(0.0–0.50 M, pH 8.2). The fractions absorbing at 240 nm were combined and lyophilized to give 106 mg of the tetrakis(triethylammonium) salt of EPSP: ^{1}H NMR (CD_3OD) δ 6.74 (d, 1, J = 3.9), 5.20 (d, 1, J = 1.3), 4.96 (ddd, 1, J = 4.0, 4.0, 8.8), 4.52 (d, 1, J = 1.0), 4.36 (ddd, 1, J = 6.2, 6.2, 7.3), 4.03 (dd, 1, J = 3.9, 8.1), 3.19 (q, 24), 3.99 (dd, 1, J = 5.2, 18.2), 2.25 (dd, 1, J = 5.9, 18.3), 1.29 (t, 36). Cation exchange (Dowex 50W-X8, Na^+ form) and lyophilization afforded 54 mg (63% yield) of **3** as the tetrasodium salt: $[\alpha]^{21}_D$ −124° (c 1.15, H_2O, pH 6.5); UV (H_2O, pH 6.5) $\lambda_{240\,nm}$ (ϵ 2550 M^{-1} cm^{-1}) based on 92% purity as determined by combustion analysis; ^{1}H NMR (D_2O) δ 6.41 (d, 1, J = 2.9), 5.05 (d, 1, J = 2.2), 4.74 (m, 1), 4.55 (d, 1, J = 2.2), 4.31 (ddd, 1, J = 5.5, 5.7, 7.3), 3.97 (dd, 1, J = 3.8, 7.7), 2.74 (dd, 1, J = 4.8, 18.5), 2.13 (dd, 1, J = 6.0, 19.1); ^{13}C NMR (D_2O) δ 174.4, 172.4, 157.0, 139.7, 133.3, 97.12, 76.23, 73.75 (d, J = 4.5), 71.43 (d, J = 3.6), 29.99; ^{31}P NMR (D_2O) δ 1.13. Anal. Calcd for $C_{10}H_9O_{10}PNa_4$: C, 29.14; H, 2.20; P, 7.52. Found: C, 26.88; H, 3.65; P, 7.31.

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Reactions of Oligoethylene Glycol Diglycidyl Ethers with Hydroxy Compounds

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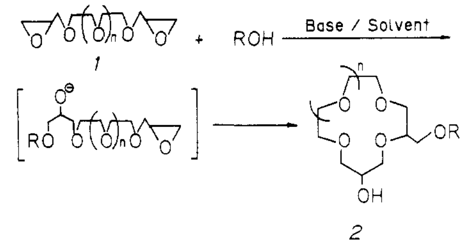
The reactions between oligoethylene glycol diglycidyl ethers and hydroxy compounds were attempted in the presence of an appropriate base. New hydroxy lariat ethers were easily obtained in the reactions with alcohols or phenols in fair to good yields depending on the kind of template metal ions.

Oligoethylene glycol diglycidyl ethers, which are prepared from epichlorohydrin and oligoethylene glycols, are interesting chemicals used as cross-linking agents in polymer chemistry by utilizing the reactivity of their two epoxy rings.[1]

In a recent patent,[2] Ovchinnikov and Chernoivanov reported the preparation of benzo crown ether derivatives by the reaction of oligoethylene glycol diglycidyl ethers with catechol. we have also previously reported the reaction of these glycidyl ethers with primary amines and ammonia in water or methanol to give a new type of monoaza crown ethers with two hydroxyl groups in fair yields.[3]

In this paper, we describe the reactions of oligoethylene glycol diglycidyl ethers with alcohols, phenols, and glycols. It was found that alkoxymethyl crown ethers with a hydroxyl group (**2**) were obtained rather selectively from the reactions with alcohols, although these reactions were anticipated to give a variety of products including addition products of the objective crown ether and the diglycidyl ether and the linear compounds such as mono- and bis(alkoxymethyl)oligoethylene glycols, and oligomers.

