[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BIRKBECK COLLEGE, UNIVERSITY OF LONDON]

UNSATURATION PHENOMENA OF ACETYLENIC ACIDS AND ESTERS

I. THE CONSTITUTION OF 2-KETO-11-UNDECYLIC ACID

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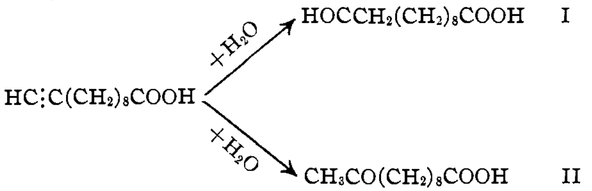
The preparation of a keto-undecylic acid has been described by Welander.[1] It was obtained by the action of moderately concentrated sulfuric acid upon 9,10-undecinolic acid. The constitution of the latter is fixed by the fact that it yields azelaic acid on oxidation,[2] so that Welander's ketonic acid might be either $CH_3CO(CH_2)_8COOH$ or $CH_3CH_2CO(CH_2)_7COOH$.

The constitution might have been settled by submitting the oxime to the Beckmann transformation and proceeding in the manner described by Baruch,[3] but Welander failed to effect the Beckmann transformation.

We set out to determine the constitution in a different way, anticipating that the same acid would be obtained by starting with 10,11-undecinolic acid described by Krafft[2] and called by him dehydro-undecylenic acid. We found that when this acid was treated with sulfuric acid in the manner described by Welander a poor yield of a keto-undecylic acid was obtained melting at 59.5° and forming an oxime melting at 68–69°.

The constitution of ethyl dehydro-undecylenate is known from the fact that it forms a silver acetylide with alcoholic silver nitrate and the free acid yields sebacic acid on oxidation.[2] The ketonic acid derived from dehydro-undecylenic acid must therefore be produced by the second of the two following reactions.



No distinctive aldehydic reactions were found for the product or in its ethyl ester.

Welander gives the melting point of his keto-undecylic acid as 49° and describes its oxime as a non-crystallizable oil. It appeared from this that his must be 3-keto-11-undecylic acid.

We then devised a method of preparing the ketonic acid from dehydro-undecylenic acid in better yield. The acetylenic acid was dissolved in

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[1] Welander, *Ber.*, **28**, 1449 (1895).

[2] Krafft, *Ber.*, **29**, 2232 (1896).

[3] Baruch, *Ber.*, **27**, 172 (1894).

glacial acetic acid and was warmed on the water-bath at 70° with mercuric acetate. During about five hours a small amount of mercurous acetate separated and was filtered off. The solution was poured into twice its volume of water and a solid separated. Recrystallization from dil. acetic acid gave a product of definite composition in the form of microcrystalline, colorless needles.

Analysis showed the crystals to be the mercuric salt of a triacetoxymercuri-keto-undecylic acid. Treatment with moderately concd. hydrochloric acid gave a quantitative yield of the keto-undecylic acid melting at 59.5°. To obtain good yields from the dehydro-undecylenic acid it was found unnecessary to isolate the mercury compound, but the whole of the acetic acid solution was treated with mineral acid and the mixture then poured into water.

The analysis of the mercury compound was carried out in three stages. The mercury was estimated by precipitation as mercuric sulfide, hydrogen sulfide being passed through an acetic acid solution containing a weighed amount of the substance. The acetoxy group was determined on a quantity of the substance, dried for several days in a vacuum desiccator at the pump, by suspending a weighed amount in lime-dried absolute alcohol and distilling from a water-bath after addition of concd. sulfuric acid. Ethyl acetate was estimated in the distillate by quantitative hydrolysis. The keto-undecylic acid was liberated from a third quantity by hydrochloric acid, extracted with ether and weighed.

The analyses fix the constitution as $(CH_3COOHg)_3C.CO(CH_2)_8COO(Hg)^1/_2$.

