acid and acetic anhydride by the method of heating the two substances in xylol under reflux gave a product which differed in its properties from that described in a previous paper[1] as made by the method of heating the acid and the acetic anhydride in excess.   It is evident that the product previously described was not pure.   To prepare the pure compound, it is necessary to heat the vanillylideneanthranilic acid with two molecular proportions of acetic anhydride in xylol solution under reflux for one hour. After distilling off the greater portion of the xylol, the acetylated metox-azine separates out on cooling in colorless sandy crystals.   Recrystallized from xylol.   Soluble in the ordinary organic solvents, except ether. M. p. 141°.

Calc. for $C_{19}H_{17}O_6N$: N, 3.97; found: N, 3.61.
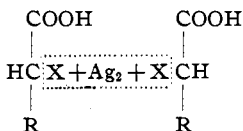
BOULDER, COLORADO.

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## THE ACTION OF FINELY DIVIDED SILVER ON α-BROMO- AND α-IODOPALMITIC ACIDS: SYNTHESIS OF TWO ISO-MERIC DITETRADECYLSUCCINIC ACIDS.

BY D. BREESE JONES.

As is well known, the reaction between finely divided silver, so called "molecular silver", and monohalogen substitution products of the fatty acids is by no means a simple one.   Besides the removal of halogen from two molecules of the substituted fatty acid and union taking place through the released affinities of the carbon atoms with formation of dibasic acids,

$$\begin{array}{cc} \text{COOH} & \text{COOH} \\ | & | \\ \text{HC} \vdots \text{X} + \text{Ag}_2 + \text{X} \vdots \text{CH} \\ | & | \\ \text{R} & \text{R} \end{array}$$

there are always formed several other products of the reaction.   Hell and his co-workers have studied the action of silver on several halogen substi-tuted fatty acids.   From ethyl α-bromoisobutyrate and silver[2] were obtained two isomeric tetramethylsuccinic acids, carbon dioxide, ethyl bromide, isobutyric acid and methylacrylic acid, while ethyl α-bromo-butyrate[3] yielded ethyl bromide, ethyl alcohol, ethyl butyrate, two di-ethylsuccinic acids, and a sirup whose composition agrees with that of hydroxysuberic acid.   Ethyl α-bromoisovalerianate with silver[4] yielded two isomeric sebacic acids, ethyl bromide, ethyl isovalerianate, and

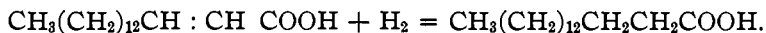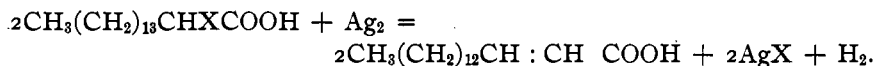[1] THIS JOURNAL, 35, 164 (1913).
[2] Hell, Ber., 10, 2229 (1877).
[3] Hell and Mühlhäuser, Ibid., 13, 473–9 (1880).
[4] Hell and Mayer, Ibid., 22, 48 (1888).

polymeric dimethylacrylic acids. Likewise ethyl α-bromopropionate[1] gave two dimethylsuccinic acids, ethyl propionate, ethyl acrylate and pyrocinchonic acid. In practically all cases two isomeric dialkylsuccinic acids were obtained.

It was accordingly deemed of interest to investigate the action of silver on halogen derivatives of higher fatty acids. In this article is described the action of silver on α-bromo-, and iodopalmitic acids. It was found that the halogen is readily removed from both bromo-, and iodopalmitic acid, either by heating alone with silver at a temperature of 130 to 140°, or by boiling the mixture in heptane. Among the products of the reaction, were obtained palmitic acid, an oil which showed properties of unsaturation, and the heretofore unknown two isomeric ditetradecyl-succinic acids.

