solid; mp 123 °C; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3 H), 3.74 (m, 2 H), 4.46, 4.74 (dd, 2 H), 4.93 (t, 1 H), 7.2 (m, 8 H); IR (KBr) 1713, 1653 cm^{-1}; MS (EI) *m/e* 276 ($M^{+\cdot}$, 70), 261 (15), 232 (34), 91 (25), 77 (15), 82 (18), 43 (100). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58, H. 5.84. Found: C, 82.42; H, 6.00.

4-(4-Chlorophenyl)-4,9-dihydronaphtho[2,3-*c*]furan-1-(3*H*)-one (15c): yield 0.67 g (45%) of a pale yellow crystalline solid; mp 160 °C; ^{1}H NMR ($CDCl_3$) δ 3.80 (m, 2 H), 4.50, 4.70 (dd, 2 H), 4.93 (t, 1 H), 7.2 (m, 8 H); IR (KBr) 1723, 1658 cm^{-1}; MS (EI) *m/e* 296 ($M^{+\cdot}$, 51), 252 (35), 217 (100). Anal. Calcd for $C_{18}H_{13}O_2Cl$: C, 72.85; H, 4.42. Found: C, 72.83; H, 4.53.

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Supplementary Material Available: X-ray data for **15a** including atomic coordinate and equivalent isotropic displacement parameters, anisotropic temperature parameters, bond lengths and angles, and physical properties data including ^{1}H and ^{13}C NMR spectra of **10c-f** and **13b-c** (15 pages). Ordering information is given on any current masthead page.

Aryl-Substituted Cyclic Homoaldol Products Derived from (α-Alkoxybenzyl)trimethylsilanes

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We have been studying the synthetic utility of α-alkoxyorganocuprate reagents in the stereoselective generation of homoaldol products. Although we were able to achieve excellent yields of 1,4-addition products to cyclic and acyclic enones,[1] and high diastereoselectivity in additions to acyclic enals,[2] the cuprate methodology was limited to alkyl-substituted α-alkoxyorganocuprates. Attempts to prepare aryl-substituted cyclic homoaldol products using aryl-substituted α-alkoxyorganocuprates were fraught with low yields and considerable amounts of undesirable dimerization of the cuprate species.[1c] In an effort to surmount the difficulties involved in the generation of aryl-substituted cyclic homoaldol products, we have investigated the potential utility of silyl-derived aryl-substituted α-alkoxy carbanions. The nucleophilic desilylation of organosilanes as a means of generating synthetically useful carbanions has been reviewed.[3] In particular, allylsilanes have been used extensively in electrophilic addition reactions.[4] Aryl anions derived from trimethylsilyl-substituted heteroaromatic silanes[5] and benzylic anions from aryl and heteroaryl benzylsilanes[6] have also been reported. In particular, Ricci and co-workers[7] described the fluoride-initiated regioselective addition of benzyltrimethylsilane to cyclohexenone, while Bennetau and co-workers[8] reported regioselective 1,2-addition of the same reagent to enals. We now wish to report highly regioselective 1,4-addition of several [α-(methoxymethoxy)benzyl]trimethylsilanes to cyclic enones.

Several substituted (α-hydroxybenzyl)trimethylsilanes were prepared in good overall yield from the appropriate benzaldehyde derivative via the reverse Brook rearrangement methodology we have described.[9] Protection of the alcohol as the methoxymethyl (MOM) ether was achieved in excellent yield under standard reaction conditions ($iPrNEt_2$, MOMCl, 0 °C).[1c] Aqueous quench of the reaction mixture of **1** and CsF in DMF provided a nearly quantitative yield of the desilylated MOM-protected benzyl alcohol **2**. In contrast to the facile reaction of α-alkoxyalkyl lithio anions with DMF,[10] no trace of the possible formylation product was detected. Direct 1,2-addition of **1** to butyraldehyde provided an 82% isolated yield of the monoprotected diol **3**. Attempted 1,2-addition of **1** to ketones provided <10% of the addition products. The silyl-derived benzyl anion was also completely unreactive toward saturated and unsaturated esters and was an inefficient nucleophile toward alkylation with allyl or benzyl bromide (<15% isolated yields). The reactivity of α-alkoxyalkyl lithio anions derived by transmetalation of the corresponding stannane[10,11] or deprotonation of carbamate derivatives of benzyl alcohol[12] toward alkylation is distinctively greater than that observed for **1**.