We then attempted to prepare Welander's ketonic acid from 9,10-undecinolic acid by the intermediate formation of a mercuric compound. The product gave analyses for the mercuric salt of a diacetoxymercuri-keto-undecylic acid. Treatment with hydrochloric acid gave a ketonic acid which melted at 49–50°. This appeared to be Welander's acid which melted at 49°. Systematic recrystallization from petroleum ether (b. p. 60–80°) led to the isolation of two pure ketonic acids having the molecular formula $C_{11}H_{20}O_3$, one melting at 59.5° identical with that prepared from dehydro-undecylenic acid, and the second melting at 43.5°. The first was obtained in fair amount but less than 1 g. of the second was isolated after recrystallization 18 times. The original 9,10-undecinolic acid melts at 59.5° but analysis and the melting point of a mixture (45–50°) showed that the two substances melting at 59.5° were not identical.

We then repeated Welander's preparation by means of sulfuric acid and obtained a product melting at 48–49°. On repeated systematic recrystallization from petroleum ether we were again able to separate two ketonic acids melting at 59.5 and 43.5° in roughly the same proportions.

It still remained to show that the predominating high-melting constituent in the mixture did not result from the presence of dehydro-undecylenic acid in the 9,10-undecinolic acid used, since both of these acetylenic acids are prepared by the action of potassium hydroxide upon 1,2-dibromo-11-undecylic acid[2] at different temperatures. Our next step was therefore to prepare pure specimens of the ethyl esters of the two acetylenic acids by repeated fractionation in a vacuum. Ethyl dehydro-undecylenate is precipitated from alcoholic solution as a silver acetylide by adding alcoholic silver nitrate, and we found that any quantity of this ester greater than 1% present in admixture with ethyl 9,10-undecinolate could be detected by the formation of a precipitate in this reaction.

A quantity of ethyl 9,10-undecinolate which failed to show turbidity with silver nitrate was dissolved in glacial acetic acid and treated with mercuric acetate. The mercury compound was isolated as before. It gave analyses for the ethyl ester of a diacetoxymercuri-keto-undecylic acid, $(CH_3COOHg)_2C_{10}H_{17}OCOOC_2H_5$.

Hydrochloric acid liberated an ester which was separated into two fractions by distillation under diminished pressure. The higher-boiling fraction, distilling at 169–170° (corr.) (12 mm.), represented about 50% of the original ester and gave on hydrolysis the ketonic acid melting at 59.5°. The lower-boiling fraction appeared with progressive rise in temperature from 158 to 169° and gave on hydrolysis a mixture from which a further amount of the acid melting at 59.5° and a small amount of that melting at 43.5° were separated by crystallization from petroleum ether.

On the evidence so far obtained, the acid melting at 59.5° must be 2-keto-11-undecylic acid and that melting at 43.5° 3-keto-11-undecylic acid.

We have succeeded in submitting the oxime of the former to the Beckmann transformation under the influence of concd. sulfuric acid. When the product was heated in a sealed tube with concd. hydrochloric acid it yielded almost the calculated amount of sebacic acid.

Experimental Part

Preparation of 1,2-Dibromo-11-undecylic Acid.—Petroleum ether (b. p. 60–80°) was treated with excess of bromine at room temperature and the mixture allowed to stand for two days. It was then washed with a solution of sodium bisulfite and dried. After distillation the purified product was used as solvent. One hundred and seventy g. of undecylenic acid (m. p. 24.5°; b. p. 168.3° at 15 mm.) was dissolved in 500 cc. of purified solvent. One hundred and fifty g. of bromine was added during one and one-half hours while cooling in a mixture of ice and salt. When about three quarters of the bromine had been added the dibromo acid began to separate. Efficient stirring was required from this point. When the whole of the bromine had been added the mixture was allowed to stand for an hour. The precipitate was filtered off at the pump and washed with 100 cc. of cold petroleum ether. The cake was broken up and transferred to a vacuum desiccator and the excess of bromine and solvent was removed during 24 hours. The white crystals melted at 38.5°; yield, 250 g. The rest of the dibromo derivative was obtained as an oil after washing the filtrate with a solution of sodium bisulfite, drying and evaporating. The yield of oil was approximately the same in a number of brominations.

