LC (silica gel, hexane–AcOEt, 10:1, 5:1); IR (KBr) 3600–2200, 1725, 1700 cm^{-1}; ^1H NMR (CCl_4) δ 0.85 (t, 3 H), 1.0–2.2 (m, 14 H), 2.2–2.7 (m, 6 H), 10.8 (br s); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 18.5 (t), 22.6 (t), 23.9 (t), 29.1 (t), 29.3 (t), 29.4 (t), 31.8 (t), 33.1 (t), 41.3 (t), 42.9 (t), 179.4 (s), 210.5 (s). Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.19; H, 10.44. Found: C, 68.33; H, 10.59.

5-Oxononanoic Acid (1c): yield 75% from 3-*n*-butyl-1,2-cyclohexanedione; mp 42.0–43.0 °C; colorless crystals purified by LC (silica gel, hexane–AcOEt, 10:1, 2:1); IR (KBr) 3600–2400, 1720, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.1–2.2 (m, 6 H), 2.2–2.7 (m, 6 H), 6.7 (br s); ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 18.6 (t), 22.3 (t), 26.0 (t), 33.0 (t), 41.3 (t), 42.6 (t), 179.3 (s), 210.5 (s). Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.83; H, 9.37.

5-Hexadecanolide (3a):[4,14] identified by using the IR and NMR spectra in comparison with those reported;[14h] ^{13}C NMR ($CDCl_3$) δ 14.2 (q), 18.5 (t), 22.7 (t), 24.9 (t), 27.8 (t), 29.36 (t), 29.44 (t), 29.48 (t), 29.52 (t), 29.58 (t), 29.63 (t), 29.65 (t), 31.9 (t), 35.9 (t), 80.7 (d), 172.1 (s).

5-Tridecanolide (3b): bp 120–130 °C (0.4 mm); IR (neat) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, 3 H), 1.12–2.30 (m, 18 H), 2.30–2.75 (m, 2 H), 4.00–4.60 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 18.5 (t), 22.6 (t), 24.9 (t), 27.8 (t), 29.4 (4 C, t), 31.8 (t), 35.7 (t), 80.6 (d), 172.1 (s); $[\alpha]^{26}_D$ +11.8° (*c* 2.02, THF) [lit.[4] $[\alpha]^{27}_D$ +45.2° (*c* 1.58, THF)]. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.38; H, 11.27.

5-Nonanolide (3c):[16] bp 70–80 °C (2 mm); IR (neat) 1740 cm^{-1}; ^1H NMR (CCl_4) δ 0.92 (t, 3 H), 1.12–2.10 (m, 10 H), 2.10–2.52 (m, 2 H), 3.90–4.40 (m, 1 H). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.25; H, 10.35.

5-Hexanolide (3d):[17] bp 80 °C (3 mm); identified by using IR and ^1H NMR spectra in comparison with those reported.[17a]

Acknowledgment. We thank Dr. Toyonari Sugimoto of Kyoto University for valuable discussions.

Registry No. **1a**, 70444-63-2; **16**, 869-99-8; **1c**, 3637-15-5; **1d**, 3128-06-1; **3a**, 59812-96-3; (+)-**3b**, 99461-66-2; (±)-**3c**, 105140-26-9; (±)-**3d**, 26991-67-3; BSA, 9048-46-8.

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2-Chloro-1-(chloromethyl)ethyl Methoxymethyl Ether as a Reagent for Acetonylation of Alcohols and Phenol

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Since the acetonyl group is a useful functional unit due to its high reactivity and versatility, introduction of this unit is one of the important operations in organic synthesis. By acetonylation, not only many kinds of elaborations are possible by successive reactions but also the property of chemicals itself can be controlled and adjusted, so it offers an effective methodology for us in designing the organic synthesis.[1] Among the many kinds of acetonylation reagents reported, alkoxyallyl bromide developed by Horning[2] and Jacobson[3] has attracted attention as the most useful acetonylation reagent at present. Although the electrophilic reactivity is high and effective for acetonylation, this reagent requires some care in its preparation and preservation, for example, high pyrolytic temperature, inevitable side reactions, difficult isolation, and unstableness to undesirable polymerization etc.[2-4]

