

ence, 0.131 g. (3.8 mmoles.) represents the amount of methanol retained by the aluminum soap after drying in a vacuum over phosphorus pentoxide. It is slightly above the 3.34 mmoles. of acid extracted, but in good agreement with the 3.79 mmoles. of dilaurate originally present. It is probable that the extracted acid is low, due to the clumping of the particles during the experiment, and subsequent failure to extract completely the freed acid.

By Precipitation in Methanol.—37.5 g. (0.1 mole) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 20 g. (0.1 mole) of lauric acid was dissolved in 200 ml. of boiling methanol; 20 ml. of concentrated ammonium hydroxide was added as quickly as possible. A very voluminous precipitate formed and 600 ml. of methanol were added to disperse the product. It was washed repeatedly with hot methanol and finally with acetone. After drying it contained 10.0% aluminum. It was treated with two portions of boiling methanol, after which it contained 10.6% aluminum. A small portion of this material was sealed in an evacuated capillary and heated. It began to decompose at 250° without melting. At 270° it softened to a brown transparent mass.

From Aluminum Hydroxide and Lauric Acid.—2.41 g. (0.01 mole) of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 ml. of distilled water and a slight excess of ammonia was added. The aluminum hydroxide was centrifuged off and washed four times with methanol; 6.0 g. (0.03 mole) of lauric acid was then added and the mixture was heated to 70° . A gelatinous white precipitate formed which began to clump together after a few minutes.

Within fifteen minutes it had formed a soft plastic mass, similar to that formed by treating dilaurate with methanol. This was dried, ground under methanol, and washed twice with hot methanol. During the second wash it again clumped together. It was washed with acetone and dried. It contained 7.8% aluminum and had almost 1.4 molecules of laurate per atom of aluminum.

Acknowledgment.—The author wishes to acknowledge the stimulating direction of Professor J. W. McBain, the many thought-provoking discussions with Drs. K. J. Mysels and G. H. Smith, and the financial assistance of the Colgate-Palmolive-Peet Company during the latter portion of this work.

Summary

The preparation and properties of aluminum mono-soaps have been described. It has been suggested that aluminum mono-soaps are polymers in which the repeating units are alumina octahedra joined by sharing edges, with the carboxyl groups occupying the remaining positions.

The structure of aluminum di-soaps has also been discussed. A polymer structure has been suggested in which alumina octahedra are joined by sharing two opposite corners, which carboxyl groups occupying the remaining four. An attempt has been made to correlate such a structure with the known properties of the di-soaps.

Aluminum tri-soaps have likewise been discussed. Possible structures have been suggested and reasons for failure hitherto to prepare them have been considered.

STANFORD UNIVERSITY, CALIF. RECEIVED JUNE 9, 1948

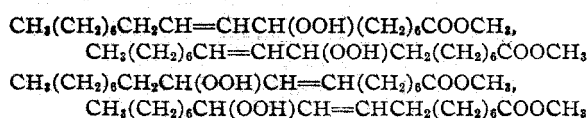
[CONTRIBUTION FROM COLGATE-PALMOLIVE-PEET CO.]

The Autoxidation of Methyl Oleate

BY JOHN ROSS, ARTHUR I. GEBHART AND J. FRED GERECHT

It has been shown that autoxidation of olefinic compounds involves, in effect, addition of a molecule of oxygen with formation of a hydroperoxide group on a carbon atom adjacent to an olefinic group. Farmer, *et al.*, further developed this view and suggested a free radical chain reaction mechanism.¹

Autoxidation, of the various resonance forms of methyl oleate, *via* such mechanism, should give rise to the structures:



