# Improvement of the Phase-Transfer Catalysis Method for Synthesis of Glycidyl Ether

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**ABSTRACT:** A convenient procedure for the synthesis of aliphatic alkylglycidyl ether has been studied. It has been found that the improved preparation of the alkylglycidyl ether can be achieved by using fatty alcohol such as octanol and octadecanol with epichlorohydrin in the presence of phase-transfer catalyst (PTC) such as 1-alkyloxypropan-2-ol-3-trimethyl ammonium methylsulfate, 1-alkyloxypropan-2-ol-3-methyldiethanolammonium methylsulfate, alkyloxy-2-hydroxypropyldimethylamine and alkyloxy-2-hydroxypropyldiethanolamine, tetrabutylammonium bromide, etc. without water and other organic solvents. This method, carried out in solid phase/organic phase (reactants and product themselves), has the following merits: (i) producing the solid by-products such as sodium chloride and sodium hydroxide which are easily removed by simple filtration, (ii) saving the amount of reactants used such as sodium chloride and phase-transfer catalyst, and (iii) increasing the yields of glycidyl ethers. The yields of octylglycidyl ether and octadecylglycidyl ether are 92.0 and 91.7%, respectively. The amount of sodium hydroxide used can be saved by from 1.5 to 0.7 molar ratio with respect to octanol in comparison with those in the conventional method using PTC.

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**KEY WORDS:** Alkylglycidyl ether, epichlorohydrin, glycerol derivatives, non-solvent, phase-transfer catalyst, surface-modifying, surfactants, two phase reaction.

The derivatives of alkylglycidyl ether with a long alkyl chain are very important intermediates in physical and pharmaceutical applications such as manufacturing softeners, antistatic agents, emulsifiers (1), drugs (2), plastic additives (3), cosmetics, pseudoceramides (4), surface-modifying agents (5), gemini-type surfactants (6), and ether lipids (7). Generally, two methods for the syntheses of glycidyl ethers are well known: (i) Lewis acid method and (ii) phase-transfer catalyst (PTC) method. The Lewis acid method consists of the halohydrin intermediate process and the dehydrochlorination process, and it has two major disadvantages, i.e., halohydrin ether formation and polymerization (8). For these reasons, the PTC method using the reaction of alcohol with epichlorohydrin in aqueous sodium hydroxide solution and *n*-hexane is known to be more useful than the Lewis acid method for the preparation of glycidyl ether. Recently, Urata *et al.* (9) has reported the yield of 72–86% for various glycidyl ethers in the presence of phase-transfer catalyst (PTC). Also, the method of Najem and Borred on (10), using epibromohydrin instead of epichlorohydrin, has been reported to have yields of 40–90% for various glycidyl ethers (10).

However, the conventional PTC method generates some by-product solution that consists of sodium hydroxide and sodium chloride. It needs an additional special device for the solidification process of the aqueous mixture solution for reuse or disposal of these chemicals. Even though the method is generally useful in small-scale synthesis, it is inconvenient in large-scale preparation because of heavy consumption of time and expenses. Therefore, a new synthetic attempt has been made to improve the yield of glycidyl ether and the feasibility of its commercial production by avoiding the use of the aqueous sodium hydroxide solution. The new synthesis of the glycidyl ethers has been achieved by using just epichlorohydrin and octanol or octadecanol as starting materials without water and other (organic) solvents.

## EXPERIMENTAL PROCEDURES

*Materials*. Epichlorohydrin (99%), hexanol (99%), octanol (99%), dodecanol (98%), tetradecanol (97%), octadecanol (99%), sodium hydroxide (97%, 20–40 mesh beads), dimethylamine (40% solution), diethanolamine (99%), dimethyl sulfate (99%), tetrabutylammonium bromide (99%) (TBAB), and tetrabutylammonium hydrogensulfate (97%) (TBAH) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Cetyltrimethylammonium chloride (98%) (CETAC) and lauryldimethylbenzylammonium chloride (98%) (LMBAC) were obtained from Il-Chil Chemical Co. (Yeochun, Korea). All these chemicals were used without further purification.

*Gas chromatography (GC)*. The GC analyses were performed on an HP 5890 gas chromatograph (Hewlett-Packard, Wilmington, DE) equipped with flame-ionization detector (FID) and DB-1HT column (0.32 mm i.d. × 30 m) (J&W Scientific, Folsom, CA). The yields of the product and by-products for the synthesis of glycidyl ether were quantified by GC with naphthalene as an internal standard. The experimental conditions for GC are as follows: carrier gas, nitrogen; column pressure, 55 kPa; carrier gas flow rate, 2.2 mL/min; split ratio, 20:1; initial oven temperature, 60°C; initial time, 3 min; ramp, 12°C/min; final time, 360°C; final time, 30 min.

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**TABLE 1**
**Analytical and Nuclear Magnetic Resonance (NMR) Spectral Data for GE-8 and GE-18[a]**

