 31.

KNORR, L., 1883.

Ber. **16**, 2593–2596; J. Chem. Soc. **46**, 334; Bull. Soc. chim. **42**, 654.

New Synthesis of Quinolin Derivatives.

By varied conditions a reaction between acetoacetic ester and anilin is obtained which forms the compound $CH_3C(NC_6H_5)CH_2CO_2C_2H_5$, which is very unstable. If the reaction be interrupted by adding sulfuric acid, γ oxy-α-methyl quinolin is obtained, which comes from the compound cited above by its losing alcohol thus: $CH_3C(NC_6H_5)CH_2$



$$CO_2C_2H_5 = C_6H_4 < \begin{array}{ll} N = & C\,CH_3 \\ & \,| \\ C(OH) : & CH \end{array} + C_2H_5OH.$$

It melts at 222 The intermediate anilin-acetoacetic acid, $CH_3C(NC_6H_5)CH_2CO_2H$, was also obtained.

KNORR, L., 1883.

Ber. **16,** 2597–2599; J. Chem. Soc. **46,** 302; Jsb. Chem. 1883, 795; Bull. Soc. chim. **42,** 655.

Action of Acetoacetic Ester on Phenylhydrazin.

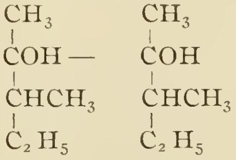
When these substances react there is formed $CH_3\,C\,(HN_2\,C_6\,H_5)\,CH_2\,CO_2\,C_2\,H_5$. If this be heated on the water bath alcohol is given off and a body $C_{10}\,H_{10}\,N_2\,O$, is left which melts at 127°; it resembles carbostyril; its constitution is unknown. When it is heated with an excess of phenylhydrazin its anhydrid $C_{20}\,H_{18}\,N_4\,O$ is produced, which from its reactions is shown to contain a hydroxyl group.

WISLICENUS, J., 1883.

Ann. Chem. **219,** 307–321; J. Chem. Soc. **44,** 966; Jsb. Chem. 1883, 980.

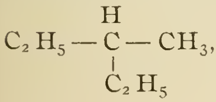
Methyl-β-butyl Ketone and its Derivatives.

Ethyl-methyl-acetoacetic ester is saponified and methyl-β-butyl ketone, $CH_3\,COCH\,(CH_3)\,(C_2\,H_5)$, obtained, it boils at 118° and has a specific gravity of .818 at 14.5°. By treating it with sodium and water two products were obtained, methyl-β-butyl carbinol, $CH_3\,CHOHCH—(CH_3)(C_2H_5)$, and methyl-β-butyl pinacone,



$$\begin{array}{ll} CH_3 & CH_3 \\ | & | \\ COH\,— & COH \\ | & | \\ CHCH_3 & CHCH_3 \\ | & | \\ C_2\,H_5 & C_2\,H_5 \end{array}$$

Methyl-β-butyl carbinol is changed into the iodid and then by substituting hydrogen for this iodin methyl-di-ethyl-methane,



$$C_2\,H_5 — \overset{H}{\underset{\underset{C_2\,H_5}{|}}{C}} — CH_3,$$

is formed.

HECKMANN, JACOB, 1883.

Ann. Chem. **220,** 128-146; Ber. **16,** 2675; J. Chem. Soc. **46,** 178; Jsb. Chem. 1883, 1147; Bull. Soc. chim. **42,** 54.

Dinitro-phenyl-acetoacetic Ester.

By treating sodacetoacetic ester with dinitro-brom-benzene, dinitro-phenyl-acetoacetic ester, $CH_3\ CO\ C\ H\ [C_6\ H_3\ (NO_2)_2]\ CO_2\ C_2\ H_5$, is produced, it is crystalline and melts at 94°. From this is produced, by potassium hydroxid, ortho-para-dinitrophenyl acetic acid, $CH_2\ C_6\ H_3\ (NO_2)_2\ CO_2\ H$, which melts at 160° and some di-nitro-toluol, $C_6\ H_3\ CH_3\ (NO_2)_2$. By means of boiling alkalis several complicated decomposition products are obtained $C_{24}\ H_{18}\ N_6\ O_{15}$, melting at 105.5° and from this, $C_{24}\ H_{16}\ K_2\ N_6\ O_{15}$, $C_{48}\ H_{32}\ N_6\ O_{19}$ and a silver salt $C_{48}\ H_{29}\ Ag_3\ N_6\ O_{19}$.

PAAL, C., 1883.

Ber. **16,** 2865–2869; J. Chem. Soc. **46,** 598; Jsb. Chem. 1883, 1220; Bull. Soc. chim. **42,** 541.

Action of Brom-acetophenon on Sodacetoacetic Ester.

These substances react with separation of sodium bromid to form $CH_3\ COCH\ (CH_2\ COC_6\ H_5)\ CO_2\ C_2\ H_5$, which easily decomposes into the acid and then into acetophenonacetone, $(C_6H_5COCH_2)CH_2COCH_3$. When acetophenonacetoacetic ester is boiled with potassium hydroxid an acid $C_{12}\ H_{10}\ O_3$, is formed by the separation of alcohol and water.

ROSER, W., 1883.

Ann. Chem. **220,** 271–278; J. Chem. Soc. **46,** 423.

Isopropyl-succinic or Pimelic Acid.

Isopropyl-succinic acid was made from acetoacetic ester, mono-chloracetic ester and isopropyl iodid, the acetyl being removed and the ester obtained being changed to the acid. This was proven to be identical with pimelic acid $CH\ (CH_3)_2—CH <\begin{matrix} CO_2\ H \\ CH_2\ CO_2\ H, \end{matrix}$ obtained from camphoric acid.

WESTENBERGER, BERNHARD, 1883.

Ber. **16**, 2991–2998; J. Chem. Soc. **46**, 581; Jsb. Chem. 1883, 978; Bull. Soc. chim. **42**, 444.

Isonitroso Bodies.

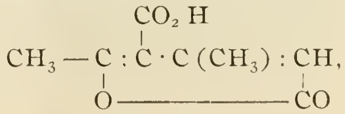
The action of hydroxylamin on acetoacetic ester is given on page 2996 of this article. From this reaction β-isonitroso-butyric ester, $CH_3C(NOH)CH_2CO_2C_2H_5$, results which is very unstable. The acid is formed from it. Isonitroso-methyl-acetoacetic ester, $CH_3C(NOH)CH(CH_3)CO_2C_2H_5$, and the corresponding ethyl- and diethyl- products were produced from the corresponding substituted acetoacetic esters, proving the reaction to be a general one.

HANTZSCH, A., 1883.

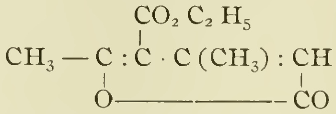
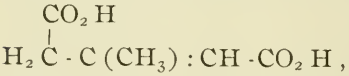
Ann. Chem. **222**, 1–46; Ber. **17**, 12 (C); Jsb. Chem. 1883, 1070; Bull. Soc. chim. **42**, 502.

Condensation Products of Acetoacetic Ester.

Acetoacetic ester treated with sulfuric acid gives a condensation product $C_{18}H_{22}O_9$, which is formed from four molecules of acetoacetic ester by the separation of three molecules of alcohol. Its formula is $C_6H_7\left\{\begin{matrix} OH & CO_2C_2H_5 \\ CO_2H & CO_2H \\ CO-O & \end{matrix}\right\}C_6H_7$. When treated with potassium hydroxid and an acid it yields two products, 1) $C_6H_7\left\{\begin{matrix} O \\ CO > \\ CO_2H \end{matrix}\right.$, called mesiten-lactone-carboxylic acid, and 2) its ethyl ester. The radical $(C_6H_9)'$ being designated as mesiten. The mesiten-lactone-carboxylic acid or isodehydracetic acid has the formula



$$CH_3 - \underset{\displaystyle \overset{|}{O}}{C} : \overset{\displaystyle CO_2H}{\overset{|}{C}} \cdot C(CH_3) : \underset{\displaystyle \overset{|}{CO}}{CH},$$

and with potassium hydroxid it yields mesityl oxid. It is a monobasic acid and many of its metallic salts were described. A few complicated salts were investigated which appeared to come from the acid, $C_6H_7\left\{\begin{array}{l}OH\\ CO_2H\\ CO_2H\end{array}\right.$. Mesiten-lactone, $C_6H_8<\genfrac{}{}{0pt}{}{O}{CO}>$, was produced and described and also oxymesitencarboxylic acid, $C_6H_8<\genfrac{}{}{0pt}{}{CO_2H}{OH}$, and its barium and calcium salts. Mesiten-lactone-carboxylic ester, $C_6H_7\left\{\begin{array}{l}O\\ CO>\\ CO_2C_2H_5\end{array}\right.$, or  $CH_3-C:\overset{\overset{CO_2C_2H_5}{|}}{C}\cdot C(CH_3):\underset{|\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad|}{CH}$ $O\text{———————}CO$, is unstable, tends to take up water, its boiling point is not constant, it boils between 270° and 310°. $C_6H_6Br\left\{\begin{array}{l}O\\ CO>\\ CO_2C_2H_5\end{array}\right.$, and also $C_6H_7\left\{\begin{array}{l}ONH_4\\ CO_2NH_4\\ CO_2C_2H_5\end{array}\right.$, were prepared and described. The latter easily loses ammonia, and when heated with water and hydrochloric acid it gives oxymesitendicarboxylic acid ester, $C_6H_7\left\{\begin{array}{l}OH\\ CO_2H\\ CO_2C_2H_5\end{array}\right.$, which melts at 76° and easily loses water to form the lactone. It forms salts of the formula $C_6H_7\left\{\begin{array}{l}OH\\ CO_2M\\ CO_2C_2H_5\end{array}\right.$, of which the copper and lead salts were described. The lactone treated with potassium hydroxid produces homo-mesaconic acid,  $H_2\overset{\overset{CO_2H}{|}}{C}-C(CH_3):CH-CO_2H$, melting at 147°. It forms acid and normal salts, the barium, calcium, copper, silver, acid potassium and acid ammonium salts were described. The author concludes that Duisberg's carbacetoacetic ester, $C_8H_{10}O_3$, is identical with his mesiten-lactone-carboxylic ester and also that the hydroxyl group does not exist in acetoacetic ester but that an intermolecular change occurs during condensation, the two acetoacetic ester molecules first lose water and are connected, then an intermolecular change forms a hydroxyl group which gives up its hydrogen to form the lactone. The author thinks the general case to be true that where such a group as $X_2C:C(OH)X$ occurs it will change into $X_2CH-COX$ but can change back to the hydroxyl form again during a reaction such as the forming of a lactone.

BEHREND, ROBERT, 1883.

Ber. **16**, 3027–3028 ; J. Chem. Soc. **46**, 583.

Action of Carbamid on Acetoacetic Ester.

These substances unite thus :

$$C_6H_{10}O_3 + (NH_2)_2CO = C_7H_{12}N_2O_3 + H_2O .$$

The product formed is crystalline and melts at 147°. Acids decompose it into acetoacetic ester and carbamid again. From it can be obtained the sodium salt of the acid $C_5H_8N_2O_3$, which is $C_5H_7NaN_2O_3$. The author is investigating the structure of the compound.

JAMES, J. WM., 1884.

Ann. Chem. **226**, 202–222 ; J. Chem. Soc. 47, 1–11 ; Ber. **17**, 604 (C).
Jsb. Chem. 1884, 1120.

Acetoacetic Ester.

According to Wedel, ethyl-acetoacetic ester is $CH_3COC_2H_5:CHCO_2R$ and sodiumethylacetoacetic ester would be $CH_3CONa:C(C_2H_5)CO_2R$, so that if it were treated with acetic acid an isomeric ethylacetoacetic ester should be obtained, but the author proves that an identical ethylacetoacetic ester is recovered. Experiments were made to determine if the order of introduction of alkyl radicals in the di-substitution products affects the products. No difference could be detected between allyl-methyl-acetoacetic ester and methyl-allyl-acetoacetic ester or between ethyl-methyl- and methyl-ethyl-acetoacetic esters. Acetylacetoacetic ester was produced from acetoacetic ester and acetyl chlorid, it boils at 200°–205° with slight decomposition. It is decomposed by water at ordinary temperatures into acetoacetic ester. The copper and nickel compounds were described. An attempt was made to substitute the hydrogen by sodium but it failed as decomposition took place. The acetyl-methyl-acetoacetic ester was prepared from methylacetoacetic ester and acetyl chlorid. Benzoyl-acetoacetic ester, $CH_3COCH(COC_6H_5)CO_2C_2H_5$, and its copper compound were prepared and described.

JONES, E. J., 1884.

Ann. Chem. **226**, 287–294; J. Chem. Soc. **48**, 376; Jsb. Chem. 1884, 1188.

Decomposition of α-Methyl-propyl-β-oxybutyric Acid by Heat.

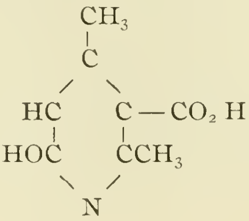
This substance, $CH_3CHOHC(CH_3)(C_3H_7)CO_2H$, is obtained by the action of sodium amalgam on methyl-propyl-acetoacetic ester. Heated to 170° it decomposes into acetaldehyde and methyl-propyl-acetic acid. When methyl-propyl-acetoacetic ester is saponified it yields methyl-α-secondary pentyl ketone, $CH_3COCH(CH_3)(C_3H_7)$, which boils at 142° to 147° and methyl-propyl-acetic acid which boils at 193°.

COLLIE, J. NORMAN, 1884.

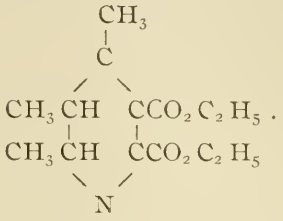
Ann. Chem. **226**, 294-322; J. Chem. Soc. **48**, 373; Ber. **18**, 25 (C); Jsb. Chem. 1884, 1116.

Action of Ammonia on Acetoacetic Ester.

Paramido-acetoacetic ester, $C_6H_{11}NO_2$, is formed which may be either $CH_3C(NH_2):CHCO_2C_2H_5$ or $CH_3C(:NH)CH_2CO_2C_2H_5$. It is easily decomposed into the substances started with. Sodium amalgam changes it into β-oxybutyric acid. It reacts with acetic acid anhydrid to produce β-acetamido-α-crotonic ester, $CH_3C(NHCOCH_3):CHCO_2C_2H_5$. When heated it condenses to $C_{10}H_{13}NO_3$ from which the acid $C_8H_9NO_3$, can be produced, which is hydroxylutidin-monocarboxylic acid,



When treated with paraldehyde and sulfuric acid it gives dihydrocollidin dicarboxylic ester,

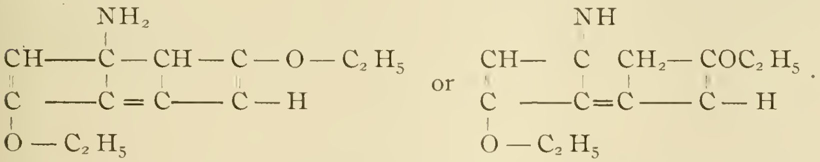


CANZONERI, F. and G. SPICA, 1884.

Gazz.* chim. **14**, 448–453; Ber. **18**, 107 (C); J. Chem. Soc. **48**, 75.

Action of Amids on Acetoacetic Ester.

Formamid reacts with acetoacetic ester to form lutidin-mono- and dicarboxylic esters and a compound $C_{12}H_{15}NO_2$, to which is attributed the formula



The results of the reaction when acetamid is used will be given later.

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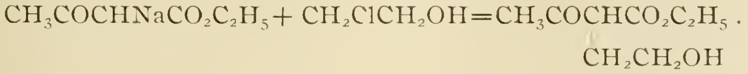
* Original article not consulted.

CHANLAROFF, MOEHSIN BEG, 1884.

Ann. Chem. **226**, 325–343; Ber. **18**, 26 (C); J. Chem. Soc. **48**, 374.

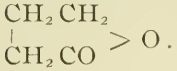
Butyrolactone.

This is quite a long article on butyrolactone which is produced from acetoacetic ester as follows:



$$CH_3COCHNaCO_2C_2H_5 + CH_2ClCH_2OH = \underset{CH_2CH_2OH}{CH_3COCHCO_2C_2H_5}.$$

This substance treated with barium hydroxid and then an acid gives $CH_2CO_2HCH_2CH_2OH$, which upon heating gives the butyrolactone,



$$\begin{matrix} CH_2CH_2 \\ | \\ CH_2CO \end{matrix} > O.$$

ELION, H., 1884.

Rec.* trav. chim. **3**, 231–270; Ber. **17**, 568 (C).

Ethyl-sodacetoacetic Ester and Sodacetoacetic Ester.

Ethyl-sodacetoacetic ester hydrate, $C_8H_{13}NaO_3 + H_2O$, and sodacetoacetic ester hydrate, $C_6H_9NaO_3 + H_2O$, were prepared. Sodium bisulfite forms a compound with acetoacetic ester but will form none with diacetyl-, ethylacetyl- and ethyldiacetyl- acetic esters. Ethyldiacetyl-acetic ester, $CH_3COC(C_2H_5)(C_2H_3O)CO_2C_2H_5$, could not be prepared from sodium diacetyl-acetic ester but could be from ethylacetoacetic ester and acetyl chlorid.

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*Original article not consulted.

HELD, A., 1884.

Compt. rend. **98**, 522–525; Bull. Soc. chim. **41**, 330; J. Chem. Soc. **46**, 727; Jsb. Chem. 1884, 1121; Ber. **17**, 204 (C).

Ethyl- and Methyl-cyanacetoacetic Esters.

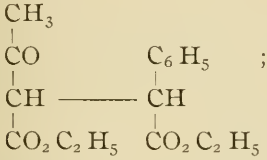
The esters could not be prepared from the cyan-acetoacetic esters but were successfully prepared by treating ethyl-acetoacetic ester and methyl-acetoacetic ester with cyanogen gas. Ethylcyanacetoacetic ester boils at 105°–110° under 15 to 2 m.m. pressure, its specific gravity is .976 at 20°. Methylcyanacetoacetic ester boils at 90°–95° under 15 to 20 m.m. pressure, and has a specific gravity of .996 at 20°. The decomposition products with potassium hydroxid show that the formulæ must be $CH_3COC(CN)(C_2H_5)CO_2C_2H_5$ and $CH_3COC(CN)(CH_3)CO_2C_2H_5$.

WELTNER, A., 1884.

Ber. **17**, 66–73; J. Chem. Soc. **46**, 746; Jsb. Chem. 1885, 1415; Bull. Soc. chim. **43**, 336.

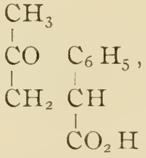
Action of Chlor- and Brom-acetone, Aceto-phenon Bromid and Phenyl-brom-acetic Acid on Acetoacetic Ester.

Chlor- and Brom-acetone act on acetoacetic ester but no definite results were obtained. Aceto-phenon bromid, $C_6H_5COCH_2Br$, acting on acetoacetic ester produces aceto-phenon-acetoacetic ester, which, when treated with sodium amalgam becomes a hydroxylactone, $CH_3CHOHCH<\begin{array}{l}CH_2\\CO_2\end{array}>CHC_6H_5$. Phenyl-brom-acetic ester and acetoacetic ester produce phenyl-aceto-succinic ester,



$$\begin{array}{ll} CH_3 & \\ | & \\ CO & C_6H_5 \\ | & | \\ CH \text{———} & CH \\ | & | \\ CO_2C_2H_5 & CO_2C_2H_5 \end{array}$$

; from this the ketone acid,



$$\begin{array}{ll} CH_3 & \\ | & \\ CO & C_6H_5, \\ | & | \\ CH_2 & CH \\ & | \\ & CO_2H \end{array}$$

is formed, and from this by the action of sodium amalgam the lactone, $\begin{array}{l}CHC_6H_5CO\\CH_2CHCH_3\end{array}> O$, is formed.

CANZONERI, F. and G. SPICA, 1884.

Gazz.* chim. **14**, 491–492; Ber. **18**, 141 (C); J. Chem. Soc. **48**, 750.

Acetyl-β-imidobutyric Ester.

By heating acetoacetic ester with acetamid and aluminum chlorid under reduced pressure there is produced acetyl-β-imidobutyric ester which melts at 64° to 65°. Its formula is

$$CH_3CO - N = C(CH_3)CH_2CO_2C_2H_5.$$

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*Original article not consulted.

PERKIN, W. H., 1884.

J. Chem. Soc. **45**, 493 and 540.

Magnetic Rotary Polarization of Compounds in Relation to Chemical Structure.

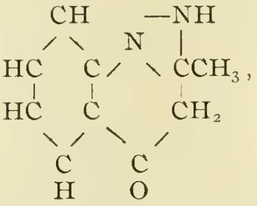
Tables of very many substances are given, among them are :— Acetoacetic ester at 16.25° specific rotation = 0.9278 and molecular rotation = 6.501. Allylacetoacetic ester at 13.9° specific rotation = 1.09022 ; molecular rotation = 10.382.

KNORR, L., 1884.

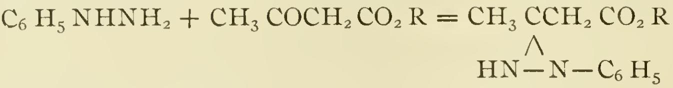
Ber. **17**, 546–552 ; J. Chem. Soc. **46**, 1153 ; Jsb. Chem., 1884, 874 ; Bull. Soc. chim. **43**, 406.

Action of Acetoacetic Ester on Phenylhydrazin. Quinizin Derivatives.*

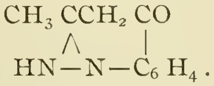
The compound $C_{10}H_{10}N_2O$, before described, is now supposed to have the formula



and is named oxymethylquinizin. The reaction between phenylhydrazin and acetoacetic esters is general and consists of two parts :—

(1) 

$$C_6H_5NHNH_2 + CH_3COCH_2CO_2R = \begin{array}{c} CH_3\,CCH_2\,CO_2R \\ \wedge \\ HN-N-C_6H_5 \end{array}$$

and (2) this loses alcohol and leaves 

$$\begin{array}{c} CH_3\,CCH_2\,CO \\ \wedge \quad | \\ HN-N-C_6H_4 . \end{array}$$

This substance was studied and a number of its derivatives described, among them were orthotoluoxymethylquinizin, paratoluoxymethylquinizin and β-napthodimethyloxyquinizin.