We have examined autoxidation of methyl oleate with oxygen in the presence of ultraviolet light

at 35° and found evidence that such is the case.²

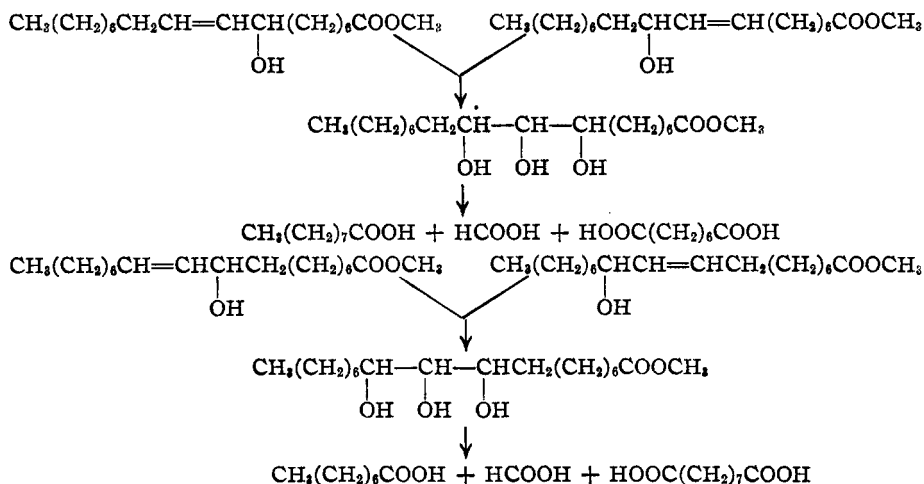
The position of the hydroperoxide group was determined as follows: The mixture of hydroperoxides of methyl oleate was reduced to methyl hydroxyoleates, hydrogenated to methyl hydroxystearates, and oxidized to methyl ketostearates. After saponification, 9- and 10-ketostearic acids were isolated pure by fractional crystallization. The 8- and 11-ketostearic acids were not isolated pure, but their presence was demonstrated by conversion to suberic and nonane dicarboxylic acids, respectively, by hydrolysis of the amides obtained by Beckmann transformation of the oxime.

Evidence for the position of the ethylenic

(2) Farmer, *et al.*, *J. Chem. Soc.*, 545 (1943), in a study of autoxidation of methyl oleate did not identify structurally any of the products of oxidation but later felt that all four hydroperoxides were probably present. In his examination of substituted cyclohexenes the structural evidence presented for the existence of four position isomers appears doubtful.

(1) W. A. Waters, *Ann. Repts. on Progress Chem. (Chem. Soc. London)*, 130, 42, 1945 (1946).

double bond was sought as follows: Dihydroxylation of the mixed hydroxy methyl oleates by performic acid gave two trihydroxy stearates, namely, 8,9,10- and 9,10,11-trihydroxystearic esters. Periodic oxidation of the mixed trihydroxystearic acids gave suberic and azelaic acids.



However, performic acid treatment of the mixed hydroxy oleates yields only 50% of trihydroxystearates. The remainder of the material suffered oxidative fission giving among other products, suberic, azelaic and sebacic acids. The appearance of appreciable amounts of acidic material is quite unusual under these conditions. Performic acid has been used with great success upon simple olefinic compounds to give almost theoretical yields of the monoformate of the dihydroxy derivative. Furthermore, ricinoleic ester under these conditions gives a 96% yield of 9,10,12-trihydroxystearic ester³ so that it appears that a non-adjacent hydroxy olefinic compound behaves normally according to the literature. The behavior of performic acid with olefinic compounds having a hydroxy group on a carbon atom directly adjacent to the olefinic group does not seem to have been examined previously. Compounds of this structure have been found to give abnormal products with other reagents. The explanation of the formation of suberic, azelaic and particularly sebacic acid must await further examination of this reaction of performic acid upon hydroxy olefins.

The relative proportion in which the isomeric hydroperoxides are formed in the case of oleic ester is of great interest. Our examination yielded the different substitution products in the order $C_{10} > C_{11} > C_8 > C_9$. However the preparation of the pure concentrated hydroperoxide and hydroxy olefinic ester undoubtedly involved selective crystallization.

Recently⁴ we had occasion to examine the addition of olefinic esters to maleic anhydride and found that the main products were those in which

addition occurred to the carbon atoms originally carrying the olefinic linkage, the latter in the final product taking up a position at the adjacent carbon atoms. There is insufficient evidence at present for regarding this addition reaction as proceeding by free radical chain mechanism.⁵

Writers in this field have introduced the term "methylenic reactivity" to describe substitution or reaction at or involving a methylene group adjacent to an olefinic linkage. We would suggest that the older term "allylic reactivity" is more inclusive and descriptive of the dynamic implications.