Very recently, in the course of study on the reactivity of epichlorohydrin under phase-transfer (PT) catalytic conditions,[5] we synthesized a series of 2-substituted 1-(chloromethyl)ethyl ethers from epoxides and chlorides in high yield in the presence of dodecyltrimethylammonium chloride under mild conditions.[6] Among them, we found 2-chloro-1-(chloromethyl)ethyl methoxymethyl ether (**1**), which can be prepared by a simple process and isolated easily by distillation, and is also stable in the air, is a superior reagent for converting various hydroxyl compounds to the corresponding acetonyl ethers.

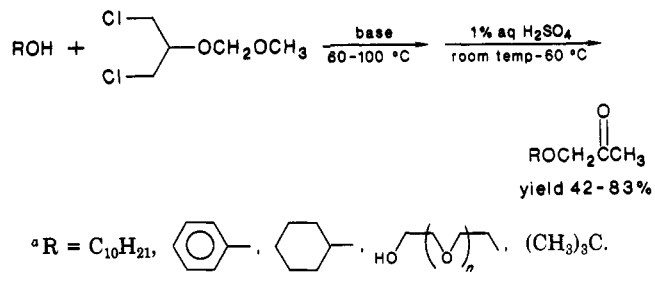
The acetonylation of hydroxyl compounds was carried out under basic conditions, generally in the presence of PT catalyst, and the successive acidic hydrolysis completed the reaction path to acetonyl ethers is shown in Scheme I.

The reaction pathway may be considered as follows (Scheme II); 2-(chloromethyl)-3,5-dioxahex-1-ene (**2**) formed through elimination of hydrogen chloride is attacked by alkoxide anion to afford **3**, which is then converted to acetonyl ether by hydrolysis in acidic medium. Compounds **2**, **3**, and acetonyl ethers **4** were isolated by distillation at reduced pressure and identified by the spectral and elemental analyses.

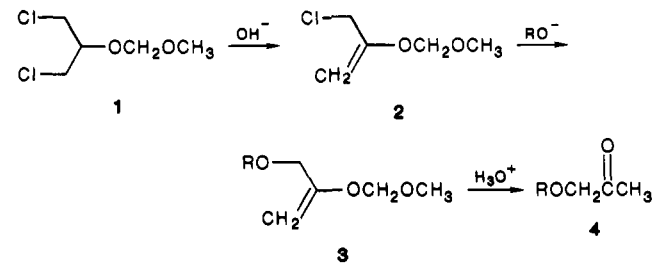
When solid sodium hydroxide (pellet form) in dioxane is employed, this reaction proceeds only in the presence of PT catalyst except for the case of oligoethylene glycol. In the latter case, the reaction proceeds smoothly even without PT catalyst. Since alkali hydroxide can be dissolved into the reaction system by solvation of metal cation with oligooxyethylene moieties of the substrate, promoted are the formation of **2**, the alkoxide anion, and then inevitably the objective compound **3**.

The hydrolysis of compounds **3** bearing hydrophobic decyl or phenyl group required relatively intensive conditions, namely at 60 °C in aqueous dioxane. In the other

Scheme I[a]