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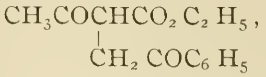
*See page 49.

PAAL, C., 1884.

Ber. **17**, 913–918 ; J. Chem. Soc. **46**, 1177 ; Bull. Soc. chim. **43**, 626.

Derivatives of Acetophenon-acetoacetic Ester.

Acetophenon-acetoacetic ester,  $\begin{matrix} CH_3COCHCO_2C_2H_5, \\ | \\ CH_2COC_6H_5 \end{matrix}$ when saponified yields acetophenonacetone, $CH_3COCH_2(CH_2COC_6H_5)$, from which were produced two isomeric compounds $C_{11}H_{10}O$, one of which melts at 41°–42°, boils at 235° to 240° and yields, on oxidation, benzoic acid. The acid $C_{12}H_{10}O_3$, previously described, gives by oxidation benzoic, acetic and carbonic acids. An oil $C_{12}H_9O_3C_2H_5$, was produced from this acid. The work is being continued.

LIEBERMANN, C. and S. KLEEMANN, 1884.

Ber. **17**, 918–921 ; J. Chem. Soc. **46**, 1120; Jsb. Chem. 1884, 1158 ; Bull. Soc. chim. **43**, 628.

Methyl-propyl-acetic Acid.

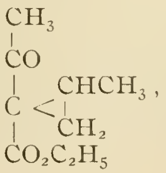
This acid, produced from methyl-propyl-acetoacetic ester which was made from methyl-acetoacetic ester and normal propyl iodid is proven to be identical with the acid of the same name produced from saccharose.

PERKIN, Jr., W. H., 1884.

Ber. **17**, 1440–1444 ; J. Chem. Soc. **46**, 1154 ; Jsb. Chem. 1884, 1081 ; Bull. Soc. chim. **44**, 538.

Trimethylene Derivatives.

Aceto-methyl-tri-methylene-carboxylic ester,



formed from acetoacetic ester and propylene bromid, boils at 210° to 215°. From it were produced the free acid and aceto-methyl-trimethylene.

PERKIN, Jr., W. H. and C. BERNHART, 1884.

Ber. **17**, 1522-1527; J. Chem. Soc. **46**, 1121.

Dehydracetic Acid.

Dehydracetic acid and hydroxylamin form dehydracetoxim, $C_7 H_8 O_3 CNOH$; dehydracetic acid and phenylhydrazin form dehydraceto phenylhydrazin, $C_8 H_8 O_3 NNH C_6 H_5$. Monobromdehydracetic acid melting at 136°-137° was obtained and if this be allowed to stand with alcoholic potash it forms hydroxyl dehydracetic acid, $C_8 H_7 O_4 OH$, which melts with decomposition at 250° to 255°. The silver salt, $C_8 H_6 O_5 Ag_2$, was formed showing the acid to be dibasic. By careful treatment of dehydracetic acid with cold potash an oil was obtained which was thought to be acetoacetic acid.

RICHTER, V. v. AND H. MÜNZER, 1884.

Ber. **17**, 1926-1930; J. Chem. Soc. **46**, 1342; Jsb. Chem. 1884, 1051; Bull. Soc. chim. **44**, 242.

Benzene-azo Ketone.

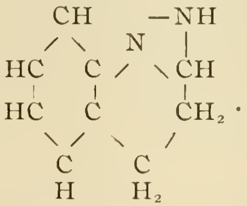
Benzene-azo-acetoacetic ester, $CH_3 CO CH (N_2 C_6 H_5) CO_2 C_2 H_5$, formed from acetoacetic ester and diazobenzene chlorid melts at 75°. When saponified no substituted acetic acid could be obtained, only the benzene-azo acetone, $CH_3 CO CH_2 N_2 C_6 H_5$, which melts at 148°-149°. In the same manner para-toluene-azo-acetoacetic ester and para-toluene-azo-acetone were produced.

KNORR, L., 1884.

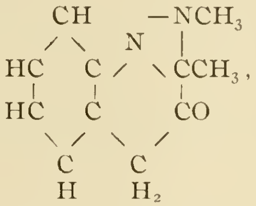
Ber. **17**, 2032–2049 ; J. Chem. Soc. **46**, 1377 ; Jsb. Chem. 1884, 877.

Constitution of Quinizin Derivatives.

Experiments were made which tend to prove the constitution of these bodies. They probably come from the hypothetical base quinizin, which is :—



Many of the derivatives were described, among them antipyrin, which is dimethyloxyquinizin,



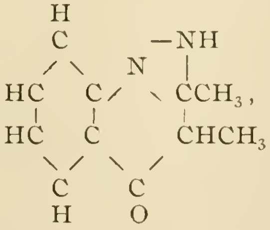
and some of its derivatives.

KNORR, L. and A. BLANK, 1884.

Ber. **17**, 2049–2052 ; J. Chem. Soc. **46**, 1380.

Action of Substituted Acetoacetic Esters on Phenylhydrazin.

Methyl-acetoacetic ester and phenylhydrazin form 2′ : 3′ dimethyloxyquinizin,



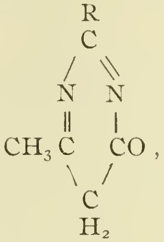
which melts at 127° to 132° It is isomeric with antipyrin. Ethylacetoacetic ester and phenylhydrazin form 2′ : 3′ methyl-ethyl-oxyquinizin which melts at 108°.

PINNER, A., 1884.

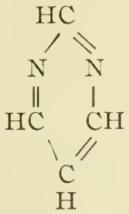
Ber. **17**, 2519–2520; J. Chem. Soc. 48, 158; Jsb. Chem. 1884, 596.

Action of Acetoacetic Ester on Amidins. Part I.

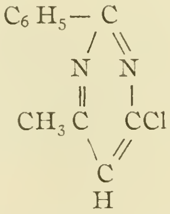
When an amidin of the formula $R - C \begin{matrix} = NH \\ - NH_2 \end{matrix}$, acts on acetoacetic ester a compound of the formula



is formed and this compound is changed by phosphorus pentachlorid into the nucleus



Benzamidin gives a compound, $C_{11}H_{10}N_2O$, which melts at 215.5°–216° and gives a platinic chlorid salt. Treated with phosphorus pentachlorid it gives $C_{11}H_9N_2Cl$, which is probably

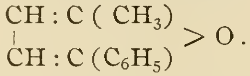
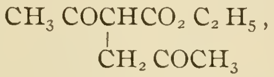


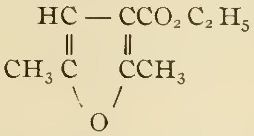
Acetamidin gives $C_6H_8N_2O$, which the author is studying.

PAAL, C., 1884.

Ber. **17**, 2756-2767 ; J. Chem. Soc. **48**, 248.

Derivatives of Acetophenonacetoacetic Ester and Acetonylaceto-acetic Ester.

One of the two isomeric compounds $C_{11}H_{10}O$, obtained by dehydrating acetophenon-acetone is named dehydraceto-phenon-acetone and given one of the three formulæ: $C_6H_5C \vdots CCH_2COCH_3$; $C_6H_5COCH_2C \vdots CCH_3$; $C_6H_5COCH_2CH_2C \vdots CH$; and the other compound is named phenyl-methyl-furfurane,  $\left.\begin{array}{l} CH:C(CH_3) \\ | \\ CH:C(C_6H_5) \end{array}\right> O$. Acetophenon-acetoacetic ester yields analogous dehydrated derivatives. Acetonyl-acetoacetic ester,  $\begin{array}{l} CH_3COCHCO_2C_2H_5, \\ \quad\ | \\ \quad CH_2COCH_3 \end{array}$ when treated with hydrochloric acid becomes pyrotritartaric ester,



A number of other derivatives of the above compounds are described, and their constitution indicated.

BEHREND, ROBERT, 1884.

Ber. **17**, 2846-2847 ; J. Chem. Soc. **48**, 246.

Derivatives of Carbamid.

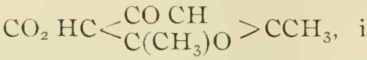
The author is investigating the products of the action of carbamid on acetoacetic ester. From the first compound formed $C_5H_8N_2O_3$, are obtained $C_5H_6N_2O_2$; $C_5H_3N_3O_6$; $C_4H_3N_3O_4$ and $C_5H_6N_4O_3$.

PERKIN, Jr., W. H., 1885.

Ber. **18**, 218-220; J. Chem. Soc. **48**, 515.

Dehydracetic Acid.

The subject of the constitution of dehydracetic acid is reviewed and the formula



$CO_2\,HC{<}\begin{matrix}CO\,CH\\C(CH_3)O\end{matrix}{>}CCH_3$,

is advanced. The methyl ester melts at 90.5°, is soluble in water and the solution is decidedly acid. From the methyl ester and sodethoxid the compound $C_8\,H_6\,Na\,CH_3\,O_4$ is formed.

JUST, FEODOR, 1885.

Ber. **18**, 319-320; J. Chem. Soc. **48**, 513; Ber. **19**, 45 (C).

New Method of Introducing Nitrogenous Radicals in Malonic and Acetoacetic Esters.

This is by the action of imido-chlorids,—benzanilidimido-chlorid, $C_6\,H_5\,Cl{=}N{-}C_6\,H_5$, for instance. The chlorin is eliminated and the remaining monad radical is substituted. The author is working in this line.

ALLEN, WM. AND ALFRED KÖLLIKER, 1885.

Ann. Chem. **227**, 107-118; J. Chem. Soc. **48**, 655; Ber. **18**, 154 (C); Jsb. Chem. 1885, 768.

Some derivatives of Triphenyl-carbinyl-bromid.

When sodacetoacetic ester is treated with triphenyl-carbinyl-bromid, $C\,Br\,(C_6\,H_5)_3$, there is produced triphenyl-carbinyl-acetoacetic ester, $CH_3\,CO\,C[C(C_6\,H_5)_3]_2\,CO_2\,C_2\,H_5$, a substance which melts at 159.5° to

160.5°. When saponified, this yields triphenyl-carbinyl ethel ether, $C_2H_5OC(C_6H_5)_3$, melting at 83°, which, treated with acetyl chlorid, gives $CH_3CO_2C(C_6H_5)_3$. Triphenyl-carbinyl-acetoacetic ester when distilled yields triphenyl methane, $CH(C_6H_5)_3$, which melts at 92° and boils at 358° to 360°.

GEUTHER, A., 1885.

Ann. Chem. **227**, 383–384.

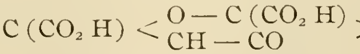
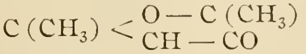
Upon the History of Acetyl-acetoacetic Esters.

After noticing the claims made by James and by Elion to the first production of these esters, the author calls attention to the fact that Lippmann produced mono- and di- acetyl-acetoacetic esters in 1869 (Ztschr. Chem. 1869, 28).

HAITINGER, L., 1885.

Ber. **18**, 452–453; J. Chem. Soc. **48**, 761.

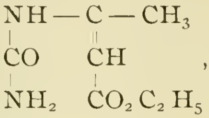
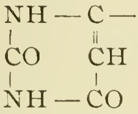
Dehydracetic Acid.

Dehydracetic acid when treated with aqueous ammonia gives $C_8H_9NO_3$ and C_7H_9NO. The former is an acid which, when heated, gives the latter, which is a weak base. When C_7H_9NO is distilled with zinc dust lutidin, C_7H_9N, boiling at 147° to 151° is obtained. Some analogous reactions of dehydracetic acid and chelidonic acid are given. Chelidonic is;  $C(CO_2H) < \genfrac{}{}{0pt}{}{O - C(CO_2H)}{CH - CO} > CH$ and dehydracetic acid is;  $C(CH_3) < \genfrac{}{}{0pt}{}{O - C(CH_3)}{CH - CO} > CCO_2H$.

BEHREND, ROBERT, 1885.

Ann. Chem. **229**, 5–31; Ber. **18**, 543 (C); Jsb. Chem. 1885, 654. Bull. Soc. chim. **46**, 360.

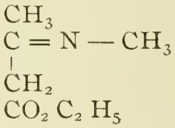
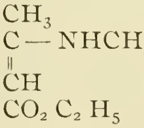
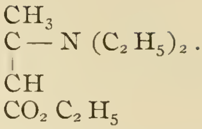
Action of Urea on Acetoacetic Ester.

By this action β Uramidocrotonic ester,  $\begin{array}{ll} \mathrm{NH} - & \mathrm{C} - \mathrm{CH_3} \\ | & \| \\ \mathrm{CO} & \mathrm{CH} \\ | & | \\ \mathrm{NH_2} & \mathrm{CO_2C_2H_5} \end{array}$, is formed. From this was formed methyluracyl,  $\begin{array}{ll} \mathrm{NH} - & \mathrm{C} - \mathrm{CH_3} \\ | & \| \\ \mathrm{CO} & \mathrm{CH} \\ | & | \\ \mathrm{NH} - & \mathrm{CO} \end{array}$, which decomposes at 270°–280° without melting. From this, trimethyluracyl, $C_7H_{10}N_2O_2$, melting point 103°; and nitrouracyl carboxylic acid, $C_5H_3N_3O_6$, were formed, and from the latter, nitrouracyl, $C_4H_3N_3O_4$; amidouracyl, $C_4H_5N_3O_2$; and oxyuracyl, $C_4H_4N_2O_3$. Amidouracyl salts give with potassium cyanate, hydroxyxanthin, $C_5H_6N_4O_3 + \frac{2}{3}H_2O$, which may be oxidized to alloxan and this reduced to alloxantin.

KUCKERT, OTTO, 1885.

Ber. **18**, 618–620; J. Chem. Soc. **48**, 751; Jsb. 1885, 1351; Bull Soc. chim. **46**, 8.

Action of Alkylamins on Acetoacetic Esters.

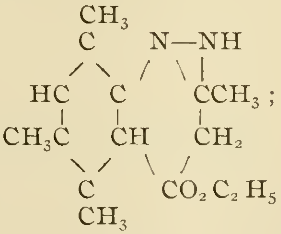
Acetoacetic ester when treated with methylamin forms two compounds according to the temperature. If kept at 0° an addition product is formed which melts at 42°–43° and easily changes into an oil, the same as the product which is formed if the temperature is not kept low. This is either  $\begin{array}{l} \mathrm{CH_3} \\ \mathrm{C} = \mathrm{N} - \mathrm{CH_3} \\ | \\ \mathrm{CH_2} \\ \mathrm{CO_2C_2H_5} \end{array}$ or  $\begin{array}{l} \mathrm{CH_3} \\ \mathrm{C} - \mathrm{NHCH_3} \\ \| \\ \mathrm{CH} \\ \mathrm{CO_2C_2H_5} \end{array}$. Diethylamin produces the compound of the formula  $\begin{array}{l} CH_3 \\ C - N(C_2H_5)_2 \\ | \\ CH \\ CO_2C_2H_5 \end{array}$. The methylamin product when treated with paraldehyde and sulfuric acid forms a condensation product $C_{15}H_{23}NO_4$, resembling dihydro-collidin dicarboxylic ester.

HALLER, S., 1885.

Ber. 18, 706–709; J. Chem. Soc. 48, 818; Jsb. Chem. 1885, 1082.

Trimethyl-quinizin Derivatives.

The following derivatives of acetoacetic ester were described :—pseudo-cumylizinacetoacetic ester, $C_{15}H_{22}O_2N_2$, which melts at 77°–78° and has the constitution :—



tetramethyl-oxyquinizin, $C_9NH_3(CH_3)_4ONH$, $[(CH_3)_4 = 1:3:4:2']$;* pentamethyl-oxyquinizin (pseudo-cumylantipyrine) $C_9NH_3(CH_3)_4ONCH_3$, $[(CH_3)_3 : NCH_3 : CH_3 : O = 1 : 3 : 4 : 1' : 2' : 4']$*] and isonitrosotetramethyl oxyquinizin, $C_{12}H_{15}O_2N_3$.

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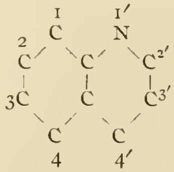
*The carbon atoms were numbered thus :—

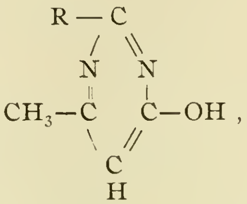


PINNER, A., 1885.

Ber. **18**, 759–763; J. Chem. Soc. **48**, 751; Jsb. Chem. 1885, 838; Bull. Soc. chim. **45**, 778.

Action of Acetoacetic Ester on Amidins. Part II.—Pyrimidins.

The formula



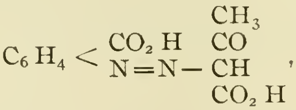
is substituted for that previously assigned to these bodies and the nucleus $C_4H_4N_2$ is termed pyrimidin. Phenyl-methyl-hydroxy-pyrimidin is further described.

GRIESS, PETER, 1885.

Ber. **18**, 960–966; J. Chem. Soc. **48**, 788.

New Researches upon Diazo Compounds.

In this article (p. 962) azo-acetoacetic-benzoic acid,



$$C_6H_4 < \begin{array}{ll} & CH_3 \\ CO_2H & CO \\ N{=}N- & CH \\ & CO_2H \end{array},$$

is described. It is produced by treating acetoacetic ester with sulfuric acid and meta diazo-benzoic acid sulphate, $C_6H_4 < \begin{matrix} CO_2H \\ N{=}N-SO_4H \end{matrix}$.

SCHILLER-WECHSLER, MAX, 1885.

Ber. **18**, 1037–1052 ; J. Chem. Soc. **48**, 900.

Anilido-pyrotartaric Acid.

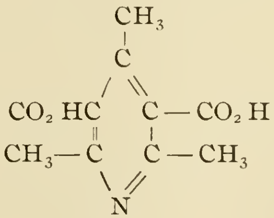
In this article mention is made of cyanhydrin of acetoacetic ester or β-cyan-β-oxybutyric ester, $CH_3C(CN)(OH)-CH_2CO_2C_2H_5$, which was produced by treating acetoacetic ester with hydrocyanic acid. It is very unstable, from it was prepared β-cyan-β-anilido-butyric ester, $CH_3C(CN)-(NHC_6H_5)CH_2CO_2C_2H_5$, by the action of anilin.

HANTZSCH, A., 1885.

Ber. **18**, 1744–1749 ; J. Chem. Soc. **48**, 1078 ; Jsb. Chem. 1885, 815 ; Bull. Soc. chim. **46**, 166.

Constitution of Synthetical Pyridin Derivatives . . . . .

After discussing the reactions of these bodies the author decides that the tri-methyl-pyridin-dicarboxylic acid obtained from ammonia, aldehyde and acetoacetic ester has the formula :



MICHAEL, R., 1885.

Ber. **18**, 2020–2029 ; J. Chem. Soc. **48**, 1244 ; Jsb. Chem. 1885, 826.

Synthesis of Pyridin Derivatives from Acetoacetic Ester, Aldehyde and Ammonia.

By using an excess of aldehyde a product different from the usual one is formed which is α—γ-lutidin-β-carboxylic ester, $C_5NH_2(CH_3)_2$

$CO_2C_2H_5$. It is an oil which boils at 246° to 247° and from it, its acid can be formed, the calcium salt of which, when distilled from lime, yields 2 : 4, lutidin. The free acid $C_5NH_2(CH_3)_2CO_2H$, can be oxidized to carbocinchomeronic acid, $C_5NH_2(CO_2H)_3$ [2 : 3 : 4], which yields cinchomeronic acid, $C_5NH_3(CO_2H)_2$ [2 : 3].

BUCHKA, K., 1885.

Ber. **18**, 2090–2093; J. Chem. Soc. **48**, 1200; Jsb. Chem. 1885, 1351.

Action of Sulfur Chlorid on Sodacetoacetic Ester.

The sulfid of acetoacetic ester $(CH_3COCHCO_2C_2H_5)_2S$, is produced by this action. It melts at 80° to 81°. The reduction or condensation of this was impossible because of its unstability. Carbonyl chlorid acts on sodacetoacetic ester to form chloracetoacetic ester.

FITTIG, R., 1885.

Ber. **18**, 2526–2527; J. Chem. Soc. **50**, 47.

Condensation of Acetoacetic Ester with Dibasic Acids.

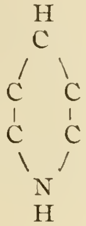
Acetoacetic ester condenses with succinic acid to form a compound $C_{10}H_{12}O_5$, which melts at 75°-76° and which is a mono-ethyl salt of a dibasic acid, $C_8H_8O_5$. This acid melts at 199° to 200°. With sodium pyrotartrate, acetoacetic ester gives the mono-ethyl ester of the acid $C_9H_{10}O_5$. Further investigations are being made in this line.

HANTZSCH, A., 1885.

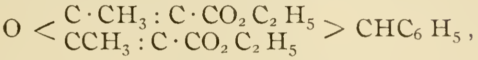
Ber. **18**, 2579–2586; J. Chem. Soc. **50**, 77; Jsb. Chem. 1885, 830.

Constitution of the Synthetical Hydro-pyridin Derivatives.

The hydrogen in these compounds has been assumed to be in connection with carbon but as Kukart has obtained a substituted hydropyridin derivative by the action of paraldehyde and sulfuric acid on the product of reaction between methyl-amin and acetoacetic ester, it follows that nitrogen must be present as an imido group which gives for the nucleus formula :



Benzylidin-diacetoacetic ester, $C_6H_5CH(C_6H_9O_3)_2$, melting at 152°–153° and dehydrobenzylidin diacetoacetic ester,



$$O < \begin{matrix} C \cdot CH_3 : C \cdot CO_2C_2H_5 \\ CCH_3 : C \cdot CO_2C_2H_5 \end{matrix} > CHC_6H_5 ,$$

melting at 87°–88° were formed from acetoacetic ester and benzaldehyde but the presence of some primary amin is necessary.

JAKSCH, R. v., 1885.

Ber. **19**, 781 (C).

Acetonurea and Diaceturea.

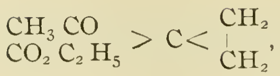
The author states that acetoacetic acid is not found in normal urine and as an explanation of its origin in diseased urine he supposes that it came from acetone by the taking up of oxygen, uniting with formic acid and then splitting off water.

PERKIN, Jr., W. H., 1885.

J. Chem. Soc. **47**, 801–855.

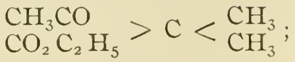
Synthetical Formation of Closed Carbon Chains.