Experimental

Purification of Methyl Oleate.—Commercial red oil or crude oleic acid (5600 g.) was heated at 200° with maleic anhydride (950 g.) for three hours in a carbon dioxide atmosphere.⁶ After cooling, 4 liters of methanol containing 40 ml. of concentrated sulfuric acid was added and the solution refluxed for two hours. After standing overnight, 4 liters of water was added and the mixture was extracted with petroleum ether. The extract was washed with potassium carbonate solution to remove acidic material, dried, and the solvent removed. The esters were distilled at 2 mm. pressure, collecting up to 170° in order to leave the maleic anhydride condensation product of polyolefinic esters in the still residue. This crude methyl oleate was then fractionated through a modified Fenske column, 100 cm. long, and a total of 2550 g. of a fraction boiling 161.2–161.8° at 1.1 mm. pressure collected. Analysis showed this to be approximately 93% methyl oleate and 5% methyl linoleate. Using the procedure of Swern, Knight and Findley,⁷ this crude ester was fractionally crystallized at low temperature in acetone solution, yielding a total of 1835 g. of methyl oleate having the analysis: *Anal.* Calcd. for $C_{19}H_{38}O_2$: I. V., 85.6; T. V., 85.0 (*cf.*⁸). Found: I. V., 85.7; T. V., 85.5. By spectrophotometric analysis it was

(5) W. G. Bickford, G. S. Fisher, Lillian Kyame and C. E. Swift, *J. Am. Oil Chem. Soc.*, **24**, **7**, 254 (1948), since this present paper was written have shown that addition occurs at carbon atom 8, 9, 10 and 11.

(6) We felt that maleic anhydride treatment offered a rapid method for eliminating polyunsaturates when present in large amounts. As a result of further work we cannot say that there are necessarily any advantages in this treatment provided a good sample of oleic acid is available.

(7) D. Swern, H. B. Knight and T. W. Findley, *Oil and Soap*, **21**, 133 (1944).

(8) Mehlenbacher, *Chem. Eng. News*, **22**, 606 (1944).

(3) Swern, Billen, Findley and Scanlan, **THIS JOURNAL**, **67**, 1788 (1945).

(4) Ross, Gebhart and Gerecht, *ibid.*, 68, 1373 (1946).

estimated that this sample of ester contained 0.09% linoleic and 0.04% linolenic esters.

Structure of Methyl Oleate Used.—In order to be certain that no isomerization of the methyl oleate had occurred as a result of the maleic anhydride or any prior treatment, a sample (14.8 g.) was converted to methyl dihydroxystearate by performic acid.⁹ A yield of 15.3 g. of solid dihydroxystearic acid, m. p. 93–93.5°, was obtained. The theoretical yield was 15.8 g. Swern, *et al.*, report m. p. 94°. Periodic oxidation of the above dihydroxystearic acid⁹ gave only azelaic acid in the dicarboxylic acid fraction.

Autoxidation of Methyl Oleate.—In a liter thin-wall pyrex erlenmeyer flask connected to an oxygen reservoir, 300 g. of methyl oleate was shaken for twenty-four hours at 35° while being irradiated with ultraviolet light from a 500-watt Hanovia lamp with a type L burner. The oxygen pressure during this time averaged about 9 cm. of mercury above atmospheric. In this manner a peroxide value¹⁰ of 250 milliequivalents per kg. was obtained which corresponded to about 4% of total methyl oleate oxidized. A total of 4570 g. of methyl oleate was oxidized in this manner.

Methyl oleate was separated from the mixture containing methyl hydroperoxido-oleate by crystallizing twice at –72° from a 10% solution in acetone,¹¹ whereby 158 g. of oil was obtained analyzing 70.1% methyl hydroperoxido-oleate.

