acetic acid by the method of Wilkinson et al.[7] Dioxane was refluxed with sodium metal and distilled. Other starting materials were commercial grade.

Intramolecular Aromatic Nuclear Acyloxylation Reaction of Phenylacetic Acid (Run 6). Into a 50-mL centrifuge tube containing a magnetic stirring bar were added phenylacetic acid (5 mmol), $K_2S_2O_8$ (8 mmol), $Pd(OAc)_2$ (0.5 mmol), dioxane (10 mL), and CH_3SO_3H (1.5 mL), and the tube was sealed under air with a No-Air stopper. Then the mixture was heated with stirring for 8 h at 100 °C. The reaction mixture was filtered to remove Pd metal and $K_2S_2O_8$, was neutralized with saturated aqueous sodium bicarbonate, and was extracted with ether. After evaporation of the ether, the products were analyzed by GLC and, in some cases, separated by column chromatography (silica gel). Yields were determined by GLC directly with the use of an internal standard (Table I). The identities of the products were proved by IR, NMR, and retention time comparison with authentic samples.

Registry No. 1, 553-86-6; phenylacetic acid, 103-82-2.

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Communications

Poly(ethylene glycols) Are Extraordinary Catalysts in Liquid–Liquid Two-Phase Dehydrohalogenation[1]

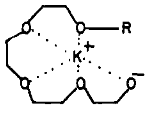
Summary: Poly(ethylene glycols) [$HO(CH_2CH_2O)_nH$, where $n > 3$] are highly active and selective in catalyzing dehydrohalogenation in organic–aqueous hydroxide two-phase systems.

Sir: We have discovered that simple poly(ethylene glycols) [$HO(CH_2CH_2O)_nH$, where $n > 3$] are highly active and selective in catalyzing dehydrohalogenation in organic–aqueous hydroxide two-phase systems.[2] In this communication we document our findings and provide data which suggest that novel polymeric alkoxides and/or hydroxides are involved.

Reaction of 0.5 mL of 2.0 M 2-bromooctane in benzene with 0.5 mL of 60% aqueous potassium hydroxide in the presence of conventional phase-transfer catalysts (10 mol % of tetrabutylammonium hydrogen sulfate or 18-crown-6) at 80 °C for 2 h produced only a modest extent of dehydrohalogenation (Table I).[3] In the absence of catalyst or in the presence of ethylene glycol, diethylene glycol, or triethylene glycol, no detectable reaction was observed. In sharp contrast, tetraethylene glycol exhibited activity comparable to that of the ammonium salt and crown ether. Pentaethylene glycol and poly(ethylene glycols) having average molecular weights of 600 and 3400 (PEG 600 and PEG 3400, respectively) all had high activity. Poly(ethylene glycol) monomethyl ether (average molecular weight 750) having half the hydroxyl content of PEG 600, converted approximately half as much organic bromide in the same time period. Replacement of both terminal hydroxyl groups with ether functionalities [PEG 600–(n-$C_4H_9)_2$] rendered the polymer essentially inactive.[4] Combination of 18-crown-6 and PEG 600 had only slightly greater activity than PEG 600 used alone. Finally, upon extended reaction with tetrabutylammonium hydrogen sulfate or 18-crown-6, 2-octanol appeared in significant yields;[5] PEG 600 and PEG 600 + 18-crown-6 afforded alkenes, exclusively.