On pages 834–835 of this long article, the author shows the many differences in behavior between acetyl tri-methylene carboxylic ester,



$$\begin{matrix}CH_3\,CO\\CO_2\,C_2\,H_5\end{matrix}>C<\begin{matrix}CH_2\\|\\CH_2\end{matrix},$$

and di-methyl-acetoacetic ester,



$$\begin{matrix}CH_3CO\\CO_2\,C_2\,H_5\end{matrix}>C<\begin{matrix}CH_3\\CH_3\end{matrix};$$

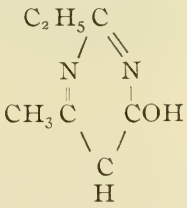
although they only differ in composition by two hydrogen atoms.

PINNER, A., 1885.

Ber. **18**, 2845-2852 ; J. Chem. Soc. **50**, 45 ; Jsb. Chem. 1885, 840 ; Bull. Soc. chim. **45**, 852.

Action of Acetoacetic Ester on Amidins. Part III.—Pyrimidins.

With the exception of formamidin all the amidins experimented with form pyrimidins ; formamidin yields cyanacetoacetic ester. Acetamidin yields di-methyl-hydroxy-pyrimidin, propionamidin yields ethyl-methyl-hydroxy-pyrimidin,



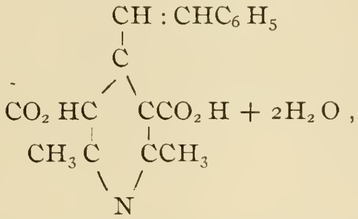
Phenyl-methyl-hydroxy-pyrimidin, $C_{11}H_{10}N_2O$; phenyl-methyl-pyrimidin, $C_{11}H_{10}N_2$; phenyl-methyl-ethoxy-pyrimidin, $C_{11}H_9(OC_2H_5)N_2$; and phenyl-methyl-pyrimidin anilid, $C_{11}H_9N_2NHC_6H_5$ were described.

EPSTEIN, W., 1885.

Ann. Chem. **231**, 1–36; J. Chem. Soc **50**, 257; Ber. **19**, 18 (C); Bull. Soc. chim. **46**, 435.

Condensation of Cinnamaldehyde with Ammonia and Acetoacetic Ester.

These substances condense to form benzylidenedihydrocollidin-dicarboxylic ester which melts at 148° to 149° and which can be oxidized to benzylidene-collidin-dicarboxylic acid,



which melts at 218° to 219° When anhydrous it melts at 241°. The potassium salt may be oxidized by potassium permanganate to lutidintricarboxylic acid which is different from the one described by Hantzsch in Ber. **15**, 2915 and **17**, 2908. By reduction it gives lutidin which is *α-α′*-dimethylpyridine, an isomer of Hantzsch's lutidin.

ENGELMANN, FRANZ, 1885,

Ann. Chem. **231**, 37–71; Ber. **19**, 16 (C); J. Chem. Soc. **50**, 258; Jsb. Chem. 1885, 1357; Bull. Soc. chim. **46**, 437.

Action of Homologues of Acetaldehyde on Ammonia and Acetoacetic Ester.

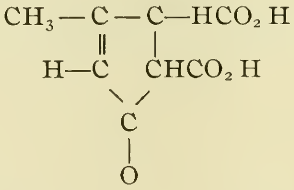
Hydroparvolin-dicarboxylic ester, $C_5NH_2(CH_3)_2C_2H_5(CO_2C_2H_5)_2$, is formed from acetoacetic ester, propaldehyde and alcoholic ammonia, it melts at 110°. By oxidation it loses its two hydrogen atoms and then by saponification parvolin-dicarboxylic acid, $C_5N(CH_3)_2C_2H_5(CO_2H)_2$, is formed which melts at 289° to 290°. Parvolin, $C_5NH_2(CH_3)_2C_2H_5$, boils at 186° and has a specific gravity of .916 at 14 Hydroisopropyl-lutidindicarboxylic ester, $C_5NH_2(CH_3)_2C_3H_7(CO_2C_2H_5)_2$, obtained by using isobutylaldehyde melts at 97 From it were obtained lutidin-dicarboxylic ester and acid. Hydroisobutyl-lutidindicarboxylic ester, $C_5N(CH_3)_2C_4H_9H_2(CO_2C_2H_5)_2$, obtained by using valeraldehyde melts at 100°. The mono-ethyl salt and free acid of isobutyl-lutidin dicarboxylic were obtained and also isobutyl-lutidin, $C_5N(CH_3)_2H_2C_4H_9$, a liquid boiling at 210° to 213°.

FITTIG, R., 1885.

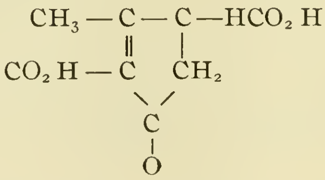
Ber. **18**, 3410–3413; J. Chem. Soc. **50**, 225.

Constitution of Carbopyrotritartaric Acid.

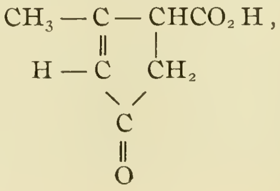
The product of the action of acetoacetic ester and succinic acid, $C_8H_8O_5$, which is isomeric with carbopyrotritartaric acid is called methronic acid and the two acids are given the following formulæ: Carbopyrotritartaric acid:



Methronic acid:



When heated they both give carbon dioxid and pyrotritartaric acid:

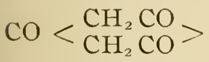


BAEYER, ADOLF, 1885.

Ber. **18**, 3454–3460 ; J. Chem. Soc. **50**, 223 ; Jsb. Chem. 1885, 1346 ; Bull. Soc. chim. **46**, 440.

Synthesis of Acetoacetic Ester and Phloroglucin.

The author discusses the constitution of sodacetoacetic ester, siding with Frankland and Duppa and Wislicenus against Geuther, showing the inconsistancies of the formula $CH_3\,CO\,Na : CH\,CO_2\,C_2\,H_5$ and inclining to Frankland and Duppa's view that sodacetic ester is formed as an intermediate product in the action of sodium on acetic ester. Phloroglucin is prepared by treating the product of the action of sodium on malonic ester with caustic potash, and the formula $CO < {CH_2\,CO \atop CH_2\,CO} > CH_2$ is suggested for it.

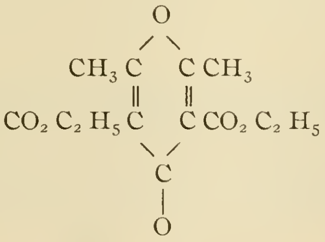


CONRAD, M. AND M. GUTHZEIT, 1886.

Ber. **19**, 19–26 ; J. Chem. Soc. **50**, 333 ; Jsb. Chem. 1886, 1331.

Action of Carbonyl Chlorid on Cupracetoacetic Ester.

Dehydro-diacetyl-acetone-dicarboxylic ester is thus produced. It is a crystalline substance melting at 79°–80°, and it has the following structural formula :



Acted upon by ammonia this compound gives lutidone-dicarboxylic ester melting at 221°; by simply substituting NH for the oxygen of the ring. Trimethyl-pyridone-dicarboxylic ester melting at 193° and phenyl-dimethyl-pyridone-dicarboxylic ester melting at 170°–171° were prepared from the dehydro-compound.

JAMES, J. WM., 1886.

J. Chem. Soc. **49**, 50–58 ; Ann. Chem. **231**, 235–244.

Action of Phosphorus Pentachlorid on Diethyl-acetoacetic Ester.

By this action diethyl-monochlor-acetoacetic ester, $CH_2 Cl—COC (C_2 H_5)_2 CO_2 C_2 H_5$, and the corresponding dichlor derivative were formed. Diethyl-monochlor-acetoacetic ester treated with sodium methoxid gave methoxy-diethyl-acetoacetic ester, $CH_2 (CH_3 O) COC (C_2 H_5)_2 CO_2 C_2 H_5$, and methoxy-methyl-ethyl acetone, $CH_2 (CH_3 O) COCH (CH_3) (C_2 H_5)$. Di-methoxy-diethyl-acetoacetic ester, $CH (CH_3 O)_2 COC (C_2 H_5)_2 CO_2 C_2 H_5$, and di-methoxy-diethyl acetone, $CH (CH_3 O)_2 COCH (C_2 H_5)_2$, were also prepared.

JAMES, J. WM., 1886.

Ann. Chem. **231**, 245-248 ; J. Chem. Soc. **50**, 333 ; Ber. **19**, 101 (C) ; Bull. Soc. chim. **46**, 758.

Synthesis of Acetoacetic Ester from Cyanacetone.

The author has repeated the experiment of Matthew * and Hodgkinson's and failed to produce any trace of acetoacetic ester from cyanacetone with hydrochloric acid or an alkali.

SOC. FOR CHEM. INDUSTRY IN BASEL, 1886.

D. P.† 39,564 of May 4th, 1886, Kl. 22 ; Ber. **20**, 443 (C).

Production of Quinizins by the Action of Hydrazobenzenes on Acetoacetic Esters.

Acetoacetic ester treated with hydrazobenzene gives phenyl-methyl-oxyquinizin which melts at 122°

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* See page 38.

†Original article not consulted.

SCHIFF, ROBERT, 1886.

Ber. **19**, 561.

Some Molecular Volumes.—Acetoacetic Ester.

B. P. = 180 –180 3. B_0 = 754.5 mm. D_4^t = specific gravity at t° compared to water at 4°. $\frac{M}{D}$ = molecular volume.

$$D_4^{0} = 1.0465$$
$$D_4^{8} = 1.0375$$
$$D_4^{55.8} = 0.9880$$
$$D_4^{79.2} = 0.9644$$
$$D_4^{135.5} = 0.9029$$

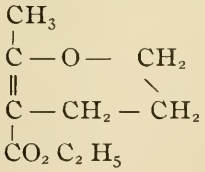
$Vt = 1. + .00109301t + .0000013895t^2 + .000000001465t^3$, from which $D_4^{180} = 0.8458$, $\frac{M}{D} = 153.34$.

PERKIN, Jr., W. H., 1886.

Ber. **19**, 1244–1247 ; J. Chem. Soc. **50**, 689 ; Jsb. Chem. 1886, 1332 ; Bull. Soc. chim. **46**, 834.

Action of Trimethylen-bromid on Sodacetoacetic Ester.

An oil $C_9H_{14}O_3$, boiling at 223° is obtained which cannot be an aceto-tetramethylen carboxylic ester because its properties when compared to the acetotrimethylen carboxylic ester and to the tetramethylen dicarboxylic ester are too irregular and because it will not react with phenylhydrazin. The author gives it the formula—



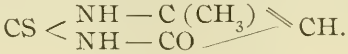
BEHREND, ROBERT, R. LIST AND A. KOHLER, 1886.

Ann. Chem. **233**, 1–15 ; Ber. **19**, 219–221 ; Ber. **19**, 395 (C) ; J. Chem. Soc. **50**, 443 ; Jsb. Chem. 1886, 549 ; Bull. Soc. chim. **46**, 544.

Condensation of Carbamids with Acetoacetic Ester.

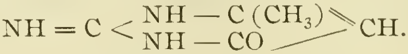
Acetoacetic ester treated with phenylcarbamid gives a compound $C_{13}H_{16}N_2O_3$, which when treated with an alkali yields acetone, alcohol, carbon dioxid and analin and when treated with an acid it yields in addition to these products ethyl phenylcarbamate, $C_9H_{11}NO_2$.

Thiocarbamid and acetoacetic ester unite to form an unstable compound which, when saponified, yields $C_5H_6N_2SO$ which is



$$CS<\begin{array}{l}NH-C(CH_3)\\NH-CO\end{array}>CH.$$

Guanidin, CN_3H_5, and acetoacetic ester form a compound $C_5H_7N_3O$, which has both acid and basic properties. Its formula probably is



$$NH=C<\begin{array}{l}NH-C(CH_3)\\NH-CO\end{array}>CH.$$

ISBERT, A., 1886.

Ann. Chem. **234**, 160–196 ; J. Chem. Soc. **50**, 1009 ; Ber. **19**, 684 (C) ; Jsb. Chem. 1886, 1328 ; Bull. Soc. chim. **47**, 585.

Acetoacetic Ester and Its Derivatives.

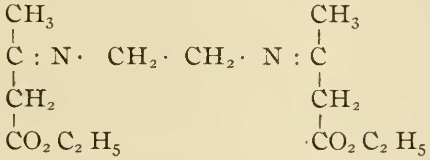
When acetoacetic ester is decomposed by sodium alkyl oxids in the presence of an alcohol, the acetate derived from the free alcohol is the chief product, while the acetate derived from the alkyl oxid is formed in smaller proportions. Resacetic acid, $C_{18}H_{22}O_5$, is formed during the same operation. Acetoacetic ester is not decomposed by ethyl or propyl alcohol at 180°, but is completely decomposed upon adding a little sodium alkyl oxid to such a mixture. The amid, $C_6H_{11}NO_2$, obtained by treating acetoacetic ester with ammonia, melts at 90° and is soluble in water. From its reactions the formula $CH_3 \cdot CO\,C_2H_5 : CH \cdot CO\,NH_2$, is assigned to it. Phosphoric chlorid acting on ethyl acetoacetic ester gives ethyl-monochlorcrotonic acid and the ethyl esters of mono- and di-chlor-ethylacetoacetic acids, and acting on methylacetoacetic ester it forms the corresponding compounds. Ethoxy-ethyl-acetoacetic ester, $(C_2H_5O)CH_2\,CO\,C_2H_5 : CH\,CO_2C_2H_5$, and ethoxy-methyl-acetoacetic ester are formed by the action of an alcoholic solution of sodium ethoxid on monochlor-ethyl and monochlor methyl-acetoacetic esters and are decomposed by alcoholic soda into ethoxy-ethyl acetone, $(C_2H_5O)CH_2COCH_2(C_2H_5)$, and ethoxy-methyl acetone, $(C_2H_5O)CH_2COCH_2(CH_3)$, which boil at 112° to 115° and 100° to 105° respectively.

SOC. FOR CHEM. INDUSTRY IN BASEL, 1886.

D. P.* 39,149 of June 5th, 1886, Kl. 12; Ber. **20,** 351 (C).

The Production of the Ester of a New Acid.

If acetoacetic ester be treated with a water solution of ethylenediamin, $C_2H_4(NH_2)_2$, they unite to form the compound,



$$\begin{array}{lcr} CH_3 & & CH_3 \\ | & & | \\ C:N\cdot & CH_2\cdot CH_2\cdot & N:C \\ | & & | \\ CH_2 & & CH_2 \\ | & & | \\ CO_2C_2H_5 & & CO_2C_2H_5 \end{array}$$

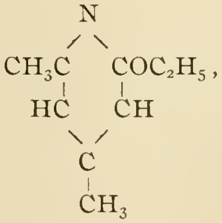
which melts at 126°, is insoluble in water but soluble in alcohols, ether, chloroform, benzene and dilute acids.

CANZONERI, F. AND G. SPICA, 1886.

Gazz.* chim. **16,** 449–453; Ber. **20,** 219 (C); J. Chem. Soc. **52,** 499.

Synthesis of Ethoxy-lutidin.

By treating acetoacetic ester in a sealed tube with an excess of ammoniacal zinc chlorid, ethoxy-lutidin,



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*Original article not consulted.

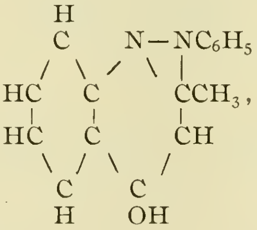
is formed, a pale yellow liquid boiling at 245° to 247°. By repeating former experiments with acetoacetic ester and formamid, a liquid boiling at 250° to 255° was obtained which was mono-lutidin-carboxylic ester and which apparently is isomeric with Michael's body of the same name which he obtained from aldehyde, aldehyde ammonia and acetoacetic ester.

MÜLLER, ALBERT, 1886.

Ber. **19**, 1771–1772; J. Chem. Soc. **50**, 899; Jsb. Chem. 1886, 1035.

Action of Acetoacetic Ester on Hydrazo-benzene.

When acetoacetic ester is treated with hydrazo-benzene, $C_6H_5NH—NHC_6H_5$, a compound $C_{16}H_{14}N_2O$. which melts at 120° and is weakly basic and acid is formed. It is probably a phenylated quinizin,



ESCALES, R. AND E. BAUMANN, 1886.

Ber. **19**, 1787–1796; J. Chem. Soc. **50**, 878.

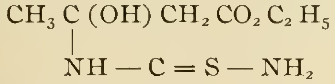
Compounds of Phenyl Mercaptan with Ketonic Acids. Phenyl Mercaptan and Acetoacetic Ester.

By treating a mixture of two molecules phenyl mercaptan and one molecule acetoacetic ester with hydrochloric acid, β dithiophenylbutyric ester, $CH_3C(SC_6H_5)_2CH_2CO_2C_2H_5$, is obtained; it melts at 57°–58°, is insoluble in water, soluble in ether, benzene and chloroform and gives a red color with concentrated sulfuric acid. When heated with an alkali it is decomposed into phenyl mercaptan and β-thio-phenyl-crotonic acid, $CH_3(SC_6H_5):CHCO_2H$, which melts at 176°–177°, is insoluble in water, soluble in benzene and hot alcohol. When heated this decomposes, giving thio-phenyl-propylene, $C_3H_5SC_6H_5$, which boils at 206°–210° and gives a blue color with sulfuric acid, which turns violet upon being heated.

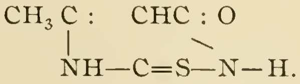
LIST, R., 1886.

Ann. Chem. **236**, 1–32; J. Chem. Soc. **52**, 127; Ber. **19**, 825 (C); Jsb. Chem. 1886, 564; Bull. Soc. chim. **47**, 587.

Action of Thiocarbamid on Acetoacetic Ester.

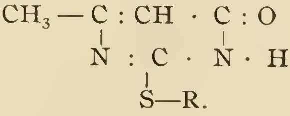
Thiomethyl-uracyl is formed, thus: $CH_3COCH_2CO_2C_2H_5 + NH_2CSNH_2 =$ 

$$\begin{array}{l} CH_3\,C\,(OH)\,CH_2\,CO_2\,C_2H_5 \\ \qquad | \\ \qquad NH - C = S - NH_2 \end{array}$$

and then water and alcohol breaking off it leaves 

$$\begin{array}{l} CH_3\,C : \quad CHC : O \\ \qquad | \qquad\quad \diagdown \\ \qquad NH - C = S - N - H. \end{array}$$

The silver, copper, mercury, potassium, and sodium salts and the methyl and ethyl esters were produced and described. The sulfur can be removed from the thiomethyl-uracyl by bromin or by silver or mercuric oxid. Thiomethyl-uracyl acetic acid, $C_7H_8N_2SO_3$, and its ethyl ester were made by using monochlor-acetic ester.

In the formation of the esters an intermolecular change is supposed to take place and the formulæ are written 

$$\begin{array}{l} CH_3 - C : CH \cdot C : O \\ \qquad\quad | \qquad\quad\;\; | \\ \qquad\quad N : C \cdot N \cdot H \\ \qquad\qquad\;\; | \\ \qquad\qquad\;\; S - R. \end{array}$$

KNORR, L., 1886.

Ann. Chem. **236**, 69–115; J. Chem. Soc. **52**, 159; Ber. **19**, 827 (C); Jsb. Chem. 1886, 1336; Bull. Soc. chim. **47**, 633.

Synthetical Experiments with Acetoacetic Ester.—Part I.

Acetoacetic ester and anilin react at ordinary temperatures to form β-phenylamido-α-crotonic ester, but at 110°–150° the anilid of acetoacetic acid is formed, which melts at 85° and gives, when distilled, diphenyl-carbamid, $CO<\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}$, which melts at 235°–236°. The anilid, when heated with chloroform and bromin, yields the anilid of monobrom-acetoacetic acid, $CH_3\,CO\,CH\,Br\,CO\,NHC_6H_5$, which melts with decomposition at 138°. Isonitroso-acetoacetic anilid, $CH_3\,CO\,C:(N\,OH)\,CO\,NHC_6H_5$, is a crystalline substance melting at 99°–100°. Reducing agents change acetoacetic acid anilid into hydroxylepidin, $C_9NH_5CH_3OH$, [4′ : 2′] which can be changed into γ-lepidin and chlorolepidin. Methoxy-lepidin formed from chlorolepidin boils at 275°–276°. Ethoxy-lepidin melts at 51 Methyl-lepidone,

$$C_6H_4<\begin{matrix}CCH_3:CH\\NCH_3\,CO\end{matrix}>,$$

may be formed from methyl anilin and acetoacetic ester. It melts at 130°, sublimes and is a strong base.

DEGEN, JOS., 1886.

Ann. Chem. **236**, 151-164; Ber. **19**, 829 (C).

Indol from Methyl-phenylhydrazin.

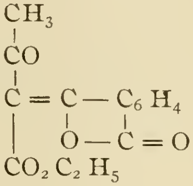
In this article an account is given of making methyl-phenylhydrazin acetoacetic ester, $CH_3C:(N_2CH_3C_6H_5)CH_2CO_2C_2H_5$, from methyl-phenylhydrazin and acetoacetic ester. The product, a yellowish red oil could not be distilled, but seemed quite stable towards water solutions of the alkalis. With alcoholic potash it was decomposed into methyl-phenylhydrazin acetoacetic acid.

BÜLOW, CARL, 1886.

Ann. Chem. **236**, 184–194; J. Chem. Soc. **52**, 144; Jsb. Chem. 1886, 1515; Bull. Soc. chim. **47**, 600.

Phthalyl-acetoacetic Ester.

This is obtained from phthalyl chlorid and acetoacetic ester and is represented thus:



It is decomposed by sulfuric acid yielding phthalyl acetic acid. Ammonia converts it into phthalyldiamid or phthalyl-imid according to the temperature. Several complicated derivatives were described, among them those formed by phenylhydrazin.

KNORR, L., 1886.

Ann Chem. **236**, 290-332; J. Chem. Soc. **52**, 275; Ber. **20**, 55 (C); Jsb. Chem. 1886, 1338; Bull. Soc. chim. **47**, 811.

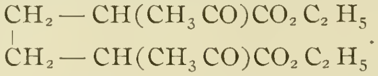
Synthetical Experiments with Acetoacetic Ester.—Part II.

