Anal. Calcd. for $C_{23}H_{29}O_2N$: N, 3.99. Found: N, 4.16.

The methyl ester, prepared by the method of E. Fischer, crystallized from acetone in white platelets, m. p. 116.5–117.5°.

1,2,3,4-Tetrahydrocarbazole.—The method of Rodgers and Carson[4] was used to prepare a colorless product, m. p. 113–114°.

β-(1,2,3,4-Tetrahydro-9-carbazolyl)-propionitrile.—This compound was prepared by the method described above in 53% yield, white needles, m. p. 115–116°.

Anal. Calcd. for $C_{15}H_{16}N_2$: N, 12.45. Found: N, 12.26.

β-(1,2,3,4-Tetrahydro-9-carbazolyl)-propionic Acid.—The method of hydrolysis described above was applied to prepare in 83% yield a granular product, m. p. 118–119°, neutral equivalent 242.0 (calcd. 243.2).

Anal. Calcd. for $C_{15}H_{17}O_2N$: N, 5.76. Found: N, 5.90.

[4] Rodgers and Carson, THIS JOURNAL, **69**, 2910 (1947).

CHEMISTRY DIVISION
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WASHINGTON, D. C. RECEIVED MARCH 28, 1950

Dimorphic Forms of 2-Hydroxymethyl-4-*t*-butyl-6-methylphenol

BY G. SPRENGLING, S. BEATTY AND K. B. ADAMS

The methylol derivative of *p*-*t*-butyl-*o*-cresol was first synthesized by K. Hultzsch by alkaline reaction of the corresponding phenol with formaldehyde.[1] Hultzsch recorded the m. p. 64° for his product. An attempt to duplicate his procedure yielded a product of m. p. 73.7–74.2° (cor.), as recrystallized from a mixture of hexane and benzene. However, rapid recrystallization of the product from hexane—in which it is less soluble—gave crystals m. p. 62.9–63.4° (cor.). Recrystallization of either product from hexane with enough benzene added to delay the beginning of crystallization until the solution had cooled to near room temperature yielded the higher-melting product again. A single crystal of the higher-melting form dropped into a melt of the other at 64° caused solidification of the melt, whereafter it melted again at 73.7–74.2°. Both forms remained unchanged on standing at room temperature for over a year.

The analyses of the two products for C and H were identical, av. 74.22% C and 9.21% H (calcd. 74.19% C and 9.34% H). Infrared spectra of the two products in CCl_4 were also identical over the range 2–15μ. However, the X-ray diffraction spectra of the powdered samples were entirely different. The interplanar spacings for the principal reflections (above $2\theta = 5°$, using Cu K_α radiation) were d = 11.6, 5.9, 5.04, 4.15 and 3.98 Å. for the higher-melting, and d = 12.3, 8.2, 4.64 and 3.82 Å. for the lower-melting form.

The two substances are therefore dimorphic, and probably monotropic forms of one compound.

It is interesting to note that infrared spectra of the two forms in the crystalline state (Nujol mull) showed small but significant differences in the hydroxyl region, possibly due to differences in bonding due to different orientation of the molecules in the crystal.

[1] Kurt Hultzsch, *J. prakt. Chem.*, **158**, 285 (1941).

CHEMICAL DEPT. RESEARCH LABS.
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E. PITTSBURGH, PA. RECEIVED APRIL 24, 1950

Concerning the Reaction of *o*-Chlorotoluene with Propylene Chlorohydrin

BY GUIDO H. STEMPEL, JR., AND BETTY SOBEL

The reaction of propylene chlorohydrin with *o*-chlorotoluene in the presence of BF_3 and P_2O_5 has been investigated by Bachman and Hellman.[1] They have found that dehydrohalogenation of the two chloroisopropyl compounds formed produces two new compounds which they have identified as 3-chloro-4-methyl- and 2-methyl-3-chloro-α-methylstyrene. In order to correlate their results with some obtained in this laboratory we have repeated their synthesis and carefully identified the products. We have found that their method yields instead 4-chloro-3-methyl- and 2-chloro-3-methyl-α-methylstyrene. We have found none of the other isomers although it is possible they were present in small quantity. It appears that the entering group is oriented ortho and para to the chlorine as is the case in the majority of other substitution reactions of *o*-chlorotoluene.

The identification of 4-chloro-3-methyl-α-methylstyrene rests upon the identity of the methylchlorobenzoic acid obtained by oxidation. We have found this acid to be 4-chloro-3-methylbenzoic acid because (1) mixtures of the acid in question with an authentic sample of 4-chloro-3-methylbenzoic acid melt at exactly the same temperature as the authentic sample and (2) melting point depressions result when the acid in question is mixed with an authentic sample of 3-chloro-4-methylbenzoic acid.

The identification of the 2-chloro-3-methyl-α-methylstyrene likewise rests upon the identity of the corresponding substituted benzoic acid. However, only *one* of the pertinent isomers, 3-chloro-2-methylbenzoic acid, has been reported. Its melting point has been variously recorded as 159°, and 156° and 154°.[2] It is obviously not possible to choose between the 2-chloro-3-methyl- and the 3-chloro-2-methyl- isomers by melting point alone in the absence of an authentic specimen for comparison, a comparison not reported by Bachman and Hellman.[1] We have positively identified the acid in question as 2-chloro-3-methylbenzoic acid by conversion of the acid to the amide, Hofmann rearrangement of the amide to the amine, acetylation of the amine and identification of the acetylated amine by mixed melting

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[1] Bachman and Hellman, THIS JOURNAL, **70**, 1772 (1948).

[2] Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 401.

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]

RESEARCH LABORATORIES OF THE
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RECEIVED APRIL 28, 1950

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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).