48.6 (C-3′), 52.0 (C-5′), 30.5 (C-6′), 55.7 (C-7′), 134.7 (C-8′), 114.5 (C-9′), 118.4 (C-10′), 110.2[a] (C-11′), 145.1 (C-12′), 136.9 (C-13′), 25.8 (C-14′), 80.2[b] (C-15′), 31.1 (C-16′), 32.7 (C-17′), 65.3[c] (C-18′), 36.5 (C-19′), 44.6[d] (C-20′), 63.9 (C-21′), 28.4 (C-22′), 47.7 (C-23′), 131.4 (C-2), 48.6 (C-3), 51.3 (C-5), 17.8 (C-6), 105.9 (C-7), 128.7 (C-8), 117.9 (C-9), 121.7 (C-10), 120.4 (C-11), 110.7[a] (C-12), 134.4 (C-13), 42.0 (C-14), 80.6[b] (C-15), 82.1 (C-16), 43.3 (C-17), 66.3[c] (C-18), 37.6 (C-19), 43.8[d] (C-20), 56.7 (C-21), 173.6 (C=O), 54.0 (CO_2CH_3), 54.0 (OCH_3) (a–d indicate assignments may be interchanged); CD (MeOH, c 0.7) $\Delta\epsilon$ 0 (224 nm), −29.0 (230), −3.7 (243), −8.7 (265), 0 (287), −1.8 (308), 0 (325).

(b) When the addition of sodium acetate was left out of the preceding procedure and the reaction mixture (starting from 250 mg of **4**) held at reflux for 1.5 h, the development of two less polar products was observed by TLC. The usual workup followed by PLC (silica; benzene–ethanol–NH_3, 89:10:1) gave 48 mg (20%) of 2′,16′:16,17-dianhydrovobtusamine, 105 mg (43%) of 16,17-anhydrovobtusamine, 21 mg (8%) of 16-isovobtusamine **5**, and 33 mg (13%) of vobtusamine **3**.

2′,16′:16,17-Dianhydrovobtusamine had the following: R_f 0.58 [emerald green (CAS)]; UV (MeOH) λ_{max} 228, 275, 314 nm (log ϵ 4.45, 4.20, 3.92); IR ($CHCl_3$) 2840, 2800, 1725 cm^{-1}; mass spectrum (265 °C), m/z 698 ($M^{+\cdot}$, 22), 560 (23), 266 (30), 149 (64), 138 (100); ^1H NMR δ 3.60 (3 H, s, $ArOCH_3$), 4.00 (3 H, s, CO_2CH_3), 6.07 (1 H, s, H-17), 6.60–7.60 (7 H, m, aromatic protons); ^{13}C NMR (inter alia) 145.3 (C-2′), 43.7 (C-6′), 50.6 (C-7′), 102.0 (C-16′), 33.5 (C-22′), 52.3 (C-23′), 38.4 (C-14), 85.7 (C-15), 127.0 (C-16), 125.2 (C-17), 163.8 (C=O).

16,17-Anhydrovobtusamine had the following: R_f 0.46 [blue (CAS)]; UV (MeOH) λ_{max} 228, 263, 312 nm (log ϵ 4.52, 4.24, 3.98); IR ($CHCl_3$) 2840, 2800, 1725 cm^{-1}; mass spectrum (250 °C), m/z 716 ($M^{+\cdot}$, 100), 698 (14), 560 (16), 421 (14), 393 (27), 149 (37), 138 (74); ^1H NMR δ 3.46 (3 H, s, $ArOCH_3$), 4.02 (3 H, s, CO_2CH_3), 6.10 (1 H, s, H-17), 6.60–6.85 (3 H, m, H-9′, H-10′, H-11′), 7.05–7.60 (4 H, m, aromatic protons); ^{13}C NMR (inter alia) 27.8 (C-22′), 47.4 (C-23′), 130.0 (C-2), 84.5 (C-15), 127.3 (C-16), 125.8 (C-17), 163.8 (C=O).

Based-Catalyzed Epimerization of Vobtusamine (3 → 5). A solution of 15 mg (0.02 mmol) of vobtusamine (**3**) in 0.5 mL of tetramethylguanidine was stirred at room temperature for 1.5 h under nitrogen, poured into water and extracted with ether. The crude reaction mixture showed a 68:32 HPLC ratio of **5** and **3**.

