Homogeneous Nonionic Detergent p-n-Nonylphenoxydecaethoxyethanol

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Abstract

A model compound representing the nonionic surfactants of the alkylphenol–ethylene oxide condensate type was prepared in high purity. The homogeneous detergent *p-n*-nonylphenoxydecaethoxyethanol was obtained as a crystalline product by a several step synthesis starting from phenol.

Introduction

STUDIES OF homogeneous nonionic surface active agents of the alkylphenol–ethylene oxide condensate type referred to products containing branched alkyl groups (1–5). In connection with the increasing emphasis on biodegradability of detergents (6), it was of interest to study the properties of homogeneous surface active agents of high purity and derived from linear alkylphenols.

This paper describes the synthesis of a model compound, *p-n*-nonylphenoxydecaethoxyethanol (undecaoxyethylene glycol mono-*p-n*-nonylphenyl ether). Starting from phenol the several-step synthesis, illustrated in Fig. 1, gave a crystalline compound of high purity.

Experimental Procedures[1]

Phenyl Pelargonate (II)

Pelargonic acid (316.5 g, 2 moles), phenol (200 g, 2.13 moles), xylene (50 ml), and triphenyl phosphite (5 g) were refluxed under a Dean-Stark water trap at a pot temperature of 190–227C. After 17 hr, 2.05 moles of water were collected in the water trap. The reaction mixture was cooled, then washed with 10% sodium hydroxide solution and water. The ester was purified by two repetitive distillations to give a fraction (320 g, 68% yield), bp 167–168C/10 mm, n_D^{25} 1.4805. The product was homogeneous on gas liquid chromatography using a column of 20% Apiezon L on Chromosorb W treated with dimethyldichlorosilane.

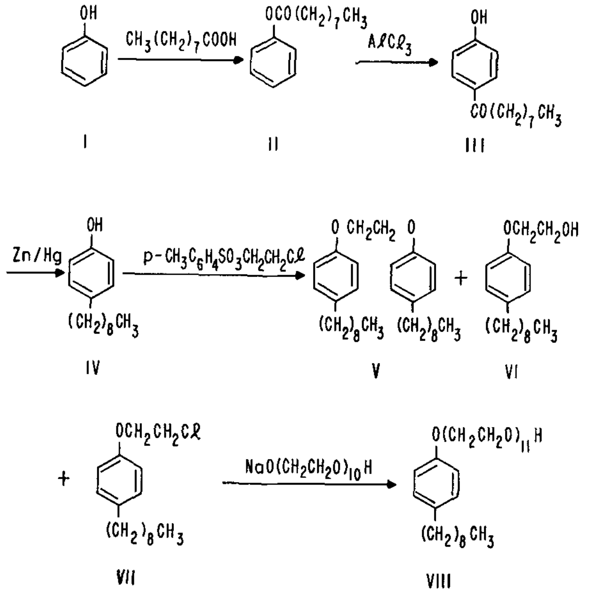

FIG. 1. Synthesis of p-n-nonylphenoxydecaethoxyethanol.

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.92; H, 9.40. Found: C, 76.97; H, 9.38.

p-Nonanoyl Phenol (III)

A mixture of phenyl pelargonate (46.9 g, 0.2 mole), nitrobenzene (250 g), and aluminum chloride (30 g, 0.226 mole) was stirred at room temperature for 2 hr and then at 60–70C for 5 hr. The mixture was poured onto ice–hydrochloric acid and extracted with ether. The ethereal solution was washed with 10% sodium hydroxide solution. The alkaline washings were acidified with hydrochloric acid and the precipitated solid extracted with ether. The ether was evaporated and the remaining material was triturated with pentane to afford *p*-nonanoyl phenol mp 54–55C (25.75 g, 55% yield). Distillation, followed by crystallization from hexane-benzene, gave the pure product, mp 55.5–56.5C (lit.[7] 54.5C). The product was homogeneous on gas liquid chromatography using a column of 20% Apiezon L on Chromosorb W containing 3% phosphoric acid.