Palmitic acid was invariably found as a product of the reaction. In one experiment with bromopalmitic acid, it comprised at least 20% of the original bromo acid taken, while in another experiment with iodopalmitic acid, 13% of the latter was converted into palmitic acid. This reduction of the original halogen acid probably takes place by abstraction of the halhydric acid, and subsequent reduction of the unsaturated acid.

$$2CH_3(CH_2)_{13}CHXCOOH + Ag_2 =$$
$$2CH_3(CH_2)_{12}CH : CH \ COOH + 2AgX + H_2.$$
$$CH_3(CH_2)_{12}CH : CH \ COOH + H_2 = CH_3(CH_2)_{12}CH_2CH_2COOH.$$

The identification of the unsaturated acid, which is a constituent of the oily product which was always obtained, could not be determined, because of the small amount available to work with. Other unsaturated compounds than 1,2-hexadecylenic acid, might also well be present. Many olefines readily polymerize, with the formation of compounds which are still unsaturated. Hell and Mayer[2] obtained polymeric dimethylacrylic acid by action of silver on ethyl bromoisovalerianate. That an unsaturated dibasic acid of the type (I) may also be formed, is shown by the formation of pyrocinchonic acid (II) from bromopropionic acid and silver[3]

$$\begin{array}{ll} R-C-COOH & C.H_3-C-COOH \\ \parallel & \parallel \\ R-C-COOH & CH_3-C-COOH \\ (I) & (II) \end{array}$$
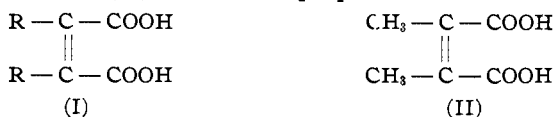
The two isomeric ditetradecylsuccinic acids obtained by action of silver on bromo-, and iodopalmitic acids, are characterized by difference in solubility and melting points. One melts at 135 to 136°, and is extremely difficultly soluble in most organic solvents, while the other melts at 95 to 96°, and is moderately soluble. When heated to about 170°,

[1] Hell and Rothberg, *Ber.*, **22**, 64 (1888).
[2] *Loc. cit.*
[3] Hell and Rothberg, *Loc. cit.*

the acid melting at 135° loses water, and is converted into an anhydride melting at 45 to 45.5°, which on hydrolysis yields the acid melting at 95°. This latter acid, on the other hand, when heated to about 150°, also loses water and is converted into an unstable anhydride, which readily transforms into the same anhydride as that obtained by heating the higher melting acid. The acid melting at 135° was formed in much the larger amount of the two, although the yield was small. The maximum yield of this acid obtained from bromopalmitic acid was 8% of the amount calculated, while a maximum yield of 13% was obtained from iodopalmitic acid. The yield was better when the constituents were boiled in heptane, than when heated alone.

Practically all of the known symmetrically substituted dialkylsuccinic acids occur in two isomeric forms, which are characterized by a considerable difference in solubility and melting point. The nature of the isomerism has been long a question of speculation. These isomers have been commonly referred to as the "fumaroid" and "maleinoid" forms. According to van't Hoff's theory, these compounds having two asymmetric carbon atoms, would be naturally expected to occur in two inactive isomeric modifications, one inactive because of external, and the other inactive because of internal compensation, as in the case of *racemic*, and *meso* tartaric acids. Furthermore, on account of the many analogies they offer with the tartaric acids, their isomerism has frequently been referred to as of the same type. Accordingly, the fumaroid form, being the less soluble and having the higher melting point, was looked upon as having the *racemic*, and the maleinoid, as having the *meso* structure. However, this assumption was considered doubtful, as no one of the inactive dialkylsuccinic acids had ever been resolved into its active components, and not all of their properties fitted in with the analogy of the tartaric acids.[1] Bischoff,[2] to account for this isomerism, advanced a theory of *dynamical isomerism*, in which he considered the equilibrium positions of the atoms and radicals joined to the two asymmetric carbon atoms.

It is rather remarkable that it was not until 1913, that one of the inactive dialkylsuccinic acids was for the first time resolved into its optically active antipodes, when Werner and Basyrin[3] succeeded in resolving one of the two inactive forms of dimethylsuccinic acid. Noyes and Kyriakides[4] have also recently resolved into its optically active forms, one of the two inactive isomeric $\alpha,\alpha'$-dimethyladipic acids. It is very significant that in both of these cases, it was the more soluble acid, and the one having the lower melting point which was decomposed into the optically

[1] Auwers, *Ann.*, **309**, 316 (1899).