Further evidence for the efficacy of poly(ethylene glycols) in promoting dehydrohalogenation is provided in Table II. Vicinal dibromides were smoothly converted to the corresponding alkynes by using 10 mol % of PEG 600. This is in marked contrast to tetrabutylammonium hydrogen sulfate where *stoichiometric* amounts of the salt are required.[6,7] Remarkably, β-bromoethyl phenyl ether, which has been reported to undergo phase-transfer-catalyzed dehydrohalogenation (benzyltriethylamminium chloride) at elevated temperatures (150 °C),[8] proceeds rapidly and quantitatively to the corresponding alkene with PEG 600 at 50 °C. Preliminary carbene generation experiments also demonstrate the synthetic potential of poly(ethylene glycols) in organic–aqueous hydroxide systems. Thus, whereas benzyltriethylammonium chloride fails to catalyze the formation of 1,1-dibromo-2-hexylcyclopropane when a benzene solution of 1-octene plus bromoform is heated with 50% aqueous sodium hydroxide at 50 °C for 20 h, PEG 600 affords a 61% isolated yield of the dibromide after 3 h at room temperature.

In addition to their synthetic value, the above results suggest that novel polymeric alkoxides 1 and/or hydroxides 2 are involved. Self-solvation is inferred by the abrupt



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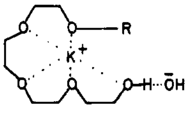

2

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

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

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[3] 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.

[4] Alkylation of PEG 600 with n-C_4H_9Cl was carried out by using procedures similar to those previously described: Gibson, T. *J. Org. Chem.* **1980**, *45*, 1095. The final polyether product was purified by column chromatography (silica gel/$CHCl_3$).

[5] Similar results have previously been reported elsewhere: Herriott, A.; Picker, D. *Tetrahedron Lett.* **1972**, 4521.

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

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

[8] Shostakovski, S. M.; Kozyrev, V. G.; Il'ina, G. I.; Bannikova, U. B. *Zh. Prikl. Khim.* **1977**, *50*, 463.

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Table I. Dehydrohalogenation of 2-Bromooctane[a]

catalyst	temp, °C	time, h	product yield, %	product distribution, %	
				alkenes (1-octene/2-octene)	2-octanol
none	80	2	0	0	0
$HO(CH_2CH_2O)_1H$	80	2	0	0	0
$HO(CH_2CH_2O)_2H$	80	2	0	0	0
$HO(CH_2CH_2O)_3H$	80	2	0	0	0
$HO(CH_2CH_2O)_4H$	80	2	41	41 (23/77)	0
$HO(CH_2CH_2O)_5H$	80	2	70	70 (27/73)	0
PEG 600	80	2	82	82 (23/77)	0
PEG 3400	80	2	78	78 (25/75)	0
$CH_3O(CH_2CH_2O)_1H$	80	2	0	0	0
$CH_3O(CH_2CH_2O)_2H$	80	2	3	3	0
$CH_3O(CH_2CH_2O)_nH$[b]	80	2	42	42 (26/74)	0
PEG 600–$(n\text{-}C_4H_9)_2$	80	2	0	0	0
$(n\text{-}C_4H_9)_4N^+HSO_4^-$	80	2	37	37 (21/79)	0
18-crown-6	80	2	22	22 (29/71)	0
18-crown-6	50	1	5	5 (27/73)	0
PEG 600	50	1	31	31 (25/75)	0
PEG 600 + 18-crown-6	50	1	49	49 (21/79)	0
$(n\text{-}C_4H_9)_4N^+HSO_4^-$	80	18	100	90 (22/78)	10
18-crown-6	80	18	86	80 (22/72)	6
PEG 600	80	18	99	99 (19/81)	0
PEG 600 + 18-crown-6	80	2	100	100 (21/79)	0
PEG 600–$(n\text{-}C_4H_9)_2$	80	18	3	3	0
none	80	18	0	0	0

[a] Reaction of 0.5 mL of 2.0 M 2-bromooctane in benzene containing 0.161 mmol of nonane (internal standard) with 0.5 mL of aqueous base (60% KOH) in the presence of 0.1 equiv of each catalyst. Product mixtures were analyzed directly by using internal-standard techniques. [b] Average molecular weight of 750.