Anal. Calcd. for $C_{11}H_{20}O_2Br_2$: Br, 46.5; equiv. wt., 344. Found: Br, 46.2; equiv. wt. (titration against standard alkali), 345.1.

Preparation of Dehydro-undecylenic Acid and 9,10-Undecinolic Acid.—Dehydro-undecylenic acid was prepared from the dibromo acid by the method of Krafft.[2] The constants of the substance given by this author were confirmed. 9,10-Undecinolic acid was obtained from the dibromo acid by the method of Welander.[1] The constants described by Welander were confirmed.

Conversion of the Acetylenic Acids into Esters.—The method of esterification at first employed was that described by Krafft[2] in which the acid is boiled under a reflux condenser with alcohol and an excess of potassium carbonate. The filtered solution containing the potassium salt was heated in pressure bottles with excess of ethyl iodide. Finally it was found to be less troublesome to reflux the acid with ten times its weight of lime-dried absolute alcohol and its own weight of concd. sulfuric acid. The mineral acid was mixed with the alcohol and the acetylenic acid added when cold. The solution was allowed to stand at room temperature before refluxing for ten hours. At the end of this time the solution was cooled and ether added. After shaking with water the ethereal solution was separated, washed with dil. sodium carbonate solution and water, dried and evaporated. The residue after distillation of the ether was fractionated under diminished pressure. The esters were collected at the following temperatures: ethyl dehydro-undecylenate, 145° (15 mm.), and ethyl 9,10-undecinolate, 197° (49 mm.).

Small quantities of the pure esters were hydrolyzed and gave the following acids: dehydro-undecylenic acid, m. p., 43°; 9,10-undecinolic acid, m. p., 59.5°.

Treatment of Dehydro-undecylenic Acid with Mercuric Acetate.—Ten g. of dehydro-undecylenic acid was dissolved in 25 cc. of glacial acetic acid in a 500cc. flask fitted with an air condenser. To this was added a solution of 39 g. of mercuric oxide in 225 cc. of glacial acetic acid. The flask was heated on the water-bath at 70 to 100° for five hours. At the end of this time the deposit of mercurous acetate was filtered off while hot and the solution cooled and poured into 250 cc. of water. The solid which separated was filtered off and recrystallized from 75% acetic acid. The colorless microcrystalline needles were drained at the pump, dried on filter paper and finally washed with ether and dried in the vacuum desiccator for at least two days on the pump. There were obtained about 1.5 g. of mercurous acetate and 45 g. of the mercuric compound.

Treatment of 9,10-Undecinolic Acid with Mercuric Acetate.—Ten g. of the acetylenic acid treated as in the preceding case with 28 g. of mercuric oxide in 250 cc. of glacial acetic acid gave a small amount of mercurous acetate and 37 g. of the mercuric compound in colorless, microcrystalline needles.

Treatment of Ethyl 9,10-Undecinolate with Mercuric Acetate.—Thirty-three g. of the ethyl ester which gave no precipitate with alcoholic silver nitrate was treated as described above with 70 g. of mercuric oxide in 500 cc. of glacial acetic acid. About 4 g. of mercurous acetate was separated, and on pouring the filtrate from this into water the product separated as a thick, amber-colored, viscous oil which solidified when shaken with water. The solid crystallized from 75% acetic acid in the form of fine needles; yield, 95 g.

Treatment of Ethyl Dehydro-undecylenate with Mercuric Acetate.—Thirty g. of the ester was treated in 600 cc. of glacial acetic acid with 95 g. of dissolved mercuric oxide. The procedure was the same as that described above.

Analysis of the Mercuric Compounds

1. Estimation of Mercury.—Approximately 0.5 g. of the substance was dissolved in hot glacial acetic acid and the solution saturated with hydrogen sulfide. Concd. hydrochloric acid was then added and the precipitated mercuric sulfide filtered through a Gooch crucible, washed with ether, dried and weighed.

