spectrometer. All reactions were run under a nitrogen atmosphere. All ethereal solvents were freshly distilled from sodium benzophenone ketyl. Flash chromatography was performed with silica gel from E. Merck (Kieselgel 60, 200–400 mesh). Diols **4a**, **5a**, **6a**, **7a**, **8a**, **9a**, and **12a** were all purchased from Aldrich Chemical Co. and used without further purification. Diols **10a** and **11a** were prepared according to the literature precedent.[12]

General Procedures Used for the Preparation of Siloxy Alcohols. Procedure A. Sodium hydride (0.27 g, 5.6 mmol) was suspended in THF (11 mL) after being washed with hexane. The diol (5.6 mmol) was added to this mixture at room temperature and stirred for 45 min at which time a large amount of an opaque white precipitate had formed. The *tert*-butyldimethylsilyl chloride was then added, and vigorous stirring was continued for 45 min. The mixture was poured into ether (100 mL), washed with 10% aqueous K_2CO_3 (30 mL) and brine (30 mL), dried (Na_2SO_4), and concentrated in vacuo. The resulting oil was purified by flash chromatography using ethyl acetate/hexane mixtures as eluent (see spectroscopic data for the exact ratio used in each case).

Procedure B. The same general experimental is followed as in procedure A except that the diol and NaH were heated together at 55 °C for 18 h prior to the addition of *tert*-butyldimethylsilyl chloride at room temperature. The silylation of diol **9a** was carried out for 2 h at room temperature, while diol **12a** was silylated for 19 h at room temperature. Workup and purification was performed as outlined in procedure A.

Procedure C. To the diol (4.81 mmol) in methylene chloride (10 mL) were added sequentially triethylamine (0.7 g, 6.9 mmol), 4-(dimethylamino)pyridine (DMAP, 100 mg), and *tert*-butyldimethylsilyl chloride (4.81 mmol) at room temperature. The mixture was allowed to stir for 4 h and then poured into ether (100 mL), washed with 10% aqueous $NaHSO_4$ (2 × 30 mL) