1 mL before analysis. The extent of monodeuteration of the product was calculated after allowance had been made for the natural abundance of carbon-13, nitrogen-15, and deuterium.

Product studies in the presence of DPE and DTBNO were carried out as described above. The diazonium salt (0.2 g) was dissolved in basic alcoholic solvent (10 mL, 0.5 M $CH_3O^-/CH_3OD$) containing either DPE (0.2 g) or DTBNO (0.2 g). In the reactions using DTBNO, nitrobenzene was used as an internal standard in place of *p*-dichlorobenzene because *p*-dichlorobenzene and DTBNO had the same retention time on the column being used.

**Acknowledgment.** We are pleased to acknowledge the assistance of Mr. J. Smith of the Department of Physical Chemistry, La Trobe University, with the gas chromatography–mass spectral analyses.

**Registry No.** $CH_3OH$, 67-56-1; $EtO^-$, 16331-64-9; $CH_3O^-$, 3315-60-4; DPE, 530-48-3; DTBNO, 2406-25-9; (*Z*)-(2-chloro-4-nitrophenyl)azo ethyl ether, 82765-37-5; (*Z*)-(2-chloro-5-nitrophenyl)azo ethyl ether, 82765-40-0; (*Z*)-(2-chloro-4-cyanophenyl)azo ethyl ether, 82765-43-3; (*Z*)-[2-chloro-5-(trifluoromethyl)phenyl]azo ethyl ether, 82765-39-7; (*Z*)-(2-chloro-5-cyanophenyl)azo ethyl ether, 82765-41-1; (*Z*)-(2,5-dichlorophenyl)azo ethyl ether, 82765-38-6; (*Z*)-(2,4-dichlorophenyl)azo ethyl ether, 83844-94-4; (*Z*)-(2-chloro-5-methoxyphenyl)azo ethyl ether, 83844-95-5; (*Z*)-(2-chloro-5-methylphenyl)azo ethyl ether, 83844-96-6; (*Z*)-(2-chlorophenyl)azo ethyl ether, 83844-97-7; ethanol, 64-17-5; 2-chlorobenzenediazonium, 17333-83-4.

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# Poly(ethylene glycols) and Poly(ethylene glycol)-Grafted Copolymers Are Extraordinary Catalysts for Dehydrohalogenation under Two-Phase and Three-Phase Conditions[1]

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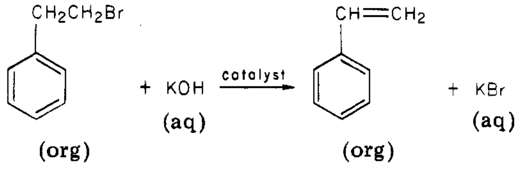
Poly(ethylene glycols) [$HO(CH_2CH_2O)_nH$, where $n > 3$] possess remarkably high activity as catalysts for dehydrohalogenation in organic–aqueous hydroxide two-phase systems, relative to classical phase-transfer agents, i.e., benzyltriethylammonium chloride and 18-crown-6. The importance of terminal hydroxyl groups together with the abrupt increase in catalyst activity and concentration in the organic layer on going from $n = 2$ to $n = 3$ and from $n = 3$ to $n = 4$ suggests the involvement of novel polymeric alkoxides I and/or hydroxides II. Moreover, the fact that maximum activity is obtained with $n \geq 5$ implies that an "18-crown-6-like" structure occurring at the terminus of the polymer chain is optimal for catalysis. Poly(ethylene glycols) grafted to cross-linked polystyrene display reasonably high activity. In preparative-scale conversions, such triphase catalysts can be recovered quantitatively by simple filtration and reused without significant loss in activity.

Phase-transfer catalysis is now established as a versatile and important synthetic technique in organic chemistry.[2] Surprisingly, however, few practical applications have been devised for dehydrohalogenation reactions and elimination processes in general. Under liquid–liquid conditions, conventional phase-transfer agents (e.g., tetraalkylammonium salts) yield synthetically useful procedures only when employed in stoichiometric quantities.[3,4] We have recently discovered that simple poly(ethylene glycols) [$HO(CH_2CH_2O)_nH$, where $n > 3$] possess extraordinary activity for *catalyzing* dehydrohalogenation in organic–aqueous hydroxide two-phase systems.[5,6] We now present the details of these findings and propose the involvement of novel polymeric alkoxides and/or hydroxides as the active catalyst(s). We further show that poly(ethylene glycols) grafted to cross-linked polystyrene yield attractive alternate procedures based on the triphase catalysis principle.[7]

## Results

**Liquid–Liquid Two-Phase Dehydrohalogenation.** In order to compare catalyst efficiency for dehydrohalogenation, we chose the conversion of (2-bromoethyl)benzene to styrene as the standard reaction (eq 1). This



(1)

organic halide has a reasonable tendency to undergo elimination and produces a single olefinic product.