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.92; H, 9.40. Found: C, 77.04; H, 9.36.

p-n-Nonylphenol (IV)

Granulated zinc (355 g) was introduced into a solution of 14.9 g of mercuric chloride in a mixture of 15 ml of concentrated hydrochloric acid and 450 ml of water. The mixture was shaken occasionally for 10 min. The liquid was decanted and the residual amalgamated zinc treated with 190 ml of concentrated hydrochloric acid. The mixture was stirred and heated under reflux while a solution of 54 g (0.23 mole) of *p*-nonanoyl phenol (III) in a mixture of 610 ml of 95% ethanol and 360 ml of concentrated hydrochloric acid was introduced over a period of 5 hr. The reaction mixture was set aside overnight and then again stirred and heated at reflux temperature while 400 ml of concentrated hydrochloric acid was added over a period of 4 hr. Afterwards, the heating under reflux continued until a sample withdrawn from the reaction mixture showed absence of the starting ketone (infrared spectroscopic analysis). The total reaction time was 8 hr. The resulting mixture was cooled, the liquid decanted, and the residual amalgamated zinc washed with ether. The combined liquids were diluted with 5 liters of water and extracted with ether. The extract was washed with water and the ether evaporated. The residual solid was distilled to give 46.2 g (91% yield) of the product (bp 122–124/0.2 mm) which, upon recrystallization from hexane, melted at 42.5–43.5C (lit.[7] mp 42.5C). The product was homogeneous on gas liquid chromatography using a column of 20% Apiezon L on Chromosorb W containing 3% phosphoric acid.

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[1] Melting and boiling points are uncorrected.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.82; H, 10.91. Found: C, 81.89; H, 11.00.

Reaction of p-n-Nonylphenyl with 2-Chloroethyl p-Toluenesulfonate

A mixture of 22 g (0.1 mole) of *p*-*n*-nonylphenol (IV) and 50 ml of 8% aqueous solution of sodium hydroxide was stirred and heated under reflux. Dioxane (25 ml) was added to dissolve the formed sodium *p*-nonylphenate. A 35.3-g (0.15-mole) sample of 2-chloroethyl *p*-toluenesulfonate was introduced over a period of 1 hr. The reaction mixture was stirred at 90–100C for an additional 4 hr. The mixture was then cooled, made alkaline with 10% caustic solution, diluted with water, and distilled to remove dioxane. The residual product was extracted with ether. The extract was washed successively with caustic, water, and finally dried. Short path distillation at 150–155C (bath temperature, 0.2 mm) gave 24 g of a solid. The distillation residue (2 g), after crystallization from hexane, gave 0.4 g of 1,2-*bis* (4-*n*-nonylphenoxy) ethane (V), mp 100.5–101.5C. No hydroxyl band was present in the infrared spectrum. The nmr spectrum determined in $CDCl_3$ showed peaks at 0.85 (triplet, 6 H, two CH_3), 1.25 [singlet, 28 H, two $-(CH_2)_7-$], 2.49 (triplet, 4 H, two $Ar-CH_2-$), 4.16 (singlet, 4 H, $-OCH_2CH_2O-$), and 6.75 and 6.98 ppm ($A_2^1B_2^1$ pattern, 8 H, both aromatic *para*-substituted ring protons).

Anal. Calcd for $C_{32}H_{50}O_2$: C, 82.40; H, 10.73. Found: C, 82.40; H, 10.64.

The distillate (24 g) was chromatographed on alumina (460 g, neutral, Brockman activity 1). Three main fractions were collected by elution. First, eluted with hexane, gave 17.9 g mp 34–35C; second, eluted with ether, gave 0.7 g mp 70–80C; and third, eluted with methanol, gave 4.1 g mp 36–37C. Each fraction was recrystallized separately from hexane. The first fraction afforded *p*-*n*-nonylphenyl-2-chloroethyl ether (VII), mp 34–35C. The product was homogeneous on gas liquid chromatography using a column of 20% Apiezon L on Chromosorb W containing 3% phosphoric acid.