| | $^1$H NMR ($CDCl_3$) | $^{13}$C NMR ($CDCl_3$) | HRMS |
|---|---|---|---|
| GE-8 | 3.71 (*dd, J* = 11.6 and 3.1 Hz, H-1), 3.49 (*m*, H-1′), 3.38 (*dd, J* = 11.6 and 5.8 Hz, H-1), 3.15 (*m*, H-2), 2.80 (*dd, J* = 4.9 and 4.3 Hz, H-3), 2.61 (*dd, J* = 4.9 and 2.9 Hz, H-3), 1.58 (*p*, H-2′), 1.26 (*m*, H-3′ – H-7′), 0.88 (*t, J* = 6.6 Hz, H-8′) | 71.78 (C-1), 71.52 (C-1′), 50.93 (C-2), 44.33 (C-3), 31.89 (C-6′), 29.77 (C-2′), 29.50 (C-4′), 29.32 (C-5′), 26.15 (C-3′), 22.72 (C-7′), 14.12 (C-8′) | Mode : El (M) 186.1620 (calcd.: 186.1620) |
| GE-18 | 3.70 (*dd, J* = 11.5 and 3.2 Hz, H-1), 3.48 (*m*, H-1′), 3.38 (*dd, J* = 11.5 and 5.7 Hz, H-1), 3.14 (*m*, H-2), 2.79 (*dd, J* = 5.0 and 4.3 Hz, H-3), 2.60 (*dd, J* = 5.0 and 2.7 Hz, H-3), 1.58 (*p*, H-2′), 1.26 (*m*, H-3′ – H-17′), 0.88 (*t, J* = 6.6 Hz, H-18′) | 71.76 (C-1), 71.49 (C-1′), 50.92 (C-2), 44.32 (C-3), 31.98 (C-16′), 29.75 (C-5′ – C-14′), 29.66 (C-2′), 29.53 (C-4′), 29.42 (C-15′), 26.13 (C-3′), 22.74 (C-17′), 14.14 (C-18′) | Mode : Cl (M + 1) 327.3259 (calcd.: 327.3263) |

[a]GE = alkylglycidyl ether. The numbers (8 and 18) refer to the chain length at the alkyl groups. See Scheme 1. EI, electron impact; HRMS, high-resolution mass spectra. CI, chemical ionization.

*Nuclear magnetic resonance (NMR) spectrometer.* $^1$H (300 MHz) and $^{13}$C (75 MHz) NMR spectra of the synthetic products were recorded on a Bruker AMX 300 NMR spectrometer (Karlsruhe, Germany). The chemical shifts are reported in δ units (ppm) with tetramethylsilane (TMS) as internal standard.

*Mass spectrometer.* High-resolution mass spectra (HRMS) were obtained on a Micromass Autospec mass spectrometer (Manchester, United Kingdom). The HRMS spectrum for octylglycidyl ether was obtained by electron impact (EI) method (40 eV) and that for octadecylglycidyl ether was obtained by chemical ionization (CI) method (methane, M + 1, 40 eV).

*Synthesis of octylglycidyl ether (GE-8).* Octanol (132 g, 1.0 mol) was heated in the reaction vessel to 40°C. Sodium hydroxide (61.9 g, 1.5 mol) and TBAB (2.00 g, 6.25 mmol) were added, and the mixture was stirred for 30 min at the same temperature. Epichlorohydrin (187 g, 2.0 mol) was added, and the temperature was kept between 38 and 42°C. The reaction was completed when the yield of the octylglycidyl ether (monitored by GC) did not increase any more with the increase of reaction time. The product was extracted twice with 250 mL of *n*-hexane and was purified by distillation (50–51°C at 0.041 mmHg). The $^1$H and $^{13}$C NMR data for GE-8 were collected with the correlated data and are summarized in Table 1 (Scheme 1) (10).

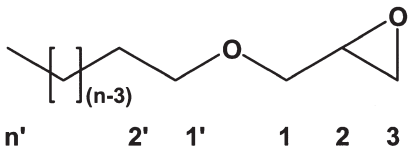
The variables for the optimal reaction condition are as follows: the amount of sodium hydroxide, from 1.0 to 2.0 mol; the amount of epichlorohydrin, from 1.2 to 3.0 mol; the amount of catalyst (TBAB), from 0.00625 to 0.05 mol; reaction temperature, from 20 to 70°C.

The other catalysts (0.015 mol) (TBAH, CETAC, LMBAC, QM, QEA, GM, and GEA; see below for definitions not already given) instead of TBAB were used to test the catalytic effects of the reaction.

*Synthesis of octadecylglycidyl ether (GE-18).* Octadecylglycidyl ether was prepared by the same method as described for the preparation of octylglycidyl ether. The reaction system consisted of octadecanol (163.9 g, 0.60 mol), sodium hydroxide (56.9 g, 1.38 mol), TBAB (1.20 g, 3.75 mmol), and epichlorohydrin (112.2 g, 1.20 mol) at 60°C. After the reaction was completed, octadecylglycidyl ether was extracted twice with 250 mL of *n*-hexane and was purified by distillation (134–136°C at 0.054 mm Hg). Table 1 shows analytical and NMR data for GE-18 (Scheme 1) (10).

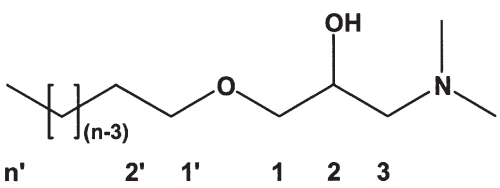
*Synthesis of catalysts*: *Alkylglycidyl ether (GE).* Alkyl groups are hexyl, octyl, dodecyl, and octadecyl, and their derivatives are GE-6, GE-8, GE-12, and GE-18, respectively. The synthesis of GE-8 and GE-18 was mentioned above. GE-6 and GE-12 were synthesized by the method of Urata *et al.* (9). GE-6 and GE-12 were purified by distillation (40°C at 0.102 mm Hg for GE-6, and 97–98°C at 0.060 mm Hg for GE-12).