[2] Bischoff, *Ber.*, **24**, 1074, 1085.

[3] Werner and Basyrin, *Ber.*, **46**, 3229 (1913).

[4] Noyes and Kyriakides, THIS JOURNAL, **32**, 1057 (1910).

active components.   It was found impossible to resolve the less soluble acid having the higher melting point.   From this it appears that, unlike the tartaric acids, the racemic, or fumaroid form of the dialkylsuccinic acids are the varieties of the low, and not of the high melting points.

It is extremely probable, therefore, that of the two ditetradecylsuccinic acids described in this article, the less soluble one melting at 135 to 136° is the *meso*, while the more soluble acid melting at 95° is the *racemic* modification.

## Experimental.

The palmitic acid, which was used in this work for the preparation of the bromo- and iodopalmitic acid, was obtained by saponification of palm oil with potassium hydroxide and decomposition of the resulting soap with hydrochloric acid.   It was fractionally distilled at 35–45 mm. The fraction boiling at 240–250° after two recrystallizations from gasoline was practically pure.   It melted at 61.5° to 62.°

α-Bromopalmitic acid was prepared according to Hell and Jordanoff's[1] method by adding dry bromine to a mixture of palmitic acid and red phosphorus.   An excess of bromine (40 cc.), which had been previously dried with concentrated sulfuric acid, was slowly dropped onto a mixture of 75 g. of palmitic acid which was intimately mixed with 3.5 g. of red phosphorus.   The reaction was carried on in the sunlight and at first was violent, the addition of every drop of bromine being attended with a flash. After most of the bromine had been added the mixture was heated on a boiling water bath until the fumes of hydrobromic acid had practically ceased.   The excess of bromine was removed by drawing a current of air through the warm mixture for a few minutes.   The reddish, oily product was then poured into about a liter of water, allowed to stand over night, extracted with petroleum ether, and the acid allowed to crystallize by spontaneous evaporation of the solvent.   No marked reaction was observed when the oily product was poured into the cold water.   (Hell records that a vigorous reaction with evolution of heat occurs at this stage.) After a few recrystallizations from petroleum ether or ligroin the bromo-palmitic acid separates in clusters of prisms which melt at 53 to 53.5°. The yield of the purified acid was 40 g.

Iodopalmitic acid was prepared by boiling for three hours 95 g. of bromo-palmitic acid, dissolved in 200 cc. of alcohol, with 70 g. of potassium iodide. After filtering off the potassium bromide, the straw-colored filtrate was evaporated nearly to dryness and the residue triturated several times with potassium iodide solution, to remove free iodine.   The iodopalmitic acid crystallized from petroleum ether in glistening scales which melted at 60 to 61°.   (Ponzio[2] gives 57°.)   Obtained a yield of 90 g.

[1] Hell and Jordanoff, *Ber.*, 24, 938 (1891).

[2] Ponzio, *Chem. Zentr.*, 82, 1361 (1911).

Action of Silver on α-Bromopalmitic Acid.—Three g. of bromopalmitic acid, dissolved in 25 cc. of heptane, was boiled with 3.1 g. of finely divided silver for nine hours in a paraffin bath. The silver was prepared by reduction of silver chloride by glucose and sodium hydroxide, and then dried at 135 to 140°. Evidence of a reaction between the silver and bromopalmitic acid was apparent within half an hour, as indicated by a change in the color and texture of the silver residue. The temperature of the boiling mixture was about 115°. The silver residue was filtered from the hot solution, and the filtrate was evaporated on a water bath to a small volume of liquid which solidified on cooling. This was then warmed with several times its volume of petroleum ether, allowed to stand for a few minutes, and the portion which remained undissolved filtered off. This white substance, which amounted to 0.08 g., melted at 120–130° to a clear oil and decomposed at 165–170° with evolution of bubbles.