Scheme II



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(2) Horning, D. E.; Kavadias, G.; Muchowski, M. *Can. J. Chem.* **1970**, *48*, 975.
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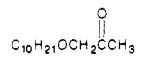
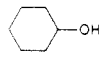
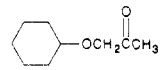
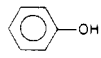
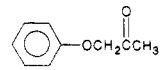
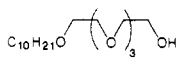
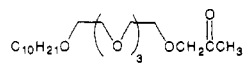
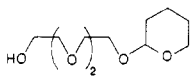
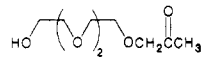
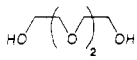
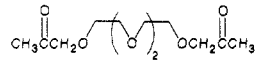
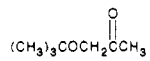
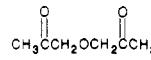
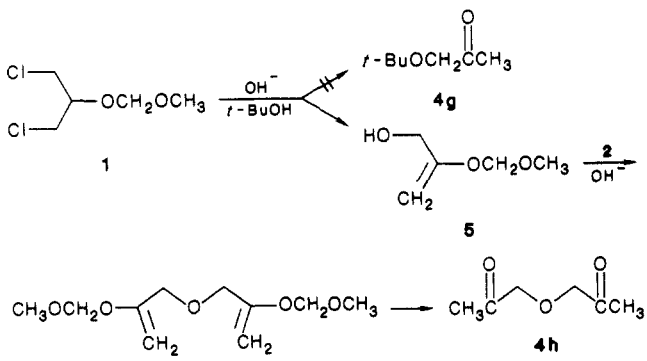
0022-3263/86/1951-5425$01.50/0

Table I. Acetonylation[a] of Alcohols and Phenol

starting matl	product	no.	yield, %	bp,[b] °C/torr
$C_{10}H_{21}OH$		4a	71	50/0.05
		4b	42	100/15
		4c	69	130/30
		4d	83	160/0.05
		4e	67	115/0.05
		4f	61	140/0.05
$(CH_3)_3COH$		4g	42[c]	54/25
H_2O		4h	58	90/30

[a] Under PT catalytic conditions, unless otherwise stated. [b] Kugelrohr distillation. [c] By *t*-BuOK–*t*-BuOH system.

Scheme III



cases, the hydrolysis was carried out at room temperature without dioxane.

It is obvious from Table I that the yield of acetonyl ether from a primary alcohol is better than that from a secondary alcohol. In the case of acetonylation of tertiary alcohol under PT catalytic conditions, the sole product obtained was diacetonyl ether (**4h**) instead of expected *tert*-butyl acetonyl ether. It is proper to consider that **2** reacted with hydroxide anion paired with quaternary ammonium cation, rather than scarce and less reactive *tert*-butoxide anion, to form allylic alcohol **5**, which then further reacted with **2** to afford **4h** in yield of 51% (Scheme III).

In an another run, diacetonyl ether (**4h**) was also prepared in yield of 58% by the hydrolytic coupling reaction of **2** in a 30% aqueous potassium hydroxide solution in the presence of PT catalyst.

However, *tert*-butyl acetonyl ether could be prepared in yield of 42% by treating **1** with potassium *tert*-butoxide in *tert*-butyl alcohol.

The yield of acetonylation for alcohols and phenol is shown in Table I.

Experimental Section

^1H NMR spectra were recorded on a JEOL JNM-PS-100 instrument in $CDCl_3$ with Me_4Si as internal standard. Mass spectra were measured on a Hitachi RMU-6E spectrometer. Infrared spectra were obtained on a Hitachi 260-10 spectrometer. All the reagents were of reagent grade and were used without further purification. 2-Chloro-1-(chloromethyl)ethyl methoxymethyl ether (**1**) was prepared according to ref 6. Evaporative distillation (Kugelrohr distillation) was performed bulb to bulb by a glass tube oven, Model GTO-205RS.

