point with an authentic specimen of 2-chloro-3-methylacetanilide. In so doing we have also established the melting points of 2-chloro-3-methylbenzoic acid and its amide.

Experimental

A mixture of methylchloro-α-methylstyrenes was prepared by the method of Bachman and Hellman.[1] Upon fractionation a 25% yield of a product I, b. p. 78–79° (7 mm.), and a 43% yield of a product II, b. p. 91–92° (7 mm.), were obtained.

A. Identification of 4-Chloro-3-methyl-α-methylstyrene

Oxidation of II.—To 20 g. of II in 150 ml. of glacial acetic acid heated to 110° was added dropwise 150 ml. of concentrated nitric acid. After refluxing for 24 hours, the flask was chilled in an ice-bath and the acid which precipitated was filtered off, washed with water, and dried. The crude acid III, m. p. 202–203°, weighed 7.9 g. (39% yield). After two recrystallizations from dilute alcohol a product, m. p. 209°, was obtained, apparently 4-chloro-3-methylbenzoic acid. A mixture of this acid with an authentic sample of 4-chloro-3-methylbenzoic acid, m. p. 209°, showed no melting point depression. The authentic sample was prepared from 4-chloro-3-methylacetophenone[3] and its structure proved by reduction with sodium amalgam to *m*-toluic acid.[4] Furthermore mixtures of II with an authentic specimen of 3-chloro-4-methylbenzoic acid, m. p. 203° (from 2-chlorocymene by oxidation[5]), gave marked melting point depressions. III must then be 4-chloro-3-methyl-α-methylbenzoic acid and II must be 4-chloro-3-methyl-α-methylstyrene.

B. Identification of 2-Chloro-3-methyl-α-methylstyrene

Oxidation of I.—The oxidation of 40 g. of I with nitric acid was carried out in the manner described for II. A 23% yield of an acid IV, m. p. 146–150°, was isolated. After one recrystallization from dilute alcohol the acid melted sharply at 153° and further recrystallizations failed to raise the melting point.

Anal. Calcd. for $C_8H_7O_2Cl$: C, 56.32; H, 4.14; neut. equiv., 170.59. Found: C, 55.63; H, 4.02; neut. equiv., 175.

Amide of IV.—Eight grams of IV was refluxed for one hour with 40 ml. of thionyl chloride. After cooling, the reaction mixture was poured into 120 ml. of cold concentrated ammonium hydroxide. The amide V which precipitated melted at 145–151°. After two recrystallizations from dilute alcohol 6.4 g. (80% yield) of a white crystalline material, m. p. 157°, was obtained.

Anal. Calcd. for C_7H_8ONCl: N, 8.26. Found: N, 8.15.

Hofmann Rearrangement of V.—To a solution of 5 g. of V in 30 ml. of methanol was added 32.5 ml. of molar sodium hypochlorite solution. After heating 2 hours, 700 ml. of water was added and the mixture was steam distilled. The oily layer which was separated from the distillate weighed 3.2 g. (75% yield). This compound VI was not further purified.

Acetylation of VI.—One gram of VI was heated with 2 ml. of acetic anhydride for one minute and cooled. The precipitate was dissolved in 6 ml. of hot water, filtered and cooled. The crude acetyl derivative melted at 132–134°. After one recrystallization from hot water the product melted sharply at 135°[6] and gave no melting point depression when mixed with an authentic sample of 2-chloro-3-methylacetanilide. 3-Chloro-2-methylacetanilide melts at 156°.[7]

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(3) Claus, *J. prakt. Chem.*, [2] **43**, 357 (1891).

(4) C. Fairbanks and G. H. Stempel, Jr., unpublished work.

(5) Vongerichten, *Ber.*, **10**, 1249 (1877).

(6) Cohen and Dakin, *J. Chem. Soc.*, **79**, 1128 (1901).

(7) Noelting, *Ber.*, **37**, 1019 (1904).

Chemistry of Epoxy Compounds. XII.[1] Coöxidation of Aldehydes and Oleic Acid, Methyl Oleate or Oleyl Alcohol

BY DANIEL SWERN AND THOMAS W. FINDLEY

In an early paper,[2] we described the preparation of 9,10-epoxystearic acid in 70–80% yield by the ultraviolet light-catalyzed coöxidation of benzaldehyde and oleic acid with air in acetone solution. Perbenzoic acid was undoubtedly the oxidizing agent, although it was not isolated.[3] This paper describes an extension of the coöxidation technique in which benzaldehyde, acetaldehyde or butyraldehyde was employed as the source of the intermediate peracid, and oleic acid, methyl oleate or oleyl alcohol was the unsaturated substance epoxidized.