The silver residue which had been filtered off, was first washed with hot petroleum ether, then extracted with boiling alcohol, and the alcoholic extract evaporated to dryness. This residue was now warmed with petroleum ether to remove traces of soluble matter, and 0.12 g. of a hard, light-colored, pulverulent substance was filtered off, which melted at 131–133° to a clear oil and decomposed with gradual effervescence at 155–160°. Altogether, there was thus obtained of this high melting product, 0.2 g., or 8% of the theoretical yield calculated for ditetradecyl-succinic acid.

The original heptane filtrate, to which was added the petroleum ether washings of the silver residue, yielded on evaporation an oil, which on cooling partially solidified forming a pasty mixture. This was stirred with ice-cold petroleum ether and filtered. By this method, 0.9 g. of a crystalline substance was separated from the oily fraction. This substance is soluble in dilute alkalies, from which it can be reprecipitated by addition of acids. After two recrystallizations from dilute alcohol, it separated in fine needles which melted sharply at 62–63°. Some of this substance mixed with pure palmitic acid melting at 62.5°, caused no lowering of the melting point, showing it to be pure palmitic acid. There was obtained 0.6 g. of this acid, which is 20% of the bromopalmitic acid originally taken. The actual percentage of palmitic acid formed is doubtless considerably more, as some must have been lost during the purification.

The petroleum ether filtrate from the palmitic acid left on evaporation a straw-colored oil. The examination of this sirupy product of the reaction is described in a subsequent paragraph.

Action of Silver on α-Iodopalmitic Acid.—The action of silver on iodopalmitic acid was carried on under the same conditions as in the case of bromopalmitic acid. The results obtained were analogous, excepting that a larger yield of the high melting acid, and a smaller amount of palmitic

acid were obtained. In one experiment 13% of the calculated yield of the former was obtained, while 13.3% of the iodo acid was converted into palmitic acid. These results suggest that iodopalmitic acid has a less tendency than the bromo acid, to split off halhydric acid, with consequently a smaller reduction to palmitic acid, and a greater tendency to lose its halogen, with the formation of the high melting acid.

**Sym-Ditetradecylsuccinic Acid** (melting at 135–6°),

$CH_3(CH_2)_{13}CH\ COOH$

| .—All of the fractions of the high melting acid,

$CH_3(CH_2)_{13}CH\ COOH$

(melting at 130–133°), obtained from several preparations as described above, were united and dissolved in boiling alcohol. On standing there soon separated from the alcoholic solution hard granular nodules, which melted to a clear oil at 133–135°, and decomposed at 170–180° with slow evolution of gas, leaving a clear, colorless oil. After one or two recrystallizations from alcohol, the substance was obtained in hard clusters, or rosets, which melted sharply at 134–135°. It can also be crystallized from hot glacial acetic acid, in the form of fine, soft aggregates which, when dry, can readily be reduced to a fine, flour-like powder.

Calc. for $C_{32}H_{62}O_4$: C, 75.29; H, 12.16. Found: C, 74.93, 74.83; H, 12.07, 11.96.

It slowly dissolves in boiling dilute ammonium hydroxide, forming a slightly opalescent solution, which, when acidified with dilute hydrochloric acid, regenerates the free acid as a light flocculent precipitate, melting at 135–136°. This acid is characterized by being extremely difficultly soluble in most solvents. It is practically insoluble in water, chloroform, acetone, carbon tetrachloride, ether, petroleum ether, benzene and ethyl acetate. It is moderately soluble in hot, but very sparingly soluble in cold alcohol. It dissolves readily in hot glacial acetic acid, but separates out again almost quantitatively on cooling. On account of these properties some trouble was encountered in purifying it. It can be best purified by dissolving in warm dilute ammonium hydroxide, precipitating with dilute hydrochloric acid and recrystallizing, first from alcohol and then from acetic acid. Thus purified it melts at 135–136°, and decomposes with bubbling at 165–170°.

