Synthesis of Surfactants from 1-Olefins *via* Bromoalkoxylation Reaction

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Alkyl β-bromoalkyl ether derivatives (I) (isomeric mixture) were prepared by the bromoalkoxylation reaction of olefins with *N*-bromosuccinimide (NBS) and appropriate alcohols. A series of nonionic surfactants was obtained by the reaction of I with glycols or ethanolamines. The distribution of two isomers (Markovnikov-type and anti-Markovnikov-type) in products was found to be slightly different from that in the starting material (I). Surface properties of several nonionic surfactants, which were prepared from I, were presented and discussed based on the difference in the structures.

KEY WORDS: Bromoalkoxylation, Markovnikov, *N*-bromosuccinimide, nonionic, olefin, surfactant, synthesis.

The bromoalkoxylation reaction of olefins with *N*-bromosuccinimide (NBS) has been known to afford the corresponding alkyl β-bromoalkyl ether derivatives in high yields as a mixture of Markovnikov and anti-Markovnikov adducts (1). This reaction is regarded as an ionic one having a bromonium ion as a transient intermediate (1). We noted the usefulness of this reaction and applied it to the syntheses of alkyl crown ethers (2,3) and bromomethyl crown ethers (4,5). If a long-chain alkyl olefin is chosen as a starting material for the bromoalkoxylation reaction, a lipophilic substance having a reactive group is obtained. Introduction of a hydrophilic group to it gives an amphipathic substance. Especially, a combination of a long-chain olefin with a long-chain alcohol constitutes a double-chain structure, which has recently attracted attention as bilayer-forming materials (6-8).

In order to clarify the effectiveness of the bromoalkoxylation reaction as a key reaction for preparing amphipathic substances, we describe the reaction of long-chain olefins with NBS and alcohols, the reactivity of alkyl β-bromoalkyl ethers with a variety of nucleophiles, and the surface properties of the nonionic surfactants obtained.

EXPERIMENTAL PROCEDURES

Synthesis of long-chain alkyl β-bromoalkyl ether (I). A mixture of long-chain olefin (0.15 mol), alcohol (2.0 mol), and NBS (0.05 mol) was stirred at 50°C for 5 hr. After the excess olefin and alcohol were removed, water (500 mL) was added to the residue. The insoluble matter was removed by filtration, and the filtrate was washed with water (150 mL × 4) and dried over $MgSO_4$. The organic layer was concentrated and purified by distillation *in vacuo* to give a slightly yellow oil. The results are summarized in Table 1.

*Synthesis of **II** by the reaction of **I** with glycols.* After sodium metal (10 mmol) was dissolved in the glycol (70 mmol), **I** (7 mmol) was added drop by drop to the mixture and the mixture was stirred at 140°C for 24 hr. After cooling the mixture to room temperature, it was neutralized with diluted HC1 and then was made slightly basic with 10% Na_2CO_3 aqueous solution. Water (100 mL) was added to the mixture and extracted with ether (200 mL × 3). The combined organic layer was dried, concentrated and purified by distillation *in vacuo.* In the case of the reaction with hexaethylene glycol, *t*-butyl alcohol was used as the solvent. The results are shown in Table 2.

*Synthesis of **III** by the reaction of **I** with amines.* A mixture of **I** (7 mmol) and ethanolamine or diethanolamine (70 mmol) was stirred at 150°C for 24 hr. After cooling the mixture to room temperature, 10% Na_2CO_3 aqueous solution (300 mL) was added to the mixture and it was extracted with dichloromethane (150 mL × 3). The organic layer was dried over $MgSO_4$, concentrated and purified by distillation *in vacuo.* The results are shown in Table 3.

*Concentration of Markovnikov-type adduct (**I-M**) by treating the mixture (**I**) with base.* A mixture of potas-

TABLE 1

Synthesis of Compounds I

Compd no.	R	R′	Yield (%)[a]	**I-M** (%)[b]	Bp (°C/torr)[c]
Ia[d]	C_6H_{13}	C_6H_{13}	90	(63)	80/0.04
Ib	C_8H_{17}	C_4H_9	91	(67)	80/0.04
Ic	$C_{10}H_{21}$	C_2H_5	75	(66)	80/0.04
Id	C_8H_{17}	C_8H_{17}	94	(64)	120/0.05
Ie	$C_{10}H_{21}$	$C_{10}H_{21}$	89	(68)	160/0.08
If	$C_{12}H_{25}$	$C_{12}H_{25}$	81	(69)	175/0.03

[a] Olefin : NBS : alcohol = 3 : 1 : 40 (mol ratio). The isolated yields are calculated based on NBS.

