3.78 (s, 3 H), 6.31 (t, 1 H, J = 1.8 Hz); IR (film) 3390, 3330, 2960, 2900, 1730, 1610, 1250 cm^{-1}; MS m/e 187 (1), 172 (100), 156 (21), 89 (51), 73 (29). Anal. Calcd for $C_8H_{17}NO_2Si$: C, 51.30; H, 9.15; N, 7.48. Found: C, 51.45; H, 9.02; N, 7.51.

Methyl (*Z*)-3-(Trimethylsilyl)-2-[(palmitoylamino)methyl]propenoate (13). **12** (100 mg, 0.5 mmol) dissolved in 1 mL of CH_2Cl_2 was cooled to 0 °C and added with a solution of 112 mg (0.05 mmol) of DCC in 1 mL of CH_2Cl_2 and 140 mg (0.5 mmol) of palmitic acid in 7 mL of CH_2Cl_2. The reaction mixture was kept overnight at room temperature and then filtered. After column chromatography (30 g of SiO_2, 230–400 mesh, eluent MeOH) 120 mg (53%) of **13** was isolated (mp 62–64 °C): ^1H NMR (C_6D_6) δ 0.23 (s, 9 H), 0.92 (t, 3 H, J = 6.6 Hz), 1.31 (bm, 26 H), 3.31 (s, 3 H), 4.12 (dd, 2 H, J = 1.5 Hz, J = 6.3 Hz), 5.06 (bt, 1 H, J = 6.3 Hz), 6.35 (t, 1 H, J = 1.5 Hz); IR (CCl_4) 3470, 2930, 2860, 1730, 1685, 1500, 1250 cm^{-1}; MS m/e 425 (2), 410 (74), 366 (20), 352 (67), 214 (25), 172 (100), 156 (74), 73 (29).

Palmitoylamide of β-Alanine Methyl Ester (14). Compound **12** was refluxed in toluene and hydroiodic acid following the procedure described by Utimoto et al.[17] Compound **14**, isolated by column chromatography (20 g of SiO_2, 230–400 mesh, eluent MeOH) shows spectral properties that are in good agreement with those described by Kashmann.[12]

(*Z*)-3-[(Trimethylsilyl)methylene]pyrrolidin-2-one (16). To a solution of (trimethylsilyl)lithium (1.50 mmol) in THF was added 70 mg (0.8 mmol) of CuCN at −23 °C. After stirring for 20 min, 320 mg (1.50 mmol) of *N*,*N*-bis(trimethylsilyl)-3-butynamine (**15**)[18] was added dropwise and kept at −23 °C for 30 min. After cooling at −40 °C and adding 15 mg (0.1 mmol) of triethyl phosphite a carbon dioxide stream (from CO_2 sublimation) was bubbled into the reaction mixture and then allowed to reach room temperature overnight. Dimethyl sulfate (190 mg, 1.5 mmol) was added at room temperature and then allowed to react for 2 h. After the usual workup and evaporation of the solvent, the crude residue was refluxed in MeOH for 2 h, affording, after column chromatography (20 g of SiO_2, 230–400 mesh, eluent EtOAc/*n*-hexane 2/1), 140 mg (55%) of **16**: ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 2.85 (td, 2 H, J = 6.9 Hz, J = 2.4 Hz), 3.42 (bt, 2 H, J = 6.9 Hz), 6.03 (t, 1 H, J = 2.4 Hz), 6.12 (bs, 1 H); IR ($CHCl_3$) 3440, 2980, 2960, 1700, 1245 cm^{-1}; MS m/e 154 (100).

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Registry No. **1**, 91375-25-6; **2**, 118832-05-6; **3**, 118799-87-4; **3a**, 118800-01-4; **4**, 118799-88-5; **5**, 118799-89-6; **6a**, 118799-90-9; **6b**, 118799-99-8; **7a**, 118799-91-0; **7b**, 118800-00-3; **8**, 118799-92-1; **9**, 118799-93-2; **10**, 118799-94-3; **11**, 118799-95-4; **12**, 118799-96-5; **13**, 118799-97-6; **14**, 52634-29-4; **15**, 88211-47-6; **16**, 118799-98-7; propargyl bromide, 106-96-7; allyl bromide, 106-95-6; 1-bromo-2-butene, 4784-77-4; vinyl bromide, 593-60-2; 2-iodothiophene, 3437-95-4.

