Phenyloctadecanol and Surface-Active Derivatives[1]

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Abstract

Phenyloctadecanol from the Friedel-Crafts reaction, like phenylstearic acid, is a viscous oil and a mixture of several position isomers. Gas-liquid chromatography of the acetophenone homologs formed by CrO_3 oxidation showed it to be a mixture of 13 position homologs, with substitution of the phenyl group at carbon atoms 5–17. A crystalline 17-phenyloctadecanol was isolated.

Reaction of oily phenyloctadecanol with dioxane-SO_3 sulfated the primary alcohol group to give sodium phenyloctadecyl sulfate $CH_3(CH_2)_xCH(C_6H_5)(CH_2)_yCH_2OSO_3Na$, where $x + y = 15$. Reaction of phenyloctadecanol with 2.4 moles of SO_3 gave an impure p-sulfophenyloctadecyl sulfate, hydrolyzed to sodium p-sulfophenyloctadecanol $CH_3(CH_2)_xCH(p\text{-}C_6H_4SO_3Na)(CH_2)_yCH_2OH$, and sulfated again with dioxane-SO_3 to disodium p-sulfophenyloctadecyl sulfate $CH_3(CH_2)_xCH(p\text{-}C_6H_4SO_3Na)(CH_2)_yCH_2OSO_3Na$. Foam, detergency, and other surface-active properties were compared with those of the p-sulfo and α-sulfo derivatives of oily phenylstearic acid.

Introduction

Phenyloctadecanol was first prepared by Sisley from benzene and oleyl acetate by the Friedel-Crafts reaction and subsequent hydrolysis (8). Protection of the hydroxyl group is unnecessary, and direct condensation of oleyl alcohol is easily possible and more convenient (1,5,7,13). Phenyloctadecanol has also been prepared by hydrogenolysis of phenylstearic acid (4).

Because of apparent similarities it was of interest to compare phenyloctadecanol with phenylstearic acid in respect to product distribution and as intermediates for anionic surface-active agents. The properties of some nonionic derivatives, from ethylene oxide, have been described (17).

Gas-liquid chromatography (GLC) of ketones from CrO_3 oxidation has been used to show the product distribution of phenylstearic acid (9) and linear phenylalkanes (10). It is an excellent method to reveal the number of position isomers but may not be quantitative because of unequal oxidative scission and differing ease of oxidation. For linear phenylalkanes the amount of 2-phenyl isomer (corresponding to 17-phenylstearic acid or 17-phenyloctadecanol) had to be revised downward and the amount of 3-phenyl increased.

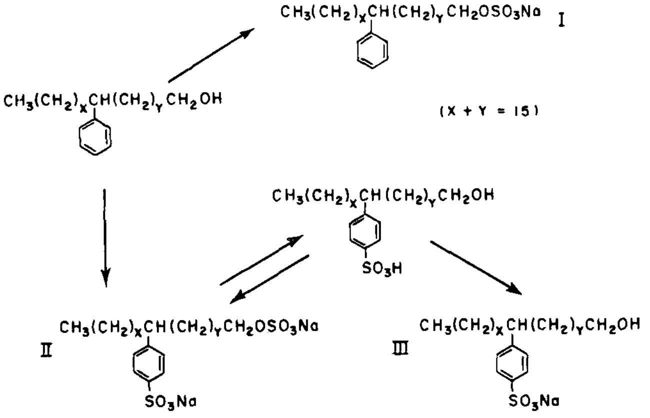

FIG. 1. Reaction sequence, phenyloctadecanol and derivatives.

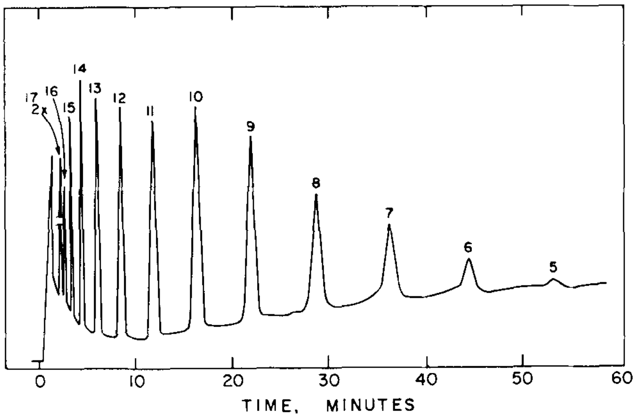

FIG. 2. Alkyl aryl ketones from phenyloctadecanol.

For application to phenyloctadecanol a larger amount of CrO_3 was used than in the case of phenylstearic acid, permitting oxidation of alcohols to carboxylic acids. Alkyl aryl ketones $CH_3(CH_2)_xCOC_6H_5$ were isolated from mixtures with monobasic, dibasic, and ω-benzoyl fatty acids and were chromatographed. Product distribution was very like that of phenylstearic acid except that one more isomer was found, namely, 5-phenyloctadecanol. It is possible that the 5-phenyl isomer may be present also in phenylstearic acid in small amounts, too small to be detected by the CrO_3 method. As with phenylstearic acid, a crystalline 17-phenyloctadecanol was isolated. The sequence of sulfation-sulfonation reactions is shown in Figure 1.