Anal. Calcd for $C_{17}H_{27}OCl$: C, 72.22; H, 9.56; Cl, 12.55. Found: C, 72.15; H, 9.39; Cl, 12.49.

The second fraction from the elution chromatography afforded 1,2-*bis* (4-*n*-nonylphenoxy)ethane, mp 100.5–101.5C identical with V, obtained from the distillation residue. The third fraction afforded 2-(4-*n*-nonylphenoxy)ethanol (VI) melting at 37–38C: $\gamma_{\max}^{CH_3OH}$ 277.5 mμ (ε1710); and infrared band appeared at 3.0 μ(OH). The nmr spectrum determined in $CDCl_3$ showed peaks at 0.85 (triplet, 3 H, $-CH_3$), 1.28 [singlet, 14 H, $-(CH_2)_7-$], 2.49 (triplet, 2 H, $Ar-CH_2-$), 3.35 (broad, 1 H, OH), 3.86 (singlet, 4 H, $-OCH_2CH_2O-$), and 6.68 and 6.94 ppm ($A_2^1B_2^1$ pattern, 4 H, aromatic *para*-substituted ring protons).

Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.27; H, 10.61. Found: C, 77.32; H, 10.58.

Tetraethylene Glycol Dichloride (X)

Tetraethylene glycol (194 g, 1 mole) was dissolved in 200 g of pyridine. The solution was vigorously stirred at 45C while thionyl chloride (262 g, 2.2 mole) was introduced over a period of 45 min. The temperature rose to 95C and the mixture was stirred for an additional 15 min. After cooling to room temperature it was extracted with ether. The ethereal solution was washed successively with aqueous sodium carbonate solution, water, and finally dried. Two repetitive distillations gave the pure product X (165.5 g, 72% yield) bp 160–163/13C mm, n_D^{20} 1.4620 (lit.[8] n_D^{20} 1.4648). The compound was homogeneous on gas liquid chromatography using a column of 25% carbowax on Chromosorb W treated with dimethyldichlorosilane.

Anal. Calcd for $C_8H_{16}O_3Cl_2$: C, 41.58; H, 6.93; Cl, 30.71. Found: C, 41.46; H, 6.84; Cl, 30.80.

Decaoxyethylene Glycol (XI)

A solution of sodium methylate (21.6 g, 0.4 mole) in 75 ml of methanol was admixed with 195 g (1.3 mole) of triethylene glycol. The mixture was stirred and heated up to 100C in vacuo to eliminate most of the methanol. Ligroin (bp 100–115C, 40 ml) was then added and partially distilled off to remove the remaining traces of methanol. The resultant monosodium triethylene glycolate was stirred and heated at 110–115C in a dry nitrogen atmosphere while tetraethylene glycol dichloride (46.2 g, 0.2 mole) was introduced over a period of 1 hr. The reaction was continued for an additional 14 hr at 110–115C. The precipitated salt was filtered off, and the filtrate (ph 8.5) neutralized with hydrochloric acid. Water, ligroin, and excess of triethylene glycol were removed by distillation under reduced pressure. The residue, upon two repetitive distillations in a short path column, gave decaoxyethylene glycol (24.1 g, 26.5% yield), bp 248–249C/0.07 mm, mp 29–30C (lit.[9] liquid at room temperature). The product, which is very hygroscopic, was stored in a desiccator over phosphoric anhydride.

