Projected Committee Work

As a result of a recent publication, "Influence of Alkali Concentration and Other Factors on the Conjugation of Natural Polyunsaturated Acids as Determined by Ultraviolet Absorption Measurements," by S. F. Herb and R. W. Riemenschneider, Eastern Regional Research Laboratory, Philadelphia, Pa., Journal of the American Oil Chemists' Society, November, 1952, Vol. XXIX, pages 456-461, the committee should investigate isomerization of fatty acids with 21% KOH, comparing the results obtained against those using the present A.O.C.S. method. The possibility of extending the method to the analysis of fats containing pentaene acids should be investigated.

A study should be made of the effect of cis-trans isomers present in hydrogenated oils on the results obtained, using the spectrophotometric method. Such a program would involve cooperative work in the infrared region to establish trans-isomer contents.

Cooperative work should be extended to encompass oils containing large quantities of preconjugated constituents. This work should probably be a joint effort with the A.S.T.M. Committee already studying the problem.

The exact program to be followed must, of course, be left to the 1953-54 Committee. The projected committee work proposed is to be considered only as a suggestion in the event that the committee should decide to embark upon an entirely different program.

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Acetylenic Compounds. I. The Dehydrohalogenation Reactions by Sodamide in Liquid Ammonia and Preparation of Some Mono-Acetylenic Substances and Their Derivatives[1,2]

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IN a previous publication Khan *et al.* (1) described the preparation of stearolic acid by dehydrobromination of dibromostearic acid with sodamide in liquid ammonia. In view of the consistently higher yields obtained by this procedure than with the alcoholic KOH reagent of Adkins (2) and others (3) (17), it seemed desirable to see if this reaction could be applied to the preparation of other acetylenic compounds. The sodamide and alcoholic KOH methods have been compared. The effect of the presence of dienoic acids was shown by using oleic acid, free of such compounds as starting material. Large-scale preparation from 3.2 moles of oleic was also accomplished with some additional precautions.

Purified tetrabromostearic acid was subjected to dehydrohalogenation by sodamide in liquid ammonia. Stearolic acid was then prepared directly from crude olive oil acids in yields of 25-30%.

Diketostearic acid has been prepared by $KMnO_4$ oxidation of the crude stearolic acid obtained from olive oil acids. Stearolic acid was qualitatively detected in mixtures by formation of diketostearic acid. Oleic acid was also detected in mixtures through the formation of stearolic acid and diketostearic acid.

The sodamide dehydrohalogenation method was successfully applied to the preparation of 6-octadecynoic acid from petroselinic acid, phenyl acetylene from styrene, and 10-undecynoic acid from 10-undecelenic acid. The yields of 6-octadecynoic acid were very high compared to those of the latter compounds.

The infrared absorption spectrum of stearolic acid was studied in order to observe absorption due to the triple bond. The freezing point curve was used to determine the absolute purity of stearolic acid.

Some suggestions have been made as to the reasons for the low yields of acetylenic compounds obtained from the unsymmetrical and short chain dibromides.

Experimental

Preparation of Stearolic Acid by Dehydrobromination of Methyl Dibromostearic Acid with Alcoholic KOH. The procedure of Adkins *et al.* (2) was followed, with five separate portions of methyl oleate (35 g., 95-97% pure). Stearolic acid was obtained only twice and in yields of 29 and 34% respectively. In addition, four batches of methyl dibromostearate, each from 35 g. of methyl oleate, were treated separately with 80 g. 85% KOH pellets and 300 ml. of one of the following alcohols: butyl, isobutyl, isoamyl, and amyl. No stearolic acid was obtained in these four experiments.

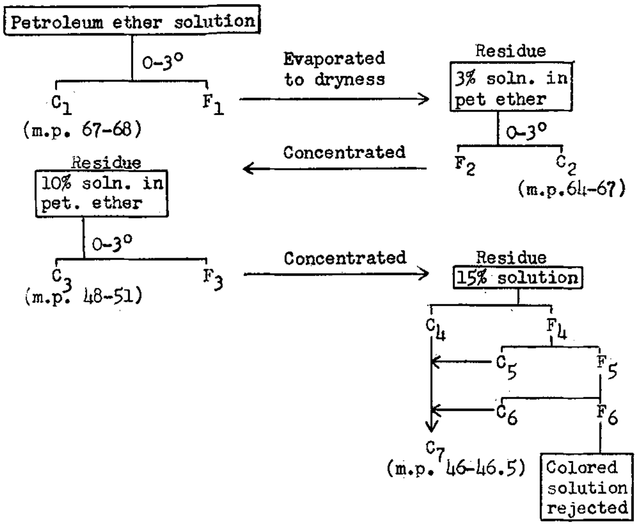

FIG. 1. Isolation of stearolic acid from dehydrobromination of olive oil fatty acids.