The first part of this article (pp 290–317) is devoted to diaceto succinic esters, the remainder to forming pyrrol derivatives from acetoacetic ester. This treated with sodium nitrite forms nitrosoacetoacetic ester which mixed with acetoacetic ester and reduced, gives dimethyl-pyrrol-di-carboxylic ester, $C_4 NH (CH_3)_2 (CO_2 C_2 H_5)_2$ [2:4:3:5]. This melts at 134°–135° and can be distinguished from its symmetrical isomer by its absence of basic properties. By eliminating one of the ethyl groups two isomeric mono-ethyl esters of dimethyl-pyrrol-dicarboxylic acid can be produced and from these (1) by eliminating ethyl, dimethyl-pyrrol-dicarboxylic acid (2) by eliminating carbon dioxid, dimethyl-pyrrol-mono-carboxylic ester. Dimethyl-pyrrol-mono-carboxylic acid and dimethyl-pyrrol, $C_4 N(CH_3)_2 H_3$, were also produced. By using the anilid of acetoacetic ester corresponding compounds were made and their properties described.

PERKIN, Jr., W. H. AND M. OBREMBSKY, 1886.

Ber. **19**, 2045–2055 ; J. Chem. Soc. **50**, 936 ; Jsb. Chem. 1886, 1397.

Upon α_1–α_2-Diacetyl–adipic Acid.

From the high-boiling residue from the action of ethylene bromid on sodacetoacetic ester the authors have isolated di-acetyl-adipic ester, which is  $\begin{array}{l} CH_2 - CH(CH_3CO)CO_2C_2H_5 \\ | \\ CH_2 - CH(CH_3CO)CO_2C_2H_5 \end{array}$. It will unite with phenylhydrazin, one molecule of $(C_6H_5N_2H)''$ displacing each atom of oxygen of the carbonyl groups. Ethylene-di-methyl-oxyquinizin is also formed. The actions of diacetyl-adipic ester with alcoholic ammonia, sulfuric acid and alcoholic potash are given.

POLONOWSKA, NATALIE, 1886.

Ber. **19**, 2402–2406 ; J. Chem. Soc. **50**, 1011 ; Jsb. Chem. 1886, 1386.

So-called Carbacetoacetic Ester.

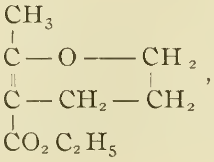
The action of hydrochloric acid on acetoacetic ester is the same as that of sulfuric producing an anhydrid, $C_{18}H_{22}O_9$, which breaks down into isodehydracetic acid and its ethyl ester (as shown by Hantzsch) so that Duisberg's so-called carbacetoacetic ester, $C_8H_{10}O_3$, must be isodehydracetic ester, $C_{10}H_{12}O_4$.

PERKIN, JR., W. H., 1886.

Ber. **19**, 2557–2561 ; J. Chem. Soc. **52**, 32 ; Jsb. Chem. 1886, 1332.

Action of Trimethylenbromid on Acetoacetic Ester.

The ester,



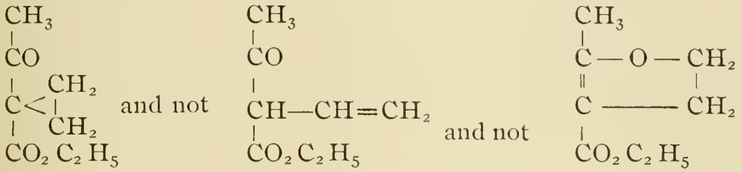
and its acid are further studied. The acid heated with water gives aceto-butyl alcohol and by distillation of this, acetobutyl alcohol anhydrid is obtained. The ester dissolves in hydrobromic acid to form brom-butyl methylketone, $CH_3CO(CH_2)_4Br$. Analogous compounds of some aromatic derivatives are cited.

PERKIN, JR., W. H. AND P. C. FREER, 1886.

Ber. **19**, 2561-2569; J. Chem. Soc. **52**, 33.

Upon Aceto-trimethylenecarboxylic Ester.

This substance was proven by its physical properties to have a trimethylene formula and thus to be:



It was united with hydrobromic acid to form omega-brom-ethyl-aceto-acetic ester, $CH_3COCH(CH_2CH_2Br)CO_2C_2H_5$, which is an oil which cannot be distilled. Saponifying this oil, aceto-propyl alcohol is obtained, $(CH_3CO)CH_2CH_2CH_2OH$, and sodium amalgam reduces this to gamma-pentylene glycol, $CH_3CHOHCH_2CH_2CH_2OH$.

WITT, OTTO N., 1886.

Ber. **19**, 2977-2978 and 3299; J. Chem. Soc. **52**, 247; Jsb. Chem. 1886, 783; Bull Soc. chim. **47**, 434.

Action of Acetoacetic Ester on Aromatic Diamins.

Acetoacetic ester heated with ortho-toluylene-diamin $C_6H_3CH_3(NH_2)_2$, gives ethenyl-toluylene-diamin, $C_6H_3CH_3 < {}^{N}_{NH} > C-CH_3$, which melts at 201°-202°.

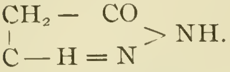
In the second communication the author acknowledges the priority of Ladenburg and Rügheimer in the preparation of this compound.

KNORR, L., 1886.

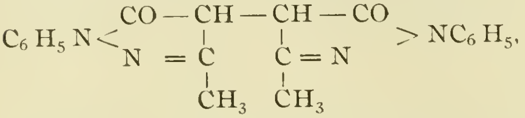
Ann. Chem. **238**, 137-219; J. Chem. Soc. **52**, 601; Ber. **20**, 259 (C).

Synthetical Experiments with Acetoacetic Ester.—Part III.

The compounds obtained from the action of phenylhydrazin on acetoacetic ester, heretofore described by the author as quinizin derivatives are now considered pyrazolone derivatives, pyrazolone being



Thus antipyrin is phenyl-dimethyl pyrazolone [1:2:3] and not di-methyl oxyquinizin Phenylmethyl pyrazolone is described. Phenyltrimethyl pyrazolone [1:3:4:4] obtained from dimethyl-acetoacetic ester melts at 55°-56° boils at 300° to 303° and is isomeric with methyl antipyrin. Disphenyl-methyl pyrazolone, [1:3:5]



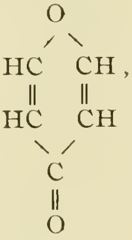
and a number of its derivatives are produced and described, among which is pyrazol blue, obtained from the above by abstracting the two hydrogen atoms from the CH groups. Some of the aromatic and nitrogen compounds of the pyrazolones are described and also some halogen compounds of antipyrin.

CONRAD, M. and M. GUTHZEIT, 1887.

Ber. **20**, 151-154; J. Chem. Soc. **52**, 502; Jsb. Chem, 1887, 1818; Bull. Soc. chim. **48**, 154.

Dimethyl=pyrondicarboxylic Ester

This substance, obtained from cupracetoacetic ester and carbonyl chlorid, formerly called dehydro-carbonyl-diacetoacetic ester is now considered to be a derivative of pyron,



in which the methyl groups occupy the 2 and 6 places and the carboxyl groups have the 3 and 5 places. It melts at 80 Alkalis decompose it into carbon dioxid and acetoacetic ester which is further decomposed to its usual decomposition products.

JAMES, J. WM., 1887,

J. Chem. Soc. **51**, 287-290; Ann. Chem. **240**, 61-66.

Formation of Cyan-acetoacetic Ester.

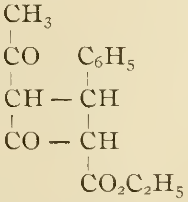
By treating monochloracetoacetic ester with potassium cyanid, potassium cyanacetoacetic ester was formed to which was given the formula $CH_2(CN)COCHKCO_2C_2H_5$. Treating this with an acid, produced cyanacetoacetic ester, a liquid which cannot be distilled under ordinary pressure. By treating dichloracetoacetic ester, called by the author $CHCl_2COCH_2CO_2C_2H_5$, with potassium cyanid no corresponding compound was formed but potassium dichloracetate, $CHCl_2CO_2K$, was the chief product.

MICHAEL, A., 1887.

Am. Chem. J. **9**, 112–124; J. prakt. Chem. **143**, 349–357; J. Chem. Soc. **52**, 672; Ber. **20**, 258 (C) and 504 (C); Jsb. Chem. 1887, 1542; Bull. Soc. chim. **48**, 520.

Addition of Sodacetoacetic Ester and Sodomalonic Ester to the Esters of Unsaturated Acids.

When sodacetoacetic ester is treated with cinnamic ester they unite directly and then split off sodium ethoxid forming a compound



$$\begin{array}{ll} \mathrm{CH_3} & \\ | & \\ \mathrm{CO} & \mathrm{C_6H_5} \\ | & | \\ \mathrm{CH} - & \mathrm{CH} \\ | & | \\ \mathrm{CO} - & \mathrm{CH} \\ & | \\ & \mathrm{CO_2C_2H_5} \end{array}$$

which is very unstable decomposing at 100 It acts as a mono-basic acid. Acetoacetic ester and citraconic ester, $C_5H_4(C_2H_5)_2O_4$, combine directly to form $C_{15}H_{24}O_7$ an unstable oil boiling at 173°–174° at 26 m. m. pressure. The author makes the point that these substances are addition products.

MICHAEL, A., 1887.

J. prakt. Chem. **143**, 449-459; Am. Chem. J. **9**, 124-129; J. Chem. Soc. **52**, 716; Ber. **20**, 320 (C); Jsb. Chem. 1887, 1536; Bull. Soc. chim **48**, 521.

Some New Reactions with Sodacetoacetic Ester.

By the action of benzoic aldehyde on sodacetoacetic ester a compound $C_{22}H_{20}Na_2O_7$ is formed which melts at 126°–127° and is soluble in alkalis. Mustard oils react with sodacetoacetic ester to form mono-thio-amids. Phenyl isocyanate forms two compounds with sodacetoacetic ester. Anhydrids of dibasic organic acids unite directly with sodacetoacetic ester: phthalic anhydrid forming

$$C_6H_4 < \begin{matrix} COCH \\ CO_2Na \end{matrix} < \begin{matrix} COCH_3 \\ CO_2C_2H_5 \end{matrix} .$$

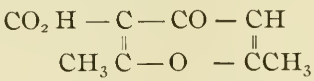
The action of phenols is to form coumarins. Ureas react to form the ureids and sulfo-ureas form the corresponding sulfo derivatives. Aldehyde ammonia forms condensation products, with sodacetoacetic ester it forms $C_8H_{12}NaNO_2$. Sodacetoacetic ester was also found to react with lactones, amidins, primary bases, guanidin, cyanamid, cyanic acid and benzoquinone.

PERKIN, Jr., W. H., 1887.

J. Chem. Soc. **51**, 484-500; Jsb. Chem. 1887, 1815.

Dehydracetic Acid.

After reviewing the work done by other chemists on this acid the author deduces the formula



$$\begin{array}{ccccccc} CO_2H & - & C & - & CO & - & CH \\ & & \| & & & & \| \\ & CH_3 & C & - & O & - & CCH_3 \end{array}$$

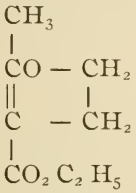
for it. The proof that it contains carbonyl is that it unites with phenylhydrazin to form $C_8H_8O_3(N_2HC_6H_5)$. It will form no acetyl derivative, therefore (two oxygen atoms being in the form of carboxyl) the fourth one must be between two carbon atoms. When carefully treated with potassium hydroxid, dehydracetic acid gives acetoacetic acid therefore it must contain two methyl groups. When treated with anilin, dehydracetic methyl ester forms lutidone derivatives, phenyl-lutidone-carboxylic methyl ester being first produced which is decomposed into phenyl lutidone, $C_5NH(OH)(CH_3)_2C_6H_5$. The bromid acetate, oxim and phenylhydrazin derivatives of dehydracetic acid were prepared and described.

FREER, P. C. AND W. H. PERKIN, Jr., 1887.

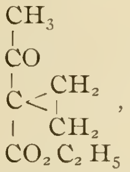
J. Chem. Soc. **51**, 820–849; Am. Chem. J. **10**, 446–457.

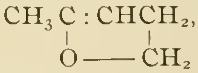
Action of Ethylene Bromid on Sodium Derivatives of Acetoacetic Ester...

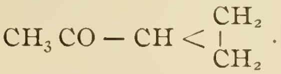
Experiments with acetoacetic ester and ethylene bromid being repeated, it was found that two substances were produced, one as before described in Ber. **19**, 2561 and the other having the formula



and being termed methyl-dehydropentone-carboxylic ester. The former is produced in much the larger quantities. Acetyltrimethylenecarboxylic ester,



(which is the one formerly described) when boiled with water gives acetopropyl alcohol, $(CH_3CO)CH_2CH_2CH_2OH$, but upon being heated it becomes acetopropyl anhydrid,  $\begin{array}{l}CH_3C:CHCH_2\\ \quad\;\; | \qquad\;\; |\\ \quad\;\; O — CH_2\end{array}$, and acetyltrimethylene,



$$CH_3CO-CH<\begin{array}{l}CH_2\\ |\\ CH_2\end{array}.$$

HALLER, A. AND A. HELD, 1887.

Compt. rend. **104**, 1627-1629; J. Chem. Soc. **52**, 799.

Cyanacetoacetic Ester.

This substance obtained by James (J. Chem. Soc. **51**, 287) is the same as that obtained by the authors in 1882 (Compt. rend. **95**, 235) by the action of cyanogen chlorid on sodacetoacetic ester. The authors give it the composition $CH_3COCH(CN)CO_2C_2H_5$, not as James gave it $CH_2(CN)COCH_2CO_2C_2H_5$.

WALLACH, O., 1887.

Ann. Chem. **241**, 288-315 ; J. Chem. Soc. **54**, 37 ; Jsb. Chem. 1887, 763; Bull. Soc. chim. **50**, 297.

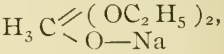
Nitrosates, Nitrosites and their Derivatives.

Amylene and nitrogen peroxid unite directly and form, not a dinitrite but a nitroso nitrate. This compound $C_5H_{10}N_2O_4$, unites with acetoacetic ester to form the crystalline compound $CH_3COCH(NOC_5H_{10})CO_2C_2H_5$.

CLAISEN, L. AND O. LOWMAN, 1887.

Ber. **20**, 651–654 ; J. Chem. Soc. **52**, 583 ; Jsb. Chem. 1887, 2050 ; Bull. Soc. chim. **48**, 394.

Preparation of Benzolacetic Ester.

Acetoacetic ester is formed in this operation which consists of mixing sodium ethoxid and benzoic ester and treating the product with acetic acid. The theory is advanced that here as well as in the ordinary production of acetoacetic ester an intermediate, addition product is formed. In the case of acetoacetic ester it would be  $CH_3C\begin{matrix}/\!\!/(OC_2H_5)_2,\\ \backslash\, O{-}Na\end{matrix}$ which is acted upon by acetic ester thus :—  $CH_3C\begin{matrix}/\!\!/(OC_2H_5)_2+\\ \backslash\, ONa\end{matrix}$ $H_2CHCO_2C_2H_5 = CH_3C(ONa):CHCO_2C_2H_5 + 2C_2H_5OH$.

CONRAD, M. AND L. LIMPACH, 1887.

Ber. **20**, 944–948 ; J. Chem. Soc. **52**, 679 ; Jsb. Chem. 1887, 1046 ; Bull. Soc. chim. **48**, 320.

Synthesis of Quinolin Derivatives from Acetoacetic Ester.

By heating anilacetoacetic ester, $CH_3C(NHC_6H_5):CHCO_2C_2H_5$, it is decomposed and besides alcohol, acetone and carbanilid, $CO:(NHC_6H_5)_2$, it forms γ-hydroxy-quinaldin, $C_6H_4C_3HOHCH_3N$, $[OH:CH_3=2':4']$, which melts at 230°-231° and distills at 360° with some decomposition. It is very bitter and gives an intensely reddish yellow color with ferric chlorid. A number of its salts and derivatives were described, phenylamidoquinaldin, methoxyquinaldin and some derivatives containing chlorin, bromin and nitrogen.

HANTZSCH, A. AND H. ZÜRCHER, 1887.

Ber. **20**, 1328–1332 ; Jsb. Chem. 1887, 1461 ; Bull. Soc. chim. **48**, 747.

Polycoumarins.

By treating polyhydric phenols with an excess of acetoacetic ester and sulfuric acid, polycoumarins are formed. Di-methyl di-coumarin, $C_6H_2 < \left\{ \begin{matrix} CCH_3 : CH \\ O \text{———} CO \end{matrix} > \right\}_2$, formed from acetoacetic ester and resorcin, $C_6H_4(OH)_2$, is a white powder almost insoluble in ordinary solvents, soluble in alkalis from which solution acids precipitate di-methyl dicoumaric acid, $C_6H_2 < \left\{ \begin{matrix} CCH_3\,CHCO_2H \\ OH \end{matrix} \right\}_2$. Acetoacetic ester treated with phloroglucin gives trimethyl tricoumarin, $C_6 < \left\{ \begin{matrix} CCH_3\,CH \\ O\text{—}CO \end{matrix} > \right\}_3$, which is also a powder difficultly soluble except in alkalis from which solution the corresponding acid is obtained. These acids easily give up water and are changed back into the lactones.

DELISLE, A., 1887.

Ber. **20**, 2008 ; J. Chem. Soc. **52**, 915 ; Jsb. Chem. 1887, 1719 ; Bull. Soc. chim. **48**, 659.

Action of Sulfur Dichlorid on Acetoacetic Ester. Preliminary Notice.

By treating acetoacetic ester with sulfur dichlorid, hydrochloric acid was given off and the mixture solidified. The new substance, $C_{10}H_{14}O_6S$, forms beautiful colorless crystals which are insoluble in water but soluble in barium hydroxid, forming a barium salt. The substance softens at 75° and melts at 90° to 91°.

BENDER, G., 1887.

Ber. **20**, 2747–2752 ; J. Chem. Soc. **54**, 53.

Action of Phenylhydrazin on Chloracetoacetic Ester.

By this action a compound $C_{12}H_{14}N_2O_2$ was formed, it is probable that $CH_3C(N_2HC_6H_5)CHClCO_2R$ is first formed which changes first into $CH_3CH(N_2C_6H_5)CHClCO_2R$ and then into $CH_3C(N_2C_6H_5):CHCO_2R$ which is β-phenylazocrotonic ester, melting at 50.5°. This can be reduced to phenylmethyl-pyrazolone.

α-Naphthylamin and chloracetoacetic ester unite to form a compound $C_{16}H_{16}NO_2Cl$, which melts at 75°.

JAPP, FRANCIS AND FELIX KLINGEMANN, 1887

Ber. **20**, 2942–2944.

Benzene-azo- and Benzenehydrazo-fatty Acids.

When sodium-methyl-acetoacetic ester is treated with diazobenzene-chlorid, $C_6H_5N_2Cl$, the diazo group takes the place of the acetyl group and benzene-α-azo-propionic ester, $C_6H_5N_2CH(CH_3)CO_2C_2H_5$, is produced. It is a yellow crystalline substance which melts at 117°. The free acid and a number of its aromatic derivatives were produced from it.

SCHIFF, HUGO, 1887.

Ann. Chem. **244**, 19–28; J. Chem. Soc. **54**, 572.

Compounds of Sugars with Aldehydes and Acetone.

Among other compounds described in this article is the one obtained from sugar and acetoacetic ester, corresponding to the formula $C_6H_{10}O_3C_6H_{12}O_6$, which is quite stable.

CONRAD, M. AND W. EPSTEIN, 1887.

Ber. **20**, 3052–3058; J. Chem. Soc. **54**, 253; Jsb. Chem. 1887, 1719; Bull. Soc. chim. **49**, 639.

Action of Ammonia on Acetoacetic Esters.

Amido-acetoacetic methyl ester, $CH_3C\cdot(NH_2):CHCO_2CH_3$, prepared from acetoacetic methyl ester and ammonia gas is a colorless crystalline substance, which melts at 85° and sublimes unchanged. Amido-ethylacetoacetic methyl ester, $CH_3C\cdot(NH_2)C(C_2H_5)CO_2CH_3$, formed from ethylacetoacetic methyl ester, melts at 36°–37°. Referring to Brandes' obtaining two compounds from this reaction the author thinks it probable that he had some acetoacetic ester with his ethyl-acetoacetic ester and so obtained the two corresponding compounds, Amido-acetoacetic esters acted upon by sodium form sodium compounds which with an alkyl iodid form amidoalkylacetoacetic esters. Amido-ethyl-acetoacetic ethyl ester formed similarly melts at 60°. Di-ethyl-acetoacetic ester will give no amid which proves that these compounds are amido-crotonic-esters and not imido-butyric esters. An interesting fact is noted in regard to the melting points of these compounds. Introducing a methyl into the *methyl* ester lowers the melting point 26° and introducing an ethyl lowers it 8°, while in the *ethyl* ester the introduction of a methyl raises the melting point 15° and the introduction of an ethyl raises it 23°.

JAPP, FRANCIS AND FELIX KLINGEMANN, 1887.

Ber. **20,** 3284–3286 and 3398–3401.

Benzene-azo- and Benzenehydrazopropionic Acids.

Discussion is taken up in regard to the constitution of the benzene-*α*-azopropionic acid, before described, and the formula is changed to $CH_3C(:NH=N—C_6H_5)CO_2H$, as it is found to be identical with phenylhydrazin pyroracemic acid.

PETERS, T., 1887.

Ber. **20,** 3318–3324; J. Chem. Soc. **54,** 253; Jsb. Chem. 1887, 3318; Bull. Soc. chim. **49,** 696.

Action of Aqueous Ammonia on Alkylated Acetoacetic Esters and of Alcohols on the Carboxylic Alkyl Group in Acetoacetic Esters.

Repeating Brandes' experiment with aqueous ammonia, the author obtained with ethyl-acetoacetic ester besides amido-ethyl-acetoacetic ester, an ethyl-acetoacetamid, $CH_3COCH(C_2H_5)CONH_2$ melting at 96° which is undoubtedly Brandes' second body. Methyl-, isobutyl- and isoamyl-acetoacetamids were obtained from the corresponding esters; they melt respectively at 73°, 85° and 127°. The author finds that the isobutyl and isoamyl esters may be readily prepared by the action of the respective alcohol on the ethyl ester, especially in the presence of a small quantity of sodium.

OTTO, ROBERT, 1888.

Ber. **21**, 89–99 ; J. Chem. Soc. **54**, 360.