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Poly(ethylene glycol)s and Their Dimethyl Ethers as Catalysts for the Reaction of Aryl Halides with Diphenylamine in the Presence of Potassium Hydroxide

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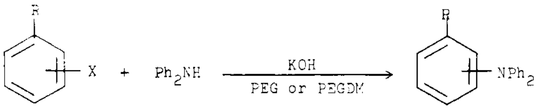
Since poly(ethylene glycol)s (PEG) and their ethers are more accessible than crown ethers or cryptands and more stable to strong alkali than onium salts at high temperature, they have been widely used as phase transfer agents (PTA) for reactions under strongly alkaline conditions.[1-12] However, there are few examples[8] of the reaction of an alkali-generated organic anion with an unactivated aryl halide in the presence of PEG or PEG ethers.

We here report on the phase-transfer reaction of unactivated aryl halides with diphenylamine (Ph_2NH) using KOH as base and PEG or PEG dimethyl ethers (PEGDM) as PTA. Recently, Gokel et al.[13] and Neumann et al.[10] have reported that one molecule of a PEG derivative can transport only one cation at a time under phase-transfer conditions. However, our kinetic and UV spectral studies have led to a different conclusion.



Results and Discussion

The reaction of PhCl or PhBr with Ph_2NH was carried out under various conditions in the presence of PEG-3000 as PTA (Table I). The reaction with PhCl produced only small amounts of Ph_3N, whereas the reaction with PhBr gave substantial yields of Ph_3N when KOH was used as base. Since the reaction was very slow with 65% aqueous KOH, 85% KOH was used. All of the additives tried had either no effect or a negative effect on the yield of Ph_3N. Addition of $PdCl_2$ gave substantial yields of biphenyl and benzene, and $CuCl_2$ gave a poor material balance of PhBr.

Neumann and Sasson[8] have reported that in the reaction of an aryl halide with alkoxide the molecular weight of PEG had significant influence on the activity. At a constant weight of PEG, higher molecular weight resulted in higher catalytic activity, and a plateau was reached at PEG-6000. Although we observed the same trend for PEG, even the low molecular weight PEGDM-400 was as efficient as PEG-6000 (Figure 1).

Accordingly, we carried out reactions of Ph_2NH with various aryl halides in the presence of PEGDM-400, continuously removing the water formed in the reaction to prevent reduction of the KOH concentration (Table II). In reactions with aryl bromides, complete conversion of Ph_2NH was observed after relatively short times, whereas reactions with aryl chlorides were considerably slower. It is well known that the cine-substitution reaction can occur in reactions of amide anions with aryl halides.[14] Our reactions gave mixtures of isomeric triphenylamine derivatives. In the reaction with *o*-dichlorobenzene, nucleophilic addition to the aryne should occur predominantly at the meta position to form the stable intermediate.

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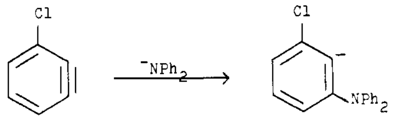


We investigated the kinetics of the reaction of Ph_2NH with PhBr in the presence of PEG or PEGDM. The reaction followed good second-order kinetics: plots of ln $([Ph_2NH]/[PhBr])$ vs time were linear. The amount of PhBr consumed was in good agreement with that of Ph_3N produced. The reaction appears to involve a benzyne

$$v = k_{obsd}[Ph_2NH][PhBr]$$

intermediate, which is unstable and highly reactive.[15] Therefore, dehydrobromination by diphenylamide anion Ph_2N^- to form the benzyne must be the rate-determining step (Scheme I). The reaction rate was independent of