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[2] Hormel Institute Publication No. 85.

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Dehydrobromination by Sodamide in Liquid Ammonia

I. *Preparation of Stearolic Acid.* a) Several dehydrobromination reactions by sodamide in liquid ammonia, using dibromides obtained from 0.5 to 1.0 mole of oleic acid, were performed. Stearolic acid was obtained in all cases in yields ranging between 55 and 58%. The yield was found to be improved if the oleic acid was made free of dienoic and other polyunsaturated compounds, as shown by the following experiment: 100 g. of oleic acid obtained by a crystallization method (1) was hydrogenated at atmospheric pressure and temperature in presence of W-6 (4, 5) Raney nickel for 1/4 hour in 5% absolute alcohol solution with constant agitation and a stream of hydrogen. After removal of the catalyst and solvent, the oleic acid, as a 5% solution in acetone, was freed from the saturates by two crystallizations, at —30° and —35° C. This oleic acid on bromination and dehydrobromination by sodamide in liquid ammonia gave stearolic acid in about 76% yield as compared to the 68% yields previously reported (1), using crystallized oleic acid. This may mean that bromides of the polyunsaturated compounds interfere with dehydrobromination of dibromostearic acid to some extent.

b) The dibromides from 900 g. of oleic acid (95-97% pure) were dehydrobrominated by sodamide in 6 to 7 liters of liquid ammonia in 12 to 14 hours, with occasional replenishment of liquid ammonia. After the usual procedure of recovery through complete acidification and crystallization from petroleum ether, almost white stearolic acid was obtained (yield 51%). Crystallization from 20-30% solution in acetone at —5° to —8° or from 8-10% solution at —20° removed the last trace of color from the acids.

c) The crude olive oil acids (100 g.) as 10% solution in petroleum ether were brominated at 0-3°C. and the precipitate was removed (6). The bromides in the filtrate (concentrated to 25-30% solution) were subjected to dehydrobromination by sodamide in liquid ammonia. The semi-solid mixture was dried under vacuum on a steam cone. The product was then refluxed with petroleum ether (2½ liters) with occasional stirring for 6 hours. The supernatant petroleum ether solution was subjected to fractional crystallizations, as shown in Figure 1.

The combined fraction C_7 (Figure 1), giving the m.p. equivalent to that of stearolic acid, was crystallized twice from petroleum ether to remove minor impurities. The overall yields were 24.9 and 31.6% in two preparations.

d) In addition to characterization by the various chemical and physical means indicated in the previous publication (1), the infra-red absorption spectrum of stearolic acid was studied (Figure 2). The slight absorption at 4.42 due to triple bond is indicative of the fact that this bond at Δ^9 in flanked on either side by balanced groups. The freezing point curve was drawn by means of a platinum resistance thermometer and Wheatstone bridge system. From this freezing point curve the absolute purity of stearolic acid was found to be in the range 99.4-99.6% and melting point 45.3°.

II. *Dehydrohalogenation of Tetrabromostearic Acid.* Pure tetrabromostearic acid (62 g., 0.1 mole) was treated with sodamide (0.8 mole) in 2 l. liquid ammonia. The product consisted almost entirely of semisolid polymers, insoluble in petroleum ether.

III. *Diketostearic Acid from Crude Olive Oil Acids.* The supernatant petroleum ether extract of crude stearolic acid (procedure I, c) was evaporated to dryness. The residue was dissolved by warming in 6 liters of water containing a slight excess of potassium hydroxide to neutralize the acids. The solution was then neutralized to phenolphthalein with 6 N H_2SO_4, and mechanically stirred with a Hershberg stirrer while permanganate solution (45 g. $KMnO_4$ in 1250 ml. of water) was added in one portion and stirred for 1 hour at room temperature (22-28°C.). The solution was decolorized by addition of excess sodium sulfite followed by acidification with 6 N H_2SO_4. The surface layer was separated from the lower water phase, washed three times with water, and heated to boiling with 1 liter of 95% alcohol. After cooling to room temperature, the insoluble residue was removed by filtration. The yellow solution was cooled to 0-3°C. to obtain yellow leaflets, m.p. 84.0-85.5°C. Another crystallization from a 3% solution in 95% alcohol at 0-3°C. gave a product melting sharply at 84.5-85.0° C. (yield, 22.0%). The mixed m.p. with an authentic sample of 9,10-diketo-stearic acid showed no depression.