General Procedure: Synthesis of Triethylene Glycol Diacetonyl Ether (4f). Into a mixture of triethylene glycol (3 g, 0.02 mol), sodium hydroxide (6.4 g, 0.16 mol, pellet), and dioxane (30 mL) was added compound **1** (7.6 g, 0.044 mol) at 60 °C during the period of 20 min with rapid stirring. After the stirring was continued for additional 3 h, solid material was removed by filtration and the solvent was removed by distillation at reduced pressure. Five milliliters of 1% aqueous sulfuric acid was added into the residue, and the mixture was stirred at room temperature for 1 h. After neutralization with sodium hydroxide solution, the product was extracted with dichloromethane and isolated by Kugelrohr distillation at reduced pressure. Triethylene glycol diacetonyl ether (**4f**) (3.2 g) was obtained as a colorless liquid in yield of 61%: bp 140 °C (0.05 torr) (Kugelrohr); ^1H NMR ($CDCl_3$) δ 2.15 (s, 6 H), 3.68 (s, 12 H), 4.12 (s, 4 H); MS, *m/e* (rel intens) 262 (M^+), 100 (100), 57 (70); IR (liquid film) 2875, 1720, 1360, 1010 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45. Found: C, 54.65; H, 8.34.

Decyl Acetonyl Ether (4a). Reaction conditions were similar to the case for **4f**, except for the use of tetrabutylammonium bisulfate as PT catalyst (5 mol % based on the alcohol) and 1.1 equiv of **1** to decyl alcohol. The hydrolysis was carried out in a mixture of 1% aqueous sulfuric acid and dioxane (1:1, v/v) at 60 °C for 1 h. Decyl acetonyl ether (**4a**) was obtained in yield of 71% as a colorless liquid: bp 50 °C (0.05 torr) (Kugelrohr); ^1H NMR ($CDCl_3$) δ 0.75–1.05 (t, 3 H), 1.10–1.80 (m, 16 H), 2.16 (s, 3 H), 3.40–3.60 (t, 2 H), 4.00 (s, 2 H); MS, *m/e* (rel intens) 214 (M^+), 57 (100), 43 (90); IR (liquid film) 2925, 1720, 1130 cm^{-1}. Anal. Calcd for $C_{13}H_{26}O_2$: C, 72.86; H, 12.33. Found: C, 73.09; H, 12.41.

Cyclohexyl Acetonyl Ether (4b). With the general procedure described above, **4b** was obtained in yield of 42% as a colorless liquid: bp 100 °C (15 torr) (Kugelrohr) [lit.[7] bp 98–98.5 °C (17 torr)]; ^1H NMR ($CDCl_3$) δ 1.04–2.04 (m, 10 H), 2.15 (s, 3 H), 3.12–3.44 (m, 1 H), 4.02 (s, 2 H); MS, *m/e* (rel intens) 157 ($M^+ + 1$), 99 (32), 83 (100), 55 (91); IR (liquid film) 2950, 1730, 1450, 1360, 1130 cm^{-1}.

Phenyl Acetonyl Ether (4c). With the general procedure described above, **4c** was isolated in yield of 69% as a colorless

(7) *Bull. Soc. Chim. Fr.* **1928**, *4*, 902. *Beilsteins Handbuch der Organische Chemie* **1944**, *EII 6*, 10.

liquid: bp 130 °C (30 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 4.47 (s, 2 H), 6.75–7.10 (m, 3 H), 7.10–7.36 (m, 2 H); MS, *m/e* (rel intens) 150 (M^+), 107 (70), 77 (100), 43 (77); IR (liquid film) 1740, 1610, 1525, 1240, 1190, 770, 700 cm^{-1}. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.75; H, 6.92.

Tetraethylene Glycol Decyl Acetonyl Ether (4d). With the general procedure described above, **4d** was obtained in yield of 83% as a colorless liquid: bp 160 °C (0.05 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 0.75–1.05 (t, 3 H), 1.20–1.60 (m, 16 H), 2.20 (s, 3 H), 3.40 (t, 2 H), 3.60–3.85 (m, 16 H), 4.20 (s, 2 H); MS, *m/e* (rel intens) 390 (M^+), 101 (70), 57 (100), 45 (60); IR (liquid film) 2900, 1720, 1470, 1350, 1120 cm^{-1}. Anal. Calcd for $C_{21}H_{42}O_6$: C, 64.58; H, 10.84. Found: C, 64.17; H, 10.98.