Scheme I

$$Ph_2NH \xrightarrow[\text{PEG or PEGDM}]{KOH} Ph_2N^-$$

$$PhBr \xrightarrow{Ph_2N^-} \text{benzyne}$$

$$\text{benzyne} + Ph_2NH \rightarrow Ph_3N$$

stirring speed above 400 rpm. The effect of catalyst type and molecular weight on reaction rate is shown in Figure 2; the quantity of catalyst was selected to give the same number of ethylene oxide units in all experiments. With PEG, the rate increased monotonically with molecular weight to a constant value at a molecular weight of ~3000 (~68 ethylene oxide units). With PEGDM, however, the rate rose to a maximum at 4–9 ethylene oxide units and then decreased to the same constant value as PEG at ~68 ethylene oxide units. This behavior of PEGDM resembles that found by Neumann and Sasson[10] in the isomerization of allylanisole.

A UV spectral study was carried out to elucidate the mechanism of the action of PEG and PEGDM. A mixture of Ph_2NH (1×10^{-3} M) in toluene (100 mL), 85% KOH (1.0 g, 15 mmol), and the indicated amount (Figure 3) of PEG and PEGDM was vigorously stirred for 20 min under reflux. After the mixture was cooled to room temperature, its difference spectrum was measured. With PEG-400, two absorption bands were observed at 320 and 362 nm (Figure 3A), whereas with PEGDM-400 and PEGDM-6000 only the band at 320 nm appeared (Figure 3B,C). The peak at 320 nm is the absorption of the ion pair $Ph_2N^-{\cdot}K^+$, which was identified in the spectrum of a THF solution of $Ph_2N^-{\cdot}K^+$ obtained from Ph_2NH and potassium. The peak at 362 nm is the absorption of the ion pair $CH_2CH_2O^-{\cdot}K^+$, which was identified by measuring the spectrum of a toluene solution of $CH_2CH_2O^-{\cdot}K^+$ obtained from PEG-400 and potassium. No absorption corresponding to $K^+{\cdot}OH^-$ (270 nm in methanol) was observed.

In the presence of KOH, PEG exists partly as $CH_2CH_2O^-{\cdot}K^+$, which is probably a crownlike complex 1, and its ability to transport $Ph_2N^-{\cdot}K^+$ to the organic phase is inferior to that of PEGDM. Furthermore, hydrogen bonding of the hydroxy groups (2) must lower the basicity of the anion Ph_2N^-. Accordingly, in the low molecular weight range, PEG produces a lower reaction rate than PEGDM. In the higher molecular weight range, the effect of the hydroxy groups becomes negligible. If, as stated by Neumann and Sasson[10] for the isomerization of allylanisole, one molecule of PEG or PEGDM complexes with only one potassium cation at a time, and ion-pair separation increases with the molecular weight of PEG or PEGDM, the absorption bands of $PEG(PEGDM){\cdot}Ph_2N^-{\cdot}K^+$ complexes should be different from each other.[16] However, no shift in the absorption maximum was observed (Figure 3). Thus the degrees of ion-pair separation in PEGDM-400·$Ph_2N^-{\cdot}K^+$ (~9 ethylene oxide units) and PEGDM-6000·$Ph_2N^-{\cdot}K^+$ (136 ethylene oxide units) complexes must be the same. Therefore the amount of complexation depends upon the total number of ethylene oxide units rather than the number of polymer chains.

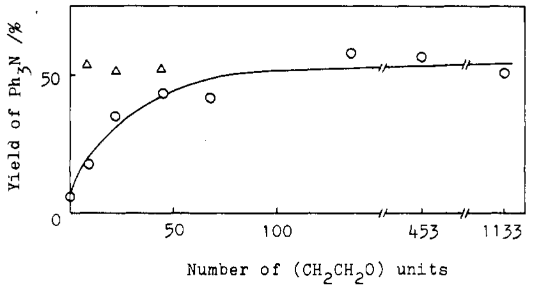


Figure 1. Plots of yields of Ph_3N vs number of ethylene oxide units in the catalyst. Reactions were carried out with Ph_2NH (8.46 g, 50 mmol), PhBr (15.70 g, 100 mmol), 85% KOH (9.90 g, 150 mmol), and a catalyst (4.00 g) at 155–160 °C for 7 h. (△) PEGDM, (○) PEG.

