SURFACTANTS & DETERGENTS TECHNICAL

Synthesis and Properties of Destructible Anionic and Cationic Surfactants with a 1,3-Dioxolane Ring

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A convenient synthetic method for the preparation of destructible surfactants containing a 1,3-dioxolane ring with various substituents is described. The substituents include carboxylate, quaternary ammonium, and several aliphatic alkyl groups, such as hydrophilic or hydrophobic groups. These novel surfactants had good surface activity, and were easily hydrolyzed under acidic conditions. They also catalyzed aliphatic halide substitution.

Surfactants are useful for micellar reactions (1,2), emulsion polymerization (3,4), phase-transfer reactions (5,6), and other organic syntheses. However, the surfactants often form troublesome emulsions during extraction of the desired products from the reaction mixture. This causes difficulty in the isolation of the products, as well as the loss of certain desired characteristics. For example, the water-resistance of the polymers obtained may decrease. Because of this, destructible surfactants have come to be of interest in recent years (7–10). Some of these surfactants have been synthesized and found to be effective as catalysts, emulsifiers, or solubilizers, but these were obtained either by use of a complicated path of synthesis (7,9) and special reagents (10), or they are mixtures of several components with different hydophilicity (8). These problems limit the use of the surfactants. We have reported on the synthesis of 1,3-dioxolane derivatives, which are easily cleaved by acids, from ketones and epoxy compounds (11). Here, we report the synthesis of destructible surfactants with satisfactory properties by a simple method.

EXPERIMENTAL PROCEDURES

The ketones (except for 10-nonadecanone) and the epoxides used were all commercially available.

Synthesis of 10-nonadecanone. 10-Nonadecanone was prepared by a modification of a published method (12). First, 52.2 g (0.30 mol) of decanoic acid was condensed at 300–320°C in the presence of 6.0 g (0.15 mol) of MgO. The crude product was purified by recrystallization from ethanol to give 27.2 g of 10-nonadecanone (yield, 64%) as white scales, mp 59°C (13); ^{1}H NMR (CDCl$_3$, δ) 0.88 (t, 6H, CH$_3$, J = 6 Hz), 1.25 (s, 28H, CH$_2$), 2.30 (t, 4H, CH$_2$C=O, J = 7 Hz); IR 2920, 1700, 1460, 1380 cm^{-1}.

Synthesis of 1,3-dioxolane ester compounds (**1a**–**e**). 2-Methyl-2-undecyl-4-ethoxycarbonyl-5-methyl-1,3-dioxolane (**1a**) was prepared by a procedure that was used for the other 1,3-dioxolane ester compounds as well. In the synthesis, 19.8 g (0.1 mol) of 2-tridecanone, 1.5 g (0.01 mol) of BF$_3$·Et$_2$O, and 30 ml of dry carbon tetrachloride were placed in a 200-ml three-necked flask fitted with a dropping funnel, a thermometer, and a condenser. Then, 13.0 g (0.10 mol) of ethyl 2,3-epoxybutyrate was added dropwise into the mixture and stirred for 30 min. The mixture was kept at 45–55°C. After the mixture was stirred at approximately 50°C for 4 hr, 40 ml of H$_2$O was added. The cooled mixture was extracted with 150 ml of diethyl ether. The organic layer that was separated was then dried over anhydrous sodium sulfate and the solvent was removed. The residue was fractionated by distillation under reduced pressure to give 8.8 g (44%) of unreacted 2-tridecanone and 16.1 g of product **1a** (yield, 49%), bp 160°C/4 mm Hg.

Synthesis of carboxylate-type surfactants (**2a**–**e**). Sodium (2-undecyl-2-methyl-5-methyl-1,3-dioxolane-4-yl)-carboxylate (**2a**) was prepared by a procedure used for the other carboxylate-type surfactants as well. In this procedure, 6.89 g (21 mmol) of **1a**, 0.80 g (20 mmol) of sodium hydroxide, and 75 ml of ethanol were placed in a 200-ml round-bottomed flask equipped with a reflux condenser. The mixture was refluxed and stirred for 4 hr. After the reaction mixture had cooled, 75 ml of water was added and the mixture was extracted with 50 ml of diethyl ether. The aqueous layer was separated, and evaporation of the solvents under reduced pressure gave 5.70 g of **2a** (yield, 91%). On concentration of the organic layer under reduced pressure, 0.19 g (3%) of unreacted **1a** was recovered.