2. **Estimation of Acetoxy Group.**—Approximately 1.5 g. of the substance was weighed and transferred to a distilling flask, the side tube of which was bent downwards at the middle of its length to make an angle of 120°. The flask was fitted with a dropping funnel and was attached to a Liebig condenser. Fifty cc. of absolute alcohol (lime-dried) mixed with 10 cc. of concd. sulfuric acid was admitted through the funnel and the flask was then heated on the water-bath and wrapped round with a duster. The distillate was collected in excess of standard 0.5 *N* alcoholic potassium hydroxide solution, and dry absolute alcohol was dropped into the flask at the same rate as that of the distillation. Fifty cc. of alcohol was added in this way and then the contents of the flask were allowed to distil to about 30 cc. The distillate was refluxed for 40 minutes and the excess of alkali titrated with 0.5 *N* acid. After each titration the solution was evaporated almost to dryness. One portion was treated for the recognition of potassium acetate and the second was diluted with water and acidified to ascertain that no turbidity appeared.

3. **Estimation of the Ketonic Acid or Ester Liberated by Treatment with Hydrochloric Acid.**—Approximately 5.0 g. of the substance was warmed with moderately concd. hydrochloric acid and the mixture then diluted with water. Esters were shaken in a flask with dil. acid, cold. No precipitate of mercurous chloride formed. The ketonic compound was extracted with ether and weighed after being washed and the solvent distilled. The residue was dried before weighing by adding a few drops of absolute alcohol and blowing out the flask at the bellows while immersed in boiling water. Two or three treatments in this way served

TABLE I

RESULTS OF THE ANALYSES

Initial acetylenic compd.	Analysis of mercuric compound		
	Hg, %	CH_3COO, %	Ketonic compd., %
Dehydro-undecylenic acid, found	65.2	16.3	18.5 $C_{11}H_{20}O_3$
Calcd. for mercuric 1-triacetoxy-mercuri-2-keto-11-undecylate	65.3	16.5	18.6 $C_{11}H_{20}O_3$
9,10-undecinolic acid (found)	61.4	14.4	24.3 $C_{11}H_{20}O_3$
Calcd. for a mercuric diacetoxymercuri-keto-undecylate	61.4	14.5	24.5 $C_{11}H_{20}O_3$
Ethyl dehydro-undecylenate, found	59.9	17.3	22.6 $C_{13}H_{24}O_3$
Calcd. for ethyl triacetoxy-mercuri-2-keto-11-undecylate	60.0	17.6	22.7 $C_{13}H_{24}O_3$
Ethyl 9,10-undecinolate, found	53.8	15.6	30.4 $C_{13}H_{24}O_3$
Calcd. for an ethyl diacetoxy-mercuri-keto-undecylate	53.8	15.8	30.6 $C_{13}H_{24}O_3$

to bring the flask to constant weight. The analyses of the ketonic compounds thus obtained are described later.

Preparation of the Ketonic Compounds without Isolation of Mercuric Compounds.—Almost quantitative yields of the ketonic compounds were obtained from the acetylenic acids and esters by treating with the amounts of mercuric oxide and acetic acid stated and then adding concd. hydrochloric acid to the whole of the solution and pouring into water. The solid separating was filtered off and then treated with ether to separate from mercurous acetate. The filtrate was extracted with ether, the ether distilled and acetic acid blown off at the bellows or distilled under diminished pressure. The products were, if solid, recrystallized from petroleum ether. Esters were extracted with ether after being poured into water and fractionated under diminished pressure.

Properties of 2-Keto-11-undecylic Acid.—The acid crystallized in fine tufts of colorless needles or in small glistening leaflets. No regularity has been observed in the occurrence of these two forms. The crystals melt sharply at 59.5°. They are moderately soluble in hot petroleum ether (b. p. 60–80°) and practically insoluble in cold. They are slightly soluble in boiling water and almost insoluble in cold. The solubility in other organic solvents is considerable.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.95; H, 10.00; equiv. wt., 200.16. Found: C, 65.89; H, 10.17; equiv. wt. (titration with standard alkali), 200.