In the absence of a catalyst, benzene solutions of (2-bromoethyl)benzene afforded no detectable styrene after vigorous stirring with 60% aqueous potassium hydroxide for 24 h at 35 °C. In the presence of 10 mol % of benzyltriethylammonium chloride, a 17% yield was obtained after 21 h. When pentaethylene glycol was employed (10 mol %), analysis of the organic layer (GLC) revealed a 63% conversion after 8 min! Table I lists observed pseudo-first-order rate constants plus catalyst and base content

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

[2] Reviews of phase-transfer catalysis: (a) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis"; Academic Press; New York, 1978. (b) Weber W. P.; Gokel, G. W. "Phase-Transfer Catalysis in Organic Synthesis"; Springer-Verlag: New York, 1977. (c) Brandstrom, A. *Adv. Phys. Org. Chem.*, 1977, *15*, 267. (d) Dehmlow, E. V. *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 493. (e) Makosza, M. *Pure Appl. Chem.* 1975, *43*, 439.

[3] Gorques, A.; LeCoq, A. *Tetrahedron Lett.* 1976, 4723.

[4] In solid–liquid two-phase dehydrohalogenations, catalytic quantities of ammonium salts have been successfully employed: Dehmlow, E. V.; Lissel, M. *Tetrahedron* 1981, *37*, 1653.

[5] For a preliminary account, see: Kimura, Y.; Regen, S. L. *J. Org. Chem.* 1982, *47*, 2493.

[6] For recent applications of poly(ethylene glycols) in two-phase organic syntheses, see: Stott, P. E.; Bradshaw, J. S.; Parish, W. W. *J. Am. Chem. Soc.* 1980, *102*, 4810. Lee, D. G.; Chang, V. S. *J. Org. Chem.* 1978, *43*, 1532. Sukata, K. *Yuki Gosei Kagaku* 1981, *39*, 443. Zupancic, B.; Kokalj, M. *Synthesis* 1981, 913. Balsubramanian, D.; Sukumar, P.; Chandani, B. *Tetrahedron Lett.* 1979, 3543. For use of poly(ethylene glycols) as *solvents* in elimination and displacement reactions, see: Lehmkuhl, H.; Rabet, F.; Hauschild, K. *Synthesis* 1977, 184. Brandstrom, A. *Acta Chem. Scand.* 1959, *13*, 610, 611. Brandstrom, A. *Ibid.* 1956, *10*, 1197. Tarchini, C.; Tran, D. A.; Jan, G.; Schlosser, M. *Helv. Chim. Acta* 1979, *62*, 635.

[7] Regen, S. L. *Angew. Chem., Int. Ed. Engl.* 1979, *18*, 421.

0022-3263/83/1948-0195$01.50/0

Table I. Liquid-Liquid Two-Phase Dehydrohalogenation of (2-Bromoethyl)benzene

| catalyst | $10^5k_{obsd}$,[a] $s^{-1}$ | % catalyst in organic layer[c] | hydroxide or alkoxide in organic layer[c,d] equiv |
|---|---|---|---|
| $PhCH_2N^+(C_2H_5)_3Cl^-$ | 2.5[b] | 0 | 0.01 |
| $HO(CH_2CH_2O)_1H$ | <0.01 | 0 | 0 |
| $HO(CH_2CH_2O)_2H$ | <0.01 | 0 | 0 |
| $HO(CH_2CH_2O)_3H$ | 1[b] | 14 | 1.0 |
| $HO(CH_2CH_2O)_4H$ | 88 | 100 | 1.0 |
| $HO(CH_2CH_2O)_5H$ | 208 | 100 | 1.0 |
| $HO(CH_2CH_2O)_{13.2}H$ | 130 | 100 | 0.5 |
| $n\text{-}C_4H_9O(CH_2CH_2O)_{13.2}n\text{-}C_4H_9$ | <0.01 | 100 | 0 |
| $CH_3O(CH_2CH_2O)_{7.2}H$ | 24 | 100 | 0.2 |
| 18-crown-6 | 4.9 | 100 | 0.02 |