Analogy between the Ketonic Acids and the Alkyl Sulfones of the Fatty Acids.

Some alkyl sulfones of the fatty acids of the formulæ $RSO_2 CO_2 H$; $RSO_2 CH_2 CO_2 H$ and $RSO_2 CH_2 CH_2 CO_2 H$ were described and the points of resemblance between them and the corresponding ketonic acids pointed out.

BERGREEN, HENRY, 1888.

Ber. **21**, 337–352 ; J. Chem. Soc. **54**, 444 ; Bull. Soc. chim. **50**, 556.

Thiocarbonyl Chlorid.

The action of thiocarbonyl chlorid on sodium and copper acetoacetic esters is given in this article (Ber. pps. 347-348) by which is produced thiocarbonylacetoacetic ester, a solid which softens at 152° and melts at 156° to 162°. The formula $[CH_3 COC (CS) CO_2 C_2 H_5]_x$ is ascribed to it, as the author thinks it is not a simple molecule. It will not react with phenylhydrazin or hydroxyl-amin. Thiocarbonyl chlorid acting on sodium methyl-acetoacetic ester produces an oil free from chlorin, which contains sulfur. It cannot be distilled and no crystalline product can be obtained from it.

BONGARTZ, J., 1888.

Ber. **21**, 478–487 ; J. Chem. Soc. **54**, 478.

Compounds of Aldehydes, Ketones and Ketonic Acids with Thioglycollic Acid.

The action of hydrochloric acid gas on a mixture of thioglycollic acid and acetoacetic ester is given in this article (Ber. p. 485) by which a white crystalline powder is formed which melts at 95° to 96°. It is acetoacetic ester dithioglycollic acid and has the formula

$$CH_3\,C\begin{cases}(SCH_2\,CO_2\,H)_2\\ CH_2\,CO_2\,C_2\,H_5\end{cases}$$

HALLER, A. AND A. HELD, 1888.

Compt. rend. **105**, 115–117 ; J. Chem. Soc. **52**, 1029.

Cyan-acetoacetic Ester.

A new method of producing this compound is given. Cyanacetic ester dissolved in alcohol is mixed with sodium dissolved in alcohol and acetyl chlorid in ether. The equation given is 2 $CH(CN)NaCO_2C_2H_5 + CH_3COCl = NaCl + CH_2(CN)CO_2C_2H_5 + CH_3COC(CN)NaCO_2C_2H_5$. This shows conclusively that the composition of the compound is that here assigned to it.

HALLER, A. AND A. HELD, 1888.

Compt. rend. **106**, 210–213 ; Bull. Soc. chim. **49**, 243 ; J. Chem. Soc. **54**, 579 ; Ber- **21**, 187 (C).

Cyan-acetoacetic Methyl Ester.

This body, $CH_3COCH(CN)CO_2CH_3$, was prepared from cyanogen chlorid and a mixture of acetoacetic methyl ester and sodium methoxid. It melts at 46.5°. It was also prepared by treating sodcyanacetic methyl ester with acetyl chlorid. The sodium and calcium compounds were prepared.

GENVRESSE, P., 1888.

Compt. rend. **107**, 687–689 ; J. Chem. Soc. **56**, 122 ; Ber. **21**, 831 (C).

Chlorin Derivatives of Acetoacetic Ester.

Dichlor-acetoacetic ester can be decomposed by hydrochloric acid into unsymmetrical dichloracetone, wherefore, (?) the formula $CHCl_2COCH_2CO_2C_2H_5$ is assigned to it. For similar reasons the trichlor-derivative is supposed to be $CCl_3COCH_2CO_2C_2H_5$, tetrachlor derivative $CCl_3COCHClCO_2C_2H_5$, and the penta-chlor derivative $CCl_3COCCl_2CO_2C_2H_5$. Two compounds containing, one, seven and the other nine atoms of chlorin were also produced, described and given the formulæ $CCl_3COCCl_2CO_2C_2H_3Cl_2$ and $CCl_3COCCl_2CO_2CHCl_4$. Acetoacetic methyl ester yields similar derivatives.

GEUTHER, A., 1888.

Ann. Chem. **244**, 190–221 ; J. Chem. Soc. **54**, 579 ; Ber. **21**, 295 (C).

Constitution of Acetoacetic, Succinosuccinic and Quinone-hydro-dicarboxylic Acids.

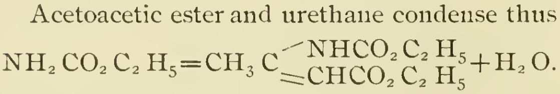
The author contends for the constitution of acetoacetic ester as $CH_3COH : CHCO_2C_2H_5$, giving as a proof of the hydroxyl group the similarity of reactions between acetoacetic ester and phenol and salicylic-ester, (1) towards potassium hydroxid and then carbon dioxid when, he states, the original substances are regained, (2) towards potassium cyanid, when potassium compounds are produced, although the potassium compounds of salicylic and succinosuccinic esters are decomposed into alcohol and the potassium salts and the acetoacetic ester compound is decomposed into alcohol and the potassium salt, which latter is then further decomposed into potassium carbonate and acetone. (3) towards ferric chlorid, as to the colors produced. He cites the easy decomposition of acetyl-acetoacetic ester as a proof that it has the formula $CH_3CO(COCH_3) : CHCO_2C_2H_5$. In the formation of sod-acetoacetic ester he supposes the intermediate bivalent group $CH_3CONa :$ is formed which unites with acetic ester liberating two atoms of hydrogen.

MEISTER, JOHANNES, 1888.

Ann. Chem. **244**, 233–253 ; J. Chem. Soc. **54**, 675 ; Ber. **21**, 427 (C).

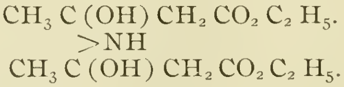
Condensation Product of Urethane and Acetoacetic Ester.

Acetoacetic ester and urethane condense thus :



$$CH_3COCH_2CO_2R + NH_2CO_2C_2H_5 = CH_3C\begin{array}{l}\nearrow NHCO_2C_2H_5\\ \searrow CHCO_2C_2H_5\end{array} + H_2O.$$

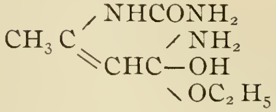
The product is the same as that produced from chlor-carbonic ester and paramido-acetoacetic ester and so is given the above formula. Alcoholic potash saponifies it giving an oil $C_{12}H_{23}NO_6$, considered as



$$\begin{array}{l} CH_3C(OH)CH_2CO_2C_2H_5. \\ \qquad > NH \\ CH_3C(OH)CH_2CO_2C_2H_5. \end{array}$$

A tribrom-derivative of the condensation product was formed but a trichlor-derivative could not be formed.

Alcoholic ammonia acts on it to form a body $C_7H_{15}N_3O_3$, which may be represented thus:—



$$CH_3C\begin{cases}NHCONH_2\\ CH\overset{NH_2}{\underset{OC_2H_5}{C}}-OH\end{cases}$$

and which is β-uramidocrotonic amid together with one molecule of alcohol. Boiling this with water decomposes it into urea, acetone, alcohol, carbon dioxid and ammonia.

MEWES, W., 1888.

Ann. Chem. **245**, 58-84; J. Chem. Soc. **54**, 817; Ber. **21**, 473 (C).

Halogen Substitution Products of Acetoacetic Ester and their Behavior with Sodethoxid.

Passing chlorin through acetoacetic ester produces the mono-, di-, tri- and tetra-chlor-acetoacetic esters which boil at 194°, 205°-207°, 223°-225°, and 245°-250° respectively. Some difficulty was found in entirely separating them from one another. The bromo-chlor-acetoacetic esters were formed by treating the chlor-acetoacetic esters with bromin and also by treating the bromo-acetoacetic esters with chlorin. Sodethoxid decomposes all of the halogen derivatives forming the mono- or di-halogen acetic esters. Bromoacetoacetic ester with sodethoxid yields succinosuccinic ester. When the chlorobrom-substitution products are treated with sodethoxid, sodium *bromid* is always formed.

KNORR, L., 1888.

Ann. Chem. **245**, 357-382; J. Chem Soc. **54**, 1111; Ber. **21**, 628 (C).

Synthetical Researches on Acetoacetic Ester. Part IV.

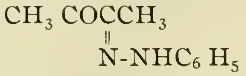
Methyl-acetoacetic anilid, $CH_3COCH(CH_3)CONHC_6H_5$, which was prepared from methyl-acetoacetic ester and anilin, melts at 138° to 140°. Sulfuric acid changes it into dimethyl-carbostyril [3′:4′], a weak acid from which the dimethyl product $C_9H_4OH(CH_3)_2N$ was obtained. Chlor-dimethyl-quinolin [$Cl:(CH_3)_2=2':3':4'$], ortho-[4′:1], meta- and para-[4′:3] dimethyl-quinolin were described together with some phenyl, nitrogenous derivatives.

JAPP, FRANCIS AND FELIX KLINGMANN, 1888.

Ber. **21**, 549-551.

Formation of Mono- and Di-hydrazin Derivatives of *α*-Di-ketones.

Methyl-acetoacetic acid and diazobenzene chlorid, $C_6H_5N_2Cl$, react and form the monophenylhydrazin derivative of diacetyl,



$$\begin{matrix} CH_3\,COCCH_3 \\ \Vert \\ N\text{-}NHC_6H_5 \end{matrix}$$

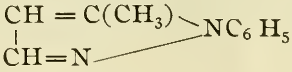
which melts at 133°. If treated with phenylhydrazin the di-phenylhydrazin derivative is formed. Ethyl-acetoacetic acid reacts similarly and gives rise to the corresponding compounds.

CLAISEN, L. AND N. STYLOS, 1888.

Ber. **21**, 1144–1149; J. Chem. Soc. **54**, 671.

Acetoacetic-aldehyde.

The sodium compound of acetoacetic-aldehyde, $CH_3COCHNaCHO$, was prepared from acetone, formic ester and sodium ethoxid. The free aldehyde could not be isolated on account of its tendancy to break down into symmetrical triacetyl benzene, which was made and described. The anilid, toluidid and napthalid of the aldehyde were prepared. Treated with phenylhydrazin, methyl-phenyl-pyrazole,



$$\begin{matrix} CH = C(CH_3) \\ | \\ CH = N \end{matrix} > NC_6H_5$$

, was obtained.

PECHMANN, H. v., 1888.

Ber. **21**, 1411-1422; J. Chem. Soc. **54**, 811.

α-Diketones.

The diketones described in this article are prepared from monoalkyl acetoacetic esters, by saponifying with dilute alkali, treating the product with sodium nitrite and sulfuric acid and after removing the alcohol by distillation, adding twenty times the volume of dilute sulfuric acid and distilling with steam. Methyl-acetoacetic ester treated in this manner gives diacetyl, $CH_3COCOCH_3$, and ethyl-acetoacetic ester gives acetyl-propionyl, $CH_3COCOCH_2CH_3$.

BEYER, C. AND L. CLAISEN, 1888.

Ber. **21**, 1697-1705.

Mixed Azo Compounds.

In this article some azo compounds are described which are formed from acetoacetic esters.

GRIESS, P. AND G. HARROW, 1888.

Ber. **21**, 2740-2743 ; J. Chem. Soc. **54**, 1313.

Action of Acetoacetic Ester on Hexamethylenetetramin.

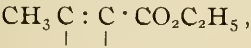
When acetoacetic ester acts on hexamethylenetetramin, $(CH_2)_6N_4$, in presence of zinc chlorid, lutidin-di-carboxylic ester and hydro-lutidin-di-carboxylic ester are formed. The latter, $C_5NHH_2(CH_3)_2(CO_2C_2H_5)_2$, melts at 170°, is neutral and is considerably decomposed upon being distilled. Treated with hydrochloric acid it gives two products, the mono- and di-ethyl esters of lutidin-dicarboxylic acid.

MICHAEL, A., 1888.

J. prakt. Chem. **145**, 473–530 ; Am Chem. J. **10**, 158–160 ; J. Chem. Soc. **54**, 1054 ; Ber. **21**, 530 (C) ; Bull. Soc. chim. **50**, 690.

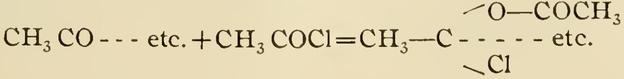
Constitution of Sodacetoacetic Ester.

By the action of chlor-carbonic ester on sodacetoacetic ester, carbethoxacetoacetic ester was produced which boils unchanged at 127° at 17m.m. pressure. No sodium derivative of this could be prepared, consequently it was considered to be an isomer of aceto-malonic ester, which does easily form a sodium derivative, and its formation was supposed to be thus :—$CH_3\,CONa:CHCO_2C_2H_5+ClCO_2C_2H_5=CH_3CO(CO_2C_2H_5):CHCO_2C_2H_5+NaCl$. In the author's opinion acetoacetic ester itself is a ketone. He gives as a formula for benzalacetoacetic ester

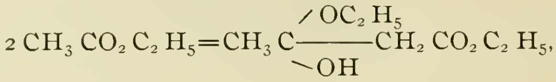
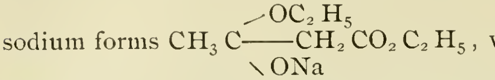
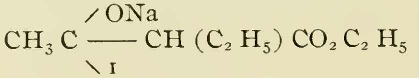


$$\begin{array}{lll} CH_3\,C & : & C\cdot CO_2C_2H_5 \\ \quad | & & | \\ \quad O & — & CHC_6H_5 \end{array}$$

which explains its loss of ketone properties and to explain the reactions between bodies analogous to acetoacetic ester such as levolinic acid, $CH_3\,COCH_2\,CH_2\,CO_2\,H$, and acetyl chlorid, he supposes an addition product thus :—



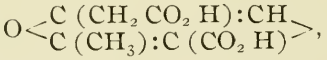
$$CH_3\,CO\text{ - - - etc.} + CH_3\,COCl = CH_3—C\begin{matrix} \nearrow O—COCH_3 \\ \text{- - - - - etc.} \\ \searrow Cl \end{matrix}$$

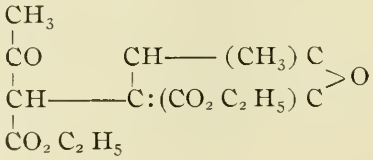
and a subsequent separation of hydrochloric acid forming a lactone. In the formation of sodacetoacetic ester an aldol polymerization is supposed to take place first, the product of which is acted upon by sodium thus :—  $2\,CH_3\,CO_2\,C_2\,H_5 = CH_3\,C\overset{\diagup OC_2\,H_5}{\underset{\diagdown OH}{\text{———}}}CH_2\,CO_2\,C_2\,H_5$, then sodium forms  $CH_3\,C\overset{\diagup OC_2\,H_5}{\underset{\diagdown ONa}{\text{——}}}CH_2\,CO_2\,C_2\,H_5$, which is again acted upon by sodium to form $CH_3\,CONaCHCO_2\,C_2\,H_5$, $NaOC_2\,H_5$ and H. If sodium be made to act on acetoacetic ester, $CH_3\,COCHNaCO_2\,C_2\,H_5$ is formed but the sodium is immediately attracted to the carbonyl group and it changes to form $CH_3\,CONa{:}CHCO_2\,C_2\,H_5$. When this last compound is treated with an alkyl iodid, $C_2\,H_5\,I$ for example, there is an addition product formed and as the group—CONa=is more positive than the group=CH—, the iodin add to the former and the ethyl adds to the =CH—group forming  $CH_3\,C\overset{\diagup ONa}{\underset{\diagdown I}{\text{——}}}CH\,(C_2\,H_5)\,CO_2\,C_2\,H_5$ from which sodium iodid separates leaving $CH_3\,COCH\,(C_2\,H_5)\,CO_2\,C_2\,H_5$.

POLONOWSKY, M., 1888.

Ann. Chem. **246**, 1-32 ; J. Chem. Soc. **54**, 1067 ; Ber. **21**, 636 (C).

Condensation of Glyoxal with Acetoacetic Esters.

By treating a mixture of glyoxal, CHOCHO, and acetoacetic ester with zinc chlorid two products are formed, (1) a part soluble in alkalis which contains methyl-furfuran carboxyacetic or sylvanecarboxyacetic acid,  $O<\begin{matrix}C\,(CH_2\,CO_2\,H){:}CH\\C\,(CH_3){:}C\,(CO_2\,H)\end{matrix}>$, which melts at 207°. The normal and acid, methyl and ethyl esters were produced and described ; (2) a part insoluble in alkalis which consists of a heavy oil and a crystalline substance, both having the composition $C_{14}\,H_{18}\,O_6$. The oil is di-ethyl-sylvane-carboxy-acetoacetic ester which is :—



JAECKLE, A., 1888.

Ann. Chem. **246**, 32–52 ; J. Chem. Soc. **54**, 1103 ; Ber. **21**, 638 (C).

Higher Homologues of the Synthetical Pyridins and Piperidins.

The normal propyl-lutidin hydrodicarboxylic ester, $C_5 NH_2 (CH_3)_2 C_3 H_7 (CO_2 C_2 H_5)_2$, obtained from normal butaldehyde and ammonia acting on acetoacetic ester and alcohol, is a crystalline substance melting at 118°. From this the normal propyl-lutidin-dicarboxylic ester, the free acid and the normal propyl-lutidin were prepared. Hexyl-lutidin hydrodicarboxylic ester was prepared from ammonia, acetoacetic ester and oenanthol, $C_6 H_{13} CHO$, and from it normal hexyl-lutidin, $C_5 NH_2 (CH_3)_2 C_6 H_{13}$. A number of piperidins were obtained from the corresponding pyridins and described.

WISLICENUS, WILHELM, 1888.

Ann. Chem. **246**, 306–309.

Synthesis of Ketone Acid Esters.

As a portion of this article the author briefly reviews the controversy as to the formation of acetoacetic ester from sodium and acetic ester. He thinks that sodium acts on alcohol to form sodethoxid and liberate hydrogen, that the sodethoxid reacts with acetic ester to produce sodacetoacetic ester and alcohol and that thus alcohol is continually produced and used up again. Some of the hydrogen is used up in secondary reactions and some is given off. He doubts the formation of a sodacetic ester as an intermediate product.

JAPP, FRANCIS R. AND FELIX KLINGEMANN, 1888.

Ann. Chem. **247**, 190–225 ; J. Chem. Soc. **53**, 519–544.

Constitution of the So-called Mixed Azo Compounds.

The compounds treated of in this article were prepared from acetoacetic esters.

PECHMANN, H. v., 1888.

Ber. **21**, 3005–3006 ; J. Chem. Soc. **56**, 42.

Condensation Product of Quinone and Acetoacetic Ester,

When quinone, $C_6 H_4 O_2$, is brought in contact with acetoacetic ester in the presence of zinc chlorid they react to form a substance $C_{16} H_{16} O_6$, which melts at 184°. This substance will not react with phenylhydrazin, benzoic chlorid, sodium ethoxid or alkyl iodids. Treated with potassium hydroxid and then an acid a crystalline dibasic acid $C_{14} H_{12} O_6$ is formed which is insoluble in ordinary solvents and sublimes without melting. The salt $C_{14} H_{10} K_2 O_6 + 2H_2O$ was prepared.

CLAISEN, L. AND W. ZEDEL, 1888.

Ber. **21**, 3397-3398 ; J. Chem. Soc. **54**, 377.

Action of Chlorcarbonic Ester on the Sodium Derivatives of Acetylacetone, Acetoacetic Ester and Malonic Ester.

The product obtained by treating acetoacetic ester with chlorcarbonic ester was thought to be the dicarboxylic ester of acetoacetic ester and to have the formula $CH_3 COC (CO_2 C_2 H_5)_2 CO_2 C_2 H_5$.*

CLAISEN, L., 1888.

Ber. **21**, 3567.

A Correction.

By further experiments the author has decided that the compound formed from acetoacetic ester and chlorcarbonic ester is the mono- not the di-carboxylic derivative of acetoacetic ester, that it is $CH_3 COCH (CO_2 C_2 H_5) CO_2 C_2 H_5$ and not $CH_3 COC (CO_2 C_2 H_5)_2 CO_2 C_2 H_5$ as stated by him in Ber. **21**, 3397.†

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*See following article.

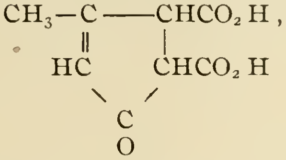
†See preceding article.

KNORR, L., 1889.

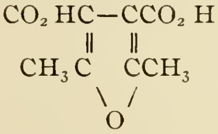
Ber. **22,** 146–152 ; J. Chem. Soc. **56,** 384.

Constitution of Carbopyrotritartaric Acid.

Fittig gives this acid the unsymmetrical formula



while the author gives it a symmetrical one :—



and says that this formula is proven by the fact that only one pyrotritartaric acid and only one hydrogen-ethyl ester can be formed from it.

RAÝMANN, B. AND K. CHODOUNSKY, 1889.

Ber. **22,** 304-305 ; J. Chem. Soc. **56,** 485.

Rhamnodiazin.

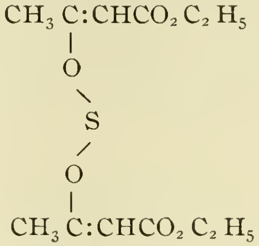
Rhamnodiazin, $C_{18}H_{32}N_2O_8$, is formed from rhamnose, $CH_3(CHOH)_4CHO$, and ammonia and acetoacetic ester in methyl alcohol solution. It melts at 186°. Other glucoses seem to yield similar compounds when treated with acetoacetic ester and ammonia.

DELISLE, A., 1889.

Ber. **22**, 306–309 ; J. Chem. Soc. **56**, 488.

Ketosulfids and Ketosulfid Acids.

The compound described in Ber. **20**, 2008, obtained from acetoacetic ester and sulfur dichlorid is found to be $C_{12}H_{18}O_6S$ intead of $C_{10}H_{14}O_6S$ and the formula



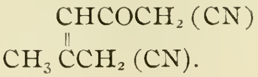
is ascribed to it.

HELD, A., 1889.

Ann. chim. phys. [6] **18**, 468–531 ; Ber. **23**, 287 (C).

Derivatives of Cyanacetoacetic Esters.