*Alkyloxy-2-hydroxypropyldimethylamine (GM).* Alkyl groups are hexyl, octyl, dodecyl, and octadecyl, and their derivatives are GM-6, GM-8, GM-12, and GM-18, respectively (Scheme 2). All the GM were synthesized by the general synthetic method (11). All of them were purified by distillation at their boiling points, respectively (GM-6, 54.5°C at 0.067 mm Hg; GM-8, 75–77°C at 0.041 mm Hg; GM-12, 123–125°C at 0.031 mm Hg; GM-18, 181–184°C at 0.035 mm Hg). The




n = 8; GE-8, n = 18; GE-18

SCHEME 1




n = 6; GM-6, n = 8; GM-8, n = 12; GM-12, n = 18; GM-18

SCHEME 2

**TABLE 2**
**Analytical and NMR Spectral Data for GM[a], GEA[b], QM[c] and QEA[d]**

| | $^1$H NMR ($CDCl_3$) | Purity (%) |
|---|---|---|
| GM-6 | 3.84 (*m*, H-2), 3.46 (*t*, *J* = 6.6 Hz, H-1′), 3.42 (*m*, H-1), 2.43 (*dd*, *J* = 12.1 and 9.8 Hz, H-3), 2.28 (*s*, N-$CH_3$), 2.24 (*dd*, *J* = 12.1 and 3.9 Hz, H-3), 1.58 (*p*, H-2′), 1.26 (*m*, H-3′ – H-5′), 0.89 (*t*, *J* = 6.7 Hz, H-6′) | 99.7 |
| GM-8 | 3.75 (*m*, H-2), 3.36 (*t*, *J* = 6.8 Hz, H-1′), 3.34 (*m*, H-1), 2.33 (*dd*, *J* = 12.4 and 9.4 Hz, H-3), 2.18 (*s*, N-$CH_3$), 2.16 (*dd*, *J* = 12.4 and 3.8 Hz, H-3), 1.49 (*p*, H-2′), 1.18 (*m*, H-3′ – H-7′), 0.79 (*t*, *J* = 6.8 Hz, H-8′) | 99.7 |
| GM-12 | 3.74 (*m*, H-2), 3.36 (*t*, *J* = 6.6 Hz, H-1′), 3.32 (*m*, H-1), 2.33 (*dd*, *J* = 12.3 and 9.8 Hz, H-3), 2.18 (*s*, N-$CH_3$), 2.16 (*dd*, *J* = 12.3 and 3.8 Hz, H-3), 1.49 (*p*, H-2′), 1.17 (*m*, H-3′ – H-11′), 0.76 (*t*, *J* = 7.2 Hz, H-12′) | 99.8 |
| GM-18 | 3.77 (*m*, H-2), 3.38 (*t*, *J* = 6.5 Hz, H-1′), 3.34 (*m*, H-1), 2.35 (*dd*, *J* = 12.3 and 9.7 Hz, H-3), 2.18 (*s*, N-$CH_3$), 2.17 (*dd*, *J* = 12.3 and 3.8 Hz, H-3), 1.51(*p*, H-2′), 1.18 (*m*, H-3′ – H-17′), 0.76 (*t*, *J* = 6.8 Hz, H-18′) | 99.8 |
| GEA-6 | 4.10 (*bs*, OH), 3.91 (*m*, H-2), 3.71 (*m*, *J* = 11.8 and 9.1 Hz, N-$CH_2CH_2$), 3.54 (*m*, *J* = 11.8 Hz, N-$CH_2CH_2$), 3.45 (*t*, *J* = 6.7 Hz, H-1′), 3.41 (*d*, *J* = 1.4 Hz, H-1), 3.39 (*d*, *J* = 2.3 Hz, H-1), 2.76 (*m*, *J* = 13.5 and 9.1 Hz, N-$CH_2CH_2$), 2.59 (*dd*, *J* = 13.2 and 9.5 Hz, H-3), 2.49–2.40 (*m*, H-3 and N-$CH_2CH_2$), 1.57 (*p*, H-2′), 1.30 (*m*, H-3′ – H-5′), 0.89 (*t*, *J* = 6.7 Hz, H-6′) | 99.3 |
| GEA-8 | 4.71 (*s*, OH), 3.84 (*m*, H-2), 3.63 (*m*, *J* = 11.6 and 9.1 Hz, N-$CH_2CH_2$), 3.46 (*m*, *J* = 11.6 Hz, N-$CH_2CH_2$), 3.37 (*t*, *J* = 6.7 Hz, H-1′), 3.33 (*d*, *J* = 5.3 Hz, H-1), 2.68 (*m*, *J* = 12.9 and 9.1 Hz, N-$CH_2CH_2$), 2.49 (*dd*, *J* = 13.3 and 9.6 Hz, H-3), 2.40–2.33 (*m*, H-3 and N-$CH_2CH_2$), 1.49 (*p*, H-2′), 1.21 (*m*, H-3′ – H-7′), 0.81 (*t*, *J* = 6.7 Hz, H-8′) | 99.1 |
| GEA-12 | 4.81 (*bs*, OH), 3.88 (*m*, H-2), 3.67 (*m*, *J* = 11.6 and 9.3 Hz, N-$CH_2CH_2$), 3.49 (*m*, *J* = 11.6 Hz, N-$CH_2CH_2$), 3.40 (*t*, *J* = 6.7 Hz, H-1′), 3.36 (*d*, *J* = 5.3 Hz, H-1), 2.72 (*m*, *J* = 13.4 and 9.2 Hz, N-$CH_2CH_2$), 2.54 (*dd*, *J* = 13.3 and 9.7 Hz, H-3), 2.43–2.35 (*m*, H-3 and N-$CH_2CH_2$), 1.53 (*p*, H-2′), 1.22 (*m*, H-3′ – H-11′), 0.81 (*t*, *J* = 6.7 Hz, H-12′) | 99.6 |
| GEA-18 | 4.86 (*bs*, OH), 3.92 (*m*, H-2), 3.71 (*m*, *J* = 11.6 and 9.0 Hz, N-$CH_2CH_2$), 3.54 (*m*, *J* = 11.8 Hz, N-$CH_2CH_2$), 3.41 (*d*, *J* = 2.5 Hz, H-1′), 3.39 (*t*, *J* = 3.5 Hz, H-1′), 3.36 (*d*, *J* = 5.3 Hz, H-1), 2.76 (*m*, *J* = 13.5 and 9.0 Hz, N-$CH_2CH_2$), 2.59 (*dd*, *J* = 13.4 and 9.7 Hz, H-3), 2.51–2.40 (*m*, H-3 and N-$CH_2CH_2$), 1.57 (*p*, H-2′), 1.22 (*m*, H-3′ – H-17′), 0.88 (*t*, *J* = 6.7 Hz, H 18′) | 99.2 |
| QM-6 | 4.36 (*m*, H-2), 3.71 (*s*, $CH_3OSO_3^-$), 3.55–3.36 (*m*, H-1′, H-1, and H-3), 3.32 (*s*, N-$CH_3$), 2.55 (*bs*, OH), 1.59 (*p*, H-2′), 1.28 (*m*, H-3′ – H-5′), 0.89 (*t*, *J* = 6.7 Hz, H-6′) | 99.5 |
| QM-8 | 4.97 (*bs*, OH), 4.37 (*m*, H-2), 3.71 (*s*, $CH_3OSO_3^-$), 3.56–3.38 (*m*, H-1′, H-1, and H-3), 3.33 (*s*, N-$CH_3$), 1.54 (*p*, H-2′), 1.27 (*m*, H-3′ – H-7′), 0.88 (*t*, *J* = 6.6 Hz, H-8′) | 98.7 |
| QM-12 | 5.78 (*s*, OH), 4.29 (*m*, H-2), 3.90 (*s*, $CH_3OSO_3^-$), 3.47–3.29 (*m*, H-1′, H-1, and H-3), 3.25 (*s*, N-$CH_3$), 1.47 (*p*, H-2′), 1.19 (*m*, H-3′ – H-11′), 0.81 (*t*, *J* = 6.6 Hz, H-12′) | 99.2 |
| QM-18 | 4.80 (*bs*, OH), 4.30 (*m*, H-2), 3.65 (*s*, $CH_3OSO_3^-$), 3.49–3.32 (*m*, H-1′, H-1, and H-3), 3.27 (*s*, N-$CH_3$), 1.46 (*p*, H-2′), 1.19 (*m*, H-3′ – H-17′), 0.81 (*t*, *J* = 6.2 Hz, H-18′) | 99.5 |
| QEA-6 | 4.70 (*bs*, OH), 4.36 (*m*, H-2), 4.06 (*m*, N-$CH_2CH_2$), 3.71 (*m*, $CH_3OSO_3$ and N-$CH_2CH_2$), 3.57 (*m*, H-1), 3.49 – 3.30 (*m*, H-1′, H-3), 3.31 (*s*, N-$CH_3$), 1.48 (*p*, H-2′), 1.28 (*m*, H-3′ – H-5′), 0.81 (*t*, *J* = 6.4 Hz, H-6′) | 99.0 |
| QEA-8 | 4.60 (*s*, OH), 4.28 (*m*, H-2), 3.99 (*m*, N-$CH_2CH_2$), 3.64 (*m*, $CH_3OSO_3$ and N-$CH_2CH_2$), 3.50 (*m*, H-1), 3.50 – 3.29 (*m*, H-1′, H-3), 3.24 (*s*, N-$CH_3$), 1.48 (*p*, H-2′), 1.20 (*m*, H-3′ – H-7′), 0.81 (*t*, *J* = 6.4 Hz, H-8′) | 99.4 |
| QEA-12 | 4.76 (*s*, OH), 4.36 (*m*, H-2), 4.06 (*m*, N-$CH_2CH_2$), 3.71 (*m*, $CH_3OSO_3$ and N-$CH_2CH_2$), 3.56 (*m*, H-1), 3.46 – 3.38 (*m*, H-1′, H-3), 3.31 (*s*, N-$CH_3$), 1.54 (*p*, H-2′), 1.26 (*m*, H-3′ – H-11′), 0.88 (*t*, *J* = 6.7 Hz, H-12′) | 98.7 |
| QEA-18 | 4.73 (*s*, OH), 4.35 (*m*, H-2), 4.06 (*m*, N-$CH_2CH_2$), 3.71 (*m*, $CH_3OSO_3$ and N-$CH_2CH_2$), 3.56 (*m*, H-1), 3.46 – 3.36 (*m*, H-1′, H-3), 3.31 (*s*, N-$CH_3$), 1.54 (*p*, H-2′), 1.25 (*m*, H-3′ – H-17′), 0.88 (*t*, *J* = 6.7 Hz, H-18′) | 99.0 |

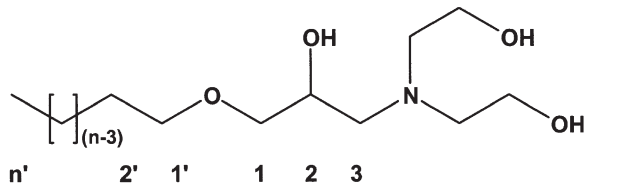
[a]See Scheme 2; GM, alkyloxy-2-hydroxypropyldimethylamine.
[b]See Scheme 3;GEA, alkyloxy-2-hydroxypropyldiethanolamine.
[c]See Scheme 4; QM, 1-alkyloxypropan-2-ol-3-trimethylammoniium methylsulfate.
[d]See Scheme 5; QEA, 1-alkyloxypropan-2-ol-3-methyldiethanolammonium methylsulfate. See Table 1 for abbreviation.

purity of GM series was determined by amine value (12). The $^1$H NMR data for GM series were collected with the correlated data and are summarized in Table 2 (Scheme 2).

*Alkyloxy-2-hydroxypropyldiethanolamine (GEA).* Alkyl groups are hexyl, octyl, dodecyl, and octadecyl, and their derivatives are GEA-6, GEA-8, GEA-12, and GM-18, respectively (Scheme 3). All the GEA were synthesized by the general synthetic method (11) except using excess 0.05 molar ratios of GE to diethanolamine. By removing the unreacted GE at the boiling point of GE, all GEA were purified, respectively. The purity of GEA series was determined by amine value (12). Table 2 shows the analytical and $^1$H NMR data for GEA series (Scheme 3).