Synthesis of bromomethyl 1,3-dioxolane compounds (**3a**–**d**). 2-Methyl-2-undecyl-4-bromomethyl-1,3-dioxolane (**3a**) was prepared by a procedure that was used for the other bromomethyl 1,3-dioxolane compounds, as well. First, 19.8 g (0.1 mol) of 2-tridecanone, 1.5 g (0.01 mol) of BF$_3$·Et$_2$O and 30 ml of dry carbon tetrachloride were placed in a 200-ml three-necked flask fitted with a dropping funnel, a thermometer, and a condenser. The mixture was then stirred and kept cooler than 60°C while 16.4 g (0.12 mol) of 1-bromo-2,3-epoxypropane was added dropwise during a one hour time period. After the mixture was stirred at 50°C for 6 hr, 40 ml of water was added and the cooled mixture was extracted wth 150 ml of diethyl ether. The organic layer was separated and dried over anhydrous sodium sulfate to remove the solvent. The crude product was purified by fractional distillation at 115°C and 3 mm Hg to give 23.7 g of **3a** (yield, 84%) as a colorless liquid.

Synthesis of (N,N-diethylaminomethyl)-1,3-dioxolane derivatives (**4a**–**d**). 2-Methyl-2-undecyl-4-diethylaminomethyl-1,3-dioxolane (**4a**) was also prepared by the procedure used for the other (N,N-diethylaminomethyl)-1,3-dioxolane derivatives. Here, 5.03 g (15 mmol) of **3a**, 3.29 g (45 mmol) of anhydrous diethylamine, and 4 ml of dry benzene were heated in a sealed tube at 140°C for 12 hr. The precipitate was filtered off and washed with benzene. The solvent was removed under reduced pressure, and 5.17 g of crude product was obtained. Of this, 4.00 g was purified by

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Kugel-Rhor distillation at 150°C and 4 mm Hg to give 3.77 g of **4a** (yield, 90%) as a pale yellow liquid.

Synthesis of surfactants of the quaternary ammonium salt type (**5a–d**). 2-Methyl-2-undecyl-4-triethylammoniomethyl-1,3-dioxolane iodide (**5a**) was prepared by a procedure used for the other surfactants of the quaternary ammonium salt type as well. In the synthesis, 2.41 g (7.4 mmol) of the tertiary amine **4a**, 1.38 g (8.8 mmol) of ethyl iodide, and 4 ml of 2-propanol were heated in a sealed tube at 80°C for 12 hr. The solvent was removed under reduced pressure and recrystallized from acetone/diethyl ether to give 3.20 g of **5a** (yield, 90%) as a white crystalline powder.

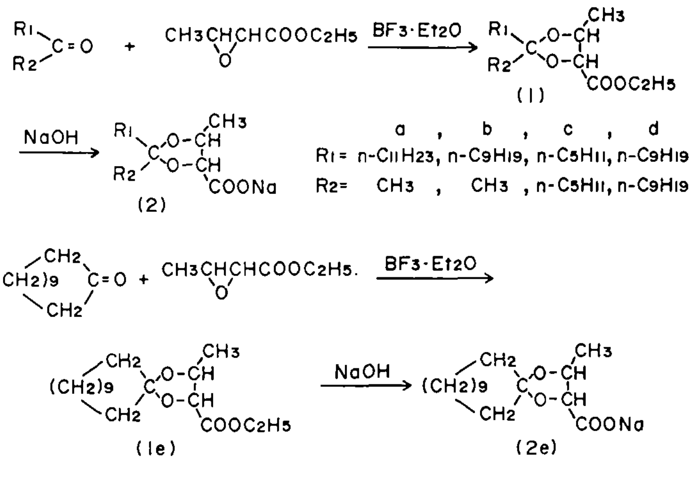
Surface tension measurements. The purified surfactants were dissolved in 5 mM aqueous NaOH. Surface tension was measured with a Du Nouy tensiometer at 25°C.

Catalytic activity in halide displacement reaction. To measure the catalytic activity, 2.6×10^{-1} mmol of surfactant, 1.0 g (5.2 mmol) of 1-bromooctane, 2.0 g (6.7 mmol) of sodium iodide, 0.5 g of dodecane as an internal standard for gas-liquid chromatography (GLC), and 3 ml of H_2O were placed in a 10-ml cylindrical vessel equipped with a Liebig condenser and were stirred at 100°C for 24 hr or 60°C for 6 hr. The 1-iodooctane generated was assayed by GLC (Shimadzu GC-R1A, OV-1, 1.5% on Chromosorb; 2-m column, 110°C).