The ethyl ester boils at 169–170° (corr.) (12 mm.). It gives no indication of enolization. The semicarbazone, prepared by adding a solution of semicarbazide hydrochloride with slightly more than the equivalent amount of sodium acetate to a solution of the acid in dil. alcohol, melts at 136.5° (corr.) after recrystallization from alcohol.

Anal. Calcd. for $C_{12}H_{23}O_3N_3$: C, 55.99; H, 9.01; N, 16.34. Found: C, 55.91; H, 9.08; N, 16.27.

The oxime prepared in the usual manner melts at 68–69°. When warmed on the water-bath for an hour with five times its weight of concd. sulfuric acid and then poured into water it is converted into a mixture of the isomeric acids $CH_3NHCO(CH_2)_8COOH$ and $CH_3CONH(CH_2)_8COOH$, melting after recrystallization from alcohol between 65 and 72°.

Anal. Calcd. for $C_{11}H_{21}O_3N$: C, 61.34; H, 9.84; N, 6.51. Found: C, 61.30; H, 9.91; N, 6.38.

Anal. (oxime). Found: C, 61.26; H, 9.90; N, 6.47.

Ten g. of the mixed acids after the Beckmann change was heated with 30 cc. of hydrochloric acid solution (saturated at room temperature) for five hours at 180–190° in a sealed tube. The contents were washed into a flask and steam distilled for 30 minutes. The contents of the flask were made alkaline and again steam-distilled for 30 minutes. The residue in the flask was concentrated to 100 cc. and acidified. Crystals separated and these were recrystallized from water. They melted at 134° and were recognized as sebacic acid by the mixed melting point of 134° with sebacic acid derived from the oxidation of dehydro-undecylenic acid. The yield of sebacic acid was 4 g.

The oxime was found to give an almost quantitative yield of 2-keto-11-undecylic acid on hydrolysis with dil. sulfuric acid.

The authors are indebted to the Government Grant Committee of the

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Summary

1. Crystalline compounds containing mercury are produced by the action of mercuric acetate in acetic acid solution upon dehydroundecylenic and 9–10 undecinolic acids and upon their ethyl esters.

2. The mercury compounds yield, after treatment with hydrochloric acid, saturated ketonic acids or esters free from mercury. Hydration at the triple bond has thus been effected.

3. Hydration in the case of dehydroundecylenic acid takes place in one direction, but in the case of 9–10 undecinolic acid in the two theoretically possible directions with formation of two isomeric ketonic acids. The ethyl esters behave in the same manner.

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UNSATURATION PHENOMENA OF ACETYLENIC ACIDS AND ESTERS

II. THE REACTION BETWEEN MERCURIC ACETATE AND SOME ACETYLENIC ACIDS AND ESTERS

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Two of the present authors have described the isolation of mercury compounds resulting from the action of mercuric acetate upon dehydroundecylenic acid and 9,10-undecinolic acid.[1]

These examples include one case in which the acetylenic bond is at the end of a carbon chain and one in which it occurs along the chain and without any associated hydrogen atom.

In the present investigation we have varied the type of acetylenic acid by studying the action of mercuric acetate upon (a) stearolic acid, (b) ricinolic acid, (c) behenolic acid, (d) methyl behenolate, (e) γ-butinene-α,α-dicarboxylic acid, (f) γ-butinene-α-carboxylic acid.

Preparation of the Acetylenic Acids

A preliminary investigation of the methods of preparation of stearolic, ricinolic and behenolic acids was considered desirable. They are obtained by brominating oleic, ricinoleic and erucic acids, respectively, the

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[4] Since this work was completed the authors have noted that Chuit, Boelsing, Hausser and Malet [*Helv. chim. Acta*, **9**, 1074 (1926)] describe the preparation of 2-keto-11-undecylic acid by oxidation of undecane-2,11-diol. The melting point recorded by these investigators is 58.5–59.5°.

[1] Myddleton and Barrett, THIS JOURNAL, **49**, 2258 (1927).