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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[19] Hager, F. D. *Organic Synthesis*; Wiley: New York, 1941; Collect. Vol. I, p 544.

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

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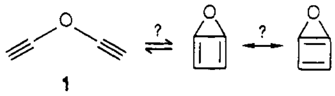
Proximal interactions[2] between two or more appropriately positioned triple bonds in a molecule are of interest for a number of reasons. These have included questions of aromaticity[3a] and the inherent potential of subsequent reaction between the interacting centers.[2] From a synthetic viewpoint,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

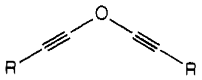
We became interested in simple C_4H_2O structures when it became apparent that little or nothing is known about diethynyl ether **1**, or its dehydrofuran valence tautomers **2**.



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 = SiMe3

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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[2] See: Misumi, S.; Kaneda, T. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; John Wiley: Chichester, 1978; Part 2.

[3] (a) Diercks, R.; Armstrong, J. C.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 268. (b) See, for example: Lecker, S. H.; Nguyen, N. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 856. (c) Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150. (d) Schore, N. E.; Najdi, S. D. *J. Org. Chem.* **1987**, *52*, 5296. (e) Neeson, S. J.; Stevenson, P. J. *Tetrahedron Lett.* **1988**, *29*, 813. (f) Sivavec, T. M.; Katz, T. J. *Tetrahedron* Lett. **1985**, *26*, 2159. (g) Grigg, R.; Scott, R.; Stevenson, P. *Tetrahedron Lett.* **1982**, *23*, 2691.

[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.

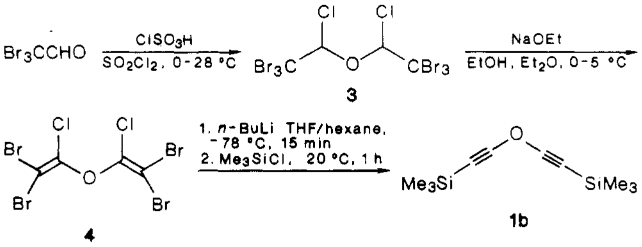
[5] Brandsma, L.; Arens, J. F. *Recl. Trav. Chim., Pays-Bas* **1962**, *81*, 510.

[6] Smithers, R. H. *Synthesis* **1985**, 556. See also Smithers, R. H. *Synth. Commun.* **1985**, *15*, 81.

[7] Miller, C. B.; Woolf, C. U.S. Patent 2803666, Aug 20, 1957. See *Chem. Abstr.* **1958**, *52*, 2047*h*.

0022-3263/89/1954-1479$01.50/0

Scheme I



minimum volume of THF. It would seem difficult to account for this observation since if the role of decreased solvent polarity was to direct toward desirable *Z* metalation[8] (lithium cis to oxygen), then substitution of THF by diethyl ether ought to improve matters.

Our reported conditions allowed isolation of **1b** as a yellow oil in 55% yield, which was stable enough to survive purification by chromatography on silica. There seeems no doubt that extra stability, whose origin is probably both steric and electronic,[9] is conferred by the trimethylsilyl groups. However, neat samples of the compound did turn brown on standing overnight at room temperature and black over a further period of a day. ^{1}H NMR monitoring of these colored samples showed the rapid demise of **1b** and a number of new $SiMe_3$ absorptions. On the other hand, samples stored in CH_2Cl_2 or $CDCl_3$ solution in a freezer compartment remained unchanged for weeks.

The spectroscopic data for **1b** were examined carefully for evidence of any intervention by the 2,5-dehydrofuran **2**. Apart from marginal differences in the UV, where long wavelength transitions between 250 and 260 nm were more intense than for (trimethylsilyl)methoxyethyne, nothing firmly inconsistent with dialkynyl ether **1b** was detected.

Experimental Section

NMR spectra were obtained on JEOL JNM-PMX60 SI and JNM-FX 100 instruments for dilute solutions in $CDCl_3$. Ultraviolet spectra were obtained on a Beckman DU-7 spectrometer in either 95% EtOH or hexane, infrared spectra on a Perkin-Elmer 1330 instrument, and mass spectra on an AEI MS 30 spectrometer with a DS 55 data system. Commercial bromal was redistilled before use as were chlorosulfonic acid and sulfuryl chloride. THF was dried and deperoxidized by using self-indicating molecular sieves, which performs both functions.[10]

Bis(2,2,2-tribromo-1-chloroethyl) Ether (3). A solution of bromal (28.1 g, 0.10 mol) in sulfuryl chloride (20 mL) was added dropwise over 45 min to a rapidly stirred solution of chlorosulfonic acid (26.8 g = 15 mL; 0.23 mol) in sulfuryl chloride (50 mL) cooled in an ice bath. The mixture was then allowed to warm slowly to room temperature and stirred overnight (18 h). [Slight generation of hydrogen halides occurs over this period, venting through a calcium chloride tube is advisable.] The deep wine-colored solution was then poured slowly on to cracked ice (~1 kg) in a large beaker with rapid stirring to control the vigorous reaction. Extraction with CH_2Cl_2 (4 × 100 mL) followed by washing with solutions of potassium bicarbonate and sodium thiosulfate (0.2 M), drying (3A moleuclar sieve powder), and removal of the solvent at reduced pressure gave a reddish-brown viscous oil containing a solid. Recrystallization from $MeOH-H_2O$ gave 14.5 g of **3** (47%) as a pale cream-colored solid, mp 95–96 °C. Recrystallization of this material from MeOH gave an analytical sample: mp 98–98.5 °C; IR (KBr) 2920, 1340, 1295, 1240, 1090 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.10 (s), the NMR indicated the presence of a single diastereomer; (found: 296.7452, Br_3C^+CHCl requires 296.7316), *m/z* 296 (26), 298 (89), 300 (100), 302 (48), 304 (7).