IV. *Qualitative Detection of Oleic Acid.* Several mixtures (1:1, 1:2, 1:4) of oleic acid (2 g.) with stearic and palmitic acids, respectively, were brominated and dehydrobrominated by sodamide in liquid ammonia. The soaps thus obtained were dissolved in water and neutralized to phenolphthalein. The presence of oleic acid was indicated by the formation of 9,10-diketostearic acid upon oxidation of the soaps with $KMnO_4$ solution as described above. In the case of mixtures of oleic acid with linoleic and linolenic acids, very dark-colored soaps were obtained, and the pH during oxidation was controlled at 7.5-8.5 by a pH meter (7). When polyunsaturated acids were present, it was found practicable to filter off tetrabromides and other polybromides before oxidation (6). In all cases the oxidation products were washed with water and heated with 95% alcohol. The filtered alcoholic solution gave on cooling 9,10-diketostearic acid. Stearolic acid was detected in mixtures by the formation of diketostearic acid. The 9,10-dihydroxy stearic acids, m.p., 95°C. (18) and 132°C. (19), 9-hydroxy, 10-keto stearic (20), and mixtures of 9-keto and 10-keto stearic acids (1, 21) do not interfere as they remain unchanged under these oxidative conditions. Furthermore 8- and 10-stearolic acids formed diketostearic acids having m.p.s in the range 93-98°C.

V. *Preparation of 6-Octadecynoic Acid.* The 28 g. of 6-octadecenoic (petroselinic) acid (16), m.p. 30-30.2°C., N.E. 281.7, I.N. 88.73, were brominated in dry ether and dehydrobrominated by sodamide in liquid ammonia. The resulting acetylenic acid was purified by two crystallizations from petroleum ether (20-25% solution at 0-3°), yield 23 g. (81.5%), m.p. 48.5-48.7°, I.N., 89.5; hydrogen uptake 2 moles/mole of substrate.

VI. *Phenyl Acetylene and 10-Undecynoic Acid.* These compounds were obtained in poor yields (45-52% and 40-42%, respectively) by sodamide dehydrohalogenation of dibromostyrene and dibromo-undecanoic acid by others (8, 9, 10). The present modified method did not improve the yields (11).

Further studies on other short chain hydrocarbons and acids are contemplated.