Regioselective 1,4-addition of several [α-(methoxymethoxy)benzyl]trimethylsilanes was obtained with cyclic enones (see Table I). The aryl-substituted cyclic homoaldol products **8-17** were obtained as mixtures of diastereomers from silanes **1** and **4-7** in 42-85% yield. Only the 2,4-dimethoxy-functionalized silane **4** produced a significant, albeit minor, amount of 1,2-addition product (<6%). Optimized reaction conditions involved in situ reaction of

(1) (a) Linderman, R. J.; Godfrey, A. *Tetrahedron Lett.* **1986**, *27*, 4553-4556. (b) Linderman, R. J.; Godfrey, A.; Horne, K. *Tetrahedron Lett.* **1987**, *28*, 3911-3914. (c) Linderman, R. J.; Godfrey, A.; Horne, K. *Tetrahedron* **1989**, *45*, 495-506.

(2) Linderman, R. J.; McKenzie, J. R. *Tetrahedron Lett.* **1988**, *29*, 3911-3914. For additional reports of α-oxygenated organocuprate reagents, see: Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1983**, *24*, 3165-3168. Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 4930-4939. Knochel, P.; Chou, T.-S.; Chen, H. G.; Yeh, M. C. P.; Rozema, M. J. *J. Org. Chem.* **1989**, *54*, 5202-5204.

(3) Furin, G. G.; Vyazankina, D. A.; Gostevsky, B. A. *Tetrahedron* **1988**, *44*, 2675-2749.

(4) See, inter alia: (a) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1-22. (b) Schinzer, D. *Synthesis* **1988**, 263-273. (c) Majetich, G.; Casares, A. M.; Chapman, D.; Behnke, M. *Tetrahedron Lett.* **1983**, *24*, 1909-1912. (d) Majetich, G.; Defauw, J.; Ringold, C. *J. Org. Chem.* **1988**, *53*, 50-68. (e) Molander, G. A.; Andrews, S. *Tetrahedron* **1988**, *44*, 3869-3888.

(5) Effenberger, F. *J. Org. Chem.* **1984**, *49*, 4687-4695.

(6) (a) Tsuzi, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1983**, 1131-1134. (b) Ogata, J.; Shimizu, S. *Synth. Commun.* **1989**, *19*, 2219-2227. (c) Ricci, A.; Degl'Innocenti, A.; Fiorenza, M. *Tetrahedron Lett.* **1982**, *23*, 577-578.

(7) Ricci, A.; Fiorenza, M.; Grifagri, M. *Tetrahedron Lett.* **1982**, *23*, 5079-5082.

(8) Bennetau, B.; Bordeau, M.; Dunogues, J. J. *Bull. Chim. Soc. Fr.* **1985**, 90-94.

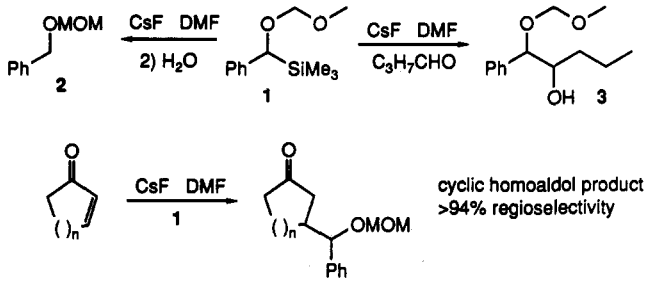
(9) Linderman, R. J.; Ghannam, A. *J. Am. Chem. Soc.* **1990**, *112*, 2392-2398.

(10) McGarvey, G. J.; Kimura, M. *J. Org. Chem.* **1985**, *50*, 4655-4657. For 1,4-additions of α-alkoxyalkyl lithio anions to unsaturated hydrazides, see: Chong, J. M.; Mar, E. K. *Tetrahedron Lett.* **1990**, *31*, 1981-1984.

(11) Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842-853.

(12) (a) Hoppe, D.; Bronneke, A. *Synthesis* **1982**, 1045-1047. (b) Barner, B.; Mani, R. S. *Tetrahedron Lett.* **1989**, *30*, 5413-5416.

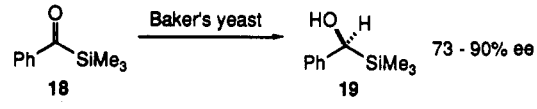
0022-3263/91/1956-5213$02.50/0



the silane and enone with CsF (catalytic or stoichiometric) in DMF. Attempts to further improve the yield of the 1,4-addition product by using a greater excess of cyclohexenone were complicated by fluoride-catalyzed dimerization of the enone.[13] Interestingly, attempts to enhance the 1,4-addition reaction of the silyl-derived anions by using in situ trimethylsilyl chloride[14] resulted only in recovery of the unreacted silane.