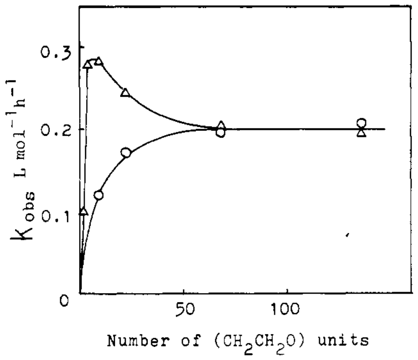
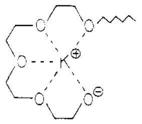


Figure 2. Plots of k_{obsd} vs number of ethylene oxide units in the catalyst. Reactions were carried out with Ph_2NH (8.46 g, 50 mmol), PhBr (15.70 g, 100 mmol), 85% KOH (9.90 g, 150 mmol), xylene (15.0 g), and a catalyst (total amount of ethylene oxide units: 90 mmol) at 119 ± 1 °C. (△) PEGDM, (○) PEG.



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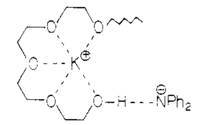

2

The reaction with PEGDM-400 was faster than that with PEGDM-6000 by a factor of ~1.4, with the same quantity of ethylene oxide units. On the other hand, the UV absorbance of PEGDM-400 was greater than that of PEGDM-6000 by a factor of 1.08. This factor is based on equal weights of the two polymers, but the number of ethylene oxide units per gram in PEGDM-400 is smaller than that in PEGDM-6000 by a factor of 0.92. Therefore, the absorbance per ethylene oxide unit in PEGDM-400 should be larger than that in PEGDM-6000 by a factor of 1.17, which is close to the ratio of reaction rates, ~1.4.

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Table I. Preparation of Ph_3N under Various Conditions Using PEG-3000[a]

PhX	temp, °C	base	additive (mmol)	yield,[b] % Ph_3N[c]	Ph_2O[d]	PhH[e]
PhCl	140–145	KOH		7 (~0.5)		
			Cu (2)	7		
			$CuCl_2$ (2)	2	~0	<1
			$NiCl_2$ (2)	6		
			$PdCl_2$ (1)	3	~0 (Ph_2; ~1)	18
			$CoCl_2{\cdot}6H_2O$ (2)	4		
PhBr	155–160	NaOH		<1		
		K_2CO_3	Cu (2)	<1		
		KOH		42 (~6)	4 (0.1)	<1 (0)
			Cu (2)	40	4	0
			$CuCl_2$ (2)	17	2	1
			$CoCl_2{\cdot}6H_2O$ (2)	37	4	<1
			$PdCl_2$ (1)	16	~2 (Ph_2; 12)	19
			$NiCl_2$ (2)	43	4	2
			$NiCl_2(PPh_3)_2$ (2)	43	5	4

[a] Unless otherwise noted, reactions were carried out with Ph_2NH (50 mmol), PhX (100 mmol), and PEG-3000 (4.0 g, 1.33 mmol) for 7 h. [b] Determined by GLC using internal standard technique. The values in parentheses are the yields in the absence of PEG-3000. [c] Based on Ph_2NH (internal standard: dibenzyl ether). [d] Beased on PhBr (internal standard: dibenzyl ether). [e] Based on PhBr (internal standard: toluene).