[a] Pseudo-first-order rate constant (±10%) for reaction of 1.5 mL of 0.2 M (2-bromoethyl)benzene in benzene containing 0.03 mmol of *n*-decane (internal standard) with 0.5 mL of 60% aqueous KOH in the presence of 0.1 equiv of catalyst at 35 °C. [b] Initial rate. [c] Analysis of a mixture of 15 mL of benzene containing 0.3 mmol of catalyst after stirring with 5 mL of 60% aqueous KOH for 1 h at 35 °C; ±10%. [d] 1 equiv is defined as 1 mol of $^-OH$ or alkoxide/mol of catalyst in the organic layer.

in the organic layer for benzyltriethylammonium chloride, 18-crown-6, and a series of poly(ethylene glycols). Ethylene glycol and diethylene glycol exhibited no detectable activity and were located entirely in the aqueous phase. Triethylene glycol partitioned partly into the organic layer, carrying with it 1 equiv of base and showed small but detectable activity. Both tetraethylene glycol and pentaethylene glycol were highly active as catalysts and were fully partitioned into the organic layer along with an equivalent amount of base. While PEG 600 (polyethylene glycol having an average molecular weight of 600 and an $n_{av}$ = 13.2), its corresponding di-*n*-butyl ether, and PEG 350 ($n_{av}$ = 7.2) monomethyl ether largely favored the organic phase, only those polyethers having hydroxyl groups extracted substantial quantities of base and were catalytically active. Benzyltriethylammonium chloride was located entirely in the aqueous phase and was very ineffective in promoting the dehydrohalogenation. In an effort to identify the nature of the extracted base, a benzene solution of pentaethylene glycol was stirred with 60% aqueous KOH and then reacted with benzyl chloride. Analysis of the product mixture by GLC and $^1H$ NMR revealed the exclusive formation of alkylated polyether; no benzyl alcohol or dibenzyl ether was detected.

**Liquid-Solid-Liquid Triphase Catalytic Dehydrohalogenation.** Triphase catalysts 1–8 were prepared by

Ⓟ—$CH_2R$

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

1a, R = $O(CH_2CH_2O)_nH$; 52% ring substitution; $n$ = 1
b, $n$ = 2
c, $n$ = 3
d, $n$ = 4
e, $n_{av}$ = 4.1
f, $n$ = 5
g, $n_{av}$ = 13.2
2a, R = $O(CH_2CH_2O)_nH$; 17% ring substitution; $n$ = 3
b, $n$ = 4
c, $n$ = 5
d, $n_{av}$ = 13.2
3, R = $O(CH_2CH_2O)_{7.2}CH_3$; 17% ring substitution
4, R = $OCH_2$-18-crown-6; 20% ring substitution
5, R = $^+N(CH_3)_2\text{-}n\text{-}C_4H_9Cl^-$; 17% ring substitution
6, R = $^+N(CH_3)_2\text{-}n\text{-}C_4H_9Cl^-$; 52% ring substitution
7, R = $^+P(n\text{-}C_4H_9)_3Cl^-$; 17% ring substitution
8, R = $^+P(n\text{-}C_4H_9)_3Cl^-$; 52% ring substitution

using standard grafting procedures starting with 1% cross-linked chloromethylated polystyrene.[8-10] A comparison of the efficacy of these polymers for reaction 1 is provided in Table II. All ammonium- and phosphonium-based resins showed no significant catalytic activity; cross-linked polystyrene bearing pendant 18-crown-6 groups was only moderately effective. In the poly(ethylene glycol) series, reasonably high activity was found with pentaethylene glycol based resins; higher and lower homologues were less active. As shown in Figure 1, observed pseudo-first-order rate constants were directly proportional to the amount of resin used. When PEG 350 monomethyl ether was grafted to polystyrene, the resulting polymer exhibited no detectable activity.