Scheme I



Scheme II

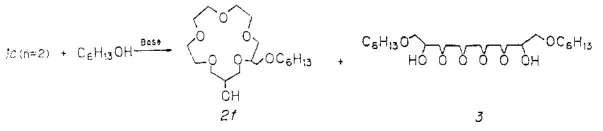


Table I. Synthesis of Alkoxymethyl Hydroxy Crown Ethers

compd	R	n	base	solvent	yield (%)
2a	$C_{12}H_{25}$	1	Li	$C_{12}H_{25}OH$	72
2b	tetrahydrofurfuryl	1	Li	t-BuOH	59
2c	CH_3	2	Na	t-BuOH	34
2d	C_3H_7	2	Na	C_3H_7OH	61
2e	$CH_2{=}CHCH_2$	2	NaOH	dioxane	53
2f	C_6H_{13}	2	Na	$C_6H_{13}OH$	50
2g	$C_{12}H_{25}$	2	Na	$C_{12}H_{25}OH$	80
2h	$C_{18}H_{37}$	2	Na	t-BuOH	48
2i	C_6H_5	2	NaOH	dioxane	46
2j	$C_{12}H_{25}$	3	Na	$C_{12}H_{25}OH$	33

The crown compounds with functional group(s) can be easily converted to polymers,[4] bis(crown ethers),[5] lariat ethers,[6] cryptands,[7] and other derivatives.[8,9] Among the functional crown ethers, synthesis and application of hydroxy crown ethers[10] have been actively investigated re-

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Table II. Examination of Template Effect in Synthesis of 2-[(Hexyloxy)methyl]-15-hydroxy-16-crown-5 (2f)

run	base	molar ratio (**1b**/base)	yield (GLC) (%) **2f**	yield (GLC) (%) **3**
1	Na	1.0/0.1	48	29
2	Na	1.0/0.2	50	25
3[a]	Na	1.0/0.2	55	24
4	Na	1.0/0.4	53	27
5	Li	1.0/0.2	32	51
6	K	1.0/0.2	10	83

[a] $NaBF_4$ was added. $NaBF_4$/**1b** = 3 (mol/mol).

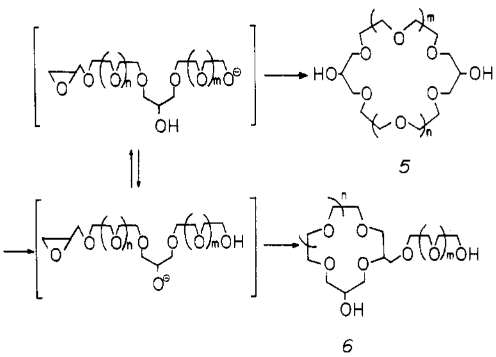
cently. Bartsch et al.[11] synthesized some hydroxy crown ethers and converted them to carboxymethyl derivatives, which show the excellent properties as ion carriers for alkali metal cations. The new reactions disclosed in this investigation should afford a simple and convenient means for the synthesis of this type of hydroxy crown ethers and the new lariat ethers useful as the ion carriers.

Results and Discussion

In these reactions, the ring-opening of one epoxy ring by an alkoxy anion gives an alkoxy intermediate, which attacks the other epoxy ring intramolecularly to give the alkoxymethyl hydroxy crown ethers **2** together with some linear byproducts (Scheme I). As the representative case, the reaction of triethylene glycol diglycidyl ether (**1c**) and threefold moles of methanol was carried out at 60 °C in *tert*-butyl alcohol in the presence of a catalytic amount of sodium *tert*-butoxide. The diglycidyl ether was completely consumed after 20 h, and 2-(methoxymethyl)-15-hydroxy-16-crown-5 (**2c**, R = CH_3) was obtained as a colorless liquid in 34% yield. In the system using dioxane and sodium hydroxide as solvent and base, the reaction rate was rather slow. The reaction was accelerated and the yield of the desired crown ether was improved when excess alcohol was used as solvent (Table I).

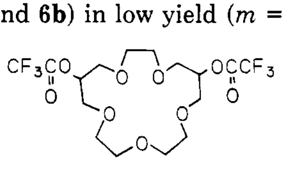
The kind of metal cations was considered to be important as the template ions.[12] In order to clarify this point, the reactions of triethylene glycol diglycidyl ether (**1c**) and a large excess of hexanol were performed by changing the kind and the amount of catalyst (Scheme II). As shown in Table II, it was found that the amount of catalyst had little affect on the yield of **2f** in the range between 10 and 40 mol % of the diglycidyl ether. However, the yields of **2f** were observed to depend on the kind of metal cation used, and sodium cation was the most suitable for the synthesis of 16-crown-5 derivative,[10p,13] whereas potassium cation preferably gave the bis[(hexyloxy)methyl]pentaethylene glycol (**3**). The use of sodium tetrafluoroborate as the template salt slightly improved the yield of crown ether **2f**.

