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$_2$)$_3$CH$_3$), 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$_2$CH=C(SC$_4$H$_9$-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$_2$)$_3$CH$_3$), 2.05 (s, 3, COCH$_3$), 6.06 (t, J = 7 Hz, 1, CH$_2$CH=C(SC$_4$H$_9$-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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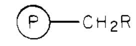
Benzyltriethylammonium chloride has enjoyed wide popularity as a catalyst for alkylation reactions in organic–aqueous hydroxide two-phase systems.[2] In an effort to expand the synthetic utility of this and related quaternary ammonium salts, attempts have recently been made to develop polymeric equivalents 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 chloro-



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)_2$$n$-$C_4H_9Cl$; 17% ring substitution
VI, R = $N(CH_3)_2$$n$-$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

methylated 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

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

judging catalyst performance in both liquid–liquid two-

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(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446).

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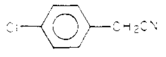
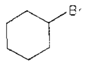
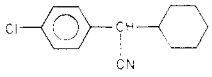
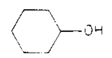
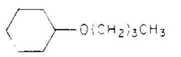
Table II. Triphase Alkylation of Nitriles, Alcohols, and Ketones Catalyzed by I

nitrile, alcohol, or ketone	organic halide	product	temp, °C	time, h	isolated yield, %
$PhCH_2CN$	$CH_3(CH_2)_3Br$	$PhCH(n\text{-}C_4H_9)CN$	23	3.0	77,[a] 74[b]
			23	24	52[c]
$PhCH(C_2H_5)CN$	$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2CPh(CN)C_2H_5$	23	5.0	76[c]
$PhC(O)CH_2Ph$	$CH_3(CH_2)_3Br$	$PhC(O)CPhH(CH_2)_3CH_3$	50	3.0	75[c]
	$CH_2{=}CHCH_2Br$	$PhC(O)CPhCH_2CH{=}CH_2$	50	3.0	76[c]
$CH_3(CH_2)_7OH$	$CH_2{=}CHCH_2Br$	$CH_3(CH_2)_7OCH_2CH{=}CH_2$	23	5.0	75[d]
	$CH_3(CH_2)_3Br$	$CH_3(CH_2)_7O(CH_2)_3CH_3$	35	5.0	79[d]
	$CH_3(CH_2)_3Br$		23	16	77[d]

[a] Reaction of 83 mmol of nitrile with 89 mmol of organic halide (see Experimental Section). [b] Yield from reused catalyst. [c] Reaction of 20 mmol of nitrile or ketone with 22 mmol of organic halide, 10 mL of 60% KOH, and 1.0 mmol of catalyst. In the case of benzylphenyl ketone, toluene (5 mL) was used as a cosolvent. [d] Reaction of 20 mmol of alcohol with 40 mmol of alkyl halide in the presence of 1 mmol of catalyst and 10 mL of 60% KOH.

phase[2] and liquid–solid–liquid three-phase systems.[3] As shown in Table I, polymer I [derived from poly(ethylene glycol) monomethyl ether, having an average number of ethylene oxide units of 16, and 17% ring-substituted chloromethylated polystyrene] showed the greatest activity. The use of shorter polyether chains and/or a higher loading of pendant groups resulted in reduced yields. In addition, resins bearing terminal hydroxyl groups were very similar to those "capped" with methyl groups (compare IV and VIII). Polymer-supported 18-crown-6 VII proved moderately efficient as a catalyst. Finally, quaternary ammonium based resins V and VI gave the poorest results. Operationally, I was very similar to benzyltriethylammonium chloride in its ability to promote the alkylation of phenylacetonitrile.

The synthetic utility of I is further demonstrated in Table II by the successful alkylation of a series of nitriles, ketones, and alcohols. In general, the yields obtained compare favorably with those of the best phase-transfer methods currently available.[14] Moreover, the catalyst could be quantitatively recovered by simple filtration and reused without any significant loss in activity.

Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and used without further purification. Resins I–VIII were prepared by using grafting procedures previously described.[10-13] Toluene was distilled over sodium under a nitrogen atmosphere. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5830A flame-ionization instrument (2 ft × 0.125 in. column, UCW-982 on Chromosorb W column). The temperature of the oil bath used was controlled (±0.5 °C) with the aid of a THERM-O-WATCH electronic controller, Model L6-1000 (I^{2}R Co., Cheltenham, PA), attached to a thermometer. ^1H NMR spectra were recorded on a Varian EM 360 L instrument. IR spectra were recorded on a Beckman Acculab 7 spectrometer. Alkylated products were identified by isolation and spectral comparison with authentic samples.