Bis(2,2-dibromo-1-chlorovinyl) Ether (4). An approximately 2 M solution of sodium ethoxide obtained from sodium (0.98 g, 42.6 mmol) in dry ethanol (21 mL) was added dropwise over 30 min to a well-cooled (ice bath) stirred solution of **4** (11.92 g, 19.3 mmol) in diethyl ether (30 mL) as previously described for related compounds.[6] Removal of solvents in vacuo followed by partitioning the oily solid between dichloromethane (50 mL) and water (10 mL), washing (0.1 M sulfuric acid), drying (3A molecular sieve powder), and removal of dichloromethane gave a brown oil. Chromatography on alumina (50 g) with hexane eluant gave 7.7 g (87%) of **4** as a white crystalline solid: mp 52–53 °C; R_f (SiO_2–hexane) 0.57; IR (Nujol) 1590, 1145–1090, 910, 850, 780, 750 cm^{-1}; UV (95% EtOH) λ_{max} 219 nm; (Found: 449.6065, $C_4Br_4Cl_2O$ requires 449.6059), *m/z* 449 (1.7), 451 (10.2), 453 (23), 455 (22), 457 (8), 459 (1).

Bis[(trimethylsilyl)ethynyl] Ether (1b). A solution of **4** (0.45 g, 1 mmol) in dry THF (1.5 mL) was added dropwise to a magnetically stirred solution of diluted *n*-BuLi (1.9 mL of 2.29 M solution in hexane, 4.35 mmol, diluted with 4 mL of hexane) over 30 min at −78 °C under argon. (Some difficulty in stirring invariably results about half way through the addition caused by the precipitation of a gum, this is overcome by briefly removing the reaction flask from the cold bath with continued stirring. Use of a heavy magnetic bar is advantageous.) After the mixture was stirred an additional 30 min, chlorotrimethylsilane (0.22 g, 2 mmol) in THF (1 mL) was added all at once, and the mixture was warmed to −20 °C for 1 h after which it was quenched by addition of saturated basic ammonium chloride solution (3 mL). Separation of the organic phase followed by washing with basic saturated ammonium chloride (1 mL), drying, and removal of volatiles on a rotary evaporator (30 °C) gave a dark oil. Flash chromatography (SiO_2–hexane) gave 116 mg (55%) of **1b** as a yellow oil after removal of solvents: R_f (SiO_2–hexane) 0.66; IR (film) 2940, 2880, 2240, 2200, 2160, 2140, 1600, 1250, 1190, 1045 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.17 (s); ^{13}C (100 MHz, $CDCl_3$) δ 78.0 (*C*–O), 27.0 (*C*–Si), −0.03 (*Me*–Si), UV (hexane) [λ_{max}, nm (ϵ)] 269 (520), 259 (750), 252 (960), 223 (6640); (found: M − Me) 195.0495, $C_9H_{15}OSi_2$ requires (M − Me) 195.0661), *m/z* 210 (0.6), 195 (3.1), 137 (9, M − $SiMe_3$), 73 (100).

(Trimethylsilyl)methoxyethyne. This material was prepared as previously reported:[11] UV (hexane) [λ_{max}, nm (ϵ)] 278 (224), 270 (256), 266 (309), 225 (405), 222 (3000).

Acknowledgment. We thank the University of Malaya for the award of a Tutorship to I.H.O.

Registry No. 1, 118921-88-3; **1b**, 118921-85-0; **2a**, 118921-89-4; **3**, 118921-87-2; **4**, 118921-87-2; (trimethylsilyl)methoxyethyne, 24082-05-1; bromal, 115-17-3.

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(8) Trans elimination in lithiated propenyl ethers also appears to be the rule. cf. (a) Smithers, R. H. *J. Org. Chem.* **1983**, *48*, 2095. (b) Lau, K. S. Y.; Schlosser, M. *J. Org. Chem.* **1978**, *43*, 1595.

(9) It appears that for acetylenes such as (trimethylsilyl)methoxyethyne there is an energetic advantage obtained by electron acceptance at Silicon through its d orbitals. In other words there is push–pull stabilization. Evidence for this has been obtained by spectral analysis and force constant calculations. See: Lararev, A. N.; Tenisheva, T. F.; Shchukovskaya, L. L.; Pal'chik, R. I. *Dokl. Akad. Nauk. SSSR* **1970**, *190*, 1106; cf. *Chem. Abstr.* **1970**, *72*, 131879*c*.

(10) Burfield, D. R. *J. Org. Chem.* **1982**, *47*, 3821.

(11) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5253.