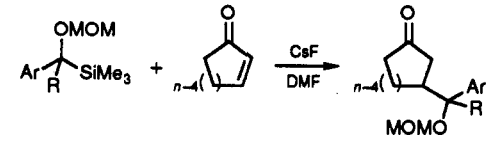
Explanation of the substantially different reactivity of α-alkoxybenzyl lithio anions[12] from that of the silyl-derived anions involves consideration of hard–soft acid–base concepts. The structure of benzyl anions in solution has been studied by a number of research groups, and a relationship of carbanion geometry and counterion has been established.[15] For example, (7-phenylnorbornyl)lithium has been found to exhibit pyramidal geometry in THF with a low barrier to inversion, while the potassium and cesium salts are planar, indicating a greater degree of charge delocalization into the aromatic ring.[16] The silyl-derived α-alkoxybenzylic anions in this study were only generated in a highly polar solvent with cesium as the counterion.[17] The resulting delocalized anion would be expected to be a soft nucleophile and therefore should be chemoselective for 1,4-addition.

Experimental evidence in support of the delocalization hypothesis has been provided by generation of 1 in enantioenriched form. Phenyl acylsilane 18 was reduced by bakers' yeast to provide optically active carbinol 19 in 73–90% ee. The yield of the asymmetric reduction was



poor (10–30%); nevertheless, sufficient material of defined % ee was available to carry out the 1,4-addition reaction.[18]

Table I. Conjugate Addition Reactions of Silyl-Derived Aryl α-Alkoxy Anions to Cyclic Enones



α-alkoxy silane				product	
Ar	R	no.	enone, n =	no.	yield (%)[a,b]
C_6H_5	H	1	5	8	68
			6	9	85
2,4-$(OCH_3)_2C_6H_3$	H	4	5	10	54
			6	11	68[c]
4-$(CH_3)C_6H_4$	H	5	5	12	67
			6	13	65
4-$(OCH_3)C_6H_4$	H	6	5	14	64
			6	15	65
C_6H_5	CH_3	7	5	16	60
			6	17	42

[a] Isolated yields of analytically pure material. Complete desilylation of the aryl α-alkoxysilane was observed in each reaction. [b] The products were isolated as a mixture of diastereomers in all cases. The diastereoselectivity for the products derived from cyclohexenone ranged from 55:45 to 61:39 (GC), while those from cyclopentenone were obtained only as 1:1 mixtures. [c] Approximately 6% of the unstable 1,2-addition product was also isolated.

The absolute configuration of enantioenriched 19 was assigned as *S* via analysis of the trimethylsilyl ^1H NMR signal chemical shift for the Mosher ester derivative.[19] (*S*)-19 of 73% ee was derivatized to (*S*)-1 as described above and employed in the CsF-catalyzed addition reaction to cyclohexenone. Methanolysis of the acetal protecting group of 9 and Mosher ester derivatization of the alcohol allowed for the determination of the % ee at the benzylic carbon. The four diastereomeric signals were resolved by ^{19}F NMR at 470 MHz to reveal a 1.5:1 diastereoselectivity for the reaction and an enantiomeric excess of only 11%.[20] Therefore, the 1,4-addition reaction had resulted in 85% racemization of the enriched chiral center. We believe that the observed racemization, coupled with the marked 1,4-regioselectivity, implies reaction predominantly by a delocalized, planar carbanion. These data do not, however, rule out rapid pyramidal inversion as a mechanism for racemization.[21]

In summary, we have reported a highly regioselective route for obtaining aryl-substituted cyclic homoaldol products by means of fluoride-induced desilylation of [(methoxymethoxy)benzyl]trimethylsilanes. In addition, our studies provide a rationale for the chemoselectivity observed for silyl-derived carbanions.

Experimental Section

General Procedures. Dimethylformamide (DMF) was doubly distilled from CaH_2 and stored over 4A molecular sieves. All reactions were carried out in flame-dried glassware under Ar. Organic reagents were purchased from Aldrich and distilled or recrystallized prior to use. Flash column chromatography was

(13) In a control experiment, CsF (0.12 g, 0.79 mmol) and cyclohexenone (0.15 mL, 1.57 mmol) were combined in dry DMF and stirred at ambient temperature for 48 h. 2-(1-Oxo-3-cyclohexanyl)]cyclohex-2-en-1-one (40%): ^1H NMR ($CDCl_3$) δ 1.50–2.50 (m, 14 H), 2.95 (m, 1 H), 6.50 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.6, 24.9, 25.9, 30.4, 37.4, 38.6, 41.1, 46.2, 141.6, 144.3, 198.3, 211.2. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.76; H, 8.39.