Triethylene Glycol Acetonyl Ether (4e). With the general procedure described above, **4e** was obtained in yield of 67% as a colorless liquid: bp 115 °C (0.05 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 2.85 (s, 1 H), 3.32–3.90 (m, 12 H), 4.25 (s, 2 H); MS, *m/e* (rel intens) 206 (M^+), 101 (25), 57 (30), 45 (100); IR (liquid film) 3500, 2900, 1720, 1140 cm^{-1}. Anal. Calcd for $C_9H_{18}O_5$: C, 52.47; H, 8.80. Found: C, 52.07; H, 8.84.

***tert*-Butyl Acetonyl Ether (4g).**[8] After metallic potassium (11.7 g, 0.3 mol) was dissolved in *tert*-butyl alcohol (200 mL), **1** (17.3 g, 0.1 mol) was added and the mixture was stirred at 80 °C for 6 h. Water (100 mL) was added at room temperature, and the organic phase was extracted with diethyl ether. The solvent was removed by distillation at reduced pressure, 10 mL of 1% aqueous sulfuric acid was added into the residue, and then the mixture was stirred at 60 °C for 30 min. The product was extracted with dichloromethane, and **4g** was isolated by Kugelrolr distillation at reduced pressure in yield of 42% (5.4 g) as a colorless liquid: bp 54 °C (25 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 9 H), 2.15 (s, 3 H), 3.92 (s, 2 H); MS, *m/e* (rel intens) 130 (M^+), 57 (100), 41 (37), 29 (26); IR (liquid film) 2970, 1720, 1380, 1200, 1110 cm^{-1}.

Diacetonyl Ether (4h). The mixture of **1** (8.7 g, 0.05 mol), 30% aqueous potassium hydroxide solution (28 g, 0.15 mol), and tetrabutylammonium bisulfate (0.85 g) was stirred at 60 °C for 50 h. After neutralization with diluted sulfuric acid and extraction with diethyl ether, the hydrolysis was carried out at room temperature for 1 h. Diacetonyl ether (**4h**) was obtained as a colorless liquid in yield of 58% (1.9 g): bp 85 °C (7 torr) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 6 H), 4.20 (s, 4 H); MS, *m/e* (rel intns) 130 (M^+), 87 (37), 57 (67), 43 (100); IR (liquid film) 2900, 1740, 1425, 1360, 1130 cm^{-1}. Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.68; H, 8.04.

Registry No. 1, 70905-45-2; **2**, 105104-40-3; **3a**, 105104-41-4; **3b**, 105104-42-5; **3c**, 105104-43-6; **3d**, 105104-44-7; **3e**, 105104-45-8; **3f**, 105104-46-9; **3g**, 105104-47-0; **4a**, 40657-11-2; **4b**, 83171-86-2; **4c**, 621-87-4; **4d**, 105104-48-1; **4e**, 105104-49-2; **4f**, 105121-45-7; **4g**, 28047-99-6; **4h**, 76089-31-1; $C_{10}H_{21}OH$, 112-30-1; C_6H_5OH, 108-95-2; $C_{10}H_{21}OCH_2(CH_2OCH_2)_3CH_2OH$, 5703-94-6; $HOCH_2(CH_2OCH_2)_2CH_2OC_5H_9O$, 60221-37-6; $HOCH_2(CH_2OCH_2)_2CH_2OH$, 112-27-6; $(CH_3)_3COH$, 75-65-0; cyclohexanol, 108-93-0.

(8) Schmitz, E.; Brede, O. *J. Prakt. Chem.* **1970**, *312*, 43; *Chem. Abstr.* **1970**, *73*, 14082x.