Table II. Triphase Dehydrohalogenation of (2-Bromoethyl)benzene[a]

| catalyst | $10^5k_{obsd}$, $s^{-1}$ | catalyst | $10^5k_{obsd}$, $s^{-1}$ |
|---|---|---|---|
| 1a | <0.01 | 2c | 30.6 |
| 1b | 1.2[b] | 2d | 14.1 |
| 1c | 13.9 | 3 | <0.01 |
| 1d | 30.0 | 4 | 5.8 |
| 1e | 18.6 (17.8)[c] | 5 | 0.3[b] |
| 1f | 35.0 (35.7)[c] | 6 | <0.01 |
| 1g | 9.4 | 7 | <0.01 |
| 2a | 3.7 | 8 | <0.01 |
| 2b | 19.2 | | |

[a] Reaction conditions were the same as described in Table I. [b] Initial rate. [c] Reused catalyst.

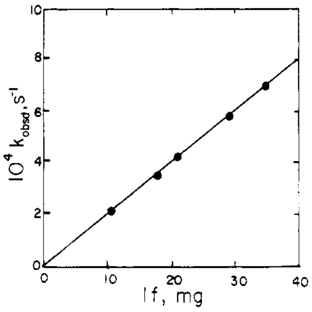

**Figure 1.** Plot of $10^4k_{obsd}$ as a function of the amount of catalyst 1f used for the dehydrohalogenation of (2-bromoethyl)benzene.

**Synthetic Applications.** Table III summarizes the yields of alkene and alkyne produced from a series of or-

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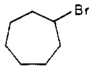
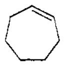
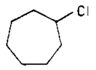
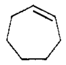
(8) Regen, S. L.; Besse, J. J.; McLick, J. *J. Am. Chem. Soc.* **1979**, *101*, 116.

(9) Regen, S. L.; Besse, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 4059.

(10) Fukunishi, K.; Czech, B.; Regen, S. L. *J. Org. Chem.* **1981**, *46*, 1218.

(11) Ugelstad, J.; Mark, P. C.; Jenson, B. *Acta Chem. Scand.* **1963**, *17*, 1455. Gokel, G. W.; Garcia, B. J. *Tetrahedron Lett.* **1977**, 317. Bartsch, R. A.; Roberts, D. K. *Ibid.* **1977**, 321. Bartsch, R. A.; Allaway, J. R.; Lee, J. G. *Ibid.* **1977**, 779.

Table III. Triphase Catalytic Dehydrohalogenation[a]

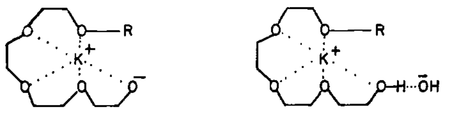
| reactant | product | catalyst | solvent | temp, °C | time, h | yield, % |
|---|---|---|---|---|---|---|
| $PhCHBrCH_2Br$ | $PhC{\equiv}CH$ | 2c | *n*-hexane | 70 | 16 | 80 |
| | | 2d | | | | 42 |
| | | 1e | | | | 95, 94,[b] 84[c] |
| | | 1f | | | | 96 |
| | | 1g | | | | 54 |
| | | 3 | | | | 9 |
| | | 4 | | | | 28 |
| $CH_3CHBr(CH_2)_5CH_3$ | 1- and 2-octenes | none | *n*-hexane | 70 | 48 | 0 |
| | | 2c | | | | 75 (20/80)[d] |
| | | 1f | | | | 82 (18/82)[d] |
| | | 1f | toluene | | | 84 (21/79)[d] |
| | | 1f | none | | | 99 (21/79)[d] |
| | | 3 | *n*-hexane | | | 5[e] |
| | | 4 | *n*-hexane | | | 18[f] |
| $CH_3(CH_2)_7CHBrCH_2Br$ | $CH_3(CH_2)_7C{\equiv}CH$ | 1f | toluene | 90 | 22 | 50 |
| | | 1f | none | | | 65 |
| $PhCH_2CH_2Br$ | $PhCH{=}CH_2$ | 1f | *n*-hexane | 70 | 1 | 96 |
| | | none | | | | 0 |
| $PhCH_2CHBrCH_3$ | $PhCH{=}CHCH_3$ | 1f | *n*-hexane | 70 | 2 | 98 |
| | | none | | | | 3 |
| *threo*-$C_4H_9CHBrCHBrC_4H_9$ | $C_4H_9C{\equiv}CC_4H_9$ | 1f | none | 90 | 22 | 95 |
|  |  | 1e | none | 70 | 16 | 94 |
| | | 1f | none | | | 95, 76[c] |
|  |  | 1e | none | | | 5 |