Coöxidation of benzaldehyde and methyl oleate gave only about 40% yields of methyl 9,10-epoxystearate. The lower yield of methyl 9,10-epoxystearate, compared to that of 9,10-epoxystearic acid,[2] can probably be attributed to unavoidable loss of product during isolation. The even lower yield (20%) of 9,10-epoxyoctadecanol in the coöxidation of oleyl alcohol and benzaldehyde, cannot yet be explained. During the reaction, however, it was observed that the gain in weight of the reaction mixture far exceeded that which could be accounted for by acidic, peroxidic or epoxy components formed. Oleyl alcohol probably combines with oxygen or other components of the reaction mixture to form compounds of unknown structure.

In coöxidations with aliphatic aldehydes, good conversion of aldehydes to the corresponding aliphatic acids (50–70%) and low yields (20% or less) of 9,10-epoxystearic acid were obtained. There is little doubt that a chain reaction occurs and a peracid intermediate[4] is formed in these reactions, but preferential oxidation of excess aldehyde may account for the low yields.

Experimental

Starting Materials.—Pure oleic acid, methyl oleate and oleyl alcohol were obtained by a previously published procedure.[5] Benzaldehyde, b. p. 74° at 20 mm. and acid number below 1, was obtained from Eastman Kodak Co. chlorine-free grade by successive washing with 5% aqueous sodium carbonate, 5% sodium chloride and then with water, followed by drying over anhydrous calcium sulfate and distillation in an all-glass apparatus. These operations were conducted in an oxygen-free atmosphere. *n*-Butyraldehyde, b. p. 73.5° and acid number below 1, was obtained by fractional distillation of the Eastman Kodak Co. purest grade in an oxygen-free atmosphere. Acetaldehyde, acid number 6, was the Eastman Kodak Co. purest grade and was used without further purification. Acetone was obtained by fractional distillation of the technical grade.

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(1) See THIS JOURNAL, **72**, 3364 (1950), for the previous paper in this series.

(2) Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).

(3) Jorissen and van der Beek, *Rec. trav. chim.*, **45**, 245 (1926), **46**, 42 (1927); van der Beek, *ibid.*, **47**, 286 (1928); Raymond, *J. chim. phys.*, **28**, 480 (1931).

(4) See Swern, *Chem. Reviews*, **45**, 1 (1949), for the numerous literature references.

(5) Swern, Knight and Findley, *Oil and Soap*, **21**, 133 (1944).

Coöxidation of Benzaldehyde and Methyl Oleate.—A solution consisting of 106 g. (1.0 mole) of benzaldehyde, 30 g. (0.1 mole) of 95% methyl oleate (containing 4% of saturated esters and 1% of methyl linoleate) and 180 ml. of acetone was coöxidized at 23–26° for twenty hours with dry air while the solution was being irradiated with ultraviolet light, as described previously.[2] It was not feasible to continue the coöxidation for more than twenty hours because of crystallization of benzoic acid in the fritted discs. The acetone solution was then cooled to –60° and the white precipitate which formed was filtered and freed of acetone. The product, which was a liquid at room temperature, was washed with 10% aqueous sodium bicarbonate, then with water, and finally dried over anhydrous calcium sulfate and filtered. The residual oil weighed 13.3 g. (42% yield) and consisted mainly of methyl 9,10-epoxystearate. Calcd. for oxirane oxygen, 5.09; sapn. equiv., 312.5. Found: oxirane oxygen,[6] 4.33%; sapn. equiv., 311.3.

Coöxidation of Benzaldehyde and Oleyl Alcohol.—Repetition of the above experiment with 26.8 g. (0.1 mole) of 99% oleyl alcohol instead of methyl oleate, and crystallization of the reaction mixture at –65°, yielded 52 g. of crude product (acid number 241). This was washed acid-free with 6 *N* aqueous sodium hydroxide. The alkali-insoluble portion was a mushy solid (19 g.) having an oxirane oxygen content of 3.45% (calcd. 5.63). Recrystallization from ethyl acetate and then diethyl ether yielded 6 g. (21% yield) of impure 9,10-epoxyoctadecanol, m. p. 42–55° (lit.[2] 54°), and oxirane oxygen, 4.66%.

The aqueous, alkaline solution was acidified while hot, filtered, and cooled to room temperature, yielding 14 g. of benzoic acid, m. p. 122°.

Coöxidation of Acetaldehyde and Oleic Acid.—Twenty-eight grams (0.1 mole) of oleic acid, 44 g. (1.0 mole) of acetaldehyde and 240 ml. of acetone were coöxidized at 0–5° for twenty-four hours while the solution was irradiated with ultraviolet light.[2] The reaction solution was washed several times with water, and the residual oil was recrystallized from acetone at –25° yielding 4 g. (13% yield) of 9,10-epoxystearic acid, m. p. 50–52° (lit.,[2] 59°). Oxirane oxygen: calcd., 5.36; found, 4.59. Neutralization equivalent: calcd., 298.5; found, 292.5. Approximately 1/2 mole of acetic acid was formed during coöxidation.