Ionization of Fluorobullvalene. Proton Rearrangements in Protonated Naphthalene

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Bullvalene[1] is a fascinating compound that undergoes a rapid, degenerate rearrangement, interchanging all atoms with an activation energy of 11.8 ± 1 kcal/mol.[2] After the first synthesis by Schröder, rearrangement was demonstrated by NMR[3] and by preparing substituted bullvalenes. For example, halogenation of bullvalene[4] produces a thermodynamic mixture of isomers. The carbocation formed from the ionization of halobullvalenes would be of great interest. If the positive charge were on the carbon along the threefold axis, it would be a bridgehead cation, which would formally be triply allylic and in homoconjugation with three cyclopropylcarbinyl centers. However, this conjugation would be *inhibited* by the lack of overlap between the p orbital and the π orbitals of the double bonds.

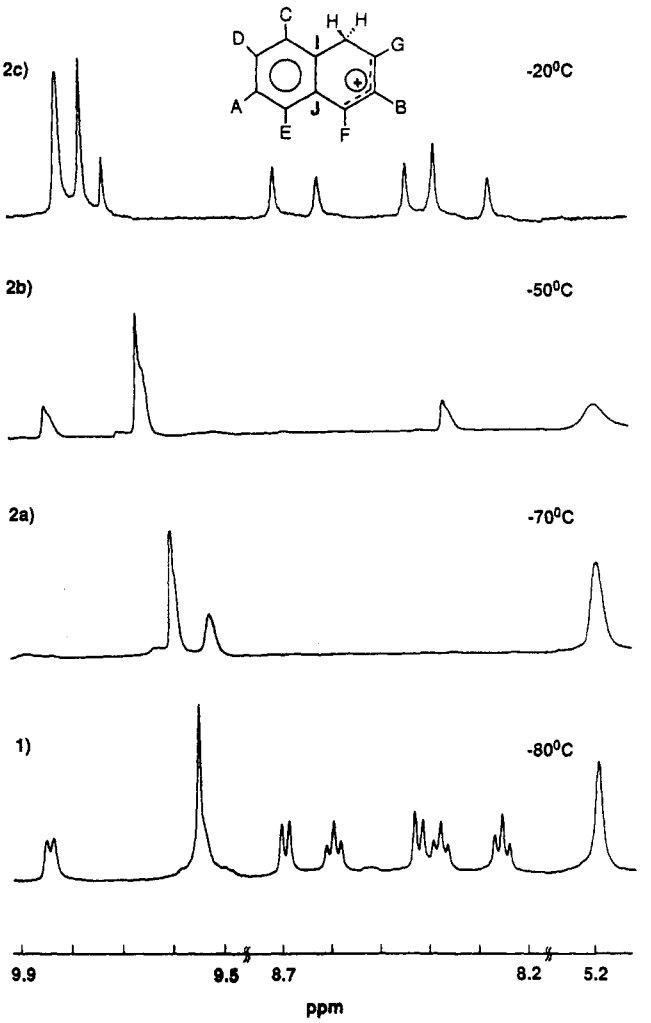

Figure 1. ^{1}H NMR at 500 MHz. (1) Cation solution resulting from addition of fluorobullvalene, at −110 °C, to SbF_5 in SO_2ClF. The sharp singlet at 9.55 ppm presumably results from HF. (2a–c) Cation solution resulting from addition of perdeuteriated naphthalene with FSO_3H and SbF_5 in SO_2ClF at indicated temperatures. Additional downfield peaks appearing at elevated temperatures presumably result from irreversible cation decomposition to unidentifiable products.

Professor Schröder generously supplied us with fluorobullvalene (fluorine is predominately along the threefold axis) and suggested that we attempt the ionization. Employing our usual procedure,[5] we codeposited it with antimony pentafluoride, under vacuum at liquid nitrogen temperatures. Addition of SO_2ClF at −110 °C resulted in a blood red solution. The solution was kept cold and transferred to an NMR tube that was placed in a precooled

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