(14) (a) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6019–6023. (b) Horiguchi, H.; Matsuzawa, S.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 4025–4028. (c) Linderman, R. J.; McKenzie, J. R. *J. Organomet. Chem.* **1989**, *361*, 31–42.

(15) Stucky, G. D. *Adv. Chem. Ser.* **1974**, *130*, 56.

(16) Peoples, P. R.; Grutzner, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 4709–4715. For similar observations, see: Abatjoglou, A. G.; Eliel, E. L.; Kuyper, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 8262–8269. Keys, B. A.; Eliel, E. L.; Juaristi, E. *Isr. J. Chem.* **1989**, *29*, 171–186.

(17) The mechanistic aspects of nucleophilic displacement of silicon as a means of generating carbanions have been investigated. (a) Eaborn, C.; Walton, D. *J. Chem. Soc., Chem. Commun.* **1975**, 931–935. (b) Damraurer, R. *J. Am. Chem. Soc.* **1984**, *106*, 7633–7634. (c) Effenberger, F.; Spiegler, W. *Chem. Ber.* **1985**, *118*, 3872–3899.

(18) To our knowledge, bakers' yeast has not been employed in the reduction of acylsilanes. For a related microbial reduction of an acylsilane, see: Tacke, R. in *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: New York, 1985; pp 252–262. The main byproduct of the bakers' yeast reduction, benzyl alcohol, presumably arises by Brook rearrangement of the (α-hydroxybenzyl)trimethysilane product. See: Brook, A. G. *Acc. Chem. Res.* **1974**, 77–84.

(19) For a description of the absolute configuration assignment method, see ref 9. For an alternative route to optically active trialkylsilyl-substituted carbinols, see: Soderquist, J. A.; Anderson, C. L.; Miranda, E. I.; Rivera, I.; Kabalka, G. W. *Tetrahedron Lett.* **1990**, *31*, 4677–4680.

(20) For a related analysis of cyclic homoaldol products, see: Linderman, R. J.; Griedel, B. *J. Org. Chem.* **1990**, *55*, 5430–5432.

(21) For lead references to carbanion stereochemistry, see references cited in refs 19 and 20. Stereoselective alkylation of benzylic lithio anions, which are stabilized by intramolecular chelation, has been reported: Beak, P.; Hunter, J. E.; Jun, Y. M.; Wallin, A. P. *J. Am. Chem. Soc.* **1987**, *109*, 5403–5412. Chan, T. H.; Pellon, P. *J. Am. Chem. Soc.* **1989**, *111*, 8737–8738.

performed on silica gel 60 (230–400 mesh ASTM) obtained from American Scientific Products. Radial preparative thin layer chromatography was carried out on a Harrison Research chromatotron. Elemental analyses were carried out by Atlantic Microlab Inc., Norcross, GA.

(α-Alkoxybenzyl)trimethylsilanes. The α-alkoxyorganosilanes were obtained via the reported reverse Brook rearrangement methodology[9] with subsequent protection of the alcohols as the methoxy methyl ethers.[1c]

(Methoxymethoxy)phenyl(trimethylsilyl)methane (1) (62% yield): ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9 H), 3.89 (s, 3 H), 4.50 (s, 1 H), 4.56 (q, 2 H, J = 6 Hz), 7.22 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −4.08, 55.25, 72.60, 94.84, 125.7, 126.0, 127.9, 140.7; IR (neat) cm^{-1} 2940, 1450, 1240. Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98. Found: C, 64.19; H, 8.95.

(Methoxymethoxy)(2,4-dimethoxyphenyl)(trimethylsilyl)methane (4) (77% yield): ^{1}H NMR ($CDCl_3$) δ −0.08 (s, 9 H), 3.37 (s, 3 H), 3.74 (s, 3 H), 3.80 (s, 3 H), 4.52 (m, 2 H), 4.89 (s, 1 H), 6.48 (m, 2 H), 7.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −4.25, 54.38, 55.35, 71.96, 94.35, 109.11, 110.4, 118.3, 132.0, 146.8, 148.3; IR (neat) cm^{-1} 2960, 1510, 1245. Anal. Calcd for $C_{14}H_{24}O_4Si$: C, 59.12; H, 8.50. Found: C, 59.18, H, 8.54.

(Methoxymethoxy)(4-methylphenyl)(trimethylsilyl)methane (5) (76% yield): ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 9 H), 2.27 (s, 3 H), 3.33 (s, 3 H), 4.40 (s, 1 H), 4.50 (q, 2 H, J = 6 Hz), 7.02 (q, 4 H, J = 10 Hz); ^{13}C NMR ($CDCl_3$) δ −3.90, 21.10, 55.39, 72.62, 94.87, 126.18, 128.76, 135.26, 137.58; IR (neat) cm^{-1} 2960, 1510, 1255. Anal. Calcd for $C_{13}H_{22}O_2Si$: C, 65.50; H, 9.30. Found: C, 65.58, H, 9.35.

