

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).

RESEARCH LABORATORY OF
MERCCK AND CO., INC.
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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 $C_{21}H_{41}Br$: 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 $C_{21}H_{41}S$: 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.

(2) Present address: Mathieson Alkali Works (Inc.), Research and Development Laboratories, Niagara Falls, N. Y.

(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).

decylbenzenesulfonate was isolated as a yellow hygroscopic solid. The yield was 41%.

Anal. Calcd. for $C_{18}H_{22}O_6S_2Ba$: Ba, 14.36. Found: Ba, 14.38.

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Polyenes. V. The Structure of Cyclocitrylidenedecyanoacetic Acid and the Purity of β -Cyclocitral¹

BY WILLIAM G. YOUNG AND SEYMOUR L. LINDEN

The absorption spectrum of cyclocitrylidenedecyanoacetic acid² obtained by the condensation of β -cyclocitral and cyanoacetic acid in aqueous sodium hydroxide, exhibits two maxima: one at 307 $m\mu$ (ϵ 4350) and the other at 223 $m\mu$ (ϵ 5500). Comparison with the spectra of other alkylidenedecyanoacetic acids² indicated that the cyclocitrylidenedecyanoacetic acid was perhaps a mixture of α - and β -isomers. However, ozonization of the compound in question failed to yield any isogeronic acid as would have been expected if an appreciable amount of α -form had been present. Only geronic acid could be isolated from the ozonization, indicating that the low maximum at 223 $m\mu$ is probably not due to the presence of the α -form.

β -Cyclocitral has been prepared several times in this Laboratory by the method of Tiemann.^{2,3} The final steps in this process involve recrystallization of the semicarbazone of the crude cyclocitral until pure β -cyclocitral semicarbazone has been obtained. The β -cyclocitral is then recovered from its semicarbazone by steam distillation in the presence of phthalic anhydride. The β -cyclocitral obtained in this way² had the following physical properties: n^{17}_D 1.4965, n^{25}_D (calcd.) 1.4933; λ_{max} , 249 $m\mu$ (ϵ 7700) in 95% ethanol. Koster⁴ reports the refractive indices of pure α - and β -cyclocitral to be 1.4691 and 1.4953 respectively at 25°. On the basis of these values the β -cyclocitral obtained previously in this Laboratory by the above described method is approximately 93% β -form.

In view of the fact that regeneration of β -ionone from its semicarbazone by steam distillation in the presence of phthalic anhydride causes partial rearrangement to the α -form⁵ it was considered possible that such a partial rearrangement could occur in the cyclocitral series also. In order to test this hypothesis, pure β -cyclocitral semicarbazone was hydrolyzed by shaking with cold dilute sulfuric acid, a procedure which has been shown to produce the purest β -ionone from its semicarbazone.^{5,6}

(1) This work was made possible by a research grant from Sharp and Dohme, Inc.

(2) Andrews, Cristol, Lindenbaum and Young, *THIS JOURNAL*, **67**, 715 (1945).

(3) Tiemann, *Ber.*, **33**, 3719 (1900).

(4) Koster, *ibid.*, **77**, 553 (1944).

(5) Young, Cristol, Andrews and Lindenbaum, *THIS JOURNAL*, **66**, 855 (1944).

(6) Heilbron, Johnson, Jones and Spinks, *J. Chem. Soc.*, 727 (1942).

The β -cyclocitral obtained in this way had the following physical properties: $n^{21.4}_D$ 1.4971, n^{25}_D (calcd.) 1.4957; λ_{max} , 249 $m\mu$ (ϵ 11600). It is apparent that the hydrolysis with cold sulfuric acid yields a product with a higher β -content than did the steam distillation method. It is highly probable that the product obtained in the cold is 100% β -cyclocitral. The extinction coefficients at 249 $m\mu$ indicate that the β -content of the cyclocitral prepared by the steam distillation method may be as low as 66%.

The hydrolysis of the β -cyclocitral semicarbazone proceeds at a much slower rate than β -ionone semicarbazone. Six normal sulfuric acid was required to accomplish the hydrolysis at an appreciable rate whereas the ionone derivative hydrolyses rapidly when shaken with two normal acid.

Ozonization of the pure β -cyclocitral yielded pure geronic acid with no trace of isogeronic acid detectable.

Experimental

Preparation of Cyclocitrylidenedecyanoacetic Acid.—Condensation of 1.0 g. of the pure β -cyclocitral ($n^{21.4}_D$ 1.4971) with cyanoacetic acid in aqueous sodium hydroxide yielded crystalline cyclocitrylidenedecyanoacetic acid whose physical properties were identical with those previously described from this Laboratory.²

Ozonization of Cyclocitrylidenedecyanoacetic Acid.—One gram of cyclocitrylidenedecyanoacetic acid was ozonized in 10 ml. of glacial acetic acid. Excess ozone appeared in the issuing stream of oxygen even at the very beginning of the ozonolysis. The ozonide was decomposed in the presence of hydrogen peroxide and treated by the procedure previously described.⁷ The crude semicarbazone obtained proved to be the geronic acid derivative. Repeated fractional extractions with hot ethyl acetate⁸ failed to reveal the presence of any isogeronic acid semicarbazone.

Hydrolysis of β -Cyclocitral Semicarbazone with Cold Sulfuric Acid.— β -Cyclocitral semicarbazone, 19.8 g., m. p. 165–166° (uncor.), was shaken under nitrogen with 100 ml. of petroleum ether and 100 ml. of 6 *N* sulfuric acid for nine hours. The ether layer was separated and the aqueous layer extracted several times with petroleum ether. The combined petroleum ether solutions were dried over anhydrous potassium carbonate. Distillation of the residue left after removal of the solvent yielded 11.2 g. (78% yield) of β -cyclocitral, b. p. 92–96° (12 mm.) (see text for other physical properties).

Ozonization of β -Cyclocitral.—Pure β -cyclocitral (11.2 g.) was ozonized in 40 ml. of acetic acid and the ozonide decomposed by pouring into 50 ml. of water containing hydrogen peroxide. After standing overnight, 50 ml. more water was added and the solution was slowly distilled until 50 ml. of distillate had collected. Three grams of unreacted β -cyclocitral was recovered as an oil in the distillate. More water was added to the still-pot residue and the solution was extracted with ether in a liquid-liquid extractor for forty-eight hours. After removal of the ether, distillation and redistillation of the residue yielded 4.6 g. (51% yield) of pure geronic acid, b. p. 133–135° (3 mm.), n^{25}_D 1.4525, neut. equiv. 173 (calcd. 172). The melting point (162–163°) of the crude semicarbazone prepared from this geronic acid indicated the absence of any impurity of isogeronic acid. This geronic acid was used in experiments reported elsewhere.⁷

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
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(7) Young and Linden, *THIS JOURNAL*, **69**, 2042 (1947).

(8) Karrer, Morf and Walker, *Helv. Chim. Acta*, **16**, 975 (1933); Karrer, Helfenstein, Wehrli and Wettstein, *ibid.*, **13**, 1094 (1930).