The first part of this article is the same as that in Bull. Soc. chim. [3]**1**, 306*. By treating cyanacetoacetic ester with ammonia, amidocyanacetoacetic ester, $CH_3C(NH_2):C(CN)CO_2R$, is obtained which melts at 188°. It is neutral wherefore the above formula is given to it. When it is treated with an alkali. sodcyanacetoacetic ester is obtained. If sulfuric acid be added to the mother liquor left after the formation of the above, a monobasic acid $C_7H_6N_2O_2$ is obtained. The sodium, barium, ammonium, silver, copper and lead salts and ethyl ester were described. When heated with hydrochloric acid, carbon dioxid is given off and another acid $C_6H_7NO_2$ is formed. The author is at work on the constitution of these acids. Ethylamin acts on cyanacetoacetic ester to produce the compound $CH_3C(NHC_2H_5):C(CN)CO_2R$ and the acid $C_9H_{10}N_2O_3$. Cyanacetoacetic ester boiled with water gives $C_8H_8N_2O$ which sublimes at 200° and is a condensation product of cyanacetone,



$$\begin{array}{l} CHCOCH_2(CN) \\ \| \\ CH_3CCH_2(CN). \end{array}$$

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*See page 105.

HALLER, A. AND A. HELD, 1889.

Compt. rend. **108**, 516-518 ; J. Chem. Soc. **56**, 588 ; Ber. **22**, 255 (C).

Monochlor-acetoacetic Esters.

Two monochlor derivatives of acetoacetic ester were formed, the *α*, and the *γ*. The latter by passing chlorin into acetoacetic ester at low temperatures. It boils at 188°-189°. It can be distinguished from the *α* product by the fact that the latter readily forms an insoluble cyanid with potassium cyanid.

HELD, A., 1889.

Bull. Soc. chim. [3] **1**, 306-311 ; Ber. **22**, 407 (C) ; J. Chem. Soc. **56**, 1141.

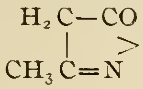
Derivatives of Cyanacetoacetic Ester.

Bromin reacts with cyanacetoacetic ester to form a dibrom derivative, $CH_2BrCOCBr(CN)CO_2C_2H_5$, a yellowish red liquid which decomposes upon being distilled even under reduced pressure. Chlorin forms with cyanacetoacetic ester $C_6H_7(CN)Cl_2O_3$, which boils at 90° to 105° with 20 to 25 m. m. pressure and decomposes spontaneously. Ethyl-cyanacetoacetic ester $CH_3COC(C_2H_5)(CN)CO_2C_2H_5$, prepared from ethyl-sodacetoacetic ester and cyanogen chlorid, boils at 103° to 105° at 25 m. m. pressure. Potassium hydroxid decomposes it into acetic and butyric acids. Methyl-cyanacetoacetic ester prepared similarly boils at 90° to 92° at 20 m. m. pressure. Potassium hydroxid decomposes it into acetic and propionic acids. Unsuccessful attempts were made to prepare cyanacetoacetic acid.

CURTIUS, TH. AND R. JAY, 1889.

J. prakt. Chem. [2] **39**, 27-58 ; Ber. **22**, 134 (C); J. Chem. Soc. **56**, 393.

Hydrazin.

On pages 51 and 52 of this article the reaction between acetoacetic ester and hydrazin hydrate, N_2H_4, H_2O, is treated of. Methyl pyrazolone, 

$$\begin{array}{l} H_2C-CO \\ \quad| \qquad \quad >NH \\ CH_3C=N \end{array}$$

is formed which is a crystalline substance melting at 215°, which will dissolve in both acids and alkalis.

BIGINELLI, P., 1889.

Gazz.* chim. **19**, 212-214 ; Ber. **22**, 688 (C) ; J. Chem. Soc. **58**, 768.

Action of Acetoacetic Ester on Cinnamaldehyde.

When acetoacetic ester, cinnamaldehyde and ethylen-diamin are mixed and heated, a reaction takes place and a crystalline substance, $C_{21} H_{26} O_6$ is formed which melts at 160°-161.° It will give a bromin derivative and is decomposed by caustic potash. Methylamin or anilin may be used in place of ethylendiamin without changing the result. If benzaldehyde be used in place of cinnamaldehyde a compound free from nitrogen is obtained but if propaldehyde is used a compound containing nitrogen is produced.

BIGINELLI, P., 1889.

Gazz.* chim. **19**, 215-217 ; Ber. **22**, 689 (C) ; J. Chem. Soc. **58**, 732.

Action of Acetoacetic Ester on Dextrose in Alcoholic Ammonia.

In this reaction two compounds are formed, $C_{16} H_{26} O_8 N$ a neutral substance which melts at 189°-190° and $C_{10} H_{16} O_5 N$, which melts at 130°-131.° The latter was formed in sealed tubes at 100° to 110.° The author is continuing the investigation of these reactions.

KIPPING, F. STANLEY AND W. H. PERKIN, Jr., 1889.

J. Chem. Soc. **55**, 330-351 ; Ber. **22**, 571 (C).

***α-ω*-diacetyl-pentane and *α-ω*-dibenzoyl-pentane.**

In the researches upon these compounds the first one was made from acetoacetic ester. Sodacetoacetic ester was treated with trimethylene bromid and after the reaction more sodium dissolved in alcohol was

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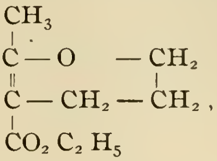
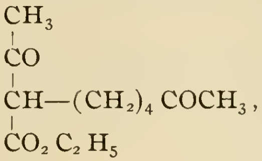
*Original article not consulted.

added. This process gave a much better yield than any other method tried. The product obtained is methyl-dehydrohexone carboxylic ester,



This is changed by hydrobromic acid into aceto-butyl-bromid, $CH_3CO(CH_2)_4Br$, and this by sodacetoacetic ester into *α-ω*-diacetylcaproate.



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH—(CH_2)_4COCH_3, \\ | \\ CO_2C_2H_5 \end{array}$$

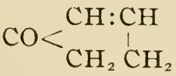
Treating this with potassium hydroxid the free acid is produced and by heating this carbon dioxid is given off and *α-ω*-diacetyl-pentane, $CH_3CO(CH_2)_5COCH_3$, is obtained. Several derivatives of this are described.

FITTIG, R., FRITZ VON EYNERN AND ADOLF DIETZEL, 1889,

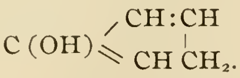
Ann. Chem. **250**, 166-211 ; J. Chem. Soc. **56**, 592 ;
Ber. **22**, 200 (C).

Condensation of β-Ketonic Esters with Dibasic Acids.

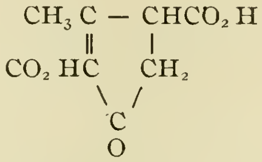
After a discussion of the constitution of the products of condensation of succinic and pyruvic acids with acetoacetic ester, it is decided that they are all derived from, either



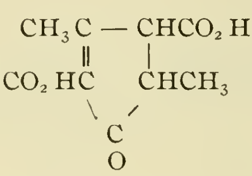
or from



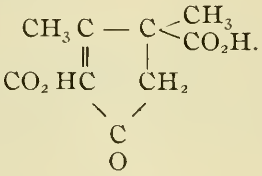
Pyrotritartaric acid is now called uvitic acid and carbpyrotritartaric acid is now called carbuvitic acid. When acetoacetic ester, acetic anhydrid and sodium succinate are heated together they give hydrogen methronic ester, $C_8H_7(C_2H_5)O_5$, a crystalline substance which melts at 75°-76°. The calcium, barium and silver salts were described. From it was prepared methronic acid,



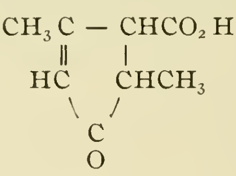
which decomposes at high temperatures to form uvic acid. Methronic diethyl ester, $C_8H_6(C_2H_5)_2O_5$, and a phenylhydrazin derivative were also described. By heating acetoacetic ester and pyruvic acid, CH_3COCO_2H, with acetic anhydrid, hydrogen methyl methronic ester is formed and from this the methyl-methronic acid which is



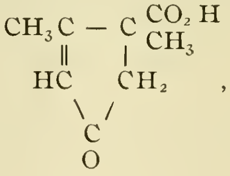
or



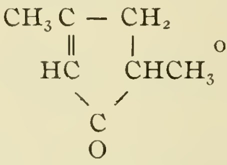
No acid salts of this are known but the normal calcium, barium and silver salts were described. Methyl-methronic diethyl ester was also described. From methyl-methronic acid were obtained methyl-uvic acid,



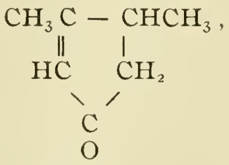
or



and dimethyl-keto-pentene,



or

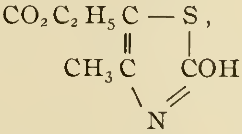


ZÜRCHER, H., 1889.

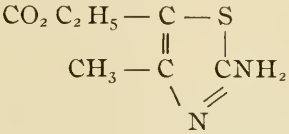
Ann. Chem. **250**, 281-294; J. Chem. Soc. **56**, 725; Ber. **22**, 258 (C).

Action of Thiocyanates and Thiocarbamids on Chlorinated Acetoacetic Esters.

Methyl-oxythiazole-carboxylic ester,



is formed from monochlor-acetoacetic ester and a metallic thiocyanate. Some of its reactions and derivatives are described. Thiocarbamid acting on monochlor-acetoacetic ester gives amidomethyl-thiazole-carboxylic ester,

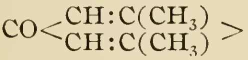


from which the free acid and some of its salts were obtained. Dichlor-acetoacetic ester reacts with barium thiocyanate to form a compound $C_{14}H_{16}O_7N_2S_2$. With thiocarbamid dichlor-acetoacetic ester does not react.

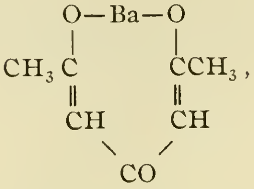
FEIST, FRANZ, 1889.

Ber. **22**, 1570-1571; J. Chem. Soc. **56**, 957; Bull. Soc. chim. [3]**3**, 657.

Dehydracetic Acid.

Dehydracetic acid when treated with hydriodic acid gives dimethylpyrone,  $CO<\begin{matrix}CH:C(CH_3)\\CH:C(CH_3)\end{matrix}>O$, which melts at 132°, boils at 248°-249°

at 719 m.m. pressure. An aqueous solution of this gives with barium hydroxid $C_7 H_8 O_3 Ba$ a (xantho) barium salt,



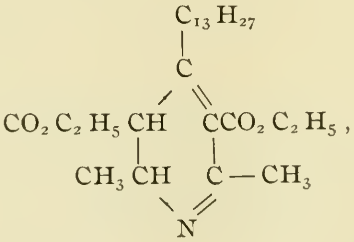
which, when treated with hydrochloric acid gives a tri-ketone $CH_3 COCH_2 COCH_2 COCH_3$, which melts at 49° and at higher temperatures gives off water and forms dimethyl-pyrone again. When the triketone is heated with ammonia, lutidone is formed.

KRAFFT, F. AND J. MAI, 1889.

Ber. **22**, 1757-1759; J. Chem. Soc. **56**, 1017.

Myristic Aldehyde.

When myristic aldehyde, $C_{13} H_{27} CHO$, ammonia and acetoacetic ester are mixed a reaction takes place and hydrotridecyl-lutidin-dicarboxylic ester,

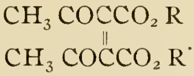


is formed, which melts at 60°. From this were formed the corresponding compounds; — tridecyl-lutidin-di-carboxylic ester, tridecyl-lutidin-di-carboxylic acid and tridecyl-lutidin.

SCHÖNBRODT, R., 1889.

Ann. Chem. **253**, 168-205 ; J. Chem. Soc. **58**, 27 ; Ber. **22**, 680 (C).

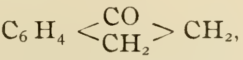
Derivatives of Acetoacetic Ester.

By passing chlorin through cupracetoacetic ester in chloroform the mono- and di-chlor derivatives were formed and the corresponding bromin derivatives were similarly formed. Iodacetoacetic ester produced from cupracetoacetic ester and iodin is an unstable oil which decomposes at 25° in a vacuum, its specific gravity is 1.705 at 14°, in alcoholic solution it gives a blood red color with ferric chlorid. Silver chlorid converts it into mono-chlor-acetoacetic ester. When treated with silver nitrite an oil is produced which gives a blood red color with ferric chlorid and sulfuric acid and which is probably nitroacetoacetic ester. Treated with phenylhydrazin it gives phenyl-methyl-nitroso-pyrazolone [1 : 3 : 4 : 5]. Sodacetoacetic ester and iodacetoacetic ester give diacetosuccinic ester. Iodacetoacetic ester and metallic silver give diacetofumaric ester,  $\begin{array}{c} CH_3\,COCCO_2\,R \\ \| \\ CH_3\,COCCO_2\,R \end{array}$. Cupracetoacetic ester boiled in benzene with sulfur gives thioacetoacetic ester. In presence of alcohol, phosphorus acts on cupracetoacetic ester to form acetoacetic ester and tri-ethyl phosphite, $P(OC_2H_5)_3$. Cupracetoacetic ester and arsenic trichlorid form cuprous chlorid, arsenic and mono-chlor-acetoacetic ester. Unsuccessful attempts were made to replace hydrogen by copper in methyl-acetoacetic ester.

GABRIEL, S. AND J. HAUSMANN, 1889.

Ber. **22**, 2017-2019 ; J. Chem. Soc. **56**, 1172.

Action of Orthocyanobenzylchlorid on Sodacetoacetic Ester.

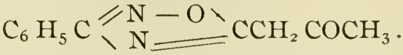
In this reaction two products are formed, a small amount of di-ortho-cyanobenzylacetoacetic ester, $CH_3COC(CNC_6H_4CH_2)_2CO_2C_2H_5$, and a much larger amount of orthocyanobenzylacetic ester, or ortho-cyanohydro-cinnamic ester, $(CNC_6H_4CH_2)CH_2CO_2C_2H_5$. The latter is a colorless, crystalline substance melting at 98°–99° which is decomposed when warmed with hydrochloric acid into α-hydrindone, carbon dioxid, alcohol and ammonia. α-Hydrindone.  $C_6H_4 < \begin{smallmatrix} CO \\ CH_2 \end{smallmatrix} > CH_2$, crystallizes and melts at 40° and boils at 243°-245°. Diortho-cyano-benzylacetoacetic ester is a colorless crystalline substance which melts at 120°.

TIEMANN, F., 1889.

Ber. **22**, 2412–2417 ; J. Chem. Soc. **58**, 44.

Action of Acetaldehyde and Acetoacetic Ester on Benzenyl-amidoxim.

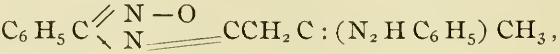
Acetoacetic ester and benzenyl-amidoxim, $C_6H_5C\begin{matrix}\diagup N-OH \\ \diagdown NH_2\end{matrix}$, react to form benzenylaceto-ethenylazoxim,



Alkalis decompose it, forming benzenyl-ethenyl-azoxim,

and acetic acid. The oxim,

and the hydrazone,



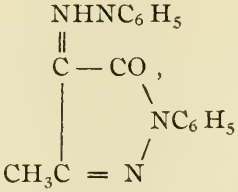
were also described.

BUCHKA, K. AND C. SPRAGUE, 1889.

Ber. **22**, 2541–2556 ; J. Chem. Soc. **58**, 28.

Thioacetoacetic Ester.

This substance, $C_{12}H_{18}O_6S$, melts at 76° and forms a sodium derivative $C_{12}H_{16}Na_2O_6S$. Schönbrodt has proven that the sulfur is joined to the *α*-carbon atom and not to oxygen. Phenylhydrazin reacts with it to form phenylmethyl-pyrazoloneketo-phenylhydrazone or phenylmethyl-pyrazolonazobenzene,



and a yellow substance which appears to be $C_{10}H_8N_2SO$. The compound which Schönbrodt describes as phenylmethyl-nitrosopyrazolone is identical with phenylmethyl-pyrazolonazobenzene. Thioacetoacetic ester unites with paratolylhydrazin and *α*-naphthylhydrazin yielding a series of complicated compounds in each case.

MICHAELIS, A. AND OSCAR BURCHARD, 1889.

Ann. Chem. **254**, 115-128.

Syntheses by Means of Sodium-phenylhydrazin. Ethylenphenylhydrazin.

In the last paragraph of this article mention is made that ethylenphenylhydrazin easily condenses with acetoacetic ester to form a beautiful crystalline substance which melts at 54° It is being investigated by the authors.

RAYMAN, B. AND O. POHL, 1889.

Ber. **22**, 3247-3249; J. Chem. Soc. **58**, 355.

Rhamnodiazin.

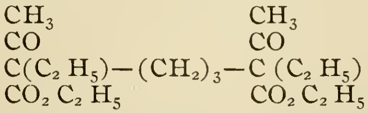
Rhamnodiazin, $C_{18} H_{32} O_8 N_2$, is further studied but no very definite results are obtained. Its constitution is probably $CH_3 (CHOH)_4 CH (N:C < \begin{smallmatrix} CH_3 \\ CH_2 CO_2 C_2 H_5 \end{smallmatrix})_2$. When rhamnose, acetoacetic ester and an amin are mixed they form rhamnosamin.

KIPPING, F. STANLEY AND W. H. PERKIN, Jr., 1890.

J. Chem. Soc. **57**, 29-38; Ber. **23**, 249 (C).

α-ω-Diacetyl-α-ω-diethylpentane.

This substance whose properties and reactions are described is obtained by treating sodacetoacetic ester with tri-methylene bromid. These substances combine to form *α*-*ω*-diacetyl-*α*-*ω*-diethyl-pimelic ester which is



$$\begin{array}{lll} CH_3 & & CH_3 \\ CO & & CO \\ C(C_2 H_5) & -(CH_2)_3- & C (C_2 H_5) \\ CO_2 C_2 H_5 & & CO_2 C_2 H_5 \end{array}$$

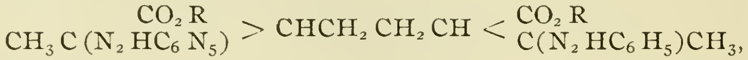
and when this is boiled with alcoholic potash there is formed *α*-*ω*-diacetyl-*α*-*ω*-diethyl-pentane, $CH_3 COCH (C_2 H_5) (CH_2)_3 CH (C_2 H_5) COCH_3$, as well as some *ω*-acetyl-*α*-*ω*-diethyl-caproic acid.

PERKIN, Jr., W. H., 1890.

J. Chem. Soc. **57**, 204-241.

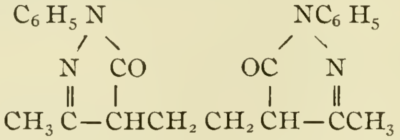
$\alpha-\alpha'$-Diacetyladipic Ester.

Sodacetoacetic ester and ethylene bromid react to form two products, (1) acetyl-trimethylene-carboxylic ester, $\begin{matrix}CH_3CO\\CO_2R\end{matrix}>C<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, and (2) $\alpha-\alpha'$-diacetyladipic ester, $\begin{matrix}CH_3CO\\CO_2R\end{matrix}>CHCH_2CH_2CH<\begin{matrix}COCH_3\\CO_2R.\end{matrix}$ The latter compound is a thick colorless oil, rather difficultly separable from impurities, which decomposes some when distilled yielding a mixture of several compounds. It will give a diphenylhydrazin derivative,



$$\begin{matrix}CO_2R\\CH_3C(N_2HC_6N_5)\end{matrix}>CHCH_2CH_2CH<\begin{matrix}CO_2R\\C(N_2HC_6H_5)CH_3,\end{matrix}$$

which melts at 145° and when heated higher gives bis-phenyl-methyl methylene-pyrazolone,



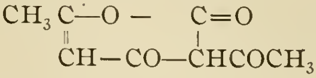
Many other reactions and derivatives of $\alpha-\alpha'$-diacetyladipic ester were given.

FEIST, FRANZ, 1890.

Ann. Chem. **257**, 253-297 ; Ber. **23**, 463 (C).

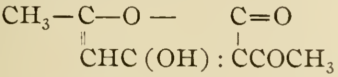
Dehydracetic Acid.

In this long article account is given of a study of dehydracetic acid made in order to determine its constitutional formula and its relation to its isomers. A large number of reactions are described and a great many of its derivatives are produced and their constitution determined. A figure is given representing the most important reactions and a table of comparisons of the three isomeric bodies $C_8H_8O_4$. They are assigned the following formulæ. For dehydracetic :—



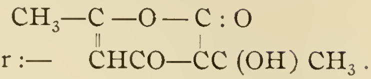
$$\begin{array}{l} CH_3C—O— \quad C=O \\ \quad\;\; \| \qquad\qquad\; | \\ \quad\;\; CH—CO—CHCOCH_3 \end{array}$$

or the tautomeric forms of :—



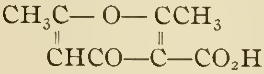
$$\begin{array}{l} CH_3—C—O— \quad C=O \\ \qquad\; \| \qquad\qquad\quad | \\ \qquad\; CHC(OH):CCOCH_3 \end{array}$$

or :—



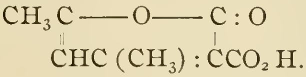
$$\begin{array}{l} CH_3—C—O—C:O \\ \qquad\; \| \qquad\quad\; | \\ \qquad\; CHCO—CC(OH)CH_3. \end{array}$$

For *α—α*-dimethyl-pyron-carboxylic acid :—



$$\begin{array}{l} CH_3C—O—CCH_3 \\ \quad\;\, \| \qquad\quad\;\; \| \\ \quad\;\, CHCO—C—CO_2H \end{array}$$

and for isodehydracetic acid :—



$$\begin{array}{l} CH_3C——O——C:O \\ \quad\;\; \| \qquad\qquad\quad | \\ \quad\;\; CHC(CH_3):CCO_2H. \end{array}$$

PETERS, THEODOR, 1890.

Ann. Chem. **257**, 339–353 ; J. Chem. Soc. **58**, 1097 ; Ber. **23**, 468 (C).

Action of Alkyl Substituted Acetoacetic Esters with Ammonia.