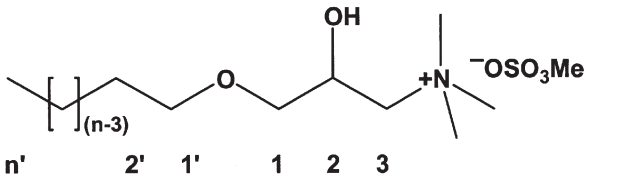
*1-Alkyloxypropan-2-ol-3-trimethylammonium methylsulfate (QM).* Alkyl groups are hexyl, octyl, dodecyl, and octadecyl, and their derivatives are QM-6, QM -8, QM-12, and QM-18, respectively (Scheme 4). All the QM were synthesized by the general synthetic method (11). The purity of QM series was determined by $^1$H NMR, i.e., the integration ratio of the separated peaks of GM (2.43–2.24 ppm) against the overlapped peaks of GM and QM (3.55–3.32 ppm). The analytical results and the $^1$H NMR data for QM series are summarized in Table 2 (Scheme 4).

*1-Alkyloxypropan-2-ol-3-methyldiethanolammonium methylsulfate (QEA).* Alkyl groups are hexyl, octyl, dodecyl, and octadecyl, and their derivatives are QEA-6, QEA-8, QEA-12, and QEA-18, respectively (Scheme 5). All the QEA were synthesized by the general synthetic method (11). The purity of QEA series was determined by $^1$H NMR, i.e., the integration ratio of the separated peaks of GEA (2.76–2.40 ppm) against the overlapped peaks of GEA and QEA (3.71–3.31 ppm). The $^1$H NMR data for QEA series were col-



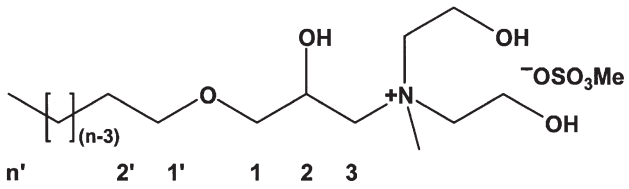

n = 6; GEA-6, n = 8; GEA-8, n = 12; GEA-12, n = 18; GEA-18

SCHEME 3




n = 6; QM-6, n = 8; QM-8, n = 12; QM-12, n = 18; QM-18

SCHEME 4




n = 6; QEA-6, n = 8; QEA-8, n = 12; QEA-12, n = 18; QEA-18

SCHEME 5

lected with the correlated data and are summarized in Table 2 (Scheme 5).

## RESULTS AND DISCUSSION

*The formation of octylglycidyl ether*: In order to develop the improved synthetic method, the effects of the following factors on the glycidyl ether formation have been considered: (i) solvent, (ii) the concentration of reactants (epichlorohydrin and sodium hydroxide), (iii) various catalysts such as amine derivatives and ammonium derivatives, and (iv) reaction temperature.

*(i) Solvent effects.* The effect of water on the formation of glycidyl ether was investigated in the binary phase system of water/*n*-hexane. In the experiments on the effect of water, we employed the optimal condition of Urata *et al.* (9). Various mixed solvents of water (0–7.2 mol) and *n*-hexane (11.6 mol) were added to the mixture of octanol (1 mol), sodium hydroxide (3 mol) (20–40 mesh beads), and TBAB (0.05 mol) at 40°C before adding epichlorohydrin (2 mol). The reaction was completed when the yield of the octylglycidyl ether did not increase any more with the reaction time. The final product components were analyzed by GC, and their GC retention times are as follows: unreacted octanol (6.87 min), 3-chloroprop-2-enylglycidyl ether (7.31 min), octylglycidyl ether (11.39 min), 1,3-dioctyloxy-2-propanol (18.88 min), and 1,3-dioctyloxy-2-propylglycidyl ether (21.04 min). The effects of mixed solvents on the yields of final product components are shown in Table 3. It is interesting to note that the yields of octylglycidyl ether showed the similar value of 84.5–85.5% regardless of the amount of the water in the mixed solvents (Table 3). By decreasing the amount of the water from 7.2 to 0 mol, the reaction time is reduced from 6 to 3.5 h, with the amount of the unreacted octanol decreased from 7.9 to 1.4%. However, the amount of 3-chloroprop-2-enylglycidyl ether was increased from 0.8 to 8.9%. This is the only disadvantage accompanied by an increase in the amount of 3-chloroprop-2-enylglycidyl ether generated from epichlorohydrin by hydrogen elimination under excess base condition (13). Therefore, the introduction of some other conditions should be considered for the formation of octylglycidyl ether without using water (see below).

On the other hand, when using the various amounts of *n*-hexane (2.9–11.6 mol) with the fixed 7.2 mol of water, each reaction time was about 6 h. The amounts of unreacted octanol (7.9–7.6%), 3-chloroprop-2-enylglycidyl ether (0.8–1.0 %), and octylglycidyl ether (84.2–84.5%) were almost constant regardless of the amount of the added *n*-hexane (Table 3). These results indicate that the change in the amount of the *n*-hexane added does not affect the formation of octylglycidyl ether. The removal of the *n*-hexane in the reaction system for the preparation could be considered. Therefore, the method for the synthesis of the glycidyl ethers was investigated in the reaction condition without water and other organic solvents

**TABLE 3**
**Solvent Effects on the Formation of Octylglycidyl Ether[a]**

| Solvents (mol) | | Reaction time | Octanol | Glycidyl ethers (%) | | 1,3-Dioctyloxy-2-propanol (%) |
|---|---|---|---|---|---|---|
| *n*-Hexane | Water | (h) | (%) | 3-Chloroprop-2-enylglycidyl ether (%) | Octylglycidyl ether | 1,3-Dioctyloxy-2-propylglycidyl ether |
| 11.6 | 7.2 | 6 | 7.9 | 0.8 | 84.5 | 2.2 | 1.5 |
| 11.6 | 1.8 | 3.5 | 2 | 6.9 | 85.5 | 0.8 | 1.5 |
| 11.6 | 0 | 3.5 | 1.4 | 8.9 | 84.6 | 0.8 | 3.3 |
| 5.8 | 7.2 | 6 | 7.9 | 0.9 | 84.5 | 1.8 | 1.7 |
| 2.9 | 7.2 | 6 | 7.6 | 1.0 | 84.2 | 1.3 | 3.6 |

[a]The reaction condition: octanol (1 mol), epichlorohydrin (2 mol), sodium hydroxide (3 mol), and tetrabutylammonium bromide (TBAB) (0.05 mol) at reaction temperature of 40°C.