Registry No. **2**, 19772-79-3; **3**, 84009-34-7; **3** (2′,16′:16,17-dianhydro), 84009-36-9; **3** (16,17-anhydro), 84009-37-0; **4**, 84009-35-8; **5**, 84048-13-5.

Conjugate Addition of 1-(Phenylthio)-1-(trimethylsilyl)-2-propene to Unsaturated Ketones

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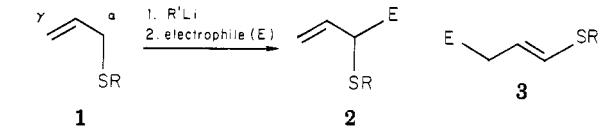
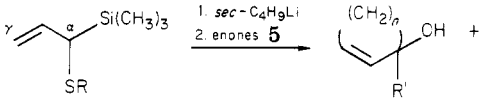
The reactions of unsymmetrical, sulfur-substituted, allyllithium reagents **1** with alkyl halides,[1] epoxides,[2] and carbonyl compounds[3] proceed with predominant α regioselectivity to give adducts **2** rather than adducts **3** (Scheme I). Exceptions to this generalization include the reactions of (alkylthio)allylcopper reagents with allylic halides,[3a,b] (arylthio)allyllithium reagents with ketones in the presence of *N,N,N′,N′*-tetramethylethylenediamine, hexamethylphosphoramide, or 1,4-diazabicyclo[2.2.2]octane,[1a] and the doubly metalated derivative of 2-propenethiol with various electrophiles.[4] In addition, the alkylation of various ketene dithioacetals exhibits similar γ regioselectivity in certain cases.[5] We recently demonstrated that 1-(phenylthio)-1-(trimethylsilyl)-2-propene (**4**) also exhibits γ regioselectivity in reactions with aldehydes and ketones,[6] and we now report the reactions of **4** with various unsaturated ketones.[7]

Scheme I



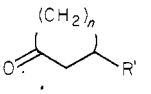
1 **2** **3**

Scheme II



4, R = C_6H_5
8, R = n-C_4H_9

6, R′ = $CH_2CH{=}C(SR)Si(CH_3)_3$



7, R′ = $CH_2CH{=}C(SR)Si(CH_3)_3$

In contrast to the high degree of α regioselectivity noted for the addition of (arylthio)- or (alkylthio)allyllithium reagents to enones,[3d] the addition of the anion of **4** to enones **5** proceeds exclusively with γ regioselectivity. Also, unlike the results reported by Binns and Haynes,[3d] 1,4-addition predominates over 1,2-addition even in the absence of hexamethylphosphoramide. With 2-cyclohexenone (**5a**), the addition furnished the γ/1,2-adduct **6** and the γ/1,4-adduct **7** (Scheme II) in a 12:88 ratio in 75% yield in the presence of hexamethylphosphoramide and in a 22:78 ratio in 61% yield in the absence of hexamethylphosphoramide. Careful scrutiny of the crude product failed to reveal any of the α/1,2- or α/1,4-adducts. Although the same degree of γ regioselectivity was maintained in other enone reactions, the proportion of 1,2- and 1,4-addition varied in a manner that was not always predictable. For example, the addition of **4** to cyclopentenone (**5c**) or cycloheptenone (**5d**) led to the γ/1,2-adducts **6** and γ/1,4-adducts **7** in 50:50 and 48:52 ratios, respectively,

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(6) Kyler, K. S.; Watt, D. S. *J. Org. Chem.* **1981**, *46*, 5182.

(7) For reactions of sulfur-substituted nucleophiles (other than allylic anions) with various unsaturated carbonyl compounds, see: (a) Mukaiyama, T.; Narasaka, K.; Furusato, M. *J. Am. Chem. Soc.* **1972**, *94*, 8641. (b) Herrmann, J. L.; Richman, J. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 3271. (c) Ostrowski, P. C.; Kane, V. V. *Ibid.* **1977**, 3549. (d) Ziegler, F. E.; Schwartz, J. A. *J. Org. Chem.* **1978**, *43*, 985. (e) Ziegler, F. E.; Tam, C. C. *Tetrahedron Lett.* **1979**, 4717.

