

at room temperature, sulfur and ammonium chloride precipitated from the reaction mixture; evaporation of the solvent gave only a tarry residue. With phenacyl bromides, however, the reaction appeared to follow a different course. The ammonium ion was not produced and 2-phenacylthio-4-arylthiazoles precipitated directly from the reaction mixtures as relatively pure hydrobromides. They were hydrolyzed to the free bases by washing with water.

Experimental³

Thiuram Disulfide.—Ammonium dithiocarbamate was prepared according to the general procedure of Miller,⁴ except that butyl or amyl alcohol was used instead of the ether-alcohol mixture. The crude product was oxidized directly by the method of Freund and Bachrach.⁵ Highest yields of the disulfide were obtained (60%) when small quantities of ammonium dithiocarbamate were used and the oxidation carried out rapidly.

Reaction of Phenacyl Bromides with Thiuram Disulfide.—In a typical experiment, a solution of 1.84 g. (0.01 mole) of thiuram disulfide and 3.98 g. (0.02 mole) of phenacyl bromide in 30 ml. of acetone was allowed to stand at room temperature, with occasional shaking, for seventy-two hours. Precipitation began within two hours. The copious precipitate was separated by filtration, washed on the filter with 10 ml. of cold acetone and finally with water until the washings gave a negative test for bromide. There was obtained 2.9 g. (93%) of 2-phenacylthio-4-phenylthiazole, which crystallized from 95% ethanol in fine white needles, m. p. 118°. No change in melting point was observed when a mixed melting point was run with a sample prepared according to the method of Buchman.²

Anal. Calcd. for C₁₇H₁₃ONS₂: N, 4.50; S, 20.58. Found: N, 4.63; S, 20.78.

The 2,4-dinitrophenylhydrazone was prepared in methanol, m. p. 151–153°.

Anal. Calcd. for C₂₃H₁₇O₄N₅S₂: N, 14.26. Found: N, 14.13.

In a similar manner, from *p*-bromophenacyl bromide and thiuram disulfide in acetone there was obtained a 94% yield of 2-(*p*-bromophenacylthio)-4-(*p*-bromophenyl)-thiazole, which crystallized as silky white needles from absolute ethanol, m. p. 146–147°.

Anal. Calcd. for C₁₇H₁₁ONBr₂S₂: N, 2.98; Br, 34.09. Found: N, 3.06; Br, 34.28.

The 2,4-dinitrophenylhydrazone was prepared in methanol, m. p. 179–181°.

Anal. Calcd. for C₂₃H₁₅O₄N₅Br₂S₂: N, 10.78. Found: N, 10.90.

(3) Melting points uncorrected.

(4) Miller, *Contrib. Boyce Thompson Inst.*, **5**, 31 (1933).

(5) Freund and Bachrach, *Ann.*, **285**, 201 (1895).

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The Decarboxylation of Opianic Acid

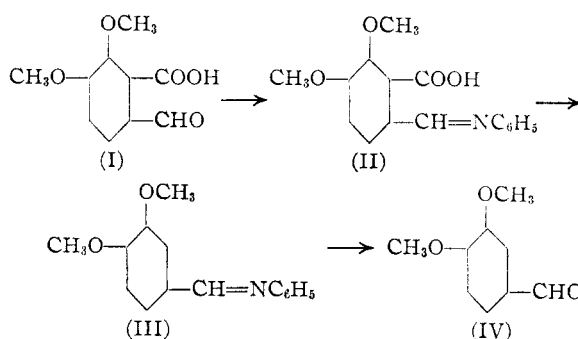
BY JOHN WEIJLARD, ELEANOR TASHJIAN AND MAX TISHLER

Opianic acid (I), a degradation product of hydrastine and narcotine, has been demonstrated to be 2-carboxy-3,4-dimethoxybenzaldehyde by con-

version into both veratraldehyde and hemipinic acid.¹

According to the literature the decarboxylation of opianic acid to veratraldehyde is difficult and the yield is poor. Under the drastic conditions employed by the previous investigators, cleavage of the ether groups occurs with the formation of vanillin, isovanillin and protocatechuic aldehyde as by-products. It is probable that lactol formation between the carboxyl and the neighboring aldehyde group is responsible for the decarboxylation difficulty.

Recent experiences in this Laboratory with the conversion of 2-carboxyindole-3-aldehyde into indole-3-aldehyde² prompted us to apply the same method to opianic acid. Accordingly, the aldehyde group of opianic acid was protected by conversion into the phenylimino derivative (II), the latter was decarboxylated to veratraldehyde anil (III) which was then hydrolyzed to veratraldehyde (IV). In this way, veratraldehyde was obtained from opianic acid in yields of around 90%.