Small-Scale Alkylation of Phenylacetonitrile. An 8-mL culture tube (Corning No. 9826) equipped with a 2 × 12.7 mm Teflon-coated magnetic stir bar was charged with phenylacetonitrile (96 mg, 0.82 mmol), *n*-bromobutane (114 mg, 0.83 mmol), I (68 mg, 0.05 mmol of polyethylene glycol), and 60% aqueous KOH (0.5 mL). The mixture was stirred at room temperature for 1.5 h. After addition of 1 mL of toluene containing 0.05 mmol of *n*-decane (internal standard) plus 2 mL of water, analysis of the organic layer indicated a 92% yield of 2-phenylhexanenitrile.

Alkylation of Phenylacetonitrile with *n*-Bromobutane. A mixture of phenylacetonitrile (9.72 g, 83 mmol), *n*-bromobutane (12.2 g, 89 mmol), I (5.04 g), and 60% aqueous KOH (40 mL) was placed in a 250-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer (standard 4-cm curved Teflon blade). After the mixture was stirred for 3 h at room temperature, 80 mL of methylene chloride and 80 mL of water were added to the flask. The contents were then filtered, and the resin was washed with methylene chloride (3 × 50 mL). The organic layer was separated, dried (Na_2SO_4), and distilled to give 11.16 g (77%) of 2-phenylhexanenitrile having a boiling point of 130–136 °C (21 mm) [lit.[15] bp 107 °C (2 mm)] and an IR spectrum which was identical with that of an authentic sample. The filtered resin was further washed with THF (100 mL), water (100 mL), and THF (100 mL) and dried [16 h, 90 °C (0.1 mm)] to give 4.85 g (96%) of recovered polymer.

Alkylation of Benzyl Phenyl Ketone with *n*-Bromobutane. A mixture of benzyl phenyl ketone (3.92 g, 20 mmol), *n*-bromobutane (3.0 g, 22 mmol), I (1.36 g), toluene (5 mL), and 60% aqueous KOH (10 mL) was stirred magnetically in a 100-mL round-bottomed flask for 3 h at 50 °C. Methylene chloride and water (40 mL of each) were added to the flask, and the organic layer was separated and dried (Na_2SO_4). Evaporation of the solvent followed by recrystallization (CH_3OH) gave 3.81 g (75%) of 2-phenylhexanophenone: mp 59–60 °C (lit.[16] mp 64 °C); ^1H NMR ($CHCl_3$) δ 0.88 (t, 3 H, CH_2CH_3), 1.05–2.37 (m, 6 H, CH_2), 4.55 (t, 1 H, CH-C=O), 7.15–8.05 (m, 5 H, Ph).

Alkylation of 1-Octanol with *n*-Bromobutane. A mixture of 1-octanol (2.61 g, 20 mmol), *n*-bromobutane (5.48 g, 40 mmol), I (1.36 g), and 60% aqueous KOH (10 mL) was placed in a 100-mL single-neck flask equipped with a 1 × $^5/_{16}$ in. Teflon-coated magnetic stir bar. After the mixture was stirred for 5 h at 35 °C, 40 mL of methylene chloride and 40 mL of water were added to the flask, and the organic layer was then separated and dried (Na_2SO_4). Evaporation of the solvent followed by distillation yielded 2.95 g (79%) of *n*-butyl *n*-octyl ether: bp 102–105 °C (20 mm) (lit.[17] bp 221.5 °C); ^1H NMR ($CDCl_3$) δ 0.6–1.05 (m, 6 H, CH_3), 1.10–1.70 (m, 16 H, CH_2), 3.37 (t, 4 H, CH_2O); IR (neat) 1115 cm^{-1} (C–O–C).

Registry No. Phenylacetonitrile, 140-29-4; *n*-bromobutane, 109-65-9; 2-phenylhexanenitrile, 3508-98-3; *p*-chlorophenylacetonitrile, 140-53-4; bromocyclohexane, 108-85-0; *p*-chloro-α-cyclohexylphenylacetonitrile, 76618-95-6; 2-phenylbutyronitrile, 769-68-6; allyl bromide, 106-95-6; 2-allyl-2-phenylbutyronitrile, 5558-62-3; benzyl phenyl ketone, 451-40-1; 2-phenylhexanophenone, 2371-23-5; 1,2-diphenyl-4-penten-1-one, 38940-36-2; 1-octanol, 111-87-5; allyl *n*-octyl ether, 3295-97-4; *n*-butyl *n*-octyl ether, 53839-23-9; cyclohexanol, 108-93-0; *n*-butyl cyclohexyl ether, 24072-44-4.

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