Coöxidation of Butyraldehyde and Oleic Acid.—Twenty-eight grams (0.1 mole) of oleic acid, 72 g. (1.0 mole) of butyraldehyde and 195 ml. of acetone were coöxidized for 24 hours at 5° while the solution was irradiated with ultraviolet light.[2] The reaction mixture was worked up as described in the preceding experiment, yielding 6 g. (20% yield) of 9,10-epoxystearic acid, m. p. 50–53°. Oxirane oxygen, 4.56; neutralization equivalent, 299.2. Approximately 2/3 mole of butyric acid was formed during coöxidation. When the reaction was conducted at 30–50°, substantially the same yield of 9,10-epoxystearic acid but larger quantities of butyric acid were obtained. In the absence of ultraviolet radiation only about 1 g. of 9,10-epoxystearic acid was isolated.

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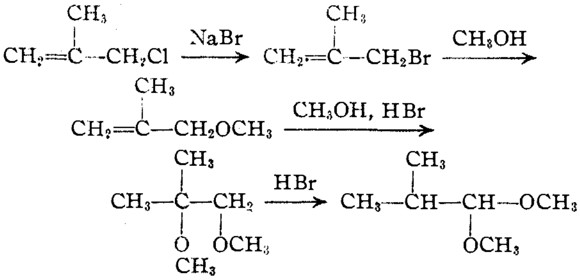
[6] Swern, Findley, Billen and Scanlan, *Anal. Chem.*, **19**, 444 (1947).

[7] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

Solvolysis and Rearrangement Reactions Accompanying the Formation of Methallyl Bromide

BY P. TEUSCHER*

In carrying out the preparation of methallyl bromide by reaction of methallyl chloride with sodium bromide in methanol, according to the method of Nichols, *et al.*,[1] the following additional products were isolated: methyl methallyl ether, 1,2-dimethoxy-2-methylpropane (isobutyleneglycol dimethyl ether) and isobutyraldehyde dimethylacetal. Various observations were made which show that these products probably are formed in the order named, in a sequence of consecutive reactions, beginning with the conversion of methallyl chloride to methallyl bromide, as shown in the chart.



$$CH_2{=}C(CH_3){-}CH_2Cl \xrightarrow{NaBr} CH_2{=}C(CH_3){-}CH_2Br \xrightarrow{CH_3OH} CH_2{=}C(CH_3){-}CH_2OCH_3 \xrightarrow{CH_3OH,\ HBr} CH_3{-}C(CH_3)(OCH_3){-}CH_2OCH_3 \xrightarrow{HBr} CH_3{-}CH(CH_3){-}CH(OCH_3){-}OCH_3$$

The pertinent experimental observations are the following: (1) The concentration of methallyl bromide passes through a maximum. At three hours reaction time, the yield of methallyl bromide was 37%, at eighteen hours 25%, and at twenty-two hours none was isolated. (2) It was shown by comparative experiments, in which the rates were followed by titration of the acid liberated, that the solvolysis of methallyl bromide in methanol occurs about one hundred times more rapidly than the solvolysis of methallyl chloride. The latter reaction, as an alternate path to methyl methallyl ether, is thus excluded and, in effect, sodium bromide is a catalyst for the etherification of methallyl chloride.

(3) The concentration of methyl methallyl ether could not be followed conveniently because of the troublesome methanol azeotrope. At eighteen hours reaction time, the yield of this product was approximately 10%. However, the appearance of this product must coincide with the developmentment of free hydrogen bromide which becomes appreciable in about two hours and is most rapid at 3–3.5 hours.

(4) The yield of 1,2-dimethoxy-2-methylpropane and of isobutyraldehyde dimethylacetal at three hours is negligible; at eighteen hours the yield of the two products together, but with the former predominating, was 15%. Under more drastic conditions, the latter is reported to be the main product.[2]

(5) Methyl methallyl ether, on refluxing with methanolic hydrogen bromide, was converted to a mixture of the glycol ether and the acetal. The acid catalyzed addition of methanol to methyl methallyl ether is a known type of reaction, as applied to isobutylene and other olefins.[3]

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* Deceased June 10, 1950.

[1] Nichols, Wrigley and Yanovski, THIS JOURNAL, **68**, 2020 (1946).

[2] Schmerling and Ipatieff, U. S. Patent 2,412,012; *C. A.*, **41**, 2070 (1947).

[3] Evans and Edlund, *Ind. Eng. Chem.*, **28**, 1186 (1936).