[a] Yields (±5%) determined by GLC and based on reactant; reaction conditions were the same as described in Table I. [b] Reuse of catalyst. [c] Isolated yield from a 20-mmol-scale reaction. [d] Ratio of 1-octene/*cis*- + *trans*-2-octene. [e] 1% of 2-octanol was produced. [f] 3% of 2-octanol was formed.

ganic halides under triphase catalytic conditions. In preparative-scale conversions, catalysts were recovered quantitatively by simple filtration and reused without significant loss in activity. Analysis of **1f**, recovered after triphase dehydrohalogenation of (2-bromoethyl)benzene, indicated no loss of resinous hydroxyl groups. In general, the yields of alkenes and alkynes were good to excellent. Only in the case of dehydrochlorination (i.e., the conversion of cycloheptyl chloride to cycloheptene) were poor results obtained.

## Discussion

Data which are reported in Table I suggest the involvement of novel polymeric alkoxides I and/or hydroxides II. Self-solvation is inferred by the abrupt increase in catalyst activity and concentration in the organic layer on going from $n = 2$ to $n = 3$ and from $n = 3$ to $n = 4$.[11] The fact that maximum activity is obtained with $n > 5$ further implies that an "18-crown-6-like" structure occurring at the terminus of the polymer chain is optimal. This probably is the result of more effective self-solvation which in turn produces increased ion-pair separation and reactivity. Polymeric hydroxyl groups are clearly essential for catalysis as demonstrated by the inability of PEG 600 di-*n*-butyl ether to extract base and to catalyze reaction 1. The exclusive formation of benzylated pentaethylene glycol upon reaction with benzyl chloride further suggests that I is the active agent.



I II

$R = H$, $(CH_2CH_2O)_{n-4}H$, $(CH_2CH_2O)_{n-4}X$ ($X$ = alkyl)

Operationally, poly(ethylene glycol)-grafted copolymers **1f** and **2c** display reasonably high activity, when compared with their soluble counterpart, i.e., pentaethylene glycol. In addition, they can be used conveniently and effectively in preparative-scale reactions. Remarkably, diethylene glycol and triethylene glycol exhibited *greater* activity after being grafted to polystyrene (**1b**,**c** and **2a**). One possible reason for this is that the pendant glycols, which are forced into proximity to one another along the polymer backbone, act together (possibly as dimers) in solvating potassium ions. Resins bearing pendant crown ethers (e.g., **4**) offer little synthetic advantage over **1f** and **2c** for dehydrohalogenation. They are more expensive, less active, and also less selective; i.e., alcohols are produced as side products (Table III).

The ready availability, low cost, and high activity of grafted copolymers such as **1f** and **2c** for dehydrohalogenation should make them very attractive candidates for laboratory and industrial use.

## Experimental Section

**General Methods.** Unless stated otherwise, all reagents and chemicals were obtained commercially and used without further purification. Resins **3**–**8** were prepared as previously described.[8-10] Chloromethylated polystyrene (1% DVB gel, 17% and 52% ring substitution, 200–400 mesh) was purchased from Bio-Rad Laboratories. Chlorocycloheptane, bromocycloheptane, (2-bromoethyl)benzene, 2-bromo-1-phenylpropane, 2-bromooctane, benzyltriethylammonium chloride, 18-crown-6, and mono-, di-, tri-, and tetraethylene glycol were purchased from Aldrich Chemical Co. Pentaethylene glycol was obtained from Columbia Scientific Co. Polyethylene glycols having average molecular weights of 200 and 600 and polyethylene glycol monomethyl ether having an average molecular weight of 350 were obtained from Polysciences. Dialkylation of PEG 600 with 1-chlorobutane was carried out by using procedures similar to those previously described.[12] The ether product was purified by column chromatography (silica gel/$CHCl_3$). Organic dibromides were prepared by bromination of the corresponding olefins in $CCl_4$. Diglyme was distilled over

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(12) Gibson, T. *J. Org. Chem.* **1980**, *45*, 1095.

sodium under a nitrogen atmosphere. Benzene, *n*-hexane, and toluene were distilled under nitrogen. 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 ($I^2R$ Co., Chetlenham, PA) attached to a thermometer. $^1H$ NMR spectra were recorded on a Varian EM 360 L instrument.