**TABLE 4**
**The Effect of the Reactants and Temperature Factors on the Formation of Octylglycidyl Ether[a]**

| Amount of reactants (mol) | | | | Reaction | | 3-Chloroprop-2- | Glycidyl ethers (%) | | 1,3- |
|---|---|---|---|---|---|---|---|---|---|
| Sodium hydroxide | Epichloro-hydrin | PTC (TBAB) | Temperature (°C) | time (h) | Octanol (%) | enylglycidyl ether (%) | Octylglycidyl ether | 1,3-Dioctyloxy-2-propylglycidyl ether | Dioctyloxy-2-propanol (%) |
| 1.0 | 2.0 | 0.00625 | 40 | 3 | 17.4 | <0.2 | 78.1 | 1.7 | 2.7 |
| 1.2 | 2.0 | 0.00625 | 40 | 3 | 10.9 | <0.2 | 84.8 | 2.3 | 2 |
| 1.5 | 2.0 | 0.00625 | 40 | 3.5 | 1.5 | <0.2 | 92.0 | 4.8 | 0.8 |
| 1.6 | 2.0 | 0.00625 | 40 | 3.5 | 1.7 | 1.1 | 92.0 | 5.4 | 0.4 |
| 1.7 | 2.0 | 0.00625 | 40 | 3.5 | 1.6 | 1.1 | 92.3 | 5 | <0.2 |
| 1.8 | 2.0 | 0.00625 | 40 | 3.5 | 1.2 | 2.4 | 91.0 | 5.6 | <0.2 |
| 2.0 | 2.0 | 0.00625 | 40 | 3.5 | 2 | 7.9 | 86.0 | 3 | 1.2 |
| 1.5 | 1.2 | 0.00625 | 40 | 3.5 | 1.6 | <0.2 | 81.0 | 1.8 | 11.2 |
| 1.5 | 1.4 | 0.00625 | 40 | 3.5 | 1.3 | <0.2 | 85.3 | 8.4 | 6.0 |
| 1.5 | 1.6 | 0.00625 | 40 | 3.5 | 1.6 | <0.2 | 87.2 | 7.4 | 1.0 |
| 1.5 | 1.8 | 0.00625 | 40 | 3.5 | 1.4 | <0.2 | 89.2 | 6.3 | 0.7 |
| 1.5 | 2.0 | 0.00625 | 40 | 3.5 | 1.5 | <0.2 | 92.0 | 4.8 | 0.8 |
| 1.5 | 3.0 | 0.00625 | 40 | 3.5 | 3.4 | 1.0 | 89.0 | 5.8 | 0.9 |
| 1.5 | 2.0 | 0.0015 | 40 | 11.5 | 3.1 | 0.9 | 90.2 | 4.5 | 1.3 |
| 1.5 | 2.0 | 0.00625 | 40 | 3.5 | 1.5 | <0.2 | 92.0 | 4.8 | 0.8 |
| 1.5 | 2.0 | 0.0500 | 40 | 3 | 1.7 | 1.3 | 90.2 | 5.1 | 0.7 |
| 1.5 | 2.0 | 0.00625 | 20 | 12 | 1.9 | 0.6 | 91.6 | 5.2 | 0.6 |
| 1.5 | 2.0 | 0.00625 | 40 | 3.5 | 1.5 | <0.2 | 92.0 | 4.8 | 0.8 |
| 1.5 | 2.0 | 0.00625 | 60 | 3.5 | 3.5 | 0.7 | 90.1 | 4.3 | 1.4 |
| 1.5 | 2.0 | 0.00625 | 70 | 3.5 | 10.5 | 1.9 | 80.0 | 2.0 | 3.0 |

[a]PTC, phase transfer catalyst. See Table 3 for other abbreviation.

by preventing the formation of 3-chloroprop-2-enylglycidyl ether with using the optimal reaction conditions, i.e., reaction mole ratio (epichlorohydrin, sodium hydroxide, and TBAB), temperature and catalyst, especially, the optimal amount of sodium hydroxide.

*(ii) The effects of reactants (sodium hydroxide and epichlorohydrin) concentration.* In the reaction condition without water and other organic solvents at 40°C, the reactants used and their amounts are octanol (1 mol), epichlorohydrin (2 mol), solid sodium hydroxide (20–40 mesh beads), and TBAB (0.00625 mol). The amount of sodium hydroxide used varied from 1.0 to 2.0 mol. Table 4 represents the yields of octylglycidyl ether, unreacted octanol, and by-products in the reaction mixture after the reaction was completed. The unreacted octanol remained more than 10% when the amount of the solid sodium hydroxide added was less than 1.2 mol. When the amount of sodium hydroxide added was between 1.5 and 1.7 mol, the yield of octylglycidyl ether reached 92.0–92.3%. The amount of 3-chloroprop-2-enylglycidyl ether increased gradually from 1.1 to 7.9% with increasing the amount of sodium hydroxide from 1.6 to 2.0 mol. Therefore, a waste of the reactant such as epichlorohydrin increases gradually with increasing the amount of the undesired 3-chloroprop-2-enylglycidyl ether derived from epichlorohydrin in excess sodium hydroxide. These results indicate that the optimal quantity of sodium hydroxide is 1.5 mol.