Methyl Hydroxyoleate.—To a solution of 157 g. of the above 70% methyl hydroperoxido-oleate in a mixture of 1600 ml. of chloroform and 2400 ml. of acetic acid there was added a saturated solution of potassium iodide (200 g. in 150 ml. water) and the mixture was vigorously stirred for five minutes. Saturated aqueous sodium sulfite solution was then added and stirring continued until the liberated iodine had been destroyed, when the mixture was transferred to a separatory funnel and allowed to separate. The chloroform layer was drawn off, washed with 2% aqueous potassium carbonate until neutral, dried, and the solvent removed *in vacuo*. There was obtained 154 g. of a light brown oily liquid which according to hydroxyl determination¹² contained 70.3% methyl hydroxyoleate. By crystallization twice from 1500 ml. of petroleum ether at –60° and –40°, respectively, there was obtained 63 g. of ester containing 98.3% methyl hydroxyoleate according to hydroxyl value and 91.4% as calculated from iodine value. The ester showed an epoxide content of 1.2% by the method of Nicolet and Poulter.¹³ By periodic acid oxidation, this ester also showed the presence of 2.5% of methyl dihydroxystearate. These amounts of epoxide and dihydroxystearate are of such low an order that they can be ignored. Making corrections for these it appears that the product contained 91.2% methyl hydroxyoleate.

A. Methyl Hydroxystearate.—Sixteen grams of the above methyl hydroxyoleate was hydrogenated at 50° and 600 p. s. i. of hydrogen with Raney nickel catalyst. After filtering off catalyst and removing solvent 16.0 g. of hydroxystearic esters was obtained.

Methyl Ketostearates.—The above hydroxystearic esters were dissolved in 50 ml. of glacial acetic acid and a solution of 3.98 g. of chromic oxide (CrO₃) in 24 ml. of 90% acetic acid was added over a period of one hour at 30–35° with stirring. Two hours later the mixture was poured into water and extracted with petroleum ether. After washing and drying, the solvent was removed and 16.0 g. of mixed ketostearic esters was obtained.

Separation and Identification of Ketostearic Acids.—The above mixed esters were saponified and the acids ob-

tained fractionally crystallized using 20% acetone in petroleum ether (b. p. 35–50°) as solvent.

9-Ketostearic acid was obtained as fine needles, m. p. 82°, and separated first as the least soluble isomer, yield 0.5 g. This was identified by mixed melting point with a known sample of 9-ketostearic acid (see B below). It also gave a semicarbazone, m. p. 118–120°, which was identical with the semicarbazone of 9-ketostearic acid.

10-Ketostearic acid was obtained as thick needles or large rhombic prisms, m. p. 72–73°, yield about 5.0 g. This was identified by mixed melting point with a known sample of 10-ketostearic acid by preparation and comparison of the semicarbazone, m. p. 101–103°, as well as by isolation of sebacic acid, m. p. 133°, from the products of Beckmann transformation of the oxime.

11-Ketostearic acid was not isolated in the pure state. The next series of crystal crops (5.0 g.) consisted of fine short needles mixed with rhombs of 10-ketostearic acid. A quantity of the rhombs was separated manually with the aid of a microscope and by preferential solubility of the fine needles in cold solvent, but the concentrated material still contained some rhombic (and probably needle form) 10-ketostearic acid. Therefore 3 g. of this product was converted to the oxime and submitted to the Beckmann transformation and from the products of hydrolysis there was isolated sebacic acid (0.4 g.) and nonanedicarboxylic acid (0.2 g.), m. p. 109–110° when recrystallized from water at 65°.

Anal. Calcd. for C₁₁H₂₀O₄: neut. equiv., 108. Found: neut. equiv., 108. The above nonanedicarboxylic acid was identified by mixed melting point with a sample, m. p. 110–111°, prepared by the method of V. Braun and Danziger,¹⁴ from nonane-1,9-diol prepared from diethyl azelate by the method of Chuit.¹⁵

8-Ketostearic acid was likewise not isolated in the pure state. The fourth series of crystal crops and final mother liquors were combined and 3.5 g. converted to the oxime and submitted to the Beckmann transformation. From the hydrolysis products of the amides there was isolated some nonane dicarboxylic acid (0.1 g.) sebacic acid (0.1 g.) and 0.1 g. of suberic acid, m. p. 139–140°, when recrystallized from acetone.