Table II. Reaction of Ph_2NH with Aryl Halides Using PEGDM-400 Catalyst[a]

ArX	time, h	temp, °C	yield,[b] %	product ratio[d]
C_6H_5Br	5	160–163	87[c]	
o-$CH_3C_6H_4Br$	8	166–167	88[c]	o:m = 35:65
m-$CH_3C_6H_4Br$	8	161–163	90[c]	o:m:p = 26:53:21
p-$CH_3C_6H_4Br$	8	165	86[c]	m:p = 53:47
p-$CH_3OC_6H_4Br$	8	158–161	48[c]	m:p = 55:45
p-ClC_6H_4Br	8	143–145	(81)[c]	m:p = 38:62
o-$Cl_2C_6H_4$	24	160–165	(53)	m = ~100
m-$Cl_2C_6H_4$	15	155–160	(71)[c]	m:p = >95:<5
p-$Cl_2C_6H_4$	15	155–160	(73)	m:p = 40:60

[a] Unless otherwise noted, reactions were carried out with Ph_2NH (25 mmol), ArX (200 mmol), 85% KOH (50 mmol), toluene (6.0 g), and PEGDM-400 (10 mmol) under reflux (removing the water formed). In the case of C_6H_5Br, toluene was omitted. [b] Isolated yields. The values in parentheses are the yields determined by GLC using internal standard technique. [c] Almost complete conversion of Ph_2NH was observed. [d] Product ratios were determined by GLC (PEG-HT, 5%, 1 m × 3 mm, 220 °C).

These results indicate that one molecule of high molecular weight PEG or PEGDM can bind more than one potassium cation. About nine ethylene oxide units are required to form a crown-type complex, and PEG and PEGDM with four to nine ethylene oxide units can most efficiently bind a potassium cation. The hydroxy groups in PEG reduce its catalytic activity because of the formation of $CH_2CH_2O^{-}{\cdot}K^{+}$ and hydrogen bonding to the anion Ph_2N^{-}.

Experimental Section

Materials. Commercial reagents were used unless otherwise indicated. PEGDM was prepared by the literature method.[17] Samples of o-, m-, and p-tolyldiphenylamine, (m- and p-methoxyphenyl)diphenylamine, and (m- and p-chlorophenyl)diphenylamine were prepared by the literature procedure.[18] All reactions were run under a nitrogen atmosphere.

General Procedure for the Reaction of PhCl or PhBr with Ph_2NH with PEG-3000 as PTA. A mixture of Ph_2NH (8.46 g, 50 mmol), PhBr (15.70 g, 100 mmol), 85% KOH (9.90 g, 150 mmol), PEG-3000 (4.00 g, 1.33 mmol), and an additive (Table I) was vigorously stirred for 7 h under reflux (155–160 °C). The mixture was cooled to room temperature, and product yields were determined by GLC (internal standard dibenzyl ether for Ph_3N and diphenyl ether; toluene for benzene).

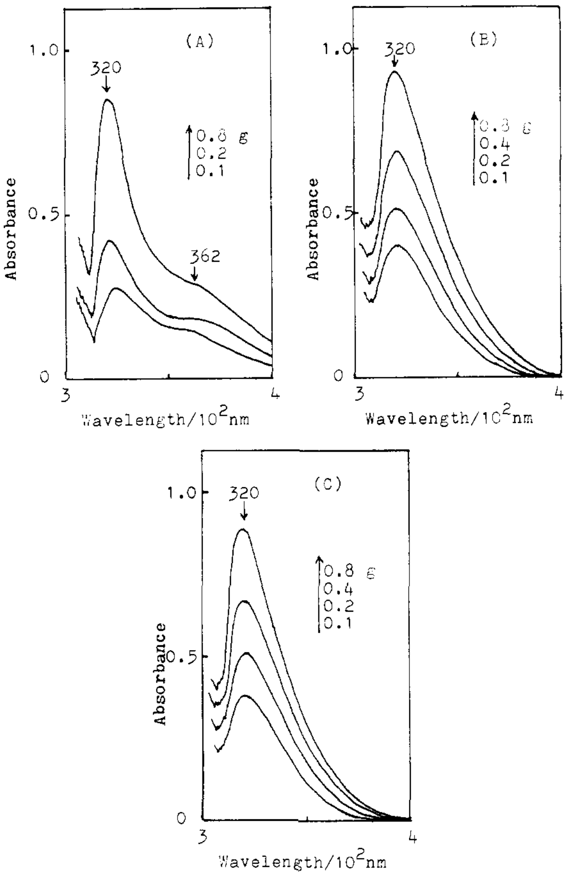

Figure 3. UV spectra of solutions of Ph_2NH, KOH, and PEG or PEGDM in toluene. (A) PEG-400, (B) PEGDM-400, (C) PEGDM-6000.