By the action of ammonia on these esters two products are formed (1) *α*-alkyl-*β*-amido-crotonic acid, $CH_3C(NH_2):CRCO_2R$, and (2) amids of alkylacetoacetic acid, $CH_3COCHRCONH_2$, but the former only is produced when anhydrous ammonia is employed. Ethyl-acetoacetic methyl ester yields ethyl-amido-crotonic methyl ester, $CH_3C(NH_2):C(C_2H_5)CO_2CH_3$, which melts at 35°–36°, and ethyl-acetoacetamid, $CH_3COCH(C_2H_5)CONH_2$, melting at 96.° Methyl-acetoacetic ester yields methyl-acetoacetamid, $CH_3COCH(CH_3)CONH_2$, melting at 73.° *α*-Methyl-*β*-amido-crotonic ester melts at 53.° Isobutyl acetoacetamid melts at 88°, *α*-isobutyl-*β*-amido-crotonic ester melts at 41°-42°, isoamyl-acetoacetamid, $CH_3COCH(C_5H_{11})CONH_2$, melts at 129° and *α*-isoamyl-*β*-amido-crotonic ester, $CH_3C(NH_2):C(C_5H_{11})CO_2C_2H_5$, melts at 50.° Diethyl-acetoacetic ester is not attacked by either anhydrous or aqueous ammonia.

PETERS, THEODOR, 1890.

Ann. Chem. **257**, 353–358 ; J. Chem. Soc. **58**, 1096 ; Ber. **23**, 468 (C).

Action of Alcohols on Acetoacetic Ester.

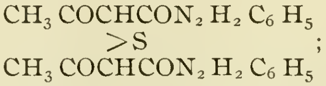
When a little sodium is dissolved in the alcohol, methyl, isopropyl and isoamyl alcohols will convert acetoacetic ester into the methyl, isopropyl and isoamyl esters respectively, slowly at ordinary temperatures but quickly if heated. Even in the absence of sodium, isopropyl and isoamyl alcohols will thus convert acetoacetic ester if the mixtures be boiled together, while methyl alcohol has no action in the absence of sodium. Ethyl-acetoacetic ester reacts similarly with these alcohols. Acetoacetic isobutyl ester, $CH_3\,COCH_2\,CO_2\,C_4\,H_9$, boils at 198°–202° and its ethyl derivative, $CH_3COCH(C_2H_5)CO_2C_4H_9$, boils at 211°–215°. Acetoacetic isoamyl ester, $CH_3\,COCH_2\,CO_2\,C_5\,H_{11}$, boils at 217°–219° and its ethyl derivative, $CH_3\,COCH\,(C_2\,H_5)\,CO_2\,C_5\,H_{11}$, boils at 226°–230°.

MICHAELIS, A. AND B. PHILIPS, 1890.

Ber. **23**, 559–561 ; J. Chem. Soc. **58**, 582.

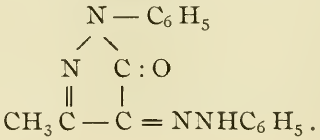
Thio-acetoacetic Ester.

This substance was prepared by treating acetoacetic ester with thionyl chlorid, $SOCl_2$; it melts at 100°–101°. When treated with an excess of phenylhydrazin it gives phenylmethylpyrazolonazobenzene which melts at 156°, but when twice the molecular proportion of phenylhydrazin is added in cold, acetic acid a compound of the composition $C_{20}\,H_{22}\,N_4\,O_4\,S$ is produced. This is probably thioacetoacetic phenylhydrazid which is



$$\begin{matrix} CH_3\,COCHCON_2\,H_2\,C_6\,H_5 \\ >S \\ CH_3\,COCHCON_2\,H_2\,C_6\,H_5 \end{matrix}\;;$$

it decomposes at 185°. When this is heated with an excess of phenylhydrazin it forms phenylmethyl pyrazolonazobenzene,



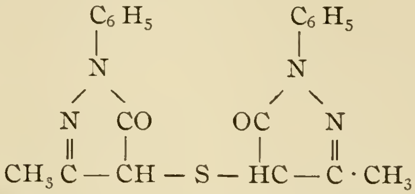
BUCKA, K. AND CH. SPRAGUE, 1890.

Ber. **23**, 847–855 ; J. Chem. Soc **58**, 796.

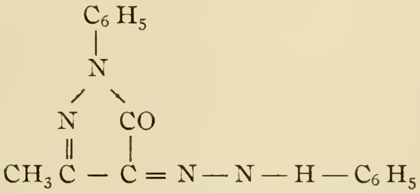
Action of Phenylhydrazin on Thioacetoacetic Ester.

When these substances react in cold, glacial acetic acid in the proportion of one molecule of thioacetoacetic ester to two molecules of phenylhydrazin they form thiophenylmethylpyrazolone,

$C_{20}H_{18}N_4SO_2 =$



and not $C_{20}H_{22}N_4SO_4$ as Michaelis and Philips state in their article (*which see). It decomposes at 183° without melting, is soluble in alkalis and forms stable salts with strong acids. When heated with an excess of phenylhydrazin it goes over into phenylmethylpyrazolone-ketophenylhydrazone which is the same as Michaelis' phenyl-methyl-pyrazolonazobenzene,



CLOEZ, C., 1890.

Compt. rend. **110**, 583–586 ; J. Chem. Soc. **58**, 739 ; Ber. **23**, 284 (C).

Hydroxytetric Acid.

By treating methyl-acetoacetic ester with bromin dibrom-methyl-acetoacetic ester, $C_6H_7Br_2(CH_3)O_3$, is formed, and when this is treated with alcoholic potash, hydroxytetric acid, $C_5H_6O_4$, is obtained,

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*See page 116.

which melts at 201°–202°. By the action of water on dibrom-methyl-acetoacetic ester in presence of barium chlorid hydroxytetric ester, $C_5H_5(C_2H_5)O_4$, is obtained, it melts at 67°–68° and has an acid reaction. By treating an alcoholic solution of hydroxytetric acid with gaseous hydrochloric acid a body boiling at 224°–226° and having the composition of hydroxytetric diethyl ester is obtained.

CLOEZ, C., 1890.

Bull. Soc. chim. [3] **3**, 602–605 ; Ber. **23**, 435 (C).

Identity of Hydroxytetric and Mesaconic Acids.

The author proves the identity of these acids by their melting points, solubility in water, volatilization, brown color given with ferric chlorid and the same reactions towards bromin and acetyl chlorid.

HALLER, A. AND A. HELD, 1890.

Compt. rend. **111**, 647–650 ; J. Chem. Soc. **60**, 171.

γ-Cyanacetoacetic Esters and their Chlor-imido Derivatives.

γ-Cyanacetoacetic ester boils at 135° to 138°, at 40 to 45 m.m. pressure, with some decomposition. Treated with hydrochloric acid in alcoholic solution the hydrochlorid of the imido ester of acetone-dicarboxylic ester, $CH_2(CO_2C_2H_5)COCH_2C(OC_2H_5)(NH),HCl$, is formed which is very unstable being decomposed by water. γ-Cyanacetoacetic methyl ester boils at 217° to 218° and when treated with hydrochloric acid in methyl alcohol it yields the hydrochlorid of the imido ester of acetondicarboxylic methyl ester + one molecule of HCl which is either $CH_2(CO_2CH_3)CH(OH)CHClC(OCH_3)(NH),HCl$ or $CHCl(CO_2CH_3)CH(OH)CH_2C(OCH_3)(NH),HCl$.

NEF, J. U., 1890.

Ann. Chem. **258**, 261–318, Am. Chem. J. **12**, 379–425; J. Chem. Soc. **58**, 983.

Tautomeric Compounds.

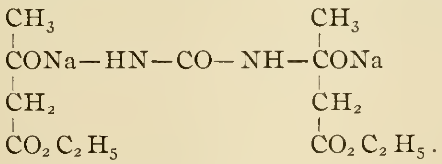
In this article acetoacetic ester is considered and the author decides that it is a tautomeric compound; that the sodium derivative has the sodium combined to oxygen, thus: $CH_3CONa:CHCO_2C_2H_5$, but that the ester itself and its alkyl derivatives have the ketonic oxygen, thus: $CH_3COCHRCO_2R$. By treating sodacetoacetic ester with benzoyl chlorid two compounds were produced, the principal one was monobenzoyl-acetoacetic ester and the minor one was dibenzoyl-acetoacetic ester, $CH_3COC(COC_6H_5)_2CO_2C_2H_5$, which has never been prepared before. It is very unstable and cannot be distilled even in vacuum.

BEHREND, R. AND PAUL ERNERT, 1890.

Ann. Chem. **258**, 360–362; J. Chem. Soc. **58**, 1240; Ber. **23**, 643(C).

Condensation of Carbamid with Acetoacetic Ester.

Carbamid condenses with sodacetoacetic ester to form a compound $C_{13}H_{22}N_2O_7Na_2$ which is probably represented by the formula



$$\begin{array}{lcccl}
CH_3 & & & & CH_3\\
| & & & & |\\
CONa & -HN- & CO & -NH- & CONa\\
| & & & & |\\
CH_2 & & & & CH_2\\
| & & & & |\\
CO_2C_2H_5 & & & & CO_2C_2H_5.
\end{array}$$

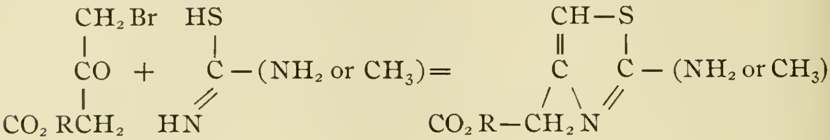
It melts at 165° and is decomposed by water. It is also decomposed, by passing carbon dioxid into its alcohol solution, into carbamid, acetoacetic ester and sodium ethyl carbonate, $NaC_2H_5CO_3$.

HANTZSCH, A., 1890.

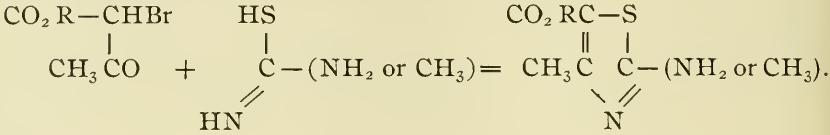
Ber **23**, 2339–2342; J. Chem. Soc. **58**, 1238.

Halogen Derivatives of Acetoacetic Ester.

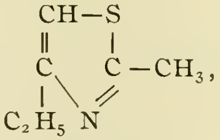
The action of thiocarbamid and thioacetamid on the halogen derivatives of acetoacetic ester are used to distinguish between the *α* and *γ* positions for the halogen thus:



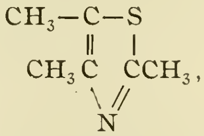
which is amido- or methyl- thiazylacetic ester and



Bromin acting on acetoacetic ester gives the *γ* product but when cupracetoacetic ester is treated with bromin the *α* product is obtained. Chlorin acting on acetoacetic ester gives the *α* product. Methyl-ethyl-thiazole,



was produced from methyl-brom-acetoacetic ester showing it to be the *γ* product and trimethyl-thiazole,



was produced from methyl-chlor-acetoacetic ester showing it to be the *α* derivative.

DITTRICH, E., 1890.

Ber. **23**, 2720–2725 ; J. Chem. Soc. **58**, 1418.

Action of Picric Chlorid on Sodacetoacetic Ester.

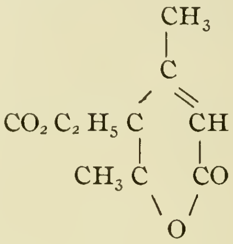
By the action of picric chlorid, $C_6H_2(NO_2)_3Cl$, on sodacetoacetic ester the mono- or di- trinitrophenyl-acetoacetic ester is formed, according to the proportion of picric chlorid used. Trinitrophenyl-acetoacetic ester, $CH_3COCH[C_6H_2(NO_2)_3]CO_2C_2H_5$, melts at 98°, dissolves in alkalis from which solution weak acids precipitate it. Di-(trinitrophenyl) acetoacetic ester, $CH_3COC[C_6H_2(NO_2)_3]_2CO_2C_2H_5$, melts at 205° with decomposition ; alcoholic potash dissolves it and acids precipitate not the same but trinitrophenyl-acetoacetic ester. When trinitrophenyl-acetoacetic ester is boiled with sulfuric acid trinitrophenyl acetone, $CH_3COCH_2[C_6H_2(NO_2)_3]$, is formed which melts at 89°. This condenses with phenylhydrazin to $C_{15}H_{13}N_5O_6$, which melts with decomposition at 125°.

ANSCHÜTZ, R., P. BENDIX AND W. KERP, 1890.

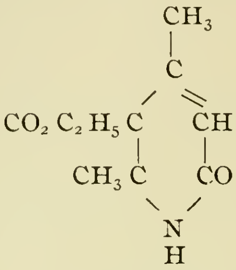
Ann. Chem. **259**, 148–186 ; J. Chem. Soc. **60**, 172 ; Ber **23**, 734 (C).

Mesitene Lactone and Isodehydracetic Acid,

Much of the work done by Hantzsch on the condensation products of acetoacetic ester has been repeated by the authors. They corroborate his formulæ for mesitene lactone and isodehydracetic acid, $(C_8H_8O_4)$, but find that the first condensation product is a mixture of isodehydracetic acid and its ethyl ester. Isodehydracetic methyl ester melts at 67° and boils at 167° under 14 m.m. pressure, it can be obtained by treating the potassium salt with methyl iodid or by condensing acetoacetic methyl ester. Unsuccessful attempts were made to prepare Hantzsch's homomesaconic acid ; by treating isodehydracetic ester with potash two acids were obtained ; (1) $C_{10}H_{12}O_4$ which melts with decomposition at 221°, is almost insoluble in ether, benzene, chloroform and cold water and but moderately soluble in boiling water. Its potassium, barium and copper salts and methyl ester were described. The second acid $C_8H_{10}O_3$, melts at 149°, is soluble in alcohol, ether and chloroform and decomposes at 160°; its barium and silver salts were described. Isodehydracetic ester is converted by warm anhydrous ammonia into the corresponding lactam, identical with the substance obtained by Collie by the condensation of β-amido-crotonic ester. The change is represented thus:

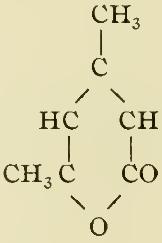


Isodehydracetic ester

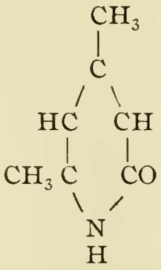


Caroxethylmesitenlactam.

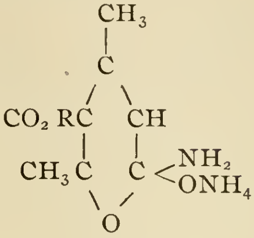
Mesitene lactone



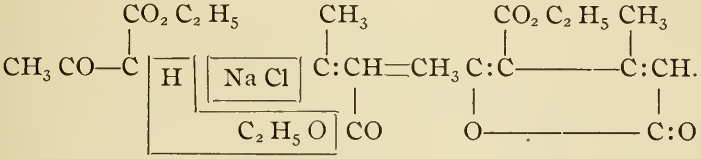
is changed by ammonia into mesitene lactam



An alcoholic ethereal solution of isodehydracetic ester treated in the cold with ammonia forms a compound $C_{10}H_{18}N_2O_4$, if moisture be excluded. It is represented thus :—



Isodehydracetic ester can be prepared from sodacetoacetic ester and *β*-chlorcrotonic ester which proves its constitution thus :—



AUTENRIETH, W., 1890.

Ann. Chem **259**, 365–373 ; J. Chem. Soc. **60**, 204.

Sulfur Derivatives of Acetoacetic, Methylacetoacetic and Ethylacetoacetic Esters.

By treating *β*-dithiophenylbutyric ester, $CH_3C(SC_6H_5)_2CH_2CO_2C_2H_5$, with sulfuric acid and potassium permanganate, *β*-diphenylsulfonebutyric ester, $CH_3C(SO_2C_6H_5)_2CH_2CO_2C_2H_5$, is obtained, it melts at 97°, is soluble in hot alcohol, ether and benzene and insoluble in water. *α*-Ethyl-*β*-diethylsulfonebutyric ester, $CH_3C(SO_2C_2H_5)_2CH(C_2H_5)CO_2C_2H_5$, formed in a similar manner from the condensation product of ethyl mercaptan and ethyl-acetoacetic ester, melts at 87°–88°. *α*-Methyl-*β*-diethylsulfonebutyric ester melts at 79°. *α*-Ethyl-*β*-dithiophenylbutyric ester, $CH_3C(SC_6H_5)_2CH(C_2H_5)CO_2C_2H_5$, is made by condensing ethyl-acetoacetic ester and phenyl mercaptan, and melts at 70°–71°. From this by the above method was prepared *α*-ethyl-*β*-diphenylsulfonebutyric ester, $CH_3C(SO_2C_6H_5)_2CH(C_2H_5)CO_2C_2H_5$, which melts at 111°.

ELION, H., 1890.

Ber. **23**, 3123–3124 ; J. Chem. Soc. **60**, 171.

Preparation and Properties of Sodacetoacetic and Sod-ethylacetoactic Esters.

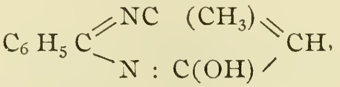
Both these substances when anhydrous are soluble in ether but both form hydrous compounds insoluble in ether. The anhydrous compounds cannot be obtained by keeping the hydrous compounds over sulfuric acid as has been stated and the author thinks that there is but one form of anhydrous sodacetoacetic ester and not two, one of which is insoluble in ether as stated by Michael.

PINNER, A., 1890.

Ber. **23**, 3820–3826 ; J. Chem. Soc. **60**, 468.

Imido Esters and their Derivatives.

Acetoacetic ester is treated with imidobenzoic ester and the chief product is found to be phenylmethyl-hydroxypyrimidin,



$$C_6H_5C\begin{array}{l}\nearrow\!\!\!\nearrow NC\ (CH_3)\searrow\!\!\!\searrow \\ \searrow N : C(OH)\nearrow\end{array}CH,$$

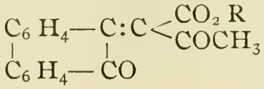
melting at 216°. The imidobenzoic ester is probably first converted into benzoic ester and ammonia thus: $C_6H_5C(NH)OC_2H_5+H_2O=C_6H_5CO_2C_2H_5+NH_3$; the ammonia acts on some imido-benzoic ester forming alcohol and benzamidin which last product unites with the acetoacetic ester.

JAPP, FRANCIS R. AND FELIX KLINGEMANN, 1891.

J. Chem. Soc. **59**, 1–26.

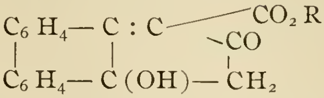
Phenanthroxylene-acetoacetic Ester.

This compound, prepared from acetoacetic ester and phenanthraquinone and given the formula,



$$\begin{array}{l}C_6H_4-C:C<\begin{array}{l}CO_2R\\ COCH_3\end{array}\\ \ |\qquad\quad\ |\\ C_6H_4-CO\end{array}$$

has been further studied. When treated with formic or sulfuric acid an isomer is formed, to which the formula,



$$\begin{array}{l} C_6H_4\text{—}C:C\begin{array}{l}\diagup CO_2R \\ \diagdown CO\end{array} \\ \;|\qquad\quad\;|\qquad\qquad\;| \\ C_6H_4\text{—}C(OH)\text{—}CH_2 \end{array}$$

is provisionally given, and which is called isophenanthroxylene-acetoacetic ester; it melts at 177°. It forms a mono-acetyl derivative, $C_{20}H_{15}(C_2H_3O)O_4$, which melts between 165° and 170°, and a monohydrazone, $C_{20}H_{16}O_3(N_2HC_6H_5)$. No pyrazolone could be obtained from this, and phenanthroxylene-acetoacetic ester does not react with phenylhydrazin. With bromin the iso compound gave $C_{20}H_{15}BrO_4$. When reduced the iso compound gave $C_{20}H_{16}O_3$, which is also produced from the phenanthroxylene-acetoacetic ester by means of hydriodic acid. This gave a phenylhydrazin derivative, $C_{20}H_{16}O_2(N_2HC_6H_5)$. When treated with hydriodic acid the iso compound gave $C_{17}H_{12}O$, which is the compound to which Japp and Streatfield * gave the formula $C_{14}H_{10}O$. It is probably a ketone containing the carbonyl group in a penta-carbon ring. Treated with an alkali the iso compound gave the iso-phenanthroxylene-acetoacetic acid, $C_{18}H_{12}O_4$, which is mono-basic. The action of acetic, propionic, sulfuric, alcoholic hydrochloric acids and of alcoholic potash and ammonia on phenanthroxylene-acetoacetic ester was determined and an account given of the experiments. The subject requires more study before the composition of these bodies can be definitely settled. The formula proposed for the iso compound explains some reactions but leaves others quite unexplained.

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* See page 39.

CLAISEN, L. AND E. HORI, 1891.

Ber. **24**, 139–140; J. Chem. Soc. **60**, 416.

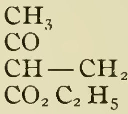
Action of Hydroxylamin on Acetoacetic Aldehyde.

By this action a compound $C_8H_{13}N_3O_3$, was produced which crystallizes in white needles, melting at 174°. It is sparingly soluble in ether, benzene and chloroform. Other compounds which were expected from this reaction were not obtained.

EMERY, W. O., 1891.

Ber. **24**, 282–286 ; J. Chem. Soc. **60**, 547.

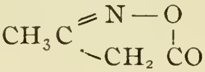
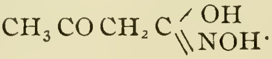
Action of β-Bromopropionic Ester on Acetoacetic Ester.

By the action of β-bromopropionic ester on sodacetoacetic ester, α-acetylglutaric ester,  $\begin{array}{l} CH_3 \\ CO \\ CH — CH_2 — CH_2\,CO_2\,C_2\,H_5 \\ CO_2\,C_2\,H_5 \end{array}$, was produced. It boils at 162° at 11 m. m. pressure and has a specific gravity of 1.071 at 20°. It reacts with ammonia and with amins, yielding amido-derivatives of α-ethylidineglutaric ester, which can be converted into lactams.

HANTZSCH, A., 1891.

Ber. **24**, 495–506 ; J. Chem. Soc. **60**, 739.

Action of Hydroxylamin on β-Ketonic Acids and β-Diketones.