Hydrolysis of surfactants. The destructibility of the surfactants was evaluated by weighing the 2-tridecanone that was obtained when the surfactant was brought into contact with the aqueous hydrochloric acid.

150 mg (0.31 mmol) of **5a**, 25 ml of aqueous 5% (w/w) HCl, and 25 ml of diethyl ether were added to a separate funnel. The mixture was shaken and left for 3 hr at 25°C. The organic layer was separated, and the aqueous layer was further extracted with three 20-ml portions of diethyl ether. The combined ether solution was dried over anhydrous sodium sulfate and evaporated under reduced pressure, giving 62 mg (0.31 mmol) of 2-tridecanone.

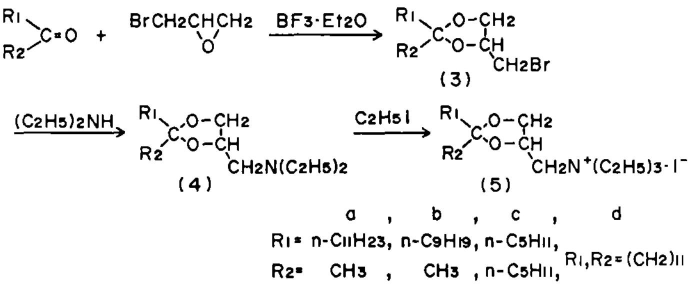
Then 407 mg (1.26 mmol) of **2a**, 25 ml of aqueous 5% (w/w) HCl, and 25 ml of ether were placed in a 100-ml flask equipped with a stopper. The mixture was stirred at 25°C for 24 hr, and treated as described above to give 250 mg (1.26 mmol) of 2-tridecanone.



SCHEME 1

RESULTS AND DISCUSSION

Surfactants were prepared by the sequences outlined in Schemes 1 and 2. The results of synthesis and analytical data from the products are summarized in Tables 1–7. The addition of epoxides to cyclododecanone produced waxy solids (**1e** and **3d**) that could be purified by crystallization from hexane/ethanol. No attempt was made to optimize the reaction conditions. Lower yields of quater-



SCHEME 2

TABLE 1

Syntheses of Compounds 1a–e and 2a–e

Compound	Yield (%)	Compound	Yield (%)
1a	49	**2a**	91
1b	37	**2b**	91
1c	26	**2c**	90
1d	33	**2d**	75
1e	47	**2e**	86

TABLE 2

Syntheses of Compounds 3a–d, 4a–d, and 5a–d

Compound	Yield (%)	Compound	Yield (%)	Compound	Yield (%)
3a	84	**4a**	90	**5a**	90
3b	83	**4b**	80	**5b**	26
3c	69	**4c**	80	**5c**	35
3d	60	**4d**	80	**5d**	60

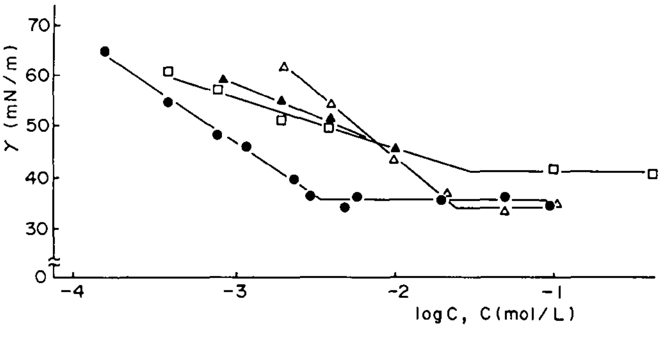


FIG. 1. Surface tension (γ) vs. log molar concentration for 2a, b, c, and e. 2a, ●; 2b, △; 2c, ▲; 2e, □.