0022-3263/83/1948-0383$01.50/0

Table I. Addition of Anions Derived from 4 or 8 to Enones 5

enone 5	anion of	% HMPA–THF	ratio of γ/1,2 and γ/1,4 products (% isolated yield)
2-cyclohexenone (5a)	4	5	12:88 (75)
3-methylcyclohexenone (5b)	4	5	57:43 (63)
cyclopentenone (5c)	4	5	50:50 (49)
cycloheptenone (5d)	4	5	48:52 (52)
5d	4	30	32:68 (63)
benzalacetone (5e)	4	5	59:41 (64)
5e	4	20	42:58 (65)
5e	8	5	53:47 (63)
chalcone (5f)	4	5	55:45 (75)

unlike the predominant γ/1,4-selectivity in the cyclohexenone case. These ratios did not change appreciably when 1-(*n*-butylthio)-1-(trimethylsilyl)-2-propene (**8**) was substituted for **4** in analogous additions or when the percentage of HMPA in the reaction medium was varied. Regeneration of the lithium alkoxide of the γ/1,2-adduct **6** (n = 3) did not result in any of the γ/1,4-adduct **7**, suggesting at least for this case that the 1,4-addition product is the result of kinetic control.[3d]

Although the presence or absence of copper(I) was reported to have little influence on the product distribution of reactions of (alkylthio)allyllithium reagents and enones,[3b] we elected to examine the organocuprates derived from **4**. We noted that the addition of copper(I) salts, particularly cuprous cyanide, in the presence of trimethyl phosphite led unexpectedly to significant increases in the γ/1,2-adduct. For example, the addition of the organolithium derivative of **4** to chalcone led to the γ/1,2- and γ/1,4-adducts in a 55:45 ratio whereas the addition of the organocuprate of **4** led to the γ/1,2- and γ/1,4-adducts in a 95:5 ratio. We do not, as yet, understand the underlying reasons for the regioselectivity change, but clearly the generalization that copper(I) promotes conjugate additions must be interpreted with some caution in dealing with sulfur-containing organometallic reagents.

Experimental Section

Infrared spectra were determined on a Beckman Microlab 600 spectrometer. The abbreviation TF denotes thin film. NMR spectra were determined on a JEOL 270-MHz spectrometer. Mass spectra were determined on either a Varian MAT CH5 or a Du Pont CEC 21-10B mass spectrometer. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

General Procedure for the Addition of the Anion of 1-(Phenylthio)-1-(trimethylsilyl)-2-propene (4) to Enones. Addition to Cyclohexenone (5a). To 287 mg (1.3 mmol) of **4** in 2.0 mL of THF at −78 °C under a nitrogen atmosphere were added 1 mL of 1.31 M *sec*-butyllithium in cyclohexane and 0.1 mL of HMPA. The orange solution was stirred for 2 h, and 96 mg (1.0 mmol) of cyclohexenone (**5a**) in 0.5 mL of THF was added. The solution was stirred an additional 4 h and quenched with 1 mL of water. The product was diluted with ether, washed with water, dried over anhydrous $MgSO_4$, and chromatographed on silica gel (1:3:5 ether–hexanes–CH_2Cl_2) to afford the γ/1,2-product **6a**: 9%; R_f 0.38; IR (TF) 3396, 1582 cm^{-1}; NMR ($CDCl_3$) δ 0.11 (s, 9, $SiMe_3$), 2.76 (d, J = 7 Hz, 2, $CH_2CH{=}C(SPh)SiMe_3$), 5.6–5.9 (m, 2, vinylic ring H), 6.83 (t, J = 7 Hz, 1, $CH_2CH{=}C(SPh)SiMe_3$), 7.1–7.5 (m, 5, aromatic H); mass spectrum (70 eV), m/e 318 (M^+), 300, 222, 167; exact mass calcd for $C_{18}H_{26}OSSi$ m/e 318.1474, found 318.1497.

Another band (R_f 0.46) was eluted to afford the γ/1,4-product **7a**: 66%; IR (TF) 1709, 1581 cm^{-1}; NMR ($CDCl_3$) δ 0.11 (s, 9, $SiMe_3$), 6.61 (t, J = 7 Hz, 1, $CH_2CH{=}C(SPh)SiMe_3$), 7.1–7.5 (m, 5, aromatic H); mass spectrum (70 eV), m/e 318, 222, 209, 208, 167.

Anal. Calcd for $C_{18}H_{26}OSSi$: C, 67.86; H, 8.23. Found: C, 67.65; H, 8.26.