Anal. Calcd for $C_{20}H_{42}O_{11}$: C, 52.40; H, 9.17. Found: C, 52.41; H, 9.18.

p-n-Nonylphenoxydecaethoxyethanol (VIII)

A mixture of decaoxyethylene glycol (8 g, 0.0174 mole), sodium methylate (0.95 g, 0.0175 mole), and methanol (60 ml) was stirred under dry nitrogen sweep. The methanol was removed by distillation and ligroin (bp 100–115C, 100 ml) added. A portion of ligroin was distilled off to remove the remaining traces of methanol. The mixture was stirred at 100–110C while a solution of 4.9 g (0.0174 mole) of *p*-*n*-nonylphenyl 2-chloroethyl ether (VII) in 50 ml of ligroin was added dropwise over a period of 2 hr. After the addition was completed, the mixture was heated at 100–110C for an additional 24 hr. The reaction mixture was cooled, diluted with acetone, and the precipitated sodium chloride filtered off. The filtrate was concentrated by distilling ligroin and acetone, and final heating of the residual liquid at 0.2 mm and 130C. The residual liquid (12.5 g) was chromatographed on a mixture of silica gel (300 g) and celite (150 g). Three main fractions were collected. The first, eluted with benzene, gave mostly unreacted chloro-compound VII, 2.6 g. The second, eluted with benzene-acetone (1:1), gave 2.7 g of the crude surface active agent VIII as a semi-solid. The third, eluted with acetone-methanol (1:1), gave 6.2 g of unreacted decaoxyethylene glycol (XI). The second fraction (2.7 g) was again chromatographed on a mixture of silica gel (40 g) and celite (20 g). Elution with 50% acetone in ether gave 1.4 g (12% yield) of undecaoxyethylene glycol mono-*p*-*n*-nonylphenyl ether (VIII), mp 32–33C. The product upon recrystallization from hexane melted at 32.5–33C; an infrared band appeared at 2.85 μ(OH). The surface tension of aqueous solutions was determined by using a DuNoüy tensiometer. The solutions were surface aged at 25 ± 0.3C for 1 hr. Critical micelle con-

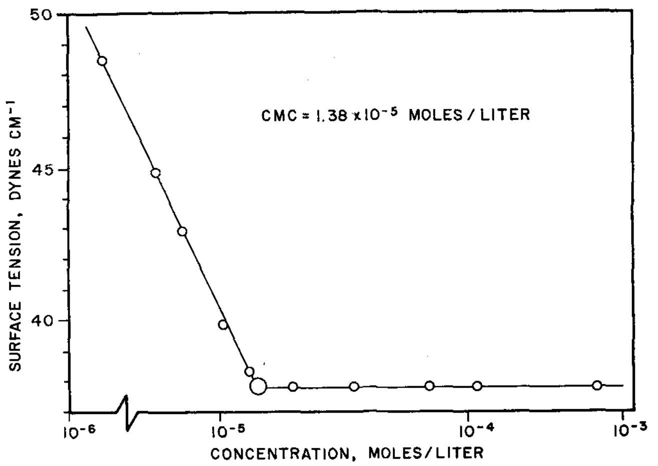

FIG. 2. Surface tension as a function of concentration for p-n-nonylphenoxydecaethoxyethanol.

centrations in water 1.38×10^{-5} moles/liter; surface tension 37.8 dynes/cm at 25C.

Anal. Calcd for $C_{37}H_{68}O_{12}$: C, 63.07; H, 9.66; mol wt, 704. Found: C, 62.94; H, 9.64; mol wt, 703 (UV spectrum in methanol; assuming that the molar absorptivity at 277.5 mμ equals that of the reference compound VI, ε1710).