(Methoxymethoxy)(4-methoxyphenyl)(trimethylsilyl)methane (6) (77% yield): ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 3.36 (s, 3 H), 3.77 (s, 3 H), 4.42 (s, 1 H), 4.53 (dd, 2 H, J = 6.6 Hz, J = 12.3 Hz), 6.83 (d, 2 H, J = 8.8 Hz), 7.08 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ −4.13, 54.87, 55.09, 71.89, 94.38, 113.3, 127.2, 132.3, 157.7; IR (neat) cm^{-1} 2940, 1450, 1245. Anal. Calcd for $C_{13}H_{22}O_3Si$: C, 61.38; H, 8.72. Found: C, 61.43, H, 8.71.

(Methoxymethoxy)phenyl(trimethylsilyl)ethane (7) (30% yield): ^{1}H NMR ($CDCl_3$) δ −0.04 (s, 9 H), 1.71 (s, 3 H), 3.40 (s, 3 H), 4.67 (dd, 2 H, J = 13 Hz, J = 6 Hz), 7.22 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −4.51, 20.34, 55.29, 75.55, 92.39, 125.31, 125.69, 127.79, 145.01; IR (neat) cm^{-1} 2940, 1450, 1240. Anal. Calcd for $C_{13}H_{22}O_2Si$: C, 65.50; H, 9.30. Found: C, 65.60, H, 9.33.

General Procedure for Addition of Silyl-Derived Aryl α-Alkoxy Anions to Electrophiles. A 1.34-mmol sample of the [α-(methoxymethoxy)benzyl]trimethylsilane was added to a flame-dried 10-mL flask and placed under vacuum for 2 h at ambient temperature to ensure the removal of adventitious water. The desired electrophile (1.5 equiv, 2.0 mmol) and 5 mL of dry DMF were then added and the flask was purged with Ar. A 0.13-mmol (0.1 equiv) sample of anhydrous (vacuum, 50 °C, 2 h) CsF was then added and the reaction mixture was stirred for 12–24 h. Reaction progress was monitored by GC analysis of aliquots of the dark brown reaction mixture. Upon completion of the reaction (consumption of the silane), the reaction mixture was quenched by the addition of 3 mL of saturated aqueous NH_4Cl and further dilution with 30 mL of water. The mixture was extracted with ether (3 × 50 mL) and the combined extracts were washed with 20 mL of saturated aqueous NaCl, dried ($MgSO_4$), and evaporated under reduced pressure. The product was purified by flash column or radial chromatography using a 3–15% ethyl acetate/petroleum ether gradient.

Silyl-Derived Aryl α-Alkoxy Anion 1,2-Addition Products. 1-(Methoxymethoxy)-1-phenylpentan-2-ol (3): ^{1}H NMR ($CDCl_3$) δ 7.36 (m, 5 H), 4.56 (m, 2 H), 4.38 (d, 1 H, J = 9 Hz), 3.75 (t, 1 H, J = 7 Hz), 3.37 (s, 3 H), 2.80 (s, 1 H), 1.54–0.81 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 129.15, 128.99, 128.89, 128.63, 128.54, 95.03, 83.11, 75.29, 74.93, 56.48, 35.10, 19.43; IR (neat) cm^{-1} 3500, 3100, 2900, 1715, 1485, 1450, 1150, 1085. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.42; H, 9.05.

Silyl-Derived Aryl α-Alkoxy Anion Conjugate Addition Products. 3-[(Methoxymethoxy)phenylmethyl]cyclopentanone (8): ^{1}H NMR ($CDCl_3$) δ 1.50–2.61 (m, 8 H), 3.35 (s, 3 H), 4.50 (m, 3 H), 7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.89, 38.07, 42.17, 43.46, 55.55, 80.94, 93.74, 126.98, 127.72, 128.24, 139.68, 218.11; IR (neat) cm^{-1} 2900, 1740, 1400, 1150. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.67; H, 7.77.

3-[(Methoxymethoxy)phenylmethyl]cyclohexanone (9): ^{1}H NMR ($CDCl_3$) δ 1.16–2.31 (m, 8 H), 3.34 (s, 3 H), 3.44 (dd, 1 H, J = 7.5 and 3 Hz), 4.43 (d, 1 H, J = 6 Hz), 4.49 (d, 2 H, J = 3 Hz), 7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.50, 28.51, 42.01, 44.56, 45.76, 56.42, 81.52, 94.67, 128.05, 128.53, 128.98, 140.26, 212.09; IR (neat) cm^{-1} 2960, 1700, 1450, 1150. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.41; H, 8.18.