[b] The content of the Markovnikov adduct.

[c] Kugel-rohr distillation.

[d] NMR ($CDCl_3$) δ 0.88 (*t*, 6H), 1.1-2.0 (*m*, 18H), and 3.2-4.2 (*m*, 5H); infrared (IR) (neat, cm^{-1}) 2930, 2850, 1460, 1380, and 1100.

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TABLE 2

Synthesis of Compounds II

Compd no.	R	R′	n	Yield (%)	Bp (°C/torr)[a]
IIa[b]	C_8H_{17}	C_4H_9	1	49[c]	120/0.05
IIb	C_8H_{17}	C_4H_9	3	48[c]	140/0.04
IIc	C_6H_{13}	C_6H_{13}	5	13[d]	185/0.05
IId	C_8H_{17}	C_4H_9	5	17[d]	170/0.04
IIe	$C_{10}H_{21}$	C_2H_5	5	15[d]	180/0.05

[a] Kugel-rohr distillation.

[b] NMR ($CDCl_3$) δ 0.78-1.02 (*m*, 6H), 1.1-1.8 (*m*, 18H), 2.2 (*bs*, 1H) 3.3-3.9 (*m*, 13H); IR (neat, cm^{-1}) 3400, 2940, 2860, 1460, 1380, and 1100.

[c] Reaction conditions: 140°C, 24 hr, Na.

[d] Reaction conditions: 80°C, 36 hr, *t*-BuONa/*t*-/BuOH.

TABLE 3

Synthesis of Compounds III

Compd no.	R	R′	R″	Yield (%)	**III-M** (%)[a]
IIIa[b]	C_8H_{17}	C_4H_9	H	79	(71)
IIIb	C_8H_{17}	C_4H_9	HO (CH_2CH_2)	72	(74)
IIIc	$C_{12}H_{25}$	$C_{12}H_{25}$	HO (CH_2CH_2)	65	(78)

[a] The content of the isomer derived from **I-M**.

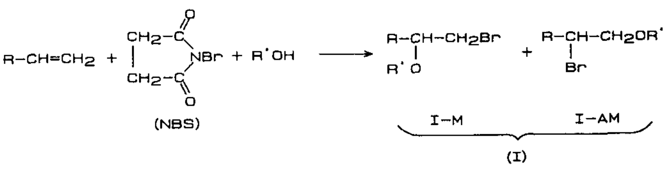
[b] NMR ($CDCl_3$) δ 0.80-1.04 (*m*, 6H), 1.1-1.8 (*m*, 18H), 2.22 (*bs*, 2H), 2.6-2.9 (*m*, 3.7H), and 3.2-3.8 (*m*, 5.3H); IR (neat, cm^{-1}) 3300, 2940, 2870, 1460, 1380, and 1100.

sium *t*-butoxide (11.2 g, 0.1 mol), methyltrioctylammonium chloride (0.81 g, 2 mmol), and **Id** (13.9 g, 0.04 mol) was stirred at room temperature for 3 hr. The mixture was neutralized with diluted HCl and then was made slightly basic with 10% Na_2CO_3 aqueous solution. Water (250 mL) was added to the mixture and it was extracted with hexane (250 mL × 2). The combined organic layer was dried over $MgSO_4$, concentrated and purified by chromatography over silica gel (hexane) to give **Id-M** as a slightly yellow oil (5.57 g, 40% yield). The content of the Markovnikov adduct in this product (**Id-M**) was calculated to be 93% based on nuclear magnetic resonance (^1H NMR). According to the similar procedure, **If-M** (95% purity) was also obtained from **If** in a 48% yield.

Measurement of surface properties. The cloud point (T_{cp}) was determined visually with a 1% aqueous solution of the surfactant. The surface tension of a surfactant solution was measured with a Wilhelmy tensiometer using a series of aqueous solutions at various concentrations. The foaming properties were evaluated with a 0.1% aqueous solution of surfactant by the semi-micro TK (Tjutjunikow-Kassjanowa) method (9). This method consists of measuring the foam volume produced by bubbling 250 mL of air over a period of 50 sec into 5 mL of the test solution.