**Synthesis of Resins 1 and 2.** Procedures similar to those previously described were used for the preparation of polymers **1a–g** and **2a–d**.[8] The following is representative. A 250-mL, one-necked, round-bottomed flask was charged with NaH (3.9 g of a 60% dispersion in mineral oil) and 96 mL of anhydrous diglyme. The mixture was cooled to 0 °C and pentaethylene glycol (48 mL) was added slowly (ca. 0.5 h). After hydrogen evolution ceased, chloromethylated polystyrene [3.0 g having a loading of 52% ring substitution (4.04 mmol of Cl/g)] was added in one portion. The mixture was shaken by hand for ca. 10 min and then placed in an oil bath maintained at 80 °C for 9 days. The mixture was then cooled to room temperature, and the polymer was removed by filtration, washed successively with THF/$H_2O$ (4:1; 5 × 20 mL) and THF (5 × 20 mL), extracted (Soxhlet) with THF for 16 h, and dried under vacuum [24 h, 80 °C (0.1 mm)] to yield 4.0 g of a grafted copolymer having 1.69 mmol of hydroxyl groups/g of dry polymer.[13] If only monoattachment of the glycol to the resin occurs, the expected hydroxyl content is 2.22 mmol/g of polymer.

The reaction conditions used for the preparation of analogous polyether grafted copolymers were the following [resin (NaH dispersion, g; glycol, mL or g; percent ring substitution of chloromethylated polystyrene used, grams added; reaction temperature, °C; reaction time, h; yield of polymer, g; mmol of OH/g expected; mmol of OH/g found]: **1a** (1.3 g; ethylene glycol, 4 mL; 52%, 1.0 g; 90 °C; 1 day; 0.8 g; 3.60 mmol; 1.60 mmol), **1b** (1.3 g; triethylene glycol, glycol, 7 mL; 52%, 1.0 g; 80 °C; 9 days; 1.1 g; 3.14 mmol; 2.44 mmol), **1c** (1.3 g; triethylene glycol, 10 mL; 52%, 1.0 g; 80 °C; 9 days; 1.4 g; 2.76 mmol; 2.3 mmol), **1d** (1.3 g; tetraethylene glycol, 13 mL; 52%, 1.0 g; 90 °C; 8 days; 1.25 g; 2.55 mmol; 2.17 mmol), **1e** (2.3 g; PEG 200, 42 mL; 52%, 1.8 g; 80 °C; 9 days; 2.6 g; 2.43 mmol; 1.98 mmol), **1g** (0.65 g; PEG 600, 20 g; 52%, 0.5 g; 80 °C; 11 days; 0.92 g; 1.23 mmol; 0.30 mmol), **2a** (0.7 g; triethylene glycol, 5 mL; 17%, 1.0 g; 90 °C; 5 days; 0.95 g; 1.29 mmol; 1.17 mmol), **2b** (0.7 g; tetraethylene glycol, 7 mL; 17%, 1.0 g; 90 °C; 8 days; 1.04 g; 1.22 mmol; 1.15 mmol), **2c** (0.5 g; pentaethylene glycol, 6 mL; 17%, 1.0 g; 80 °C; 10 days; 1.15 g; 1.16 mmol; 1.05 mmol), **2d** (0.5 g; PEG 600, 15 g; 17%, 1.0 g; 80 °C; 12 days; 1.35 g; 0.82 mmol; 0.30 mmol).

**Small-Scale Dehydrohalogenations.** Typically, an 8-mL culture tube (Corning No. 9826) equipped with a 3 × 12.7 mm Teflon-coated magnetic stir bar was charged with 1.5 mL of 0.2 M (2-bromoethyl)benzene in benzene containing 0.03 mmol of *n*-decane (internal standard) plus 0.03 mmol of catalyst. Aqueous potassium hydroxide (60%, 0.5 mL) was then added and the tube placed in an oil bath maintained at 35 °C. The contents of the tube were stirred magnetically, and the organic layer was analyzed for styrene as a function of time. When insoluble polymeric catalysts were employed, the resins (0.03 mmol of hydroxyl) were stirred initially for 15 h at 35 °C with the benzene solution of organic bromide in the absence of aqueous KOH. Except for ammonium- and phosphonium-based catalysts, kinetic runs were carried out to 30–70% conversion. With the ionic catalysts, clean pseudo-first-order kinetics was not obeyed, and the rate constants were determined from the very early stages of the reaction (<5%).