TABLE 3

Analytical and Spectral Data of Compounds 1a-e

Compound	Elemental analysis Found (Calcd) C (%)	H (%)	^1H NMR ($CDCl_3$, δ)[a]	IR (cm^{-1})
1a	69.76 (69.47)	11.03 (11.05)	0.90 (t, 3H, CH_3, J = 6 Hz), 1.10-1.70 (m, 26H, CH_2, $COOCCH_3$, and CH_3C-CCOO), 1.57 (s, 3H, $CH_3C\langle{}^{O}_{O}$), 4.25 (q, 2H, $COOCH_2$, J = 7 Hz), 4.57 (m, 2H, OCHCHO)	2920 1760 1100
1b	67.96 (67.96)	10.90 (10.74)	0.90 (t, 3H, CH_3, J = 6 Hz), 1.10-1.70 (m, 22H, CH_2, $COOCCH_3$, and CH_3C-CCOO), 1.57 (s, 3H, $CH_3\langle{}^{O}_{O}$), 4.25 (q, 2H, $COOCH_2$, J = 7 Hz), 4.55 (m, 2H, OCHCHO)	2920 1760 1100
1c	67.70 (67.96)	10.85 (10.74)	0.90 (t, 6H, CH_3, J = 6 Hz), 1.10-1.70 (m, 22H, CH_2, $COOCCH_3$, and CH_3C-CCOO), 4.25 (q, 2H, $COOCH_2$, J = 7 Hz), 4.55 (m, 2H, OCHCHO)	2920 1760 1100
1d	72.42 (72.77)	11.72 (11.72)	0.90 (t, 6H, CH_3, J = 6 Hz), 1.10-1.70 (m, 38H, CH_2, $COOCCH_3$, and CH_3C-CCOO), 4.25 2H, $COOCH_2$, J = 7 Hz), 4.55 (m, 2H, OCHCHO)	2920 1760 1100
1e	69.09 (69.12)	10.42 (10.32)	1.10-1.70 (m, 28H, CH_2, $COOCCH_3$, and CH_3C-CCOO), 4.20 (q, 2H, $COOCH_2$, J 7 Hz), 4.50 (m, 2H, OCHCHO)	2920 1760 1100

[a]Tetramethylsilane (TMS) was used as the internal standard.

TABLE 4

Analytical and Spectral Data of Compounds 2a-e

Compound	Elemental analysis Found (Calcd) C (%)	H (%)	^1H NMR (D_2O, δ)[a]	IR (cm^{-1})
2a	63.20 (63.33)	9.53 (9.69)	0.90 (t, 3H, CH_3, J = 6 Hz), 1.05 1.80 (m, 23H, CH_2 and CH_3C-CCOO), 1.50 (s, 3H, $CH_3C\langle{}^{O}_{O}$), 3.95 (m, 1H, MeCH-O), 4.50 (d, 1H, $OCHCOO^-$, J = 3 Hz)	2920 1610 1100
2b	61.21 (61.20)	9.53 (9.34)	0.90 (t, 3H, CH_3, J = 6 Hz), 1.10-1.80 (m, 19H, CH_2 and CH_3C-CCOO), 1.50 (s, 3H, $CH_3C\langle{}^{O}_{O}$), 3.95 (m, 1H, MeCH-O), 4.50 (d, 1H, $OCHCOO^-$, J = 3 Hz)	2920 1610 1100
2c	61.23 (61.20)	9.55 (9.34)	0.90 (t, 6H, CH_3, J = 6 Hz), 1.10-1.90 (m, 19H, CH_2 and CH_3C-CCOO), 4.00 (m, 1H, MeCH-O), 4.55 (d, 1H, $OCHCOO^-$, J = 3 Hz)	2920 1610 1100
2d[b]	67.63 (67.95)	10.82 (10.66)	0.90 (t, 6H, CH_3, J = 6 Hz), 1.05-1.70 (m, 35H, CH_2 and CH_3C-CCOO), 4.15 (m, 1H, MeCH-O), 4.55 (d, 1H, $OCHCOO^-$, J = 3 Hz)	2920 1610 1100
2e	62.64 (62.72)	9.04 (8.88)	1.10-2.00 (m, 25H, CH_2 and CH_3C-CCOO), 4.00 (m, 1H, MeCH-O), 4.55 (d, 1H, $OCHCOO^-$, J = 3 Hz)	2920, 1610 1100

[a] Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as the internal standard.
[b]TMS was used as the internal standard and Me_2SO-d^6 as solvent.