The concentration of epichlorohydrin also has the important effect on the formation of glycidyl ether. The various amount of epichlorohydrin (1.2–3.0 mol) was added to the reaction mixture solution with 1.5 mol of sodium hydroxide optimized as mentioned above. Table 4 shows the yields of octylglycidyl ether, octanol, and by-product as a function of the amount of the epichlorohydrin added. The amount of the undesired 1,3-dioctyloxy-2-propanol increased proportionally from 1.0 to 11.2% with decreasing the amount of the added epichlorohydrin from 1.6 to 1.2 mol. Accordingly, in order to prevent the formation of the undesired 1,3-dioctyloxy-2-propanol and/or polymerization, the amount of epichlorohydrin more than 1.6 mol was used in the reaction for octylglycidyl ether. The yield of octylglycidyl ether increased gradually from 81.0 to 92.0% with increasing amount of the added epichlorohydrin from 1.2 to 2.0 mol. The use of excess epichlorohydrin (3 mol) did not increase the yield of glycidyl ether, but did increase the amount of the unreacted octanol and 3-chloroprop-2-enylglycidyl ether. Therefore, these results indicate that the optimal amount of epichlorohydrin is 2.0 mol for the efficient formation of the octylglycidyl ether.

*(iii) The catalyst effects*. Generally, PTC is used in a binary solvent system due to its solubility in both solvents. The conventional PTC methods to obtain glycidyl ether or glycidyl ester are the reaction in aqueous phase/organic phase (*n*-hexane) (9) or solid phase/organic phase (toluene) (14). However, our reaction system contains neither aqueous phase nor organic phase (*n*-hexane or toluene). For this reason, the solubility reaction of TBAB to the reactants and octylglycidyl ether was tested. TBAB (0.001 mol) is dissolved clearly in octanol (0.1 mol), epichlorohydrin (0.1 mol), and octylglycidyl ether (0.1 mol) at 40°C, respectively. Therefore, the reactants and products themselves play the role of solvent, replacing other organic solvents. Thus, our reaction system consists of solid phase/organic phase (reactants and product).

As mentioned above, the various amounts of TBAB (0.0015–0.05 mol) were added to the reactant mixture with

**TABLE 5**
**Test of Various Catalysts for the Formation of Octylglycidyl Ether[a]**

| Catalyst | Reaction time (h) | Octanol (%) | 3-Chloroprop-2-enylglycidyl ether (%) | Glycidyl ethers (%) | | 1,3-Dioctyloxy-propan-2-ol (%) |
|---|---|---|---|---|---|---|
| | | | | Octylglycidyl ether | 1,3-Dioctyloxy-2-propylglycidyl ether | |
| QM-6 | 4 | 1.6 | <0.2 | 90.4 | 6.0 | 1.0 |
| QM-8 | 5 | 0.9 | <0.2 | 89.4 | 7.5 | 0.4 |
| QM-12 | 9 | 2.2 | <0.2 | 89.6 | 6.8 | 1.5 |
| QM-18 | 8 | 0.9 | <0.2 | 88.9 | 7.7 | 0.4 |
| QEA-6 | 5 | 1.3 | 0.3 | 91.4 | 4.5 | 0.8 |
| QEA-8 | 9 | 2.9 | <0.2 | 89.3 | 5.9 | 1.4 |
| QEA-12 | 9 | 2.2 | <0.2 | 88.1 | 8.0 | 1.8 |
| QEA-18 | 9 | 1.7 | <0.2 | 91.1 | 6.1 | 1.1 |
| CETAC | 3 | 0.8 | 0.6 | 92.4 | 5.7 | 0.6 |
| LMBAC | 4 | 0.6 | 1.6 | 89.3 | 6.0 | 0.5 |
| TBAH | 12 | <0.2 | <0.2 | 92.0 | 6.0 | <0.2 |
| GM-6 | 4 | <0.2 | <0.2 | 93.2 | 4.8 | <0.2 |
| GM-8 | 5 | 1.3 | 0.4 | 90.9 | 6.2 | 0.5 |
| GM-12 | 5 | 1.4 | <0.2 | 91.9 | 6.2 | 0.5 |
| GM-18 | 5 | 1.2 | 0.6 | 89.6 | 6.4 | 0.5 |
| GEA-6 | 3 | 1.1 | <0.2 | 92.9 | 5.1 | 0.8 |
| GEA-8 | 24 | 1.8 | <0.2 | 92.7 | 4.3 | 0.6 |
| GEA-12 | 24 | 2.3 | <0.2 | 91.9 | 4.1 | 0.8 |
| GEA-18 | 24 | 1.9 | <0.2 | 93.0 | 3.8 | 0.5 |

[a]The reaction condition: octanol (1 mol), epichlorohydrin (2 mol), sodium hydroxide (1.5 mol), and catalyst (0.015 mol) at reation temperature of 40°C. CETAC, cetyltrimethylammonium chloride; LMBAC, lauryldimethylbenzylammonium chloride; TBAH, tetrabutylammonium hydrogensulfate. See Table 2 for other abbreviations.

the optimized amounts of the sodium hydroxide and epichlorohydrin. After the reaction was completed, the yields of octylglycidyl ether, octanol, and by-products were quantified by GC, and their results are shown in Table 4. When the amount of the added TBAB was 0.0015 mol, the amount of unreacted octanol was 3.1%. When the amount of the TBAB added was 0.0016, 0.00625, and 0.05 mol, respectively, the yields of octylglycidyl ether were almost the same (90.2–92.0%) regardless of the amount of the TBAB added. The reaction time increased gradually from 3.0 to 11.5 h with decreasing amount of added TBAB, from 0.05 to 0.0015 mol. However, variation of the amount of TBAB (0.00625–0.05 mol) used did not affect the reaction time very significantly (3.0–3.5 h). In order to determine the optimal amount of the added TBAB for the preparation of the octylglycidyl ether, we chose the amount of the catalyst to derive the short reaction time (0.00625 and 0.05 mol) and then minimize the amount of the catalyst used (0.0015 and 0.00625 mol). These results indicate that the optimal quantity of TBAB for its preparation is 0.00625 mol.