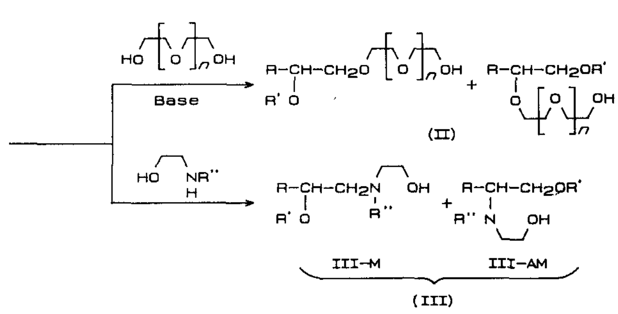
RESULTS AND DISCUSSION

Synthesis. The bromoalkoxylation reaction of the long-chain olefin with NBS and the excess alcohol gave the corresponding alkyl β-bromoalkyl ether derivative (**I**) as a mixture of Markovnikov-type (**I-M**) and anti-Markovnikov-type (**I-AM**) in a high yield (Scheme 1). The ratios of two isomers were determined based on the integrated values of ^1H NMR data. The results are shown in Table 1. The contents of **I-M** are 63-69% and are regarded to be almost constant in spite of the different alkyl groups.



SCHEME 1

In order to evaluate the reactivity of **I**, the reactions with glycols and ethanolamines were carried out (Scheme 2). The results are shown in Tables 2 and 3. The yields of the reaction of **Ib** with diethylene and tetraethylene glycols were 49% and 48%, respectively (Table 2). On the other hand, the yields of the reaction of **Ib** with ethanolamine and diethanolamine were 79% and 72%, respectively (Table 3). The contents of M-type of **III** were also calculated based on the ^1H NMR data. Though the content of M-type of **Ib** was 67%, the reaction products, **IIIa** and **IIIb**, contained 71% and 74% of M-type isomer, respectively. These results showed a slight increase of the content of M-type isomer in products. In elimination of hydrogen bromide from alkyl bromide, the reaction rate for the secondary bromide is known to be much faster than that for the primary one. Accordingly, the increase of the content of M-type isomer means the increase of the extent of the elimination compared with the substitution. The difference in the content of M-type isomer between **Ib** and **IIIa** or **IIIb** was, however, rather small. The difference in the yields between **II** and **III** also reflects the difference in the extent of the elimination reaction. This elimination reaction can be applied for preparing the alkyl bromide (**I**) having a higher content of M-type



SCHEME 2

isomer. In the presence of a phase transfer catalyst, **I** was reacted with potassium *t*-butoxide. In the course of the reaction, the starting material was recovered and purified. The yields recovered were 40% for **Id** and 48% for **If**. The contents of M-type isomer obtained from **Id** and **If** were 93% and 95%, respectively.

Surface properties. Surface properties and foaming properties of **IIc**, **IId** and **IIe** are summarized in Tables 4 and 5, respectively, with the data for **IV**, which is chosen as the reference. **IIc**, **IId** and **IIe** are nonionic surfactants and possess the same molecular weight.

Generally speaking, when the position of the hydrophilic group locates near the center of the hydrophobic group in an ionic surfactant, which consists of only one-chain alkyl group, the critical micelle concentration (CMC) of the surfactant increases (11). We also found the similar trend in the case of the surfactants that are half-ester derivatives of maleic acid (12). As for nonionic surfactants, the comparison of the surface properties of the ethylene oxide adducts of 1- and 7-tridecanols was reported by Kuwamura *et al.* (13), though the ethylene oxide chains were not homogeneous. The latter showed a higher CMC and a lower T_{cp} compared with the former. The comparison of the properties among **IIc**, **IId** and **IIe**, which have the same oxyethylene chain, is expected to give important information about the relation between the structure and the surface properties. Although it is not easy to discriminate the boundary between the hydrophilic and the lipophilic parts because they contain an oxygen atom in the double chain structure, the position of the hydrophilic group approaches the center of the hydrophobic group as the following order: **IIe** > **IId** > **IIc**. T_{cp} decreases according to the same order: **IIe** > **IId** > **IIc**. The solubility of nonionic surfactants in water is determined by the extent of hydration to the ether oxygen of the oxyethylene chain. The hydration to the ether oxygen, which is the nearest to the hydrophobic group, is considered to be sterically hindered by the bulkiness of the hydrophobic group (14). These results are reasonably explained by considering that the extent of the steric hindrance increases when the hydrophilic group approaches the center of the hydrophobic group. The CMC of **IId** was higher than that of **IIe** (Fig. 1). The structure of **IIe** is considered to have an ethoxy group to the β-position of hexaethylene glycol monododecyl ether (**IV**). Introduction of ethoxy group lowered the hydrophlicity estimated by the T_{cp} data and increased the CMC value possibly because of making the branched structure. The branched structures also lowered the foaming properties. The fact that the position of the hydrophilic group to the hydrophobic group highly affected the surface properties strongly suggests the importance of molecular design of the surfactants.