**Action of Heat on the Above Acid. Formation of Ditetradecylsuccinic**

$CH_3(CH_2)_{13}CH\ C:O$
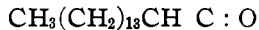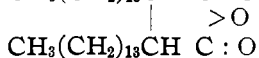
**Anhydride,** | >O .—The ditetradecylsuccinic acid, con-

$CH_3(CH_2)_{13}CH\ C:O$

tained in a short test tube, was heated to 180° in a sulfuric acid bath, and maintained at that temperature until the formation of bubbles had largely subsided. The temperature was finally raised to about 200°, at which point the evolution of gas had entirely ceased. During the heating, which occupied about three-quarters of an hour, the substance was stirred

with a platinum wire. The thick, slightly yellow oil solidified on cooling, to a hard crystalline cake. Loss of water during the heating:

Subst., 0.492; loss of weight on heating, 0.018. Calc. for $C_{32}H_{62}O_4$: $H_2O$, 3.53. Found: 3.65.

The crude product melted at 42–43.5°. It was purified by dissolving it in ether, and then adding a little more than an equal volume of absolute alcohol. On cooling in ice water it separated in fine, white, asbestos-like needles, which melted sharply at 45–45.5° to a clear oil.

Calc. for $C_{32}H_{60}O_3$: C, 78.05; H, 12.20. Found: C, 77.71; H, 12.07.

This anhydride is extremely soluble in ether and practically insoluble in cold alcohol and water.

**Hydrolysis of the Above Anhydride and Its Conversion into a Ditetradecylsuccinic Acid Melting at 95°.**—This anhydride is quite stable even toward boiling water. When warmed with water it melted, forming a clear layer of oil. Even after boiling for four or five minutes, the oil remained on the surface of the water apparently unchanged. On cooling the oil solidified, forming a crystalline crust which melted at 45°. The water remained perfectly clear, showing that not a trace of hydrolysis had occurred. The anhydride was accordingly boiled for about three-quarters of an hour with 75 cc. of potassium hydroxide (1%). It readily dissolved, forming a milky, or opalescent solution. After filtering and acidifying with dilute hydrochloric acid, a light flocculent precipitate separated. This was dissolved in a small amount of ether, and the solution placed in a freezing mixture of ice and salt. There soon separated a light flocculent precipitate. This substance melted at 95°, forming a slightly turbid oil which became clear at 96–97°. It decomposed at 145–150° with evolution of bubbles.

Calc. for $C_{32}H_{62}O_4$: C, 75.29; H, 12.16. Found: C, 75.10; H, 12.34.

It readily dissolves in warm dilute ammonium hydroxide, and is reprecipitated when acidified with hydrochloric acid. This acid is characterized, in comparison with the acid melting at 135–136°, by a greater degree of solubility in most of the common organic solvents. It is rather sparingly soluble in cold alcohol, and is more soluble in warm ether than in warm alcohol. It will not separate, however, from an extremely concentrated alcoholic solution. It is difficultly soluble in petroleum ether. It can be crystallized from glacial acetic acid, from which it separates as a light precipitate which, when dry, can be readily reduced to a fine powder. Especially striking is the behavior of the oil obtained by heating the acid a few degrees above its point of decomposition. If the acid is decomposed in a capillary tube, the resulting oil does not solidify on standing for a short time at room temperature. But on sudden cooling, by plunging the capillary into ice water, it solidifies. As soon as it is removed from the ice water it again melts to a clear oil at room temperature. When this

oil, however, is now slightly warmed by merely holding between the fingers, it quickly solidifies and then melts at 43–45°. Owing to the very small amount of substance available, it was impossible to make a closer study of these remarkable changes. They suggest, however, the formation of a low melting, unstable anhydride of the acid melting at 95°, which easily changes into the same anhydride as that obtained by heating the higher melting acid.

The properties of the acid melting at 95°, and its composition as indicated by analysis, show it to be a ditetradecylsuccinic acid isomeric with the acid which melts at 135–136°. The analogy with dimethylsuccinic acid and α,α-dimethyladipic acid, in both of which cases the more soluble acid, and the one having the lower melting point of the two inactive isomeric forms, were resolved into the optically active antipodes,[1] indicates that this ditetradecylsuccinic acid just described is probably the *racemic*, while its isomer melting at 135–136° is the *meso* modification.