To investigate the effect of various PTC on the glycidyl ether formation, TBAB (0.00625 mol) was replaced by the following catalysts (0.015 mol). The tested catalysts were the derivatives of alkylamines and alkylammonium salts, i.e., TBAH, CETAC, LMBAC, QM-6, QM-8, QM-12, QM-18, QEA-6, QEA-8, QEA-12, QEA-18, GM-6, GM-8, GM-12, GM-18, GEA-6, GEA-8, GEA-12, and GEA-18. The solubilities of the catalysts in the reactants and octylglycidyl ether were tested. All of them (0.002 mol) are dissolved clearly in octanol (0.1 mol), epichlorohydrin (0.1 mol), and octylglycidyl ether (0.1 mol) at 40°C, respectively. Therefore, the reactants and product themselves play the role of solvent to replace other organic solvents. The QM, QEA, GM, GEA series can be easily synthesized as represented in the Experimental Procedures section (Tables 2 and 5). The above optimized reaction system using the catalysts instead of TBAB produced octylglycidyl ether with the yield of 88.1–93.2% (Table 5). The reaction time increased by increasing the alkyl chain length of our synthesized catalysts (QM, QEA, GM, and GEA series).

*(iv) The temperature effects*. Under the optimized molar ratio of reactants as mentioned above, the reaction temperature was varied from 20 to 70°C. Table 4 represents the amount of the components in product mixture as a function of the temperature. In the reaction at 20 and 40°C, the yields of the octylglycidyl are the high value of 91.6 and 92.0%, respectively. The reaction time at 20 and 40°C was about 12 and 3.5 h, respectively. As the reaction temperature rose from 40 to 70°C, the yield of octylglycidyl ether was decreased from 92.0 to 80.0%, and the amount of unreacted octanol increased from 1.5 to 10.5%. The reaction at high temperature drops the yield of octylglycidyl ether because of the exothermic reaction. It was supposed the reverse reaction, which progresses from octylglycidyl ether to octanol at high temperature (60 and 70°C), caused these phenomena, as shown by the decreasing yield of octylglycidyl ether with rising reaction temperature. At the reaction temperature of 70°C, the formation of a tiny amount of octanol (about 1% for 1 h) was confirmed by GC from the reaction system using reactants of octylglycidyl ether (0.20 mol), sodium hydroxide (0.10 mol), sodium chloride (0.20 mol), and TBAB (0.0013 mol). This is the probe of reverse reaction occurring at high temperature. Therefore, the optimized temperature for the formation of

**TABLE 6**
**The Standard Deviation for the Formation of Octylglycidyl Ether[a]**

| Order | Octanol (%) | 3-Chloroprop-2-enylglycidyl ether (%) | Glycidyl ethers (%) | | 1,3-Dioctyloxy-2-propanol (%) |
|---|---|---|---|---|---|
| | | | Octylglycidyl ether | 1,3-Dioctyloxy-2-propylglycidyl ether | |
| 1 | 1.5 | <0.2 | 92.0 | 4.8 | 0.8 |
| 2 | 1.9 | <0.2 | 92.0 | 4.3 | 0.6 |
| 3 | 1.5 | <0.2 | 91.7 | 4.6 | 0.6 |
| 4 | 1.6 | <0.2 | 92.3 | 4.9 | 0.8 |
| 5 | 1.2 | <0.2 | 91.2 | 6.0 | 0.7 |
| Average value | 1.5 | —[b] | 91.8 | 4.9 | 0.7 |
| Standard deviation | 0.4 | —[b] | 0.4 | 0.7 | 0.1 |

[a]The reaction condition: octanol (1.0 mol), epichlorhydrin (2.0 mol), sodium hydroxide (1.5 mol), and TBAB (0.00625 mol), temperature 40°C. See Table 3 for abbreviation.
[b]Not determined.

octylglycidyl ether is 40°C in the reaction condition using reactants of octanol (1.0 mol), epichlorohydrin (2.0 mol), sodium hydroxide (1.5 mol), and TBAB (0.00625 mol). To provide the estimate of the standard deviation, five repetitive experiments were carried out in the optimized reaction condition. The average value and standard deviation of octylglycidyl ether yield are 91.8 and 0.42%, respectively (Table 6).

*II. The formation of octadecylglycidyl ether.* As mentioned above, glycidyl ether has been conventionally synthesized by the Lewis acid method or the PTC method in the water/*n*-hexane system. However, especially, these methods do not give rise to the high yield of the alkylglycidyl ether having long-chain alcohol such as an octadecanol. Then the present reaction system using the PTC method without water and other organic solvents was applied to the synthesis of octadecylglycidyl ether. The reaction temperature of 60°C was used to liquify octadecanol (melting point: 60°C). The effects of sodium hydroxide and epichlorohydrin for the formation of octadecylglycidyl ether were similar to those of previous octylglycidyl ether except the added amount of sodium hydroxide. In the optimal reaction condition using reactants of octadecanol (0.60 mol), epichlorohydrin (1.2 mol), sodium hydroxide (1.4 mol), and TBAB (0.0038 mol) at 60°C, the yields of the components and the retention time in the product mixture are as follows: 3-chloroprop-2-enylglycidyl ether (1.5%, 7.31 min), unreacted octadecanol (0.7%, 18.21 min), octadecylglycidyl ether (91.7%, 20.85 min), 1,3-dioctadecyloxy-2-propylglycidyl ether (3.8%, 33.68 min) (the molar ratio of octadecanol/epichlorohydrin/sodium hydroxide/TBAB = 1:2.3:2:0.00625).

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