Adducts of 3-Methylcyclohexenone (5b). γ/1,2-Product 6b: IR (TF) 3400, 1590 cm^{-1}; NMR ($CDCl_3$) δ 0.12 (s, 9, $SiMe_3$), 1.76 (s, 3, vinyl CH_3), 2.74 (d, J = 7 Hz, 2, $CH_2CH{=}C(SPh)SiMe_3$), 5.44 (m, 1, $CH{=}C(CH_3)$), 6.84 (t, J = 7 Hz, 1, $CH_2CH{=}C(SPh)SiMe_3$); mass spectrum (70 eV), m/e (relative intensity) 332 (M^+, 100), 222 (27), 221 (64), 167 (13); exact mass calcd for $C_{19}H_{28}OSSi$ m/e 332.1631, found 332.1637.

γ/1,4-Product 7b: IR (TF) 1706, 1583 cm^{-1}; NMR ($CDCl_3$) δ 0.10 (s, 3, $SiMe_3$), 1.05 (s, 3, CH_3), 6.76 (t, J = 7 Hz, $CH_2CH{=}C(SPh)SiMe_3$); mass spectrum (70 eV), m/e (relative intensity) 332 (M^+, 2), 314 (53), 231 (100), 222 (30), 167 (7); exact mass calcd for $C_{19}H_{28}OSSi$ m/e 332.1631, found 332.1628.

Adducts of Cyclopentenone (5c). The adducts were inseparable, and analysis of NMR signals for $SiMe_3$ groups indicated a ca. 1:1 ratio of γ/1,2- and γ/1,4-adducts.

Adducts of Cycloheptenone (5d). γ/1,2-Product 6d: IR (TF) 3400, 1581 cm^{-1}; NMR ($CDCl_3$) δ 0.11 (s, 9, $SiMe_3$), 6.60 (t, J = 7 Hz, 1, $CH_2CH{=}C(SPh)SiMe_3$); mass spectrum (70 eV), m/e (relative intensity) 332 (M^+, 5), 314 (22), 222 (100), 167 (21); exact mass calcd for $C_{19}H_{28}OSSi$ m/e 332.1631, found 332.1633.

γ/1,4-Product 7d: IR (TF) 1698, 1581 cm^{-1}; NMR ($CDCl_3$) δ 0.11 (s, 9, $SiMe_3$), 6.60 (t, J = 7 Hz, 1, $CH_2CH{=}C(SPh)SiMe_3$); mass spectrum (70 eV), m/e (relative intensity) 332 (M^+, 52), 293 (19), 281 (35), 269 (29), 223 (21), 131 (99), 119 (100); exact mass calcd for $C_{19}H_{28}OSSi$ m/e 332.1631, found 332.1636.

Adducts of Benzalacetone (5e). γ/1,2-Product 6e: IR (TF) 3420, 1580 cm^{-1}; NMR ($CDCl_3$) 0.11 (s, 9, $SiMe_3$), 1.51 (s, 3, CH_3), 2.89 (d, J = 7 Hz, 2, $CH_2CH{=}C(SPh)SiMe_3$), 6.37, 6.70 (2 d, J = 16 Hz, $CH{=}CHC_6H_5$), 6.83 (t, J = 7 Hz, 1, $CH_2CH{=}C(SPh)SiMe_3$); mass spectrum (70 eV), m/e 367, 350, 222, 147, 73.

Anal. Calcd for $C_{22}H_{28}OSSi$: C, 71.68; H, 7.66. Found: C, 71.52; H, 7.75.

γ/1,4-Product 7e: IR (TF) 1715, 1582 cm^{-1}; NMR ($CDCl_3$) δ 0.01 (s, 9, $SiMe_3$), 2.09 (s, 3, $COCH_3$), 6.49 (t, J = 7 Hz, 1, $CH_2CH{=}C(SPh)SiMe_3$); mass spectrum (70 eV), m/e 368, 310, 222, 134, 73.

Anal. Calcd for $C_{22}H_{28}OSSi$: C, 71.68; H, 7.66. Found: C, 71.76; H, 7.66.

Adducts of Chalcone (5f). γ/1,2-Product 6f: IR (TF) 3453, 1579 cm^{-1}; NMR ($CDCl_3$) δ 0.11 (s, 9, $SiMe_3$), 2.43 (s, 1, OH), 3.32 (d, J = 7 Hz, 2, $CH_2CH{=}C(SPh)SiMe_3$), 6.60, 6.89 (2 d, J = 16 Hz, 2, $CH{=}CHC_6H_5$), 6.80 (t, J = 7 Hz, 1, $CH_2CH{=}C(SPh)SiMe_3$), 7.1–7.6 (m, 15, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 412 ($M^+ - H_2O$), 222, 209 (base), 105.