Anal. Calcd. for C₈H₁₄O₄: neut. equiv., 87. Found: neut. equiv., 87.7.

The suberic acid was identified by mixed melting point with a known sample.

B. Preparation of 9- and 10-Ketostearic Acids.—Ten grams of methyl 9,10-epoxystearate¹⁶ was dissolved in 700 ml. of ethanol and the solution carefully neutralized to phenolphthalein with caustic soda; 3.5 g. of Raney nickel was added and hydrogenation carried out on a shaking machine at 25°; 600 ml. of hydrogen at S. T. P. was absorbed. After filtering, the solvent was removed and 10 g. of hydroxy ester was recovered. This ester was oxidized with 14 ml. of a solution of chromic acid in acetic acid containing 0.16 g. of chromic oxide per ml., stirring for one hour at 30–35° and two hours at room temperature. The oxidation mixture was then poured into 300 ml. of water and the product extracted with petroleum ether. About 10 g. of methyl ketostearate was obtained as a pale yellow liquid. This was saponified and the keto acids recovered.

The keto acids were fractionally crystallized from acetone-petroleum ether mixture (1:2).

9-Ketostearic acid was obtained as lustrous plates, m. p. 81.5°, yield 0.21 g. Behrend¹⁷ obtained this acid, m. p. 83°, and proved the structure by obtaining azelaic acid, decanoic acid, ω-aminoöctanoic acid and nonylamine through the Beckmann transformation of the oxime.

The semicarbazone of 9-ketostearic acid, which was prepared and crystallized from alcohol, melted at 118–120°.

Anal. Calcd. for C₁₉H₃₇O₃N₃: N, 11.83. Found: N, 11.7.

(9) J. Ross, A. I. Gebhart and J. F. Gerecht, *THIS JOURNAL*, **67**, 1275 (1945).

(10) C. H. Lea, *J. Soc. Chem. Ind. (London)*, **65**, 289 (1946).

(11) C. E. Swift, F. G. Dollear and R. T. O'Connor, *Oil and Soap*, **23**, 355 (1946).

(12) C. L. Ogg, W. C. Porter and C. O. Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945).

(13) B. H. Nicolet and T. C. Poulter, *THIS JOURNAL*, **52**, 1186 (1930).

(14) V. Braun and Danziger, *Ber.*, **45**, 1975 (1912).

(15) Chuit, *Helv. Chim. Acta*, **9**, 265 (1926).

(16) Findley, Swern and Scanlan, *THIS JOURNAL*, **67**, 412 (1945).

(17) Behrend, *Ber.*, **29**, 808 (1896).

10-Ketostearic acid was obtained as needles or rhombic prisms, m. p. 71°, yield 8.5 g. This acid gave a semicarbazone, m. p. 101–103°, crystallized from alcohol.

Anal. Calcd. for $C_{15}H_{27}O_3N_2$: N, 11.83. Found: N, 11.9.

Baruch¹⁸ obtained this acid, m. p. 75°, and proved its structure. A sample of our keto acid, m. p. 71°, was converted to the oxime and by Beckmann transformation yielded sebamic acid, m. p. 133°.

C. Beckmann Transformation on Oxime of 12-Ketostearic Ester.—In order to ascertain the conditions for the Beckmann transformation upon long chain ketoximes the following examination was carried out. This is described in detail since to our knowledge it has not been previously reported for this readily available compound.

Methyl 12-Hydroxystearate.—Methyl ricinoleate, b. p. 189–191° at 1 mm. pressure, was prepared by fractional distillation of methyl esters of castor oil acids. The ester (227 g.) was hydrogenated directly using Raney nickel catalyst in a shaking bomb at 100° and 600 p. s. i. initial hydrogen pressure. The product was dissolved in 250 ml. of methanol, filtered and crystallized at 0°. After recrystallization from methanol 194 g. of pure methyl 12-hydroxystearate was obtained, m. p. 57–58°.