Experimental Section

Phenyloctadecanol

Phenyloctadecanol was prepared by carefully adding $AlCl_3$ in portions in 1.1 molar ratio to a stirred solution of purified oleyl alcohol in a 6 molar ratio of benzene. The temperature rose to 60C. The mixture was stirred one hour, hydrolyzed, and distilled to give phenyloctadecanol as a viscous colorless oil $b_{0.3}$ 184C–193C, yield 63%. A crystalline solid, shown by oxidation to acetophenone to be 17-phenyloctadecanol mp 44.1C–45C, was isolated by repeated crystallization from acetone at −28C. Refluxing in acetic anhydride gave 17-phenyloctadecyl acetate mp 34.9C–35.5C. Infrared analysis showed absence of the hydroxyl group. GLC of the acetate, which indicated a purity of 99.3%, was not entirely satisfactory because the low vapor pressure made it necessary to operate near the high-temperature limit (310C for an SE 30 column).

Oxidation. CrO_3 (4 g) was added in the course of 2 min to 2 g of phenyloctadecanol in 30 ml of glacial acetic acid at 20C. The solution was refluxed 10 min

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TABLE I
Isomeric Phenylstearic Acids and Phenyloctadecanols[a]

Carbon number on the aliphatic chain	Phenylstearic acids	Phenyloctadecanols
17	14.9	9.9
16	2.6	3.3
15	4.3	5.2
14	6.8	6.9
13	8.1	7.8
12	9.8	9.4
11	11.7	10.6
10	15.1	13.5
9	13.4	12.9
8	7.8	9.6
7	3.6	6.7
6	1.8	3.6
5	0.0	0.7

[a] Values are given as mole %.

and cooled to 20C. Water and ethyl ether (20 ml each) were added, and the mixture was transferred to a separatory funnel containing 100 ml of a saturated Na_2SO_4 solution. The ether layer was washed, separated, washed with 50 ml of 2N NaOH solution saturated with Na_2SO_4, and washed twice with 50 ml each of saturated Na_2SO_4 solution while maintaining the ether volume at about 10 ml. The ether layer was then separated, concentrated to about 1.5 ml, dried over anhydrous Na_2SO_4, and analyzed by GLC. A somewhat lower CrO_3 ratio, previously used for phenylstearic (9), gave less complete oxidation of phenyloctadecanol to alkyl aryl ketones.

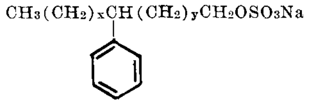
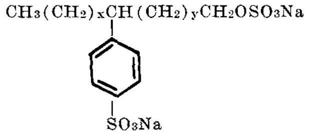
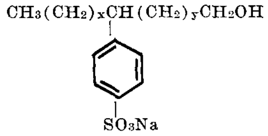
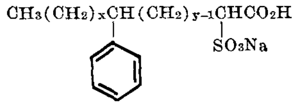
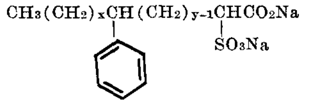
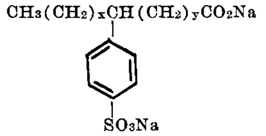
Chromatography. The chromatographic separations were carried out on an F & M dual column programmed-temperature gas chromatograph Model 720. An 8-ft stainless steel column containing 20% silicone rubber SE 30 was used. Acetophenone, propiophenone, valerophenone, hexanophenone, decanophenone, laurophenone, and hexadecanophenone were used as reference standards. Separation of the ketones from the oxidation of phenyloctadecanol is shown in the chromatogram of Figure 2, a programmed run from 188C–230C at 1C/min. The peak numbers are the points of attachment of the benzene ring on the aliphatic chain.

Product distribution, as shown in Table I and Figure 3, is quite similar for phenylstearic acid and phenyloctadecanol. The principal difference is the presence of the 5-phenyl isomer, and a smaller amount of the 17-phenyl isomer is formed in the case of phenyloctadecanol. In each case about two-thirds of the mixture are isomers with the phenyl group at carbon atoms 8–13. The presence of the hydroxyl rather than the carboxyl group in the molecule permits greater formation of more internal isomers (5,6 and 7-phenyl isomers).

Surface-Active Derivatives

Sulfation and Sulfonation. Sulfation of phenyloctadecanol with 1.02 equivalents of 1:1 dioxane-SO_3 at 0 to 5C gave sodium phenyloctadecyl sulfate (I, Figure 1) as a colorless hygroscopic solid: found 5.07% Na, calculated for $C_{24}H_{41}NaO_4S$ 5.13. Infrared spectra showed absence of the hydroxyl group.