Scheme III



The reaction of phenol with **1** in dioxane also gave the phenoxymethyl hydroxy crown ether in fair yield.

On the other hand, the reaction of diglycidyl ethers with glycols may afford the crown ethers with two hydroxyl groups (Scheme III). The reaction of an equimolar amount of ethylene glycol (**4a**, $m = 0$) and diethylene glycol diglycidyl ether (**1b**, $n = 1$) was tried in *tert*-butyl alcohol and a colorless oil, which is considered to be a mixture of two isomeric crown derivatives (**5a** and **6a**: $m = 0, n = 1$) from MS and NMR, was obtained in 24% yield. The oil was esterified with trifluoroacetic acid and the product was analyzed by ^1H NMR and estimated to contain nearly equal amounts of two hydroxy crown derivatives (**7** and **8**) from the integration ratio (8.5:5.3) of the two absorptions at δ 5.25 ($CF_3COOCH<$) and 4.45 ($CF_3COOCH_2CH_2$). The combination of diethylene glycol and diethylene glycol diglycidyl ether (**1b**) also gave the crown ether mixtures (**5b** and **6b**) in low yield ($m = n = 1$, 12%). Obviously in these cases, two kinds of alkoxy anions generated in the course of reaction have about the same reactivity and their competitive intermolecular attack to the epoxy rings of other molecules may predominantly give linear oligomers rather than the cyclic products.



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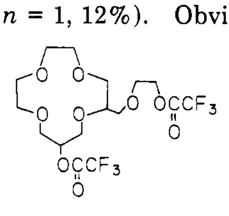

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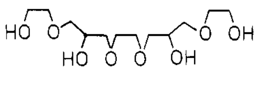

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On the other hand, α,α'-bis[(hydroxyethoxy)methyl]triethylene glycol (**9**) was obtained as a single isolable

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product in 75% yield from the reaction between ethylene glycol diglycidyl ether (**1a**) and excess ethylene glycol (**4a**) in the presence of tetrabutylammonium hydrogen sulfate.

Experimental Section

The ^1H NMR spectra were taken at 100 MHz on a JEOL JNM-PS 100 spectrometer using tetramelthylsilane as the internal standard. The infrared spectra were obtained on a Hitachi 260-10 spectrometer. The mass spectra were measured with a Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV.

Materials. *Oligoethylene glycol diglycidyl ethers 1* were prepared by the previously reported procedure.[14] Alcohols, phenols, and glycols were commercially obtained.

2-[(Dodecyloxy)methyl]-12-hydroxy-13-crown-4 (2a). To a solution of lithium metal (35 mg, 0.005 mol) in dodecyl alcohol (112 g, 0.6 mol) was added diethylene glycol diglycidyl ether (**1b**) (2.18 g, 0.01 mol), and the resulting mixture was heated at 60 °C for 20 h. The progress of the reaction was checked by GLC. The solution was concentrated. Water (50 mL) was added to the residue and the solution was extracted with dichloromethane (300 mL). The solvent was concentrated and distilled in a Kugelrohr apparatus under reduced pressure (170 °C/0.01 torr) to give a colorless liquid: IR (neat) 3440, 2930, 2860, 1470, 1360, 1300, 1260, 1130, 950, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.89 (t, 3 H), 1.04–1.68 (m, 20 H), 3.01 (s, 1 H), 3.23–4.20 (m, 20 H); MS, *m/e* (relative intensity) 404 (M^+, 7), 386 (8), 241 (12), 205 (51), 187 (21), 99 (52), 89 (80), 87 (93), 57 (100), 45 (86).

Anal. Calcd for $C_{22}H_{44}O_6$: C, 65.31; H, 10.96. Found: C, 65.65; H, 11.03.