TABLE 5

Spectral Data of Compounds 3a-d

Compound	^{1}H NMR (CDCl$_3$, δ)[a]	IR (cm^{-1})
3a	0.88 (t, 3H, CH_3, J = 6 Hz), 1.10-1.60 (m, 23H, CH_2 and $CH_3C{<}^{O}_{O}$), 3.22-4.32 (m, 5H, $OCHCH_2O$ and CH_2Br)	2920 1110
3b	0.90 (t, 3H, CH_3, J = 6 Hz), 1.10-1.85 (m, 19H, CH_2 and $CH_3C{<}^{O}_{O}$), 3.10-4.60 (m, 5H, $OCHCH_2O$ and CH_2Br)	2920 1110
3c	0.90 (t, 6H, CH_3, J = 6 Hz), 1.10-1.90 (m, 16H, CH_2) 3.05-4.60 (m, 5H, $OCHCH_2O$ and CH_2Br)	2920 1100
3d	1.20-1.90 (m, 22H, CH_2), 3.08-4.50 (m, 5H, $OCHCH_2O$ and CH_2Br)	2920 1110

[a] TMS was used as the internal standard.

TABLE 6

Analytical and Spectral Data of Compounds 4a-d

Compound	Elemental analysis Found (Calcd) C (%)	H (%)	N (%)	^{1}H NMR (CDCl$_3$, δ)[a]	IR (cm^{-1})
4a	73.58 (73.34)	12.77 (12.61)	4.24 (4.27)	0.70-1.70 (m, 32H, CH_3, CH_3, CH_3C-N, $CH_3C{<}^{O}_{O}$, and CH_2), 2.55 (q, 6H, NCH_2, J = 7 Hz), 3.20-4.40 (m, 3H, $OCHCH_2O$)	2920 1210 1070
4b	72.20 (72.19)	12.29 (12.45)	4.65 (4.68)	0.70-1.70 (m, 28H, CH_3, CH_3C-N, $CH_3C{<}^{O}_{O}$, and CH_2), 2.60 (q, 6H, NCH_2, J = 7 Hz), 3.20-4.40 (m, 3H, $OCHCH_2O$)	2920 1210 1080
4c	72.16 (72.19)	12.37 (12.45)	4.68 (4.68)	0.70-1.70 (m, 28H, CH_3, CH_3C-N, and CH_2), 2.60 (q, 6H, NCH_2, J = 7 Hz), 3.20-4.40 (m, 3H, $OCHCH_2O$)	2920 1210 1090
4d	73.29 (73.26)	11.92 (11.97)	4.63 (4.50)	1.00 (t, 6H, CH_3C-N, J = 7 Hz), 1.20-1.80 (m, 22H, CH_2), 3.55 (q, 6H, NCH_2, J = 7 Hz), 3.20-4.40 (m, 3H, $OCHCH_2O$)	2920 1210 1080

[a] TMS was used as the internal standard.

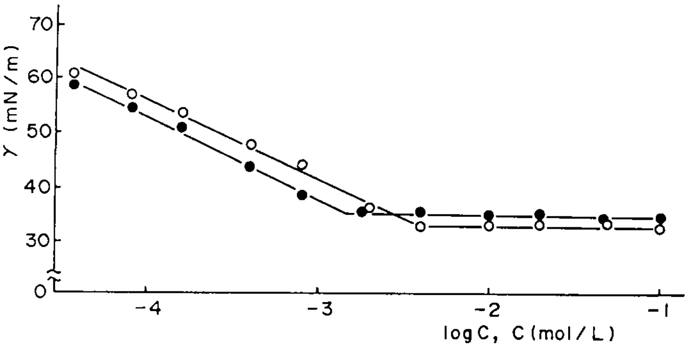
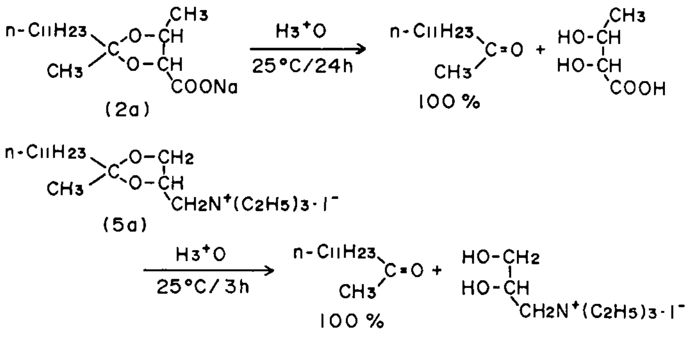


FIG. 2. Surface tension (γ) vs. log molar concentration for 5a and b. 5a, ●, at 40°C; 5b, ○, at 25°C.