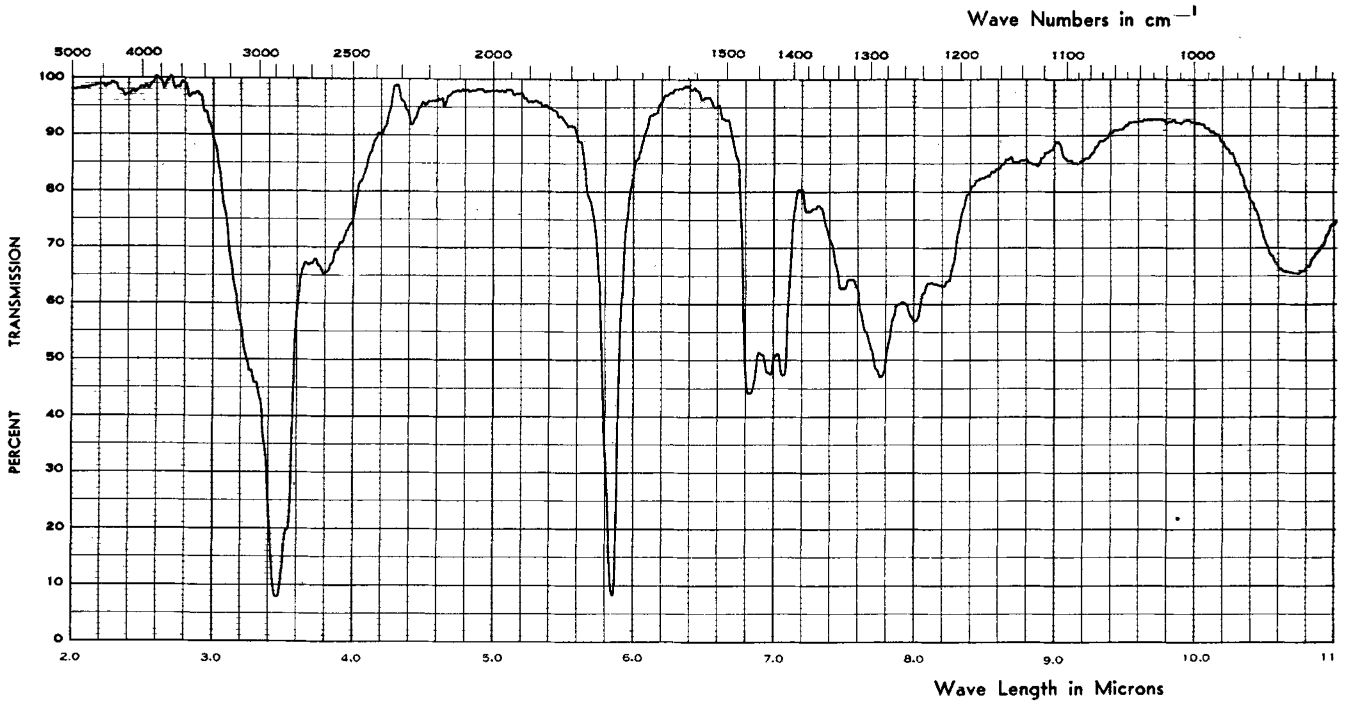


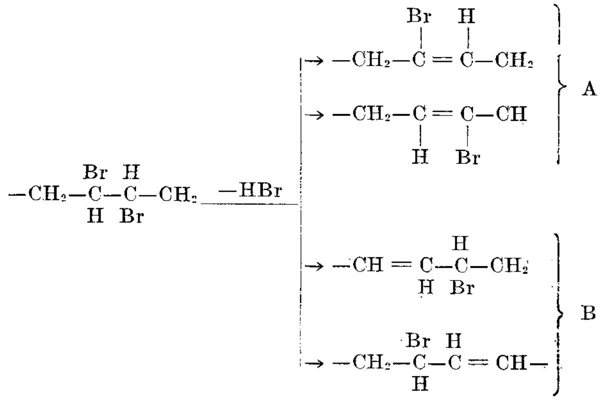
FIG. 2. Infrared absorption spectrum of stearolic acid.

Discussion

It seems that polyacetylenic compounds may not be prepared by dehydrohalogenation reactions. The tetrabromides from linoleic acid form insoluble polymers exclusively, indicating that stearolic acid can be made directly from crude fatty acids containing small amounts of these polyunsaturated compounds. This has led to the preparation of this acid and its derivative, 9,10-diketo stearic acid, from olive oil fatty acids without much difficulty.

Several other observations are evident from this study: a) As a dehydrobrominating reagent, sodamide in liquid ammonia gives better yields than alcoholic KOH; b) symmetrical dibromides of comparatively long carbon chain form the acetylenic compounds more smoothly than the unsymmetrical ones; c) activated (unsymmetrical) dibromides are involved in side reactions.

Overbeck (15) showed that during dehydrobromination of dibromostearic acid with alcohol KOH, monobromo-olefinic compounds were first obtained through elimination of one mole of HBr. The author did not indicate which one of the several possible isomers was preferentially formed.



$$-CH_2-\overset{Br}{\underset{H}{C}}-\overset{H}{\underset{Br}{C}}-CH_2 \xrightarrow{-HBr} \begin{cases} -CH_2-\overset{Br}{C}=\overset{H}{C}-CH_2 \\ -CH_2-\underset{H}{C}=\underset{Br}{C}-CH \end{cases} A \qquad \begin{cases} -CH=C-\overset{H}{\underset{Br}{C}}-CH_2 \\ -CH_2-\overset{Br}{\underset{H}{C}}-\overset{H}{C}=CH- \end{cases} B$$

When the second mole of HBr is removed, A would be expected to give 9-stearolic acid and allenic compounds while only conjugated dienes and allenes could result from B. However 9-stearolic acid as well as the 8- and 10-isomers could also be formed through rearrangement of the allenic compounds obtained from A and B. In any case it can be expected that A would yield more 9-stearolic than B. From the results obtained in this study it appears that more A is formed at the low temperature of the sodamide procedure than with the high alkali concentration and high temperature required for KOH dehydrobromination. This would explain the high yields of 9-stearolic obtained by the sodamide method and also the conjugated dienoic products obtained by Moruyama and Suzuki (14), using alcoholic KOH.