General Procedure for the Reaction of Ph_2NH with Aryl Halides. A mixture of Ph_2NH (4.23 g, 25 mmol), PhBr (31.40 g, 200 mmol), 85% KOH (9.90 g, 150 mmol), and PEGDM-400 (4.28 g, 10 mmol) was heated under reflux (160–163 °C) with vigorous stirring for 5 h. Water was removed continuously by passing the vapor through a column (6 g of $^1/_8$ in. 4A molecular sieve pellets) under the reflux condenser. The mixture was cooled to room temperature, water (30 mL) and benzene (60 mL) were added, and the two layers were separated. The organic layer was washed with 5% aqueous HCl (2 × 25 mL) and brine (3 × 70 mL). After removal of the benzene and excess PhBr, the residue was distilled under reduced pressure to give 5.33 g (87%) of Ph_3N,

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[17] Sukata, K. *Yuki Gosei Kagaku Kyokai Shi* **1981**, *39*, 86.
[18] Gauthier, S.; Frechet, J. M. J. *Synthesis* **1987**, 383.

bp 157-160 °C (1 mmHg). Recrystallization gave pure Ph_3N, mp 126-127 °C [lit.[19] bp 195-205 °C (10-12 mmHg), mp 126 °C).

Reaction of Ph_2NH with *p*-Bromotoluene. A mixture of Ph_2NH (4.23 g, 25 mmol), *p*-bromotoluene (34.21 g, 200 mmol), PEGDM-400 (4.28 g, 10 mmol), 85% KOH (9.90 g, 150 mmol), and toluene (6 g) was refluxed with vigorous stirring for 8 h (166-167 °C). After workup as above, distillation gave 5.91 g of crude product, bp 140-150 °C (0.4 mmHg). Purification by column chromatography (15 cm, SiO_2 Merck 60, eluted with benzene/hexane, 1:3) gave 5.69 g (88%) of a mixture of *m*-tolyldiphenylamine and *p*-tolyldiphenylamine in a ratio of 35:65 (PEG-HT, 5% 1 m × 3 mm, 220 °C).

Kinetic Measurements. A mixture of Ph_2NH (8.46 g, 50 mmol), PhBr (15.70 g, 100 mmol), PEGDM-400 (4.28 g, 10 mmol; total ethylene oxide units 90 mmol), xylene (15.0 g), and dibenzyl ether as internal standard was heated to 115 °C, and 85% KOH (9.90 g, 150 mmol) was added. The resulting mixture was heated at 119 ± 1 °C with stirring (800 rpm). The organic layer was analyzed by GLC at intervals (PEG-HT 5%, 1 m × 3 mm, 180 °C). Rate constants were calculated by a least-squares computer program from the equation

$$kt = [1/(C_0^B - C_0^A)](\ln C^B/C^A - \ln C_0^B/C_0^A)$$

where

$$C^A = [Ph_2NH],\ C^B = [PhBr].$$

UV Spectra. A solution of Ph_2NH in toluene (1×10^{-3} M, 100 mL, control solution), 85% KOH (1.0 g, 15 mmol), and the indicated weight of catalyst (Figure 3) was vigorously stirred for 20 min under reflux. The mixture was cooled to room temperature, and the organic layer was filtered through glass fiber paper. The difference spectrum of this solution was measured with a JASCO UVIDEC-660 spectrometer with a 1-cm quartz cell. UV spectra of $Ph_2N^-{\cdot}K^+$ in THF, obtained from Ph_2NH and potassium, and of $CH_2CH_2O^-{\cdot}K^+$ in toluene, obtained from PEG-400 and potassium, were also measured.

Acknowledgment. We thank Nihon Tokushu Kagaku Kogyo Co., Ltd., for permission to publish this article. We are also greatful to Prof. W. J. le Noble (Senior Editor) for his helpful support in editing the manuscript.