3-[(Methoxymethoxy)(2,4-dimethoxyphenyl)methyl]cyclopentanone (10): ^{1}H NMR ($CDCl_3$) δ 1.81–2.72 (m, 7 H), 3.22 (s, 3 H), 3.83 (s, 3 H), 3.90 (s, 3 H), 2.45 (m, 2 H), 4.97 (overlapping doublets, 1 H, J = 6 Hz), 6.53 (m, 2 H), 7.22 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.37, 38.26, 42.65, 55.19, 55.77, 73.69, 94.15, 98.06, 104.23, 120.71, 127.98, 158.28, 160.13, 219.54; IR (neat) cm^{-1} 2970, 1720, 1950, 1480, 1440, 1270. Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.07; H, 7.59.

3-[(Methoxymethoxy)(2,4-dimethoxyphenyl)methyl]cyclohexanone (11): ^{1}H NMR ($CDCl_3$) δ 1.21–2.50 (m, 9 H), 3.37 (s, 3 H), 3.75 (s, 3 H), 3.75 (s, 3 H) 4.48 (s, 2 H), 4.90 (d, 1 H, J = 6 Hz), 6.48 (m, 2 H), 7.16 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.91, 26.53, 41.39, 44.11, 55.25, 55.83, 74.57, 94.35, 104.17, 120.03, 128.17, 158.22, 160.13, 212.27; IR (neat) cm^{-1} 2970, 1710, 1950, 1480. Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.26; H, 7.89.

3-[(Methoxymethoxy)(3-methylphenyl)methyl]cyclopentanone (12): ^{1}H NMR ($CDCl_3$) δ 1.61–2.32 (m, 6 H), 2.35 (s, 3 H), 3.36 (s, 3 H), 3.40 (m, 1 H), 4.45 (dd, 1 H, J = 6, 3 Hz), 4.50 (m, 2 H), 7.17 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.07, 26.08, 38.26, 42.46, 43.63, 55.68, 81.04, 93.83, 127.14, 129.11, 136.74, 137.71, 218.12; IR (neat) cm^{-1} 2950, 1740, 1400, 1150. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.63; H, 8.14.

3-[(Methoxymethoxy)(3-methylphenyl)methyl]cyclohexanone (13): ^{1}H NMR ($CDCl_3$) δ 1.21–2.20 (m, 8 H), 2.40 (s, 3 H), 2.65 (d, 1 H, J = 12 Hz), 3.36 (s, 3 H), 3.47 (dd, 1 H, J = 6, 3 Hz), 4.48 (m, 3 H), 7.21 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.94, 24.69, 27.63, 41.23, 43.95, 44.95, 55.91, 80.62, 93.80, 128.44, 128.89, 136.35, 137.38, 211.10; IR (neat) cm^{-1} 2950, 1710, 1150, 1020. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.03; H, 8.51.

3-[(Methoxymethoxy)(3-methoxyphenyl)methyl]cyclopentanone (14): ^{1}H NMR ($CDCl_3$) δ 1.22–2.21 (m, 8 H), 2.68 (d, 1 H, J = 12 Hz), 3.37 (s, 3 H), 3.81 (s, 3 H), 4.48 (m, 3 H), 6.81–7.22 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 26.02, 38.19, 42.55, 43.62, 55.13, 55.61, 80.78, 93.64, 113.77, 128.33, 131.73, 159.29, 218.84; IR (neat) cm^{-1} 2900, 1740, 1610, 1510. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.16; H, 7.67.

3-[(Methoxymethoxy)(3-methoxyphenyl)methyl]cyclohexanone (15): ^{1}H NMR ($CDCl_3$) δ 1.20–2.60 (m, 8 H), 2.68 (d, 1 H, J = 12 Hz), 3.37 (s, 3 H), 3.81 (s, 3 H), 4.48 (m, 3 H), 6.81–7.22 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 24.79, 27.70, 41.36, 44.21, 45.11, 55.19, 55.74, 80.49, 93.83, 113.67, 128.57, 131.44, 159.23, 220.12; IR (neat) cm^{-1} 2900, 1740, 1610, 1510. Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 67.40; H, 8.36 (satisfactory combustion analysis not obtained).