Methyl 12-Ketostearate.—The above ester (60 g.) was dissolved in 160 ml. of glacial acetic acid at 30° and 11.1 g. of chromic anhydride dissolved in 50 ml. of 80% acetic acid was gradually added with stirring. The reaction mixture was stirred for an additional two hours and then poured into water and the solid ester extracted with Skellysolve F, washed, dried and recovered. After recrystallization from methanol 52 g. of methyl 12-ketostearate, m. p. 45–46°, was obtained.¹⁹

Oxime of Methyl 12-Ketostearate.—The above ester (12 g.) was dissolved in 90 ml. of 80% alcohol, and solutions of 6.7 g. of hydroxylamine hydrochloride in 30 ml. of 80% alcohol and 10 g. of sodium acetate in 30 ml. of 80% alcohol were added, when the mixture was refluxed for two and one-half hours and then stood at 30° overnight. The alcohol was then distilled off and the residual oil taken up in ether, washed and dried. The oxime was obtained as 12 g. of oil and was not further purified.

Beckmann Rearrangement of Oxime.—The above crude oxime was added to 60 ml. of concentrated sulfuric acid and heated on steam-bath one hour. After cooling, the reaction mixture was poured into water. The solid amides which were filtered and washed weighed 12 g.

Hydrolysis of Amides.—This was carried out by heating the above amides with 60 ml. of 20% caustic potash in a bomb at 175–200° for three hours. The hydrolysis products were isolated in the order: (a) Monocarboxylic acid, by steam distillation of acidified hydrolysis mixture. Recovered 1.5 g. of *n*-heptanoic acid. *Anal.* Calcd. for $C_7H_{14}O_2$: neutral equivalent, 130. Found: neutral equivalent, 131. The *p*-toluidide had m. p. 80°. Reported *n*-heptanoic-*p*-toluidide, m. p. 81°. (b) Dicarboxylic acid, by ether extraction of acidified hydrolysis mixture after removal of (a). Recovered 6 g. of decane dicarboxylic acid. This was recrystallized from ethylene dichloride and had m. p. 127–128°. Reported m. p. was 127–128°. *Anal.* Calcd. for $C_{12}H_{22}O_4$: neutral equivalent, 115. Found: neutral equivalent, 116.5. (c) Amine, by making alkaline aqueous liquor from (b) and extraction with ether. Recovered 1 g. hexylamine, b. p. 127–128°. Reported b. p. 129–130°. (d) Amino acid, by acidifying the alkaline solution from above with acetic acid, adding ammonia until just alkaline and filtering the amino acid which precipitated as a solid (1.5 g.). This ω -aminoundecanoic acid recrystallized from water and had m. p. 183–184°.

Anal. Calcd. for $C_{11}H_{23}O_2N$: N, 6.96. Found by Kjeldahl: N, 6.80.

It was found that for the Beckmann rearrangement of the oximes of these keto acids concentrated sulfuric acid

was more reliable than phosphorus pentachloride in ether and good yields of amides were obtained without any reversion to the keto acid, which sometimes occurred with the phosphorus pentachloride.

D. Action of Performic Acid on Methyl Hydroxyoleates.—Performic acid was prepared using the method of Swern, *et al.*² To 20 g. of 98% methyl hydroxyoleates dissolved in 320 ml. of 98% formic acid, 40.2 ml. of hydrogen peroxide (32%) was added. The reaction temperature was not allowed to exceed 40°. When the temperature began to drop the reaction mixture was left overnight at room temperature. The product was poured into water, saturated with sodium chloride and the separated oil extracted with ether. The ether solution was washed with water, then with acidified ferrous sulfate solution to remove peroxide and finally with 2% potassium carbonate to remove acidic material.

The neutral ether-soluble portion was recovered as an oil which was deformedylated by refluxing in 150 ml. of methanol containing 1% sulfuric acid. This reaction mixture was poured into water and the solid which precipitated was taken up in ether, washed free of acid and dried. Evaporation of the ether yielded 10.6 g. of white solid which was crude methyl trihydroxystearates. This was purified by extraction with one-liter of petroleum ether for forty-five minutes, cooling and filtering. There was obtained 5.6 g. of insoluble solid which by periodate analysis was 96% pure methyl trihydroxystearates. A portion was saponified and converted to the acid which melted at 115–120°.