Anal. Calcd for $C_{27}H_{30}OSSi$: C, 75.30; H, 7.02. Found: C, 75.16; H, 7.07.

γ/1,4-Product 7f: IR (TF) 1684, 1595, 1579 cm^{-1}; NMR ($CDCl_3$) δ 0.03 (s, 3, $SiMe_3$), 2.87 (m, 2, $CH_2CH{=}C(SPh)SiMe_3$), 3.32 (d, J = 7 Hz, 2, CH_2COPh), 3.62 (m, 1, CHPh), 6.50 (t, J = 7 Hz, 1, $CH_2CH{=}C(SPh)SiMe_3$), 7.2–8.2 (m, 15, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 430, 222, 105 (base).

Anal. Calcd for $C_{27}H_{30}OSSi$: C, 75.30; H, 7.02. Found: C, 75.16; H, 7.06.

1-(*n*-Butylthio)-1-(trimethylsilyl)-2-propene (8). The procedure[5] described for the preparation of **4** was repeated with 28.6 g (0.22 mol) of allyl *n*-butyl thioether, 158 mL of 1.4 M *sec*-butyllithium (0.22 mol), and 52 g (0.48 mol) of chlorotrimethylsilane to afford 19.3 g (43%) of **8**: bp 77–79 °C (3.8 mm); IR (TF) 1617 cm^{-1}; NMR ($CDCl_3$) δ 0.10 (s, 9, $SiMe_3$), 0.90 (m, 3, $S(CH_2)_3CH_3$), 2.70 (d, J = 10 Hz, $CHCH{=}CH_2$), 4.85–5.15 and 5.55–5.8 (m, 3, vinylic H); mass spectrum (70 eV), m/e (relative intensity) 202 (M^+, 16), 145 (51), 73 (100).

Anal. Calcd for $C_{10}H_{22}SSi$: C, 59.33; H, 10.96. Found: C, 59.30; H, 11.01.

In addition, 16.8 g (37%) of (*E*)-1-(*n*-butylthio)-3-(trimethylsilyl)-1-propene was obtained: bp 88–89 °C (3.8 mm); IR (TF) 1600 cm^{-1}; NMR ($CDCl_3$) δ 0.03 (s, 9, $SiMe_3$), 0.91 (t, J = 7 Hz, 3, $S(CH_2)_3CH_3$), 5.5–5.9 (m, 2, vinylic H); mass spectrum (70 eV), m/e (relative intensity) 202 (M^+, 14), 145 (50), 73 (100).

Anal. Calcd for $C_{10}H_{22}SSi$: C, 59.33; H, 10.96. Found: C, 59.36; H, 11.03.

Addition of 1-(*n*-Butylthio)-1-(trimethylsilyl)-2-propene (8) to Benzalacetone (5e). The procedure described for the addition of 4 to enones was repeated with 8 and 5e to afford γ/1,2-product: IR (TF) 3420, 1600, 1580 cm^{-1}; NMR ($CDCl_3$) δ 0.17 (s, 9, $SiMe_3$), 0.90 (t, J = 7 Hz, 3, $S(CH_2)_3CH_3$), 1.42 (s, 3, $C(OH)CH_3$), 6.15, 6.76 (2 d, J = 16.5 Hz, 2, $CH{=}CHPh$), 6.35 (t, J = 7 Hz, 1, $CH_2CH{=}C(SC_4H_9\text{-}n)Si(CH_3)_3$), 7.1-7.5 (m, 5, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 202 (50), 147 (100), 93 (24), 73 (69).

Anal. Calcd for $C_{20}H_{32}OSSi$: C, 68.90; H, 9.25. Found: C, 69.09; H, 9.30.

γ/1,4-Product: IR (TF) 1716 cm^{-1}; NMR ($CDCl_3$) δ 0.09 (s, 3, $SiMe_3$), 0.91 (t, J = 7 Hz, 3, $S(CH_2)_3CH_3$), 2.05 (s, 3, $COCH_3$), 6.06 (t, J = 7 Hz, 1, $CH_2CH{=}C(SC_4H_9\text{-}n)Si(CH_3)_3$), 7.2-7.5 (m, 5, aromatic H); mass spectrum (70 eV), m/e (relative intensity) 348 (M^+, 13), 201 (100), 73 (98).