Results and Discussion

The model compound *p-n*-nonylphenoxydecaethoxyethanol (VIII) was prepared in high purity by the sequence of reactions outlined in Fig. 1. Direct esterification of phenol (I) with pelargonic acid in the presence of triphenyl phosphite catalyst following the method (10) applied to substituted phenols, gave phenyl pelargonate (II). Fries' rearrangement of the ester II provided crystalline *p*-nonanoylphenol (III) (7). Reduction of the ketone III by the Clemmensen method gave pure *p-n*-nonylphenol (IV) (7). The chloroderivative VII, *p-n*-nonylphenyl-2-chloroethyl ether, was obtained by treating the *p-n*-nonylphenol with 2-chloroethyl *p*-toluenesulfonate following the method of Gingras and Bayley (11). The reaction gave, in addition to the desired product VII, 2 other compounds. One of these by-products, 1,2-*bis*(4-*n*-nonylphenoxy) ethane (V), was probably formed by Williamson synthesis from *p*-nonylphenol and the chloro compound VII. Its structure was proved by elemental and spectroscopic analyses. No hydroxyl group was present in the infrared spectrum. The nmr spectrum revealed 4 hydrogens of the ethylenedioxy group and the 8 hydrogens of the 2 *para*-substituted benzene rings. The other compound isolated from the reaction mixture was 2-(4-*n*-nonylphenoxy) ethanol (VI), produced probably by hydrolysis of the chloroethoxy compound VII. Analytical and spectral data supported the structure VI. The infrared spectrum showed a hydroxyl band (3.0 μ). The nmr spectrum exhibited 1 hydroxyl hydrogen, 4 hydrogens of the ethylenedioxy group, and 4 hydrogens of the *para*-substituted benzene ring.

The decaoxyethylene glycol (XI), required for the last phase of the synthesis, was obtained by the following two-step reaction.

$$\underset{\text{IX}}{HO(CH_2CH_2O)_4H} \xrightarrow{SOCl_2} \underset{\text{X}}{Cl(CH_2CH_2O)_3CH_2CH_2Cl}$$

$$\xrightarrow{2NaO(CH_2CH_2O)_3H} \underset{\text{XI}}{HO(CH_2CH_2O)_{10}H}$$

Treatment of tetraoxyethylene glycol (IX) with thionyl chloride gave tetraoxyethylene glycol dichloride (X), according to the method of Rempp (8). Condensation of the dichloride X with 2 mole-equivalents of monosodium salt of triethylene glycol gave decaoxyethylene glycol (XI) as a solid. The product is very hygroscopic and has been reported (9) to be a liquid at room temperature, probably because it forms a hydrate readily.

The final product, *p-n*-nonylphenoxydecaethoxyethanol (VIII) was prepared by condensing *p-n*-nonylphenyl-2-chloroethyl ether (VII) with decaoxyethylene glycol (XI) in the presence of sodium methylate. The crystalline detergent VIII was obtained in low yield because several purification procedures were necessary. Also, a large part of the starting compounds failed to condense despite prolonged reaction time. Its molecular weight was determined by ultraviolet absorption, which showed a benzenoic maximum of 277.5 mμ. In calculating the molecular weight, the molar absorptivity was assumed to equal that of 2-(4-*n*-nonylphenoxyl) ethanol (VI) by analogy with similar products (1).

The critical micelle concentration of detergent VIII was determined by surface tension measurements. The surface tension versus concentration curve, presented in Fig. 2, exhibits a sharp inflection which confirms high purity of the surface active agent.

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REFERENCES

1. Kelly, J., and H. L. Greenwald, J. Phys. Chem. *62*, 1096–1098 (1958).
2. Becher, P., J. Colloid Sci. *16*, 49–56 (1961).
3. Schick, M. J., S. M. Atlas and F. R. Eirich, J. Phys. Chem. *66*, 1326–1333 (1962).
4. Crook, E. H., D. B. Fordyce and G. F. Trebbi, J. Phys. Chem. *67*, 1987–1994 (1963).
5. Mansfield, R. C., and J. E. Locke, JAOCS *41*, 267–272 (1964).
6. Winton, J., Chemical Week, May 30, 111–126 (1964).
7. Sandulesco, G., and A. Girard, Bull. Soc. Chim. France *47*, 1300–1314 (1930).
8. Rempp, P., Bull. Soc. Chim. France, 844–847 (1957).
9. Perry, S. Z., and H. Hibbert, Can. J. Chem. *14*(B), 77–83 (1936).
10. Jaruzelski, J. J., M. Kolobielski and C. S. Sheppard, US Patents 3,184,425 and 3,205,270 (1965).
11. Gingras, B. A., and C. H. Bayley, Can. J. Chem. *35*, 599–604 (1957).

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