Experimental

3,4-Dimethoxy-2-carboxy-(1)-phenyliminomethyl Benzene; Opianic Acid Anil.³—To a solution of 63 g. of opianic acid (0.3 mole) in a mixture of 300 cc. of alcohol and 300 cc. of 4% aqueous sodium hydroxide at 70° was added 28 g. of aniline (0.3 mole). The mixture was stirred five minutes at this temperature and then cooled to 3°. About 110 cc. of 10% hydrochloric acid was then added in a thin stream with efficient stirring. The anil precipitation was complete when the reaction was slightly acid to congo red. The product was filtered, washed free from chloride with water and dried at 70° to constant weight; yield 81.0 g. (94.6%), m. p. 188–190°. After recrystallization from alcohol, the compound melted at 191.5–192.5°.

Anal. Calcd. for C₁₆H₁₅O₄N: N, 4.91. Found: N, 5.03.

3,4-Dimethoxy-1-phenyliminomethylbenzene; Veratraldehyde Anil.—A mixture of 50 g. of the unrecrystallized opianic acid anil and 2 g. of powdered copper bronze was held at 195–205° for ten minutes, at which time the carbon dioxide evolution was complete. The cooled reaction mixture was used for the hydrolysis step.

For analytical purposes the product from a 1-g. run was dissolved in 20 cc. of boiling absolute alcohol, the solution

(1) Beckett and Wright, *J. Chem. Soc.*, **29**, 281 (1876); Wegscheider, *Monatsh.*, **3**, 356 (1882); Schorigin, Issaguljanz and Below, *Ber.*, **64**, 274 (1931).

(2) Shabica, Howe, Ziegler and Tishler, *THIS JOURNAL*, **68**, 1156 (1946). See also Boyd and Robson, *Biochem. J.*, **29**, 555 (1935).

(3) Although the anil was previously prepared [Liebermann, *Ber.*, **19**, 2284 (1886)], our procedure is recorded as it is different.

was treated with charcoal, filtered and chilled. The product weighed 0.4 g.; m. p. 78.5–79.5°.⁴

Anal. Calcd. for $C_{15}H_{15}O_2N$: C, 74.59; H, 6.26; N, 5.80. Found: C, 74.30; H, 6.31; N, 6.08.

Veratraldehyde.—The entire reaction mixture from above was dissolved in 400 cc. of 5% acetic acid and boiled under reflux for one hour. The mixture was cooled and filtered. The insoluble product was triturated with ether and the filtered ether extract was washed with dilute sodium hydroxide and with water. The veratraldehyde was obtained as a solid residue by evaporation of the ether; wt. 27.7 g., 95% yield; m. p. 44°, mixed m. p. with an authentic sample showed no depression.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05; H, 6.06. Found: C, 65.40; H, 5.84.

(4) Previously prepared from veratraldehyde by Noelting, *Ann. chim.*, [8] **19**, 538 (1910).

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Aliphatic and Aromatic Sulfonates of Phenyl- octadecane

BY B. B. SCHAEFFER² AND A. J. STIRTON

The barium salts of sulfonic acids related to the phenylstearic acid of Nicolet and de Milt³ were prepared for the purpose of cooperating with the Naval Research Laboratory,⁴ in evaluating lubricating oil additives. The steps in the synthesis of barium phenyloctadecanesulfonate and of barium octadecylbenzenesulfonate are described below. In the Friedel and Crafts reaction of benzene with oleic acid, oleyl alcohol or an alkyl oleate, in the presence of aluminum chloride, the product is a viscous oil which does not easily crystallize. Apparently it is a mixture of at least two isomers (the 9- and the 10-phenyl derivatives).⁵ The double bond may migrate during the reaction to increase the number of possible isomers. The sulfation of oleic acid, an analogous reaction, leads not only to 9- and 10-hydroxystearic acids but also to other isomeric hydroxy acids.⁶

Experimental

Phenyloctadecanol.—Phenyloctadecanol may be prepared from an alkyl phenylstearate or from oleyl acetate as described by Sisley,⁷ but it is more readily prepared directly from oleyl alcohol. Oleyl alcohol, purity 83.4%, 0.58 mole, was dissolved in 500 ml. of benzene and added gradually over a period of four hours to a stirred suspension of 0.64 mole of aluminum chloride in 225 ml. of benzene at not over 35°. The mixture was heated and stirred for ten hours at 65°, cooled and hydrolyzed with dilute hydrochloric acid. Phenyloctadecanol was isolated as a fraction

distilling at 180–198° at 0.15 mm., n_D^{20} 1.4940. The yield was 62%. The over-all yield was lower when phenyloctadecanol was prepared from oleyl acetate (31%) or by the Bouveault–Blanc reduction of butyl phenylstearate (17%).