Registry No. C_6H_5Br, 108-86-1; *o*-$CH_3C_6H_4Br$, 95-46-5; *m*-$CH_3C_6H_4Br$, 591-17-3; *p*-$CH_3C_6H_4Br$, 106-38-7; *p*-$CH_3OC_6H_4Br$, 104-92-7; *p*-ClC_6H_4Br, 106-39-8; *o*-$Cl_2C_6H_4$, 95-50-1; *m*-$Cl_2C_6H_4$, 541-73-1; *p*-$Cl_2C_6H_4$, 106-46-7; Ph_2NH, 122-39-4; Ph_3N, 603-34-9; *o*-$CH_3C_6H_4NPh_2$, 4316-55-6; *m*-$CH_3C_6H_4Ph_2$, 4316-54-5; *p*-$CH_3C_6H_4NPh_2$, 4316-53-4; *m*-$CH_3OC_6H_4NPh_2$, 20588-62-9; *p*-$CH_3OC_6H_4NPh_2$, 4316-51-2; *m*-$ClC_6H_4NPh_2$, 106336-13-4; *p*-$ClC_6H_4NPh_2$, 4316-56-7; PhCl, 108-90-7.

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Bis[(trimethylsilyl)ethynyl] Ether: A Moderately Stable C_4H_2O Derivative

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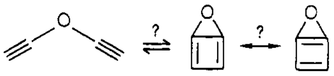
Proximal interactions[2] between two or more appropriately positioned triple bonds in a molecule are of interest for a number of reasons. These have included questions of aromaticity[3a] and the inherent potential of subsequent reaction between the interacting centers.[2] From a synthetic viewpoint, this area has been explored particularly successfully with use of transition metal complexes[3b-g] to initiate cycloaddition.

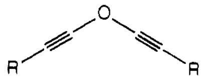
We became interested in simple C_4H_2O structures when it became apparent that little or nothing is known about diethynyl ether 1, or its dehydrofuran valence tautomers 2.



1 2a 2b

We were particularly encouraged to initiate experimental work by the results of INDO calculations[4] on 1 and 2, which suggested that **2a** is favored energetically over 1, while **2b** appeared a highly unsatisfactory structure, not surprisingly perhaps in view of its oxirene-cyclobutadiene (twice antiaromatic) character.

As it turned out, compound **1a** had actually been made by Brandsma[5] some 25 years ago, but the reported bromination-dehydrobromination sequence starting from dipropenyl ether had failed for structures lacking the terminal alkyl groups. In addition, the reported property of **1a** of exploding at room temperature did not appear to recommend it as a likely candidate for further investigation.



1a: R = Me
b: R = $SiMe_3$

We report herein a simple three-step sequence of quite general utility for preparation of derivatives of 1 through intermediacy of its dianion, and in particular the isolation and characterization of the reasonably stable bis[(trimethylsilyl)ethynyl] ether **1b**.

The synthesis summarized in Scheme I is a modification of our earlier procedure for synthesis of alkoxyacetylenides.[6] Initial attempts to prepare the hexabromo ether **3** by the procedure reported for chloral[7] gave extremely poor yields (~5%). However, the use of sulfuryl chloride as solvent markedly improved matters. This presumably reflects the assistance of the inorganic chloride in transferring chloride ion to intermediate cations. Interestingly, we noticed that running the last step (**4** → **1b**) in high concentrations of *n*-BuLi in THF gave black reaction solutions and numerous side products, and substitution of THF by diethyl ether seemed to make matters even worse. Optimum conditions were obtained by initially diluting *n*-BuLi to about 1 M with hexane and using a

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(4) The difference in total energy between 1 and **2a** was calculated to be 0.10 Hartree in favor of **2a**. The electronic energy did not converge for **2b**. We thank Dr. S. Brumby of the School of Chemical Sciences, The Australian National University, for carrying out these calculations using Program No. 274 from the Quantum Chemistry Program Exchange.

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