**Examination of the Sirupy Residues Obtained by the Action of Silver on Bromo- and Iodopalmitic Acid.**—The sirupy residues, obtained by the action of silver on the halogen acids, were united and dissolved in aqueous potassium hydroxide (1%). The solution was just neutralized with dilute hydrochloric acid and a slight excess of barium chloride solution added. A copious precipitate formed. This product after standing *in vacuo* over sulfuric acid for several days had somewhat of a sticky, rubberlike consistency. It was extracted in a Soxhlet extractor with ether for several hours, whereupon a considerable portion of the substance went into solution. (See below for the ether-soluble portion.) The ether-insoluble portion, after drying, consisted of hard lumps which were ground in a mortar, and decomposed with dilute hydrochloric acid by heating on a water bath. An oil separated which on cooling solidified to a hard crust. This was broken up, washed several times with water, dried *in vacuo* over sulfuric acid, and extracted in a Soxhlet apparatus with petroleum ether. A grayish white residue remained undissolved in the capsule.

The petroleum-ether extract on evaporation yielded a white crystalline residue, which after one crystallization from ligroin, and another from alcohol, was identified as palmitic acid. It melted sharply at 62.5–63°.

The grayish white residue which remained undissolved by the petroleum ether, was dissolved in a small amount of alcohol. On standing, a substance separated in the form of light flocculent aggregates, which melted at 90–93° to a thick, translucent liquid, gradually clearing and becoming a perfectly clear oil at 115°. It decomposed with bubbling at about 150°. Despite all attempts to further purify it, it could not be obtained to melt to a *clear oil* at a definite temperature. It is, however, identical in all other respects with the lower melting ditetradecylsuccinic acid, and

[1] Noyes and Kyriakides, *Loc. cit.*; Werner and Basyrin, *Ibid.*

is undoubtedly the same acid, but containing a trace of some impurity which persistently clings to it.

The ether extract, obtained by extraction of the barium salts, yielded on spontaneous evaporation of the ether a straw-colored residue having the consistency of vaseline. This was decomposed by warming in a water bath with dilute hydrochloric acid, and the clear oil which separated, extracted with ether. By spontaneous evaporation of the ether, there was obtained a clear, yellow oil. This oil readily decolorizes bromine water, and is soluble in dilute alkalies, from which it is regenerated when acidified. It showed no tendency to crystallize until after standing for about three months, when a crystalline substance separated. The crystals were spread on a porous plate to remove the adhering oil, and then washed with a little cold alcohol, whereby the substance was obtained nearly white. After two recrystallizations from acetic acid, and another from ether in a freezing mixture, it melted at 86–90° to a slightly turbid oil which became perfectly clear at 100° and decomposed with bubbling at about 150°. It dissolves easily in warm dilute ammonium hydroxide, and is reprecipitated in a flocculent form when acidified with hydrochloric acid. This substance shows all of the properties of the ditetradecylsuccinic acid which melts at 95°.

The oil from which the above acid was obtained showed strong properties of unsaturation. Unfortunately, the amount available was so small that further investigation of it was impossible.

MADISON, WIS.

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## THE CONSTITUTION OF ACETYLACETONE-THIOUREA.

BY WILLIAM J. HALE AND ARTHUR G. WILLIAMS.

The constitution of acetylacetone-urea has been shown by de Haan,[1] and again by one of us,[2] to accord primarily with the formula advanced by Evans[3] and at the same time to exist in a tautomeric imino, or colorless form. The ordinary product was considered quinoid in structure and possessed a decided yellow color. The condensation of thiourea with acetylacetone is described by Evans[4] as proceeding in exactly analogous manner to the condensation of urea with this diketone and yielding two distinct condensation products. From the properties of these two products it seemed that their exact structures might be open to question. de Haan has shown conclusively that the so-called diurimido-acetylacetone

[1] Rec. trav. chim., 27, 162 (1908).
[2] THIS JOURNAL, 36, 104 (1914).
[3] J. prakt. Chem., [2] 48, 489 (1893).
[4] Ibid., 48, 503 (1893).