Anal. Calcd. for $C_{18}H_{36}O_6$: neutral equivalent, 332. Found: neutral equivalent, 338.

Calcd. for $C_{18}H_{38}O_2(OH)_3$: hydroxy equivalent, 110.7. Found: 112.5.

The acidic fraction of this reaction was recovered as 10 g. of thick liquid material upon acidification and extraction of the potassium carbonate washings above. These acid esters were saponified with alcoholic caustic potash and the acids were recovered. The monocarboxylic acids were separated by steam distillation. A total of 5.0 g. of volatile acids was collected which after fractional redistillation in vacuum were found to boil from 87–100° at 0.7 mm. and these fractions had neutral equivalents varying from 153–167.

The material non-volatile with steam was taken up in 500 ml. of boiling water and filtered. A small amount (0.7 g.) of solid insoluble in water proved to be trihydroxystearic acid. The filtrate was fractionally crystallized and the following acids were separated and identified.

Sebamic Acid.—This separated at 60° from the water solution. A yield of 1.0 g. was obtained which upon recrystallizing from a 50% mixture of dioxane and water had m. p. 131–132.5°. *Anal.* Calcd. for $C_{16}H_{32}O_4$: neutral equivalent, 101. Found: neutral equivalent, 101. It gave a diphenacyl ester m. p. 81°. The identity was proved by mixed melting point of the acid and the diphenacyl ester with pure specimens, respectively.

Azelaic Acid.—This separated at 25° from the water solution. A yield of 2.6 g. of acid was obtained which melted at 105–106° after recrystallization from benzene and then methyl acetate. *Anal.* Calcd. for $C_9H_{16}O_4$: neutral equivalent, 94. Found: neutral equivalent, 93. Identity was confirmed by mixed melting points of acid and diphenacyl ester (m. p. 70–71°) with pure specimens, respectively.

Suberic Acid.—This was obtained upon concentration of the aqueous mother liquor. Yield was approximately 1.1 g. after recrystallization from acetone, m. p. 140–141°. *Anal.* Calcd. $C_8H_{14}O_4$: neutral equivalent, 87. Found: neutral equivalent, 86. Its identity was confirmed by mixed melting points of acid and diphenacyl ester (m. p. 107.5°) with pure specimens of these.

Periodate Oxidation of Above Mixed Trihydroxystearic Acids.—Six grams of the above acid was dissolved in 60 ml.

(18) Baruch, *Ber.*, **27**, 174 (1894).

(19) Rene and Perrotte, *Compt. rend.*, **199**, 358 (1934).

(20) Huntress-Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, N. Y., 1941, pp. 143, 150, 153.

of ethanol and treated with 8.5 g. of periodic acid in 60 ml. of ethanol with cooling and then kept at room temperature for thirty minutes.

The reaction mixture was poured into water and extracted with ether. The acid half-aldehydes were separated from the normal aldehydes by aqueous carbonate washing of the ether extract, and were subsequently separately oxidized to the carboxylic acid by treatment with peracetic acid.⁹ There was thus recovered 2.47 g. of liquid monocarboxylic acids which were not further examined.

From the carbonate extract there was obtained 2.81 g. of mixed dicarboxylic acids after oxidation of the half aldehydes. These acids were separated by maceration with anhydrous ether. The portion insoluble in ether (0.6 g.) was washed with benzene and then crystallized from acetone to give a pure acid which was identified as suberic acid, m. p. 140–141° by mixed melting point with an authentic sample. *Anal.* Calcd. for $C_8H_{14}O_4$: neut. equiv., 87.0. Found: neut. equiv., 88.0.

The ether soluble fraction was crystallized from water and then from methyl acetate. 0.58 g. of pure acid was obtained which was identified by analysis and mixed melting point with a known sample as azelaic acid, m. p. 105–106°. *Anal.* Calcd. for $C_9H_{16}O_4$: neut. equiv., 94. Found: neut. equiv., 95.