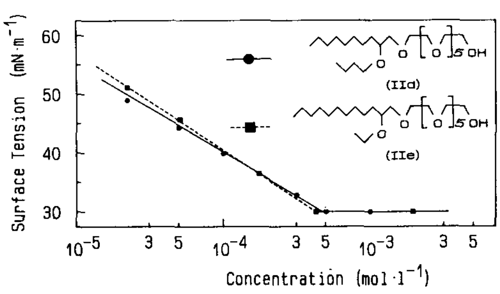


FIG. 1. The surface tension-concentration plots for IId **and** IIe.

TABLE 4

Surface Properties of Compounds IIc, IId, IIe **and** IV

Compd no.	T_{cp}(°C)	10^4 CMC (mol · l^{-1})	γ_{CMC} (mN · m^{-1})	10^2A (nm^2)
IIc	4	—	—	—
IId	27	4.6	30	61
IIe	39	4.0	30	56
IV[a]	49	0.85	32	52

[a] Hexaethylene glycol monododecyl ether: reference 10.

TABLE 5

Foaming Properties of Compounds IId, IIe **and** IV

		Foaming volume/mL					
Compd no.	Temp. (°C)	0″	30″	1′	1′ 30″	2′	5′
IId	20	160	60	20	0	—	—
IIe	20	90	30	10	0	—	—
IV[a]	20	250	220	160	140	100	0

[a]Hexaethylene glycol monododecyl ether; reference 10.

REFERENCES

1. Jovtscheff, A., H. Reinheckel, K. Haage and R. Pomakowa, *Monatsh. 97*:1620 (1966).
2. Okahara, M., M. Miki, S. Yanagida, I. Ikeda and K. Matsushima, *Synthesis* 854 (1977).
3. Mizuno, T., Y. Nakatsuji, S. Yanagida and M. Okahara, *Bull. Chem. Soc. Jpn. 53*:481 (1980).
4. Nakamura, T., Y. Nakatsuji and M. Okahara, *J. Chem. Soc. Chem. Commun.* 219 (1981).
5. Nakatsuji, Y., T. Mori and M. Okahara, *Tetrahedron Lett. 25*:2171 (1984).
6. Kunitake, T., and Y. Okahata, *J. Am. Chem. Soc. 102*:549 (1980) and references cited therein.
7. Okahata, Y., and T. Seki, *Yukagaku 34*:820 (1985).
8. Okahata, Y., *Acc. Chem. Res. 19*:57 (1986) and references cited therein.
9. Yano, W., and W. Kimura, *Yukagaku 11*:138 (1962).
10. Masuyama, A., K. Akiyama and M. Okahara, *J. Am. Oil Chem. Soc. 64*:1040 (1987).
11. Rosen, M.J., *Surfactants and Interfacial Phenomena*, 2nd edn., John Wiley & Sons, New York, NY, 1988, p. 133.
12. Ikeda, I., S. Kawamuko, M. Okahara and S. Komori, *Nippon Kagaku Kaishi* 261 (1976).
13. Kuwamura, T., and H. Takahashi, *Proc. Intern. Congr. Surface Active Substances* 7th (Moscow), Vol. 1, 1976, p. 33.
14. Aizawa, M., and S. Suzuki, in *Surfactants: Properties, Application, Chemical Ecology*, edited by A. Kitahara, Y. Tamai, S. Hayano and I. Hara, Kodansha Scientific, Tokyo, Japan, 1979, p. 15.

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