Phenyloctadecyl Bromide.—Dry hydrogen bromide, generated by the action of bromine on tetralin, was led into 1.4 moles of phenyloctadecanol for a period of nine hours at 100–110° until 1.64 moles had been absorbed. The mixture was washed successively with sulfuric acid, 50% methanol, 15% aqueous ammonia and 50% methanol, separated and dried over calcium chloride and then fractionated by vacuum distillation. Phenyloctadecyl bromide was isolated as a yellow oil distilling at 182–194° at 0.02 mm., n_D^{20} 1.4995. The yield was 45%.

*Anal.*⁸ Calcd. for $C_{23}H_{41}Br$: Br, 19.52. Found: 19.59.

The method using phosphorus tribromide in carbon tetrachloride led to greater emulsion difficulties, contamination with phosphorus compounds, under-bromination, and the necessity of separating the bromide from the alcohol when both were high boiling liquids.

Phenyloctadecyl Mercaptan.—The bromide was converted to the mercaptan by thiourea by the method of Urquhart, Gates and Connor⁹ in a yield of 79%. Phenyloctadecyl mercaptan was isolated as an almost colorless oil with a slight mercaptan odor, distilling at 203–211° at 0.5 mm., n_D^{20} 1.4988, d_4^{25} 0.9066.

Anal. Calcd. for $C_{23}H_{46}S$: S, 8.84; mol. refr., 117.12. Found: S, 8.55; mol. refr., 117.36.

Barium Phenyloctadecanesulfonate.—The mercaptan (0.1 mole) was oxidized in acetone solution by the gradual addition of 0.7 mole of potassium permanganate during three hours of refluxing. Acetone was removed, concentrated hydrochloric acid was added to the residue, and the mixture was extracted with ethyl ether. The ether layer was continuously extracted with water for seventy-two hours. The aqueous extract was neutralized with sodium hydroxide and evaporated; the residue was dissolved in water and precipitated with barium chloride. The precipitate was washed with alcohol, dissolved in xylene and reprecipitated with acetone as barium phenyloctadecanesulfonate, a yellow hygroscopic solid. The yield was 27%.

Anal. Calcd. for $C_{18}H_{32}O_6S_2Ba$: Ba, 14.36. Found: Ba, 14.11.

Phenyloctadecane.—Phenyloctadecyl bromide (0.27 mole) was added dropwise during thirty minutes to 0.3 mole of magnesium turnings in 500 ml. of anhydrous ethyl ether. The mixture was warmed slightly to start the reaction, then refluxed for four hours. The flask was surrounded by an ice-bath, and the contents were hydrolyzed by the careful addition of 100 ml. of a cold 14% ammonium chloride solution, followed by 100 ml. of 5% hydrochloric acid. The ether solution was washed until the washings were neutral, and dried over sodium sulfate; then the ether was removed and the residue vacuum distilled. Phenyloctadecane was obtained as an almost colorless liquid, distilling at 145–152° at 0.08 mm., n_D^{20} 1.4862, d_4^{20} 0.8744. Molecular refractivity: theoretical, 109.43; found, 108.61. The yield was 49%.

Barium Octadecylbenzenesulfonate.—Phenyloctadecane (0.2 mole) was added dropwise during fifteen minutes with stirring to 157 g. of concentrated sulfuric acid, the temperature rising to 36°. The mixture was heated and stirred for two hours at 50°, cooled, poured into water and then extracted with ethyl ether. The ether layer was extracted with water, the water extract was neutralized with sodium hydroxide, evaporated and extracted with alcohol, and the alcoholic solution was evaporated, yielding the crude sodium salt. The crude sodium salt was converted to the barium salt by barium chloride, and barium octa-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

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(3) Nicolet and de Milt, *THIS JOURNAL*, **49**, 1103 (1927).

(4) Anacosta Station, Washington, D. C.

(5) Harmon and Marvel, *THIS JOURNAL*, **54**, 2515 (1932).

(6) Schaeffer, Roe, Dixon and Ault, *ibid.*, **66**, 1924 (1944).

(7) Sisley, *Chim. industrie*, Special No., 763 (April, 1934).

(8) Analyses by the Analytical and Physical Chemistry Division, Eastern Regional Research Laboratory.

(9) Urquhart, Gates and Connor, "Organic Syntheses," **21**, 36 (1941).