Summary

1. The products of autoxidation of methyl oleate at 35° in the presence of ultraviolet light have been examined.

2. The position of substitution of the hydroperoxido groups has been determined by conversion to the corresponding ketostearic acids. Substitution has been shown to occur at carbon atoms C_8 , C_9 , C_{10} and C_{11} .

3. Evidence has been obtained that a double bond shift occurs in the formation of two of the above hydroperoxido substitutions so that in all four compounds the olefinic group is adjacent to the hydroperoxido group. In the peroxidation and double bond shift only the carbon atoms C_8 , C_9 , C_{10} and C_{11} are involved.

4. The products identified strongly support a chain reaction mechanism sequence involving allylic resonance of the two free radicals initially possible.

JERSEY CITY, N. J.

RECEIVED JUNE 28, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

Oxidation of Some Aliphatic Alcohols with Chromic Acid

BY WILLIAM A. MOSHER AND ESLEY O. LANGERAK¹

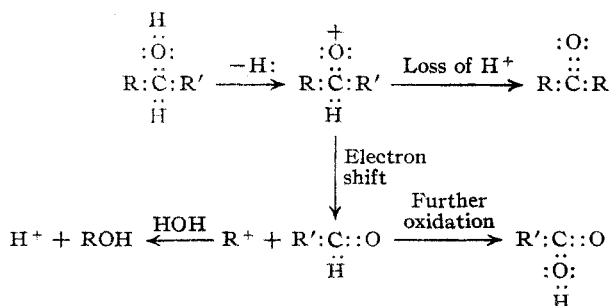
Mosher and Whitmore² recently reported the isolation of *t*-amyl alcohol from the chromic acid oxidation of methyl-*t*-amylcarbinol and isopropyl-*t*-amylcarbinol and *t*-butyl alcohol from the oxidation of methyl-*t*-butylcarbinol. A tentative mechanism involving the new concept of an intermediate containing an electronically-deficient oxygen atom was proposed. Work has been continued on this general problem by a careful search for anomalous oxidation products from other secondary aliphatic alcohols.

The secondary alcohols referred to above all have a neopentyl carbon in the alpha position to the hydroxyl-bearing carbon atom. It is probably due to the weak electron-attracting power of this type of group³ and to the "steric strain"⁴ that the splitting occurs to any appreciable extent. The first extension of the above work was to study the oxidation of secondary alcohols which had carbon atoms of lower substitution in the alpha position. The oxidation of ethyl-*s*-butylcarbinol with chromic anhydride in 80% aqueous acetic acid gave 63% of the corresponding ketone, 1% *s*-butyl alcohol, and about 1% methyl ethyl ketone probably formed by the oxidation of some of the *s*-butyl alcohol. The similar oxidation of methyl-*n*-amylcarbinol gave 83% of the corresponding ketone and a trace of *n*-amyl acetate presumably formed from the esterifica-

tion of the corresponding alcohol or carbonium ion.

The question of the second part of the molecule formed by the split has been clearly answered in the case of *n*-propyl-*t*-butylcarbinol. The oxidation of this alcohol gave 41% of the corresponding ketone, 4% *n*-butyraldehyde and a corresponding amount of *t*-butyl alcohol. Traces of aldehyde have been isolated in other aliphatic alcohol oxidation but further oxidation to acid appears to be the usual course.

In the case of secondary aliphatic alcohols it would appear that some cleavage at the carbon alpha to the hydroxyl-bearing carbon is a general phenomenon. The amount of cleavage observed decreases as the electron attracting power of the group increases and the steric strain decreases. The proposed mechanism is written below in generalized form for any secondary alcohol.



(1) F. G. Cottrell Research Fellow in chemistry.

(2) Mosher and Whitmore, *THIS JOURNAL*, **70**, 2544 (1948).

(3) Whitmore and Bernstein, *ibid.*, **60**, 2626 (1938).

(4) H. C. Brown, *et al.*, *ibid.*, **66**, 435 (1944).