In addition, Adkins (2) pointed out that, with the KOH reagent, insufficient heating during the removal of amyl alcohol yields a product which still contains brominated derivatives that prevent crystallization of pure stearolic acid and therefore cause low yields.

The reasons for the effective and smooth dehydrohalogenation by sodamide in liquid ammonia may be attributed to its strong base character, strong enough to dehydrohalogenate at —33°C. The low temperature of liquid ammonia eliminates the difficulties noted in the case of the alcoholic KOH reaction. Addition of organic solvents to liquid ammonia does not improve the yields and is often detrimental although small amounts of ether may increase the reaction rate slightly (12).

With the unsymmetrical and activated dibromides, such as 10,11-dibromo-undecanoic acid and bromostyrene, the monobromo-olefins first formed are not as much stabilized by hyperconjugation as the symmetrical ones and may therefore enter into other side reactions, possibly polymerization, isomerization (12). In addition, debromination may also occur (12, 13), yielding the original olefin through removal of two bromine atoms.

No isomerization of a mono-acetylenic compound, 3-nonyne, in the presence of sodamide in liquid ammonia has been observed by Vaughn and others (17). It is also known that the *balanced disubstituted monoacetylenes* undergo less rearrangement in the presence of sodamide in liquid ammonia (12) than the unsymmetrical compounds. This may explain the low yields of phenyl acetylene and 10-undecynoic acid obtained in this study.

From these results it may be concluded that the dehydrohalogenation reaction by sodamide can be effectively applied to α,β-dibromo compounds and not to other polybromo-derivatives. Such reaction runs smoothly without appreciable side reactions if the bromine atoms are located close to the middle of the C-chain of a comparatively large molecule.

Summary

The advantages of dehydrohalogenation by sodamide in liquid ammonia over the alcoholic potassium hydroxide method are noted. The sodamide reaction is found to be a mild and quite suitable reaction for the preparation of mono-acetylenic acids (especially those having long and balanced alkyl groups on either side of the triple bond) by dehydrobromination of the dibromides obtained from the corresponding olefinic compounds. Dehydrobromination of tetrabromostearic acid was unsuccessful. A large laboratory scale preparation of stearolic acid has been accomplished. Stearolic acid and 9,10-diketo-stearic were prepared from the crude olive oil acids. A procedure for detecting oleic acid and stearolic acid in mixtures has been outlined. The sodamide dehydrohalogenation method has been successfully applied to the preparation of 6-octadecynoic acid (for the first time from a natural source, petroselinic acid), phenyl acetylene and 10-undecynoic acid from their parent olefinic compounds. An explanation for the low yields of the last two substances has been offered.

Acknowledgment

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Supply and Consumption of Oils and Fats[1]

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THE best data (1) available on the production and the consumption of visible oils and fats have been compiled and are presented herewith in two sections. The first is on a world basis and the second is for the U.S.A. It should be emphasized that only visible oils and fats are considered and that the data for the world as a whole necessarily include some estimates. Furthermore no adjustment has been made for differences in the world carry-over from one year to the next, which means that production and consumption are treated as interchangeable terms. Even with these limitations however we accept the figures given as being reasonably accurate, probably within the range of ±10%. For the convenience of the reader the data are shown in terms of pounds per capita when this is practicable.

I. The pre-war world average annual production and consumption of visible fats was around 20-22 lb. per capita. During the war it fell to about 15 lb., but it has now risen to about 23 lb. Approximately 60% comes from vegetable seeds and 40% from animal sources. A high proportion, possible 85%, is considered to be of edible quailty as produced, not necessarily by U. S. standards but as judged by the standards of the areas involved. The more important of the individual oils and fats are shown in Table I.

It is estimated that 70-80% of the total production is consumed in the countries of origin and only 20-30% moves into the international markets. Western Europe is the main market for the fats that cross national boundaries, for most of the western European nations depend on imported fats to make up their deficits. Ireland, Spain, and Denmark are the only nations in this group that produce as much as they consume. Pre-war, the others produced on the average about 50% of their requirements, but Great Britain produced only 10%. At the present time these countries are probably doing somewhat better than

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[1] Presented before the Regional Meeting of the American Institute of Chemical Engineers, Cincinnati, O., April 24, 1953.