3-[1-(Methoxymethoxy)-1-phenyl-1-ethyl]cyclopentanone (16): ^{1}H NMR ($CDCl_3$) δ 0.81–2.21 (m, 10 H), 3.60 (s, 3 H), 4.60 (m, 2 H), 7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.98, 23.82, 38.65, 40.20, 49.96, 55.58, 81.03, 92.25, 125.95, 127.05, 128.15, 145.01, 219.13; IR (neat) cm^{-1} 2900, 1740, 1100. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.62; H, 8.17.

3-[1-(Methoxymethoxy)-1-phenyl-1-ethyl]cyclohexanone (17): ^{1}H NMR ($CDCl_3$) δ 1.40–2.33 (m, 12 H), 3.55 (s, 3 H), 4.51 (m, 2 H), 7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 20.56, 24.85, 25.82, 41.20, 43.04, 50.70, 55.54, 81.49, 92.18, 126.40, 127.11, 128.08, 143.91, 211.08, IR (neat) cm^{-1} 2900, 1710, 1450. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.16; H, 8.51.

(S)-α-(Trimethylsilyl)benzenemethanol (19). A suspension of 260 g of bakers' yeast in 200 mL of water and 2.92 g (0.016 mol) of phenyl trimethylsilyl ketone was stirred for 12 h at 32 °C. The crude product was isolated by centrifuging the suspension and decanting. The supernatant was then extracted with ethyl acetate (10 × 100 mL), and the combined ethyl acetate fractions were filtered through Celite, washed with saturated aqueous NaCl, and dried ($MgSO_4$). The solvent was removed under reduced pressure to yield 4.2 g of a viscous yellow oil. The crude product contained a large quantity of high molecular weight impurities. Successive flash chromatography using a 0–10% ethyl acetate/petroleum ether gradient purified this material to homogeneity (330 mg, 10% yield).

R Mosher Ester of (*S*)-(trimethylsilyl)phenylmethanol: ^1H NMR ($CDCl_3$) major isomer 0.036, minor isomer 0.026 (s, 9 H), 3.52 (s, 3 H), 5.81 (s, 1 H), 7.00–7.59 (m, 5 H); ^{19}F NMR (470 MHz) ($CDCl_3$) major isomer −71.65, minor isomer −71.32.

3-(Hydroxyphenylmethyl)cyclohexanone. A solution of **9** (31 mg, 0.12 mmol) in 10 mL of a 5:1 methanol/water solution containing 4 drops of concd. HCl was refluxed for 6 h and neutralized via the addition of sodium bicarbonate solution (to pH 8). The crude reaction mixture was concentrated under reduced pressure and the residue was extracted with ether (3 × 50 mL). The combined ether fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified via radial chromatography, using a 10–25% ethyl acetate/petroleum ether gradient.

R Mosher ester of 3-(Hydroxyphenylmethyl)cyclohexanone: ^1H NMR ($CDCl_3$) δ 1.11–2.61 (m, 17 H), 3.44–3.52 (m, 4 H), 5.67 (m, 1 H), 7.1–7.8 (m, 10 H); ^{19}F NMR (470 MHz) ($CDCl_3$) δ −71.17, −71.25, −71.52, −71.60.

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Benzofuroxan Photochemistry: Direct Observation of 1,2-Dinitrosobenzene by Steady-State Spectroscopy. A New Photochromic Reaction

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The synthesis of a 1,2-dinitrosoarene was first claimed in 1886. However it was clear from its physical properties that 1,2-dinitrosobenzene (II), and related arenes, were better represented by the benzofuroxan structure (I), which was first proposed in 1912.[1] Even to date there is still confusion between benzofuroxans and 1,2-dinitrosoarenes. For example, benzotrifuroxan is incorrectly depicted as hexanitrosobenzene.[2] Benzofuroxans substituted in the 5- and 6-positions are known and can thermally interconvert, presumably through the dinitrosobenzene intermediate, while the 4-substituted compound does not usually interconvert with the thermodynamically less stable 7-isomer. A number of studies on the photochemistry and thermochemistry of benzofuroxans have resulted in the proposal of 1,2-dinitrosoarenes as intermediates. Low-temperature ^1H NMR studies on the thermal isomerization of unsymmetrical benzofuroxans gave an activation energy ΔG^* for tautomerisation of about 15 kcal mol^{-1},[3] and anisyl azide has been successfully employed as a trap for 1,2-dinitrosobenzene from thermolysis of benzofuroxan at 155 °C.[4] A more recent report has found persistent radicals from benzofuroxan photolysis.[5] However, in all of the above studies there was no direct observation of the 1,2-dinitrosobenzene intermediate. Our recent studies on the photochemistry of matrix-isolated nitrosobenzene, which efficiently ejects nitric oxide and generates phenyl radical,