Table II. PEG 600 Catalyzed Dehydrohalogenation[a]

reactant	product	aqueous base	temp, °C	time, h	yield,[b] %
$PhCHBrCH_2Br$	$PhC{\equiv}CH$	KOH	70	1	84
		NaOH	70	1	51
$CH_3(CH_2)_7CHBrCH_2Br$[c]	$CH_3(CH_2)_7C{\equiv}CH$	KOH	80	3	72 (61)
		NaOH	80	3	66 (56)
$PhCH_2CH_2Br$[c]	$PhCH{=}CH_2$	NaOH	23	0.5	99 (83)
c-HxCHBrCH$_2$Br[c]	c-HxC≡CH	NaOH	80	5	68 (52)
erythro-$C_4H_9CHBrCHBrC_4H_9$[c]	$C_4H_9C{\equiv}CC_4H_9$	NaOH	80	18	5
threo-$C_4H_9CHBrCHBrC_4H_9$[c]	$C_4H_9C{\equiv}CC_4H_9$	NaOH	80	18	93 (78)
$PhOCH_2CH_2Br$[c]	$PhOCH{=}CH_2$	KOH	50	3	92 (70)

[a] Reaction of 1.0 mmol of organic halide dissolved in 0.25 mL of benzene with 0.5 mL of 50% NaOH or 60% KOH catalyzed by 0.06 g (0.1 mmol) of PEG 600; preparative-scale reactions were performed with 20 mmol of organic halide, 5 mL of benzene, 10 mL of aqueous hydroxide, and 1.2 g of PEG 600. [b] GLC yield; numbers in parentheses refer to isolated yields from preparative-scale reactions. In all reactions, the complete disappearance of starting material was observed. Unreacted vinyl bromide plus alkyne accounted for the total mass balance in the case of the vicinal dibromides. [c] No organic solvent used.

appearance of activity on going from $n = 3$ to $n = 4$.[9,10] The fact that maximum catalytic activity is obtained with $n \geq 5$ further implies that an "18-crown-6-like" structure occurring at the terminus of the polymer chains is optimal.[11] The high selectivity toward alkene formation coupled with the dependence of activity on hydroxyl groups, however, clearly indicates that the reactive base differs from hydroxide ion found in 18-crown-6/KOH complexes. All of these observations, taken together, strongly suggest that **1** and/or **2** is (are) the active agent(s).

Quaternary ammonium salts have been proposed as the catalysts of choice in several organic–aqueous two-phase reactions.[3,12] The greater inherent stability of poly(ethylene glycols) toward base coupled with the results presented herein provide ample justification for examining further the scope of these polyethers in organic synthesis.[13] Such studies, as well as the development of analogous triphase catalysts, are now in progress in our laboratories.[14]

Registry No. $HO(CH_2CH_2O)_1H$, 107-21-1; $HO(CH_2CH_2O)_2H$, 111-46-6; $HO(CH_2CH_2O)_3H$, 112-27-6; $HO(CH_2CH_2O)_4H$, 112-60-7; $HO(CH_2CH_2O)_5H$, 4792-15-8; $HO(CH_2CH_2O)_nH$, 25322-68-3; $CH_3O(CH_2CH_2O)_1H$, 109-86-4; $CH_3O(CH_2CH_2O)_2H$, 111-77-3; $CH_3O(CH_2CH_2O)_nH$, 9004-74-4; $BuO(CH_2CH_2O)_nBu$, 31885-97-9; $Bu_4N^+HSO_4^-$, 32503-27-8; 18-crown-6, 17455-13-9; 2-bromooctane, 557-35-7; (1,2-dibromoethyl)benzene, 93-52-7; 1,2-dibromodecane, 28467-71-2; (2-bromoethyl)benzene, 103-63-9; (1,2-dibromoethyl)cyclohexane, 81602-60-0; *erythro*-5,6-dibromodecane, 81602-61-1; *threo*-5,6-dibromodecane, 80262-80-2; (2-bromoethoxy)benzene, 589-10-6.

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Received January 26, 1982

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