SCHEME 3

TABLE 7

Analytical and Spectral Data of Compounds 5a-d

Compound	Elemental analysis Found (Calcd) C (%)	H (%)	N (%)	^1H NMR ($CDCl_3$, δ)[a]	IR (cm^{-1})
5a	54.57 (54.65)	9.62 (9.59)	2.80 (2.90)	0.88 (t, 3H, CH_3, J = 6 Hz), 1.10-1.85 (m, 32H, $CH_3C\text{-}N^+$, CH_2, and $CH_3C{<}^{O}_{O}$), 3.65 (q, 8H, $CH_2\text{-}N^+$, J = 7 Hz), 4.00-4.80 (m, 3H, $OCHCH_2O$)	2920 1160 1080
5b	52.74 (52.74)	9.25 (9.29)	3.07 (3.08)	0.88 (t, 3H, CH_3, J = 6 Hz), 1.10-1.85 (m, 28H, $CH_3C\text{-}N^+$, CH_2, and $CH_3C{<}^{O}_{O}$), 3.65 (q, 8H, $CH_2\text{-}N^+$, J = 7 Hz), 4.00-4.80 (m, 3H, $OCHCH_2O$)	2920 1160 1080
5c	52.75 (52.74)	9.27 (9.29)	3.14 (3.08)	0.88 (t, 6H, CH_3, J = 6 Hz), 1.10-1.80 (m, 25H, $CH_3C\text{-}N^+$ and CH_2), 3.65 (q, 8H, $CH_2\text{-}N^+$, J = 7 Hz), 4.00-4.80 (m, 3H, $OCHCH_2O$)	2920 1160 1090
5d	53.90 (53.96)	9.36 (9.06)	3.10 (3.00)	0.90-1.90 (m, 31H, CH_3, $CH_3C\text{-}N^+$ and CH_2), 3.65 (q, 8H, $CH_2\text{-}N^+$, J = 7 Hz), 3.90-4.90 (m, 3H, $OCHCH_2O$)	2920 1160 1090

[a] TMS was used as the internal standard.

TABLE 8

Halide Displacement of 1-Bromooctane to 1-Iodooctane[a,b]

Catalyst	Yield (%)	Catalyst	Yield (%)
2a	35	5a	70
2b	40	5b	58
2c	50	5c	55
2d	30	5d	6
2e	8	TBAB[c]	14

[a] 2a-e were at 100°C for 24 hr.

[b] 5a-d were at 60°C for 6 hr.

[c] Tetrabutylammonium bromide was at 60°C for 6 hr.

nizations of methyl-nonyl and dipentyl derivatives were due to the poor yield during crystallization from the solvent. The process of synthesis was economical, and the starting materials were all commercially available.

The surface tension, γ, of aqueous solutions of the surfactants at 25°C, was plotted against the logarithm of the concentration (Figs. 1 and 2). The curves had inflection points, and the surface activity of these surfactants increased as the length of the alkyl chain increased. Measurement of the surface tension of the dipentyl derivative 2c failed because of its limited solubility in water, and also because the critical micelle concentration was not obtained. The surfactants **2d**, **5c**, and **5d** are not shown because of their slight solubility in water.

Catalysis by the surfactants in the halogen exchange reaction of 1-bromooctane with sodium iodide was studied. The catalytic activity increased as the length of the alkyl chain of the surfactants increased (Table 8). The activity of the cationic surfactants was greater than that of the anionic surfactants. The reason was probably that the reaction is accelerated more by the phase-transfer catalytic action of the cationic surfactants.

Examination of the destructibility of these surfactants gave the results shown in Scheme 3. Compound 5a was emulsified in a hydrochloric acid solution when shaken in a separatory funnel. After 3 hr, the solution had separated into two phases, and the surfactant had decomposed. The anionic surfactant 2a did not decompose when occasionally shaken during a 24 hr time period under the same conditions. This compound had low surface activity for emulsification in acidic solution; and the carboxylic acid compound formed on acidification of the anionic surfactant with hydrochloric acid that was highly soluble in the diethyl ether. However, when the same mixture was continuously stirred for 24 hr by a magnetic stirrer in a flask with a stopper, the anionic surfactant decomposed completely.

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