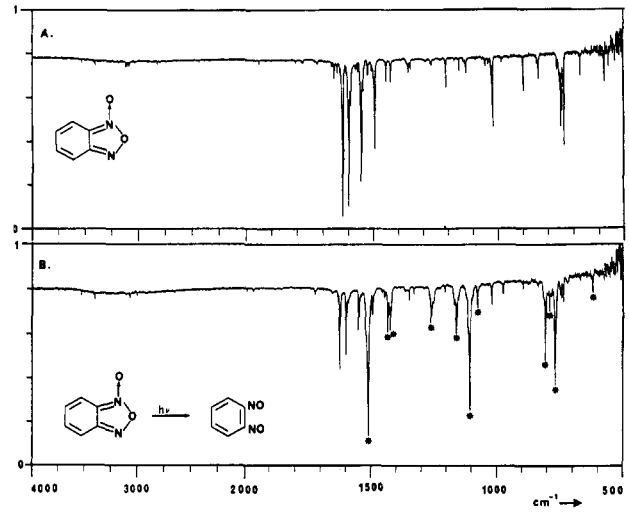
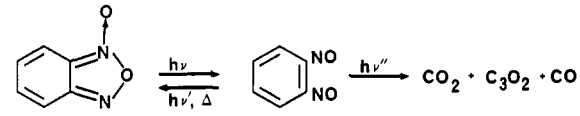


Figure 1. IR spectra recorded from photolysis of benzofuroxan in Xe at 14 K: (A) benzofuroxan; (B) after 2 h photolysis at 366 nm. (Bands in spectrum B that are marked with an asterisk appear after photolysis, disappear after warming the matrix to 70 K, and are assigned to 1,2-dinitrosobenzene.)

Scheme I. Products from Photolysis of Benzofuroxan at 14 K



I II

prompted an examination of the photochemistry of benzofuroxan, which may undergo an analogous reaction via the 1,2-dinitrosobenzene intermediate and be a new precursor for benzyne.[6] We report here the photochemistry of benzofuroxan in inert matrices and as thin films at cryogenic temperatures, the direct observation of 1,2-dinitrosobenzene, and the photochromic behavior of this system at 12–80 K.

Benzofuroxan was deposited from a side arm, at ambient temperature, with a constant stream of inert gas, onto a CsI window at 32 K (Ar) or 60 K (Xe) for about 20 min. The sample was cooled to 14 K at 1 K min^{-1} and gave a clear matrix. The infrared spectrum in xenon (Figure 1) shows principal bands at 1622, 1599, 1547, and 1492 cm^{-1}, typical for the furoxan ring, along with less intense bands at lower frequencies. Irradiation of this sample at λ = 366 nm for 0.5 to 2.0 h caused all of these bands to decrease and new bands centered at 1515, 1102, 805, and 795 cm^{-1} to appear. Warming the matrix to 80 K resulted in a minor loss of sample and caused the 1515 cm^{-1} band and related bands to disappear and the benzofuroxan bands to reappear. In separate experiments the 1515 cm^{-1} species was generated as above and photolysis of these samples with λ = 254 or 313 nm at 14 K resulted in almost complete reversion to benzofuroxan. Similar results were obtained in argon matrices except that the thermal reversion could not be completed due to sample loss above temperatures of 40 K. Thus this photochemically and thermally reversible process represents a new photochromic reaction. It is well known that monomeric aromatic *C*-nitroso compounds have a characteristic strong N=O stretching frequency at 1490–1520 cm^{-1} and bands at 1100 and 800 ± 50 cm^{-1} associated with C–N vibration.[7] The facts that

(1) For a review of benzofuroxan chemistry, see: Boulton, A. J.; Ghosh, P. B. *Advances in Heterocyclic Chemistry*, Vol. 10; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1969; p 1.
(2) Aldrich Chemical Catalog, 1990–1991, p 702.
(3) Mallory, F. B.; Mannatt, S. L.; Wood, C. S. *J. Am. Chem. Soc.* **1965**, *87*, 5433.
(4) Bulacinski, A. B.; Scriven, E. F. V.; Suschitzky, H. *Tetrahedron Lett.* **1975**, 3577.
(5) Lin, S.-K. *J. Photochem. Photobiol. A. Chem.* **1988**, *45*, 243.
(6) Hatton, W. G.; Hacker, N. P.; Kasai, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 227.
(7) (a) Bradley, G. M.; Strauss, H. L. *J. Phys. Chem.* **1975**, *79*, 1953. (b) Gowenlock, B. G.; Luttke, W. *Q. Rev.* **1958**, *12*, 321.

0022-3263/91/1956-5216$02.50/0