**Dehydrohalogenation of 1,2-Dibromo-1-phenylethane.** A mixture of 5.3 g (20 mmol) of 1,2-dibromo-1-phenylethane, 1.03 g of **1e**, 20 mL of *n*-hexane, and 20 mL of 60% aqueous potassium hydroxide was placed in a 100-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer (standard 4-cm curved Teflon blade). The flask was immersed in an oil bath maintained at 70 °C, and the mixture stirred for 16 h. The mixture was then cooled to room temperature and filtered, and the resin was washed successively with 50 mL of water, 100 mL of *n*-hexane, and 100 mL of $CH_2Cl_2$. The aqueous portion of the filtrate was extracted with 50 mL of $CH_2Cl_2$ and combined with the organic filtrate. After being dried overnight ($Na_2SO_4$), the organic layer was then distilled to give 1.7 g (84%) of phenylacetylene having a boiling point of 136–138 °C (lit.[14] bp 138.4–138.8 °C) and an IR spectrum identical with that of an authentic sample. Resin **1e** was quantitatively recovered from the product mixture.

**Base Concentration in the Organic Layer.** A 40-mL culture tube was charged with 0.3 mmol of soluble catalyst, 15 mL of benzene, and 5 mL of 60% aqueous KOH. The two-phase mixture was stirred for 1 h at 35 °C, and an aliquot of the organic phase (typically 4 mL) was then added to 10 mL of water. The two-phase mixture was vigorously stirred and titrated with 0.015 M HCl with phenolphthalein as the indicator.

**Catalyst Concentration in the Organic Layer.** A 40-mL culture tube was charged with 0.3 mmol of soluble catalyst, 0.1 mmol of mesitylene (internal standard), 15 mL of benzene, and 5 mL of 60% aqueous KOH. The two-phase mixture was stirred for 1 h at 35 °C, and the organic layer was analyzed directly by $^1H$ NMR (when ethylene glycol, diethylene glycol, and triethylene glycol were examined, the benzene solution was concentrated under reduced pressure prior to analysis). Integration of the ethylene oxide protons relative to the methyl protons of mesitylene was used to judge the catalyst concentration in the organic layer.

**Reaction of Pentaethylene Glycol Derived Base with Benzyl Chloride.** After a mixture of pentaethylene glycol (0.43 mmol), benzene (6 mL), and 60% aqueous KOH (2 mL) was stirred for 1 h at 35 °C, a portion of the organic layer (1.5 mL) was removed and allowed to react with 0.11 mmol of benzyl chloride for 48 h at 70 °C. Direct analysis of the product mixture by $^1H$ NMR with mesitylene (0.14 mmol) as an internal standard ($\delta$ 2.1, s, $CH_3$) indicated that 50% of the organic chloride ($\delta$ 4.1, s, $CH_2Ph$) had been converted to benzyl ether groups ($\delta$ 4.3, s, $OCH_2Ph$). Analysis by GLC also showed that 50% of the benzyl chloride remained and that no benzyl alcohol or dibenzyl ether was produced.

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**Registry No.** $PhCHBrCH_2Br$, 93-52-7; $CH_3CHBr(CH_2)_5CH_3$, 557-35-7; $CH_3(CH_2)_7CHBrCH_2Br$, 28467-71-2; $PhCH_2CH_2Br$, 103-63-9; $PhCH_2CHBrCH_3$, 2114-39-8; *threo*-$C_4H_9CHBrCHBrC_4H_9$, 80262-80-2; $PhCH_2N^+(C_2H_5)_3Cl^-$, 56-37-1; $HO(CH_2CH_2O)_4H$, 112-60-7; $HO(CH_2CH_2O)_5H$, 4792-15-8; 18-crown-6, 17455-13-9; bromocycloheptane, 2404-35-5; chlorocycloheptane, 2453-46-5; benzyl chloride, 100-44-7; poly(ethylene glycol), 25322-68-3; polystyrene, 9003-53-6.

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(13) Hydroxyl content was determined by using methods previously described.[8]

(14) Vaughn, T. H. *J. Am. Chem. Soc.* **1934**, *56*, 2064.