Anal. Calcd for $C_{20}H_{32}OSSi$: C, 68.90; H, 9.25. Found: C, 69.08; H, 9.33.

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Registry No. **4**, 78905-13-2; **5a**, 930-68-7; **5b**, 1193-18-6; **5c**, 930-30-3; **5d**, 1121-66-0; **5e**, 122-57-6; **5f**, 94-41-7; **6a**, 84029-01-6; **6b**, 84029-03-8; **6d**, 84029-05-0; **6e**, 84029-07-2; **6f**, 84029-09-4; **7a**, 84029-02-7; **7b**, 84029-04-9; **7d**, 84029-06-1; **7e**, 84029-08-3; **7f**, 84029-10-7; **8**, 84029-11-8; (*E*)-1-(*n*-butylthio)-3-(trimethylsilyl)-1-propene, 84029-12-9; 1-(trimethylsilyl)-1-(butylthio)-4-methyl-6-phenylhexa-1,5-dien-4-ol, 84029-13-0; 7-(trimethylsilyl)-7-(butylthio)-4-phenylhept-6-en-2-one, 84029-14-1.

Poly(ethylene glycol)-Grafted Copolymers as Synthetic Equivalents of Benzyltriethylammonium Chloride for Triphase Catalytic Alkylation[1]

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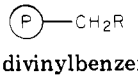
Benzyltriethylammonium chloride has enjoyed wide popularity as a catalyst for alkylation reactions in organic–aqueous hydroxide two-phase systems.[2] In an effort to expand the synthetic utility of this and related quaternary ammonium salts, attempts have recently been made to develop polymeric equivalents for use in analogous triphase conversions.[3-5] Commercial anion-exchange resins bearing pendant quaternary ammonium groups exhibit modest triphase catalytic activity for C-alkylation of phenylacetonitrile.[3] Similar polymers have also been used successfully in alkylating benzyl methyl ketone.[4] Because of their susceptibility toward dequaternization, however, the ultimate value of these resins for practical organic synthesis appears questionable.[6] Polymer-supported crown ethers and cryptands can also function as triphase catalysts for alkylation reactions and are clearly preferable in terms of chemical stability and reusability.[4] They are, however, far more difficult and expensive to prepare.[7-9] In this paper we report synthetic results which show that simple poly(ethylene glycols) grafted to cross-linked polystyrene are remarkably active and stable triphase catalysts for the alkylation of nitriles, ketones, and alcohols.

Table I. Monoalkylation of Phenylacetonitrile with 1-Bromobutane[a]

catalyst	conversion, %	yield,[b] %
none	0.3	0.3
I	96, 94,[c] 97[d]	92
II	71	63
III	74	70
IV	58	55
V	30, 18[c]	22
VI	24	22
VII	65	64
VIII	54	52
$PhCH_2N(C_2H_5)_3Cl$	96	94

[a] Reaction of 0.82 mmol of phenylacetonitrile with 0.83 mmol of *n*-bromobutane plus 0.5 mL of 60% aqueous KOH and 0.05 mmol of catalyst for 1.5 h at 23 °C. [b] GLC yield. [c] Yield from reused catalyst. [d] Yield from second reuse of catalyst.

Resins I–VIII were prepared from commercial chloromethylated polystyrene by using standard grafting procedures.[10-13] For comparison of their efficacies for promoting alkylation, the conversion of phenylacetonitrile to 2-phenylhexanenitrile was chosen as a standard reaction (eq 1). This transformation has been used extensively in judging catalyst performance in both liquid–liquid two-



polystyrene gel-1% divinylbenzene (200-400 mesh)

I, R = $O(CH_2CH_2O)_{16}CH_3$; 17% ring substitution
II, R = $O(CH_2CH_2O)_7CH_3$; 17% ring substitution
III, R = $O(CH_2CH_2O)_{16}CH_3$; 52% ring substitution
IV, R = $O(CH_2CH_2O)_7CH_3$; 52% ring substitution
V, R = $N(CH_3)_2n\text{-}C_4H_9Cl$; 17% ring substitution
VI, R = $N(CH_3)_2n\text{-}C_4H_9Cl$; 52% ring substitution
VII, R = OCH_2-18-crown-6; 20% ring substitution
VIII, R = $O(CH_2CH_2O)_{6.4}H$; 52% ring substitution

$$PhCH_2CN + CH_3(CH_2)_3Br \rightarrow PhCH(n\text{-}C_4H_9)CN \quad (1)$$

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