TABLE II
Surface-Active Properties

		cmc[a] %	Ca++ stability[b] ppm $CaCO_3$	Wetting time[c] 0.1% seconds	Foam height[d] 0.25% 60C mm	Detergency 0.25% 60C ΔR[e]
I	 $CH_3(CH_2)_xCH(CH_2)_yCH_2OSO_3Na$	.01	1180	77	170	36
II	 $CH_3(CH_2)_xCH(CH_2)_yCH_2OSO_3Na$ SO_3Na	.02	>1800	166	165	19
III	 $CH_3(CH_2)_xCH(CH_2)_yCH_2OH$ SO_3Na	.01	830	28	170[f]	29
A	 $CH_3(CH_2)_xCH(CH_2)_{y-1}\underset{SO_3Na}{CH}CO_2H$	.008	540	105	185	33
B	 $CH_3(CH_2)_xCH(CH_2)_{y-1}\underset{SO_3Na}{CH}CO_2Na$	.056[g]	320	125	210	32
C	 $CH_3(CH_2)_xCH(CH_2)_yCO_2Na$ SO_3Na	.10	630	14	165[f]	18

[a] Critical micelle concentration, surface-tension method.
[b] Modified Hart method (16).
[c] Draves test (2), 3-g hook.
[d] Ross-Miles test (6).
[e] Increase in reflectance after washing standard soiled cotton (3) in the Terg-O-Tometer for 20 min, 10 swatches/liter. For comparison, ΔR for sodium dodecyl sulfate = 23.
[f] Unstable foam. All other values stable for 5 min.
[g] Critical micelle concentration by dye titration.

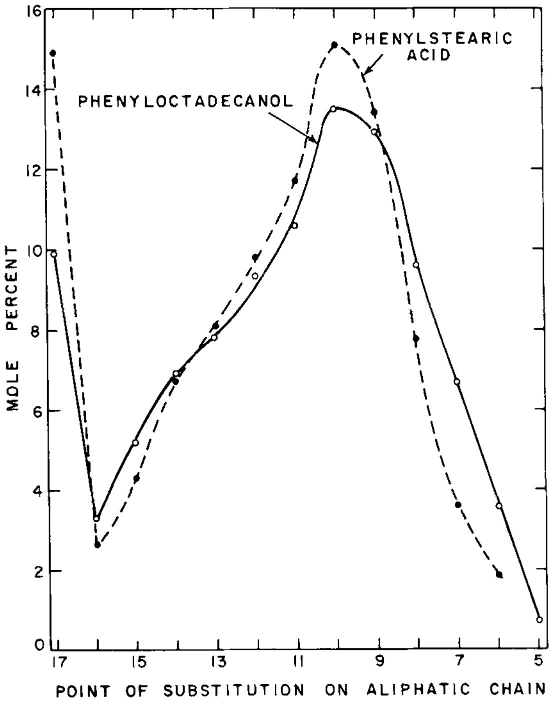


FIG. 3. Product distribution for phenyloctadecanol and phenylstearic acid.

Sulfation and sulfonation of phenyloctadecanol with excess SO_3 (2.4 molar ratio) gave the impure sulfo-sulfate (II), hydrolyzed by refluxing with constant boiling HCl to give the acid form of III as a brown sirup: found, N.E. 429, calculated for $C_{24}H_{42}O_4S$ 427. Neutralization with NaOH gave sodium p-sulfophenyloctadecanol (III) as a light brown solid:found 5.15% Na, calculated for $C_{24}H_{41}NaO_4S$ 5.13. Sulfation of III with 1.02 equivalents of 1:1 dioxane-SO_3 at 0 to 10C gave disodium p-sulfophenyloctadecyl sulfate (II) as a hygroscopic straw-colored solid:found 8.41% Na, calculated for $C_{24}H_{40}Na_2O_7S_2$ 8.35.

Properties. Several surface-active properties were measured and compared with those for the α-sulfo (14) and p-sulfo (12) derivatives of phenylstearic acid, as recorded in Table II.

Discussion

Table II permits an examination of the relation between structure and surface-active properties, obscured somewhat because the six compounds are mixtures of isomers. Values for the cmc are not entirely trustworthy because of this. The distance between the hydrophilic group and the end of the hydrophobic chain is a single value for I, A, and B but is an average of those of the several isomers for II, III, and C. The cmc is greater for polyelectrolytes.

All of the compounds are easily soluble and except for B, which has a Krafft point of 32C, form clear 1% solutions at 0C. All have good or excellent Ca^{++} stability except for B. Only III and C are fairly good wetting agents. Except for B the compounds have only moderate foaming properties. Compounds with the hydrophilic group at the end of the molecule are the best detergents (I, A, and B). None of the six were good lime soap-dispersing agents. A fat-splitting test, carried out as described for sulfoxylstearic acid (11), showed that only the p-sulfo compounds II, III, and C were effective. Hydrolysis of the sulfate can be expected under these conditions. α-Sulfo acids are not effective because they are more soluble in the aqueous than the oil phase.

Sodium phenyloctadecyl sulfate (I) is a good detergent much more easily soluble than sodium octadecyl sulfate. Arylation, like additive chlorination and other modifications (15), is another means for increasing the solubility of tallow alcohol sulfates.

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