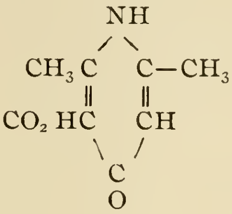
By the action of hydroxylamin on acetoacetic ester in alkaline solution and subsequent acidification the chief product is methyl-isoxazolone,  $CH_3C\begin{array}{l} \diagup\!\!= N — O \\ \qquad\quad\ | \\ \diagdown CH_2\ \ CO \end{array}$, which melts at 169°–170° and is a base towards strong acids. In alkaline solutions it is partially changed into oximidobutyric acid, $CH_3\,C : (NOH)\,CH_2\,CO_2\,H$. By the action of hydroxylamin on acetoacetic ester in neutral or acid solution, an oil is obtained which, on being hydrolyzed, gives a crystalline substance, $C_{20}\,H_{26}\,N_4\,O_7$, which melts at 140° and can be changed by hydrolysis into methylisoxazolone. By the action of hydroxylamin on acetoacetic ester in ammoniacal solution an unstable product was obtained which may be the hydroxamic acid of acetoacetic acid,  $CH_3\,CO\,CH_2\,C\begin{array}{l} \diagup OH \\ \diagdown\!\!\diagdown NOH \end{array}$.

COLLIE, J. NORMAN, 1891.

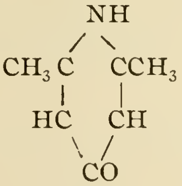
J. Chem. Soc. **59**, 172–179.

Action of Heat on β-Amidocrotonic Ester.

When this substance is distilled a small amount of substance is always left which has been found to be $C_{10}H_{13}NO_3$, the ethyl ester of an acid, $C_8H_9NO_3$, which is dimethyl-pyridone-monocarboxylic acid,



The ester, $C_{10}H_{13}NO_3$, melts at 163°-164° and boils with slight decomposition at 240° to 250°. It does not form a compound with phenylhydrazin or hydroxylamin. With bromin it forms $C_{10}H_{12}BrNO_3$; with PCl_5 it gives $C_{10}H_{12}NO_2Cl$, which can be changed into chlorolutidin boiling at 177° to 180°. The acid $C_8H_9NO_3$, melts at 257°-258° and is converted into *α-α'*-dimethyl-pyridone,



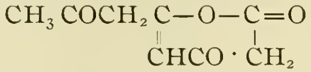
This was also prepared from dehydracetic acid. Phosphorus pentachlorid acts on *α-α'*-dimethyl-pyridone to form chlorolutidin boiling at 178°-179°. *α-α'*-Dimethyl-pyridin or lutidin was obtained in four ways, (1) by the action of nascent hydrogen on chloroludidin; only a little could be formed in this way; (2) from vapors of chlorolutidin and zinc dust in an atmosphere of hydrogen; (3) from chlorolutidin made from dehydracetic acid; (4) from the potassium salt of lutidone-monocarboxylic acid heated with an excess of solid potassium hydroxid. By oxidation of the lutidin, dipicolinic acid, $C_5H_3N(CO_2H)_2$, was obtained.

COLLIE, J. NORMAN, 1891.

J. Chem. Soc. **59**, 179–189.

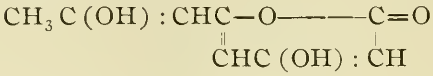
Constitution of Dehydracetic Acid.

The author, having studied this acid and its reactions, determines that Feist* did not present the correct formula for it and proposes the formula

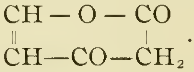


$$\begin{array}{l}CH_3COCH_2C{-}O{-}C{=}O\\ \qquad\qquad\quad\ \| \qquad\quad\ \ |\\ \qquad\qquad\quad CHCO\cdot CH_2\end{array}$$

or the tautomeric form

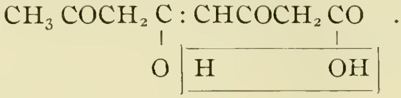


$$\begin{array}{l}CH_3C(OH):CHC{-}O{-}{-}{-}{-}C{=}O\\ \qquad\qquad\qquad\quad \| \qquad\qquad\quad |\\ \qquad\qquad\qquad CHC(OH):CH\end{array}$$

By this formula he thinks that all of its reactions, the most important ones of which he illustrates, can best be explained. He considers it as built up on the nucleus of *α*-oxypyrone,  $\begin{array}{l}CH-O-CO\\ \| \qquad\qquad\ \ |\\ CH{-}CO{-}CH_2\end{array}$. Its formation from acetic acid is illustrated thus:—

$$CH_3CO\boxed{OH\quad H}CH_2CO\boxed{OH\quad H}CH_2CO\boxed{OH\quad H}CH_2COOH$$

and then



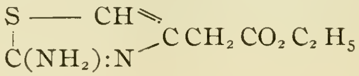
$$\begin{array}{l}CH_3COCH_2C:CHCOCH_2CO\ .\\ \qquad\qquad\quad\ |\qquad\qquad\quad\ \ |\\ \qquad\qquad\quad O\ \boxed{H\qquad\quad OH}\end{array}$$

STEUDE, M., 1891.

Ann. Chem. **261**, 22–47 ; J. Chem. Soc. **60**, 742

Thiazole Derivatives from Bromacetoacetic Ester.

The thiazole derivatives obtained from bromacetoacetic ester and thio-carbamid and thiacetamid are isomeric with those obtained if chloracetoacetic ester be used, but those obtained both ways can be converted into *μ*-amido-*α*-methyl-thiazole or *α*-*μ*-dimethyl-thiazole as the case may be. This proves that bromacetoacetic ester has the formula $CH_2BrCOCH_2CO_2R$. *μ*-Amido-thiazylacetic ester,



$$\begin{array}{l}S{-}{-}{-}CH\diagdown\\ |\qquad\qquad\quad\ CCH_2CO_2C_2H_5\\ C(NH_2):N\diagup\end{array}$$

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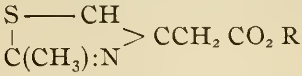
* See page 114.

obtained from bromacetoacetic ester and thiocarbamid melts at 94 , the free acid melts at 130°. Thiacetamidoacetic ester, $CH_2(SC\,NH\,CH_3)COCH_2CO_2C_2H_5$, is formed besides μ-methyl-thiazylacetic ester from bromacetoacetic ester and thiacetamid in alcoholic solution. Methyl-thiazylacetic ester,



$$\begin{matrix} S - CH \\ | \\ C(CH_3):N \end{matrix} > CCH_2CO_2R$$

boils at 238° to 240°. γ-Thiacetoacetoacetic ester, $CH_2(SCOCH_3)CO\,CH_2CO_2R$, results when thiacetamidacetoacetic ester hydrobromid is warmed with water. It boils at 155° at 15 m. m. pressure. A compound, probably of the formula $CO_2RCH_2C \Big\langle \begin{matrix} CH - S \\ SCH \end{matrix} \Big\rangle CCH_2CO_2R$, was also described.

PECHMANN, H. v. AND M. DÜNSCHMANN, 1891.

Ann. Chem. **261**, 162–166; J. Chem. Soc. **60**, 672.

Decomposition of Acetone-dicarboxylic Ester.

When acetone-dicarboxylic ester, $CO_2C_2H_5CH_2COCH_2CO_2C_2H_5$, is changed to the potassium salt and then boiled with water, acetoacetic ester is produced which is identified by being treated with phenylhydrazin and changed into methyl-phenylpyrazolone.

JAEGER, J., 1891.

Ann. Chem. **262**, 365–372; J. Chem. Soc. **60**, 1007.

Condensation of Guanidin with β-Ketonic Esters.

Guanidin carbonate and acetoacetic ester condense to form imido-methyl-uracyl, $CH \Big\langle \begin{matrix} CO\ NH \\ C(CH_3)NH \end{matrix} \Big\rangle C:NH$, which melts with decomposition at 270°. The hydrochlorid, nitrate and sulfate were described. Dibromohydroxyimidomethyl-uracyl, $NH \Big\langle \begin{matrix} C(NH)NH \\ COC(Br_2) \end{matrix} \Big\rangle CCH_3OH$, is formed together with bromimidomethyluracyl, $C_5H_6BrN_3O$, when imidomethyl-uracyl is heated with bromin; it melts at 160°. When imidomethyluracyl is heated with an excess of methyl iodid a compound, $(C_5H_6N_3OCH_3)_2HI$, is obtained, which melts at 212° and can be converted into methyl-imidomethyl-uracyl, $C_5H_6N_3OCH_3$, which melts at 312°. Imidodimethyluracyl formed from guanidin carbonate and methyl-acetoacetic ester melts at 320°, and imido-phenyl-uracyl formed from guanidin carbonate and benzoylacetic ester melts at 294°.

BREDT, J., 1891.

Ber. **24**, 603–605; J. Chem. Soc. **60**, 712.

Action of Sodacetoacetic Ester on Benzalmalonic Ester.

By this reaction in alcoholic solution at 0 a crystalline sodium compound is formed which when decomposed by an acid gives a compound $C_{18}H_{20}O_6$, which is sparingly soluble in water and melts with decomposition at 155°.

OTTO, R. AND A. RÖSSING, 1891.

Ber. **24**, 685–687; J. Chem. Soc. **60**, 712.

Action of Sodium Phenylmercaptid on Chloracetoacetic Ester.

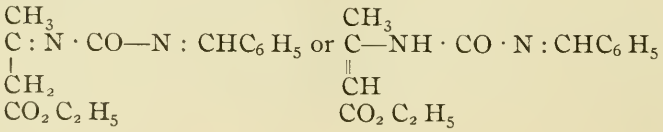
When equivalent quantities of these substances are made to react in alcoholic solutions, an oil is obtained, which will not crystallize and has but a feeble odor. It appears to be thiophenylacetoacetic ester, $CH_3COCH(SC_6H_5)CO_2C_2H_5$.

BIGINELLI, P., 1891.

Ber. **24**, 1317–1319; J. Chem. Soc. **60**, 908.

Aldehydeuramids of Acetoacetic Ester. Part 1.

Molecular proportions of acetoacetic ester, benzaldehyde and carbamid are allowed to react and a crystalline compound melting at 207°-208 is obtained. It is either



$$\begin{array}{l} CH_3 \\ C:N\cdot CO{-}N:CHC_6H_5 \\ | \\ CH_2 \\ CO_2C_2H_5 \end{array} \quad \text{or} \quad \begin{array}{l} CH_3 \\ C{-}NH\cdot CO\cdot N:CHC_6H_5 \\ \| \\ CH \\ CO_2C_2H_5 \end{array}$$

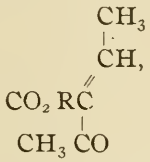
but probably is the latter. The same substance can be formed from uramidocrotonic ester and benzaldehyde. It is very stable as it is not affected by strong acids or alkalis in the cold. Heating it with potassium hydroxid gives benzyl alcohol, benzaldehyde, ammonia and potassium carbonate, besides an unknown solid substance. Salicylaldehyde, cinnamaldehyde, furfuraldehyde, cumaldehyde and others react similarly.

BEYER, C., 1891.

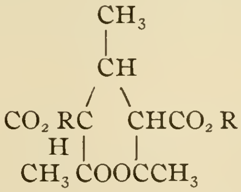
Ber **24**, 1662–1670; J. Chem. Soc. **60**, 1090.

Hantzsch's Pyridin Synthesis,

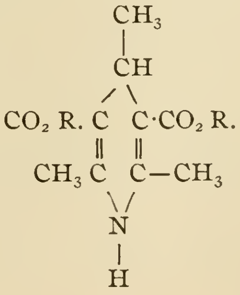
The author believes that in these reactions acetoacetic ester and aldehyde first react to form ethylidin-acetoacetic ester,



and that this then unites with acetoacetic ester to form ethylidin-diacetoacetic ester,



which unites with ammonia to form dihydrocollidin-dicarboxylic ester,



Ethylidinacetoacetic ester and paramido-acetoacetic ester were mixed in molecular proportions and united to form dihydrocollidin-dicarboxylic ester. Several other experiments were performed and several pyridin derivatives made and described. They all agreed with these reactions.

FREER, P. C., 1891.

Am. Chem. J. **13**, 308–322; J. Chem. Soc. **60**, 1181.

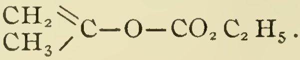
Constitution of Aliphatic Ketones and the Action of Sodium on Acetone.

The constitution of acetoacetic ester is discussed at length and mention is made of the work done by different chemists upon it. Acetic ester dried over calcium chlorid and by being boiled over phosphorus pentoxid is found to react with sodium readily which inclines the author to believe in the intermediate sodacetic ester. A comparison of the properties and reactions of tetric acid and acetoacetic ester seems to show that the former contains a hydroxyl group and the latter does not. In the sodium derivative the author believes the sodium is joined to the oxygen, therefore that its constitution is different from that of acetoacetic ester itself. This is shown by the fact that sodaceto-acetic ester will form addition products with unsaturated compounds like cinnamic ester while the acetoacetic ester itself will not.

FREER, PAUL C. AND GEO. O. HIGLEY, 1891.

Am. Chem. J. **13**, 322–326; J. Chem. Soc. **60**, 1182.

Action of Chlorcarbonic Ester on Acetone Sodium.

By this action a colorless oil boiling at about 125° was obtained which appears to be an isomer of acetoacetic ester. It is insoluble in water, miscible with alcohol and ether and does not react with phenyl hydrazin or ferric chlorid. On boiling with hydro chloric acid it is decomposed into carbon dioxid, alcohol and acetone. The authors suggest for it the formula  $\begin{matrix} CH_2 \\ CH_3 \end{matrix}\!\!>\!C{-}O{-}CO_2\,C_2\,H_5$.

WALDEN, P., 1891.

Ber. **24**, 2025–2039; J. Chem. Soc. **60**, 1187.

Tetric and Oxytetric Acids and their Homologues.

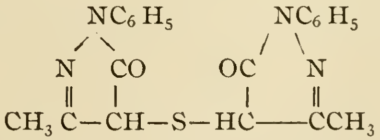
Experiments were performed attempting to determine whether tetric acid and its homologues contain the carboxylic group but no definite conclusions were reached. Oxytetric acid and its homologues were shown to be alkyl substituted fumaric acids, thus oxytetric is mesaconic or methyl fumaric, oxypentic is ethyl fumaric, etc. The acids described by Demarcay as hydroxytetric, etc., are identical with alkyl succinic acids, hydroxytetric is methyl succinic and hydroxypentic is ethyl succinic, etc. The acids are all obtained from the bromated alkyl aceto-acetic esters.

SPRAGUE, CHARLES T., 1891.

J. Chem. Soc. **59**, 329–343.

Thiacetoacetic Ester.

This substance was produced and after carefully determining the melting point it was found to be between 75° and 78°. By the action of phenylhydrazin four bodies were produced :—(1) thiophenyl-methyl-pyrazolone ; (2) Knorr's phenylmethyl-pyrazolone-azobenzene ; (3) a substance, $C_{10}H_9$* N_2SO ; (4) Knorr's bisphenyl-methyl-pyrazolone. The first one is



it is a weak base, dissolves in alkalis and weak acids reprecipitate it. If it be heated with phenylhydrazin the other three above mentioned compounds are produced. To the third product the author gave the formula $C_{10}H_8$* N_2SO, but states that Höltzcka has since proven it to be bisulphid of phenylmethyl pyrazolone $(C_{10}H_9N_2O)_2S_2$. A method was given for preparing a good yield of each one of the four products.

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* A disagreement, $C_{10}H_8N_2SO$ is probably correct

COLLIE, J. NORMAN, 1891.

J. Chem. Soc. **59**, 617–621.

Some Reactions of Dehydracetic Acid.

In the preparation of dehydracetic acid by passing acetoacetic ester through a red-hot iron tube, there were formed, besides the dehydracetic acid, acetone, alcohol, carbon dioxid, ethylene and a residue. Acetoacetic methyl ester similarly treated gave large quantities of dehydracetic acid, but ethylacetoacetic ester gave none at all. Dehydracetic acid is slightly decomposed by water into carbon dioxid and dimethylpyrone. When boiled with hydrochloric acid it is totally decomposed into carbon dioxid and a compound, $C_7 H_{11} O_3 Cl$, which melts at 83 –85 and is acid in water solution. Barium and copper salts of dehydracetic acid were prepared, the former corresponded most nearly with $(C_8 H_9 O_5)_2 Ba$ and was considered to be the salt of tetracetic acid, $CH_3 CO CH_2 CO CH_2 CO CH_2 CO_2 H$; and the latter corresponded to $C_{24} H_{25} O_9 N_3 Cu$, being formed by ammonia and copper acetate. Hydrocyanic acid has no action on dehydracetic acid.

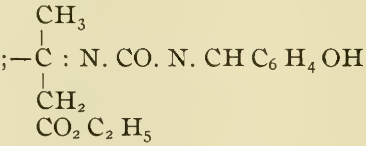
BIGINELLI, P., 1891.

Ber. **24**, 2962–2967; J. Chem. Soc. **62**, 56.

Aldehydeuramids of Acetoacetic Ester. Part II.

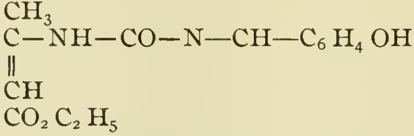
In the continuation of the subject it is found that two isomers, corresponding to the two formulæ given in the first article on this subject,* are always produced. The compounds

$C_{14} H_{16} N_2 O_4$;



$$\begin{array}{l} CH_3 \\ | \\ -C : N. CO. N. CH\, C_6 H_4 OH \\ | \\ CH_2 \\ CO_2 C_2 H_5 \end{array}$$

and



$$\begin{array}{l} CH_3 \\ C-NH-CO-N-CH-C_6 H_4 OH \\ \| \\ CH \\ CO_2 C_2 H_5 \end{array}$$

formed from carbamid, salicylaldehyde and acetoacetic ester, and the similar compounds, $C_{17} H_{22} N_2 O_3$, formed from cumaldehyde, $C_6 H_4 (C_3 H_7) COH$, carbamid and acetoacetic ester ; $C_{16} H_{18} N_2 O_3$, obtained by using cinnamaldehyde, and $C_{12} H_{14} N_2 O_4$, obtained by using furfural dehyde, are produced and described.

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* See page 130.

CONRAD, M. AND L. LIMPACH, 1891.

Ber. **24**, 2990-2992, J. Chem. Soc. **62**, 78.

Synthesis of Quinolin Derivatives by means of Alkyl Acetoacetic Esters.

Methyl-acetoacetic methyl ester and anilin, when mixed and allowed to stand, form phenyl-amido-methyl-crotonic methyl ester. By quickly heating this, it is changed into dimethyl-hydroxyquinolin, $C_9NH_4(CH_3)_2OH$, $[(CH_3)_2 : OH = 2' : 3' : 4']$. Methyl-ethyl-hydroxy-quinolin is produced similarly from phenyl-amido-ethyl-crotonic methyl ester.

NEF, J. U., 1891.

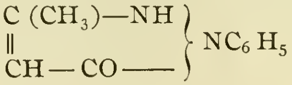
Ann. Chem. **266**, 52–138; J. Chem. Soc. **62**, 140.

Acetoacetic Ester.

A large number of experiments are performed relative to determining the constitution of acetoacetic ester and the position of the sodium in the sodium derivative, and the conclusions drawn are that acetoacetic ester is not a ketone but is represented by $CH_3COH : CHCO_2C_2H_5$ and that in the sodium derivative the sodium is joined to oxygen. If by heating the sodacetoacetic ester with an alkyl halogen the alkyl is substituted for the sodium, the reaction should be more energetic if the heavier metals, such as copper or lead, be in the acetoacetic ester in place of sodium, but solutions of the copper or lead derivatives of acetoacetic ester do not react with ethyl iodid at ordinary temperatures—which proves that no direct substitution of the metal takes place. The author supposes an intermediate addition product to be formed with an alkyl iodid, for example, with benzylchlorid, $CH_3CONaClCH(CH_2C_6H_5)CO_2R$ is first formed and then HCl splits off leaving $CH_3CONa : C(CH_2C_6H_5)CO_2R$ and by continued action $CH_3CONaClC(CH_2C_6H_5)_2CO_2R$ and then $CH_3COC(CH_2C_6H_5)_2CO_2R$ are formed. As proof of the existence of hydroxyl in acetoacetic ester its acid properties and its behavior towards phenyl hydrazin, ammonia and the amids are mentioned, also the fact that acetoacetic ester and its mono-alkyl derivatives are not reduced by treatment with sodium in ethereal solution while the diethyl derivative is converted into diethyl-hydroxybutyric ester. The substitution of the α-hydrogen atom affects the compound according to the character of the substituted group, making it more alcoholic or more acidic as that group is more or less positive than hydrogen. By the action of phenylhydrazin on acetoacetic ester phenyl-β-hydrazo-crotonic ester, $CH_3C(N_2H_2C_6H_5):CHCO_2R$, melting at 50 is formed and by heating this with mercuric oxid phenyl-β-azocrotonic ester, $CH_3C(N_2C_6H_5):CHCO_2R$, melting at 51° is obtained. The product obtained by the action of bromin on acetoacetic is a mixture of the α and the γ bromderivatives. α-Brom-methyl-acetoacetic ester, $C_7H_{11}BrO_3$, boiling at 107° at 30 m.m. pressure, is obtained by treating sodmethyl-acetoacetic ester or methyl-acetoacetic ester with bromin. When this is heated in a sealed tube tetric acid is formed for which the author gives the formula

$$CH_2 : C(OH)\,CCH_3 < \begin{matrix} OCO \\ COO \end{matrix} > CCH_3\,C(OH) : CH_2$$

α-Bromethylacetoacetic ester, $C_8H_{13}BrO_3$, is prepared similarly and is described. Dibenzoyl-acetoacetic ester, $C_{20}H_{18}O_5$, and triacetylacetic ester, $CH_3COC(CH_3CO)_2CO_2R$, and acetylcarbintricarboxylic ester, $CH_3COC(CO_2R)_2CO_2R$, are also described. A large number of pyrazolone derivatives are prepared and studied, and the author decides that their acid properties are due to the presence of an imido group. The formula for phenylmethyl-pyrazolone he gives as



$$\left.\begin{matrix} C(CH_3)\text{—}NH \\ \| \\ CH\text{—}CO\text{——} \end{matrix}\right\} NC_6H_5$$

PECHMANN, H. v., 1891.

Ber. **24**, 3600; J. Chem. Soc. **62**, 296.

Preparation of Dehydracetic Acid.

By treating acetondicarboxylic acid with acetic anhydrid, a substance either isomeric or identical with the carboxylic acid of dehydracetic acid is produced. This may be easily changed into dehydracetic acid by dissolving in soda, evaporating to dryness and precipitating the aqueous solution with acetic acid.

AUTHOR INDEX.

SUBJECT INDEX.