2-(Tetrahydrofurfuryl)-12-hydroxy-13-crown-4 (2b). To a solution of lithium metal (21 mg, 0.003 mol) in *tert*-butyl alcohol were added tetrahydrofurfuryl alcohol (3.06 g, 0.03 mol) and **1b** (2.18 g, 0.01 mol), and the resulting mixture was heated at 60 °C for 30 h. After the solution was neutralized with hydrochloric acid, the solvent was evaporated off. According to the similar workup mentioned above **2b** was isolated as a colorless oil (1.88 g, 59%): bp 150 °C/0.01 torr (Kugelrohr); IR (neat) 3450, 2880, 1460, 1360, 1300, 1260, 1130, 950, 920, 880 cm^{-1}; NMR ($CDCl_3$) δ 1.44–2.15 (m, 4 H), 3.16–4.20 (m, 24 H); MS, *m/e* (relative intensity) 320 (M^+, 5), 302 (3), 205 (17), 145 (18), 89 (42), 87 (47), 85 (78), 71 (100), 45 (92).

Anal. Calcd for $C_{15}H_{28}O_7$: C, 56.23; H, 8.81. Found: C, 55.81; H, 8.98.

2-(Methoxymethyl)-15-hydroxy-16-crown-5 (2c): bp 130 °C/0.01 torr (Kugelrohr); IR (neat) 3430, 2890, 1460, 1360, 1300, 1250, 1120, 940 cm^{-1}; NMR ($CDCl_3$) δ 1.93 (s, 1 H), 3.34 (s, 3 H), 3.37–4.08 (m, 22 H); MS, *m/e* (relative intensity) 294 (M^+, 3), 276 (2), 249 (25), 133 (37), 101 (21), 89 (54), 87 (66), 45 (100).

Anal. Calcd for $C_{13}H_{26}O_7$: C, 53.05; H, 8.90. Found: C, 52.58; H, 9.15.

2-[(Propyloxy)methyl]-15-hydroxy-16-crown-5 (2d): bp 135 °C/0.01 torr (Kugelrohr); IR (neat) 3430, 2930, 2870, 1460, 1360, 1300, 1260, 1120, 950 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.34–1.87 (m, 2 H), 3.20–4.21 (m, 25 H); MS, *m/e* (relative intensity) 322 (M^+, 3), 304 (1), 279 (7), 249 (28), 133 (49), 89 (66), 87 (73), 57 (61), 45 (100).

Anal. Calcd for $C_{15}H_{30}O_7$: C, 55.88; H, 9.38. Found: C, 55.53; H, 9.41.

2-[(Allyloxy)methyl]-15-hydroxy-16-crown-5 (2e). To a stirred suspension of triethylene glycol diglycidyl ether (**1c**) (5.25 g, 0.02 mol) and sodium hydroxide (0.8 g, 0.02 mol) in dioxane (60 mL) was added allyl alcohol (1.45 g, 0.025 mol) in dioxane (60 mL) at 60 °C, and the reaction mixture was heated at 60 °C for 5 days. The solvent was evaporated and the residue was neutralized with hydrochloric acid. The objective compound was isolated according to the similar workup with **2a**: bp 130 °C/0.01 torr (Kugelrohr); IR (neat) 3440, 3060, 2850, 1640, 1440, 1340, 1290, 1250, 1110, 990, 930 cm^{-1}; NMR ($CDCl_3$) δ 3.29 (s, 1 H), 3.40–4.10 (m, 24 H), 5.10–5.40 (m, 2 H), 5.70–6.08 (m, 1 H); MS, *m/e* (relative intensity) 320 (M^+, 2), 289 (4), 249 (24), 231 (5), 133 (38), 101 (24), 89 (54), 87 (65), 57 (49), 45 (100).

Anal. Calcd for $C_{15}H_{28}O_7$: C, 56.23; H, 8.81. Found: C, 56.01; H, 8.90.

2-[(Hexyloxy)methyl]-15-hydroxy-16-crown-5 (2f): bp 140 °C/0.005 torr (Kugelrohr); IR (neat) 3430, 2930, 2870, 1470, 1360, 1300, 1260, 1120, 950, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.10–1.78 (m, 8 H), 2.96 (s, 1 H), 3.12–4.08 (m, 24 H); MS, *m/e* (relative intensity) 364 (M^+, 6), 346 (2), 321 (3), 249 (44), 133 (69), 101 (37), 89 (84), 87 (73), 57 (69), 45 (100).

Anal. Calcd for $C_{18}H_{36}O_7$: C, 59.32; H, 9.96. Found: C, 59.09; H, 10.08.

2-[(Dodecyloxy)methyl]-15-hydroxy-16-crown-5 (2g): bp 200 °C/0.01 torr (Kugelrohr); IR (neat) 3450, 2950, 2870, 1470, 1350, 1300, 1250, 1120, 940, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.89 (t, 3 H), 1.14–1.40 (m, 20 H), 3.21 (s, 1 H), 3.34–4.08 (m, 24 H); MS, *m/e* (relative intensity) 448 (M^+, 8), 430 (3), 405 (3), 249 (71), 133 (68), 101 (36), 89 (70), 87 (75), 57 (98), 45 (100).

Anal. Calcd for $C_{24}H_{48}O_7$: C, 64.25; H, 10.78. Found: C, 64.60; H, 10.89.

2-[(Octadecyloxy)methyl]-15-hydroxy-16-crown-5 (2h): bp 210 °C/0.005 torr (Kugelrohr); IR (neat) 3440, 2920, 2860, 1470, 1350, 1300, 1250, 1130, 950, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.87 (t, 3 H), 1.14–1.67 (m, 32 H), 3.24–4.16 (m, 25 H); MS, *m/e* (relative intensity) 532 (M^+, 8), 524 (3), 489 (2), 249 (70), 133 (72), 101 (44), 89 (84), 87 (87), 57 (98), 45 (100).

Anal. Calcd for $C_{30}H_{60}O_7$: C, 67.63; H, 11.35. Found: C, 67.20; H, 11.47.

2-(Phenoxymethyl)-15-hydroxy-16-crown-5 (2i). To a stirred suspension of triethylene glycol diglycidyl ether (**1c**) (5.25 g, 0.02 mol) and sodium hydroxide (0.8 g, 0.02 mol) in dioxane (50 mL) was added phenol (2.35 g, 0.025 mol) in dioxane (50 mL) at 60 °C, and the reaction mixture was heated at 60 °C for 3 days. The solvent was evaporated and the residue was neutralized with hydrochloric acid. The workup was done according to the similar method for **2a**: bp 180 °C/0.01 torr; IR (neat) 3440, 3060, 2870, 1600, 1500, 1450, 1350, 1290, 1250, 1120, 940, 760 cm^{-1}; NMR ($CDCl_3$) δ 3.26 (s, 1 H), 3.40–4.08 (m, 22 H), 6.82–7.02 (m, 3 H), 7.14–7.36 (m, 2 H); MS, *m/e* (relative intensity) 356 (M^+, 3), 263 (24), 249 (13), 133 (58), 101 (26), 89 (47), 87 (51), 59 (35), 57 (43), 45 (100).

Anal. Calcd for $C_{18}H_{28}O_7$: C, 60.66; H, 7.92. Found: C, 60.19; H, 8.12.

2-[(Dodecyloxy)methyl]-18-hydroxy-19-crown-6 (2j): bp 220 °C/0.005 torr; IR (neat) 3420, 2930, 2860, 1470, 1360, 1300, 1250, 1120, 950, 730 cm^{-1}; NMR ($CDCl_3$) δ 0.87 (t, 3 H), 1.10–1.72 (m, 20 H), 3.32–4.09 (m, 29 H); MS, *m/e* (relative intensity) 492 (M^+, 4), 474 (1), 449 (1), 293 (33), 219 (25), 177 (16), 133 (42), 89 (92), 87 (92), 57 (80), 45 (100).

Anal. Calcd for $C_{26}H_{52}O_8$: C, 63.38; H, 10.64. Found: C, 63.06; H, 10.49.

Examination of Template Effect in the Reaction of Hexyl Alcohol and 1c. To a stirred solution of an appropriate amount of alkali metal in hexyl alcohol (50 mL, 0.4 mol) was added triethylene glycol diglycidyl ether (**1c**) (2.62 g, 0.01 mol), and the mixture was heated at 60 °C for 20 h. At this stage, **1c** was completely consumed. The solvent was evaporated and water (20 mL) was added to the residue. The mixture was extracted with dichloromethane (150 mL) and the dichloromethane was concentrated. The ratio of **2f** and **3** was determined on the basis of the peak areas of GLC analyses (Shimadzu GC 3BT; internal standard: **2a**; 1.1 m × 3 mm column packed with 5% SE-30 on Celite 545 (60–80 mesh), TCD, H_2 carrier, 265 °C).

Mixture of 9,16-Dihydroxy-1,4,7,11,14-pentaoxacycloheptadecane (5a) and 2-[(2-Hydroxyethoxy)methyl]-12-hydroxy-13-crown-4 (6a). To a stirred solution of sodium metal (69 mg, 0.003 mol) in *tert*-butyl alcohol (50 mL) was added ethylene glycol (0.93 g, 0.015 mol) and diethylene glycol diglycidyl ether (**1b**) (2.18 g, 0.01 mol), and the mixture was heated at 60 °C for 30 h. The mixture was neutralized with hydrochloric acid and the solvent was evaporated. The workup was done according to the similar method for **2a**: bp 140 °C/0.01 torr (Kugelrohr); IR (neat) 3380, 2860, 1450, 1350, 1290, 1240, 1130, 980, 940, 880 cm^{-1}; NMR ($CDCl_3$) δ 3.05 (s, 2 H), 3.30–4.31 (m, 22 H); MS, *m/e* (relative intensity) 280 (M^+, 5), 262 (2), 237 (3), 191 (8), 163 (16), 145 (10), 101 (38), 89 (29), 87 (76), 45 (100).

Anal. Calcd for $C_{12}H_{24}O_7$: C, 51.42; H, 8.63. Found: C, 51.51; H, 8.81.

Mixture of 8,19-Dihydroxy-1,4,7,11,14,17-hexaoxacycloeicosane (5b) and 2-[(2-(2-hydroxyethoxy)ethoxy)methyl]-

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[14] Gu, X.-P.; Ikeda, I.; Okahara, M. *Synthesis* 1985, 649.

15-hydroxy-16-crown-5 (6b): Yield 12%; bp 160 °C/0.01 torr (Kugelrohr); IR (neat) 3370, 2890, 1460, 1350, 1250, 1130, 980, 930, 900 cm^{-1}; NMR ($CDCl_3$) δ 3.08–4.20 (m, 28 H); MS, *m/e* (relative intensity) 324 (M^+, 4), 306 (2), 205 (12), 163 (14), 145 (19), 101 (28), 89 (50), 87 (62), 45 (100).

Anal. Calcd for $C_{14}H_{28}O_8$: C, 51.84; H, 8.70; Found: C, 52.17; H, 8.98.

3,7,10,14-Tetraoxahexadecane-1,5,12,16-tetrol (9). To a stirred solution of sodium metal (46 mg, 0.002 mol) in ethylene glycol (**4a**) (50 mL) were added ethylene glycol diglycidyl ether (**1a**) (1.74 g, 0.01 mol) and tetrabutylammonium hydrogen sulfate (0.34 g, 0.001 mol), and the mixture was heated at 60 °C for 15 h: bp 170 °C/0.01 torr; IR (neat) 3370, 2860, 1460, 1360, 1250, 1130, 950, 900 cm^{-1}; NMR ($CDCl_3$) δ 3.12–4.20 (m, 26 H); MS, *m/e* (relative intensity) 299 (M^++1, tr), 223 (10), 205 (36), 119 (78), 101 (61), 87 (64), 57 (45), 45 (100).

Anal. Calcd for $C_{12}H_{26}O_8$: C, 48.31; H, 8.78. Found: C, 47.86; H, 8.92.

Asymmetric Conjugate Addition of Organometallic Reagents to Chiral Vinyl Sulfoximines

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The chiral vinyl sulfoximines 1 and 2 (R′ = C_6H_5, CH_3, *n*-Bu, $C_6H_5CH_2CH_2$) have been prepared; they undergo conjugate addition reactions with organometallic reagents with high asymmetric induction. These conjugate addition adducts have been converted to chiral 3-alkylalkanoic acids in high enantiomeric excess (>90%).

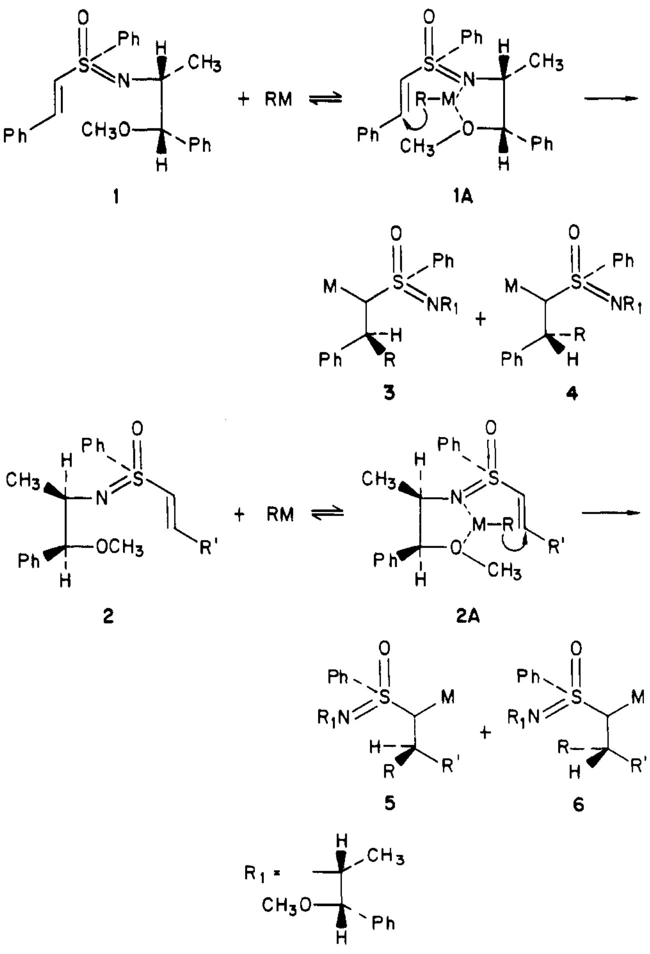
In recent years, a variety of chiral electrophilic olefinic substrates that undergo conjugate addition by organometallic reagents with high asymmetric induction[1] have been prepared. These substrates have allowed for the preparation of chiral 3-alkykalkanoic acids[1b–e,h] and 3-alkylcycloalkanones[1e–g] and their derivatives[1a] in high (>95%) enantiomeric excess (ee). We report here a study of the conjugate addition of organometallic reagents to chiral vinyl sulfoximines and demonstrate the potential of these substrates for enantioselective synthesis.

By analogy with the chemistry of vinyl sulfones,[2] it was expected that vinyl sulfoximines would undergo smooth conjugate addition with organometallic reagents. The chiral vinyl sulfoximines **1** and **2**, being bidentate ligands for coordination with an organometallic reagent (RM, Scheme I), should ensure high asymmetric induction in the conjugate-addition step. It was expected that the resulting carbanionic intermediates (**3**, **5**) would be readily manipulated to give a variety of chiral substrates.[3]

Synthesis of Chiral Vinyl Sulfoximines 1 and 2

(+)-Norephedrine[4] was converted to (1*S*,2*R*)-2-amino-1-methoxy-1-phenylpropane (**7**) by standard procedures.[5] Treatment of benzenesulfinyl chloride (2 equiv) in CH_2Cl_2 at 0 °C with **7** (1 equiv) and Et_3N (2 equiv) gave the diastereomeric sulfinamides **8** and **9** (3:1 respectively) as an inseparable mixture by TLC (Scheme II). Treatment of this mixture with *N*-chlorobenzotriazole[8] in THF at 0–23 °C[9] and then sodium phenoxide in DMF[7c] gave a mixture (1.8:1) of diasteromeric phenylsulfonimidates **11** which was homogeneous by TLC, in 85% overall yield from **7**. Not unexpectedly,[7c] racemization at sulfur had occurred in the intermediate sulfonimidoyl chloride **10**. The mixture of phenysulfonimidates **11** was treated with methyllithium to give chromatographically separable (*SS*)-(+)-sulfoximine **12** (14%, $[\alpha]^{18}{}_D$ +88.8° (CH_2Cl_2, *c* 0.024)) and (*SR*)-(+)-sulfoximine **13** (28%, $[\alpha]^{18}{}_D$ +19.2° (CH_2Cl_2, *c* 0.03)).

Scheme I[a]



[a] a, R′ = C_6H_5; b, R′ = CH_3; c, R′ = *n*-Bu; d, R′ = $CH_2CH_2C_6H_5$.

The sulfoximines **12** and **13** were converted to (*SS*)-vinyl sulfoximine **1** and (*SR*)-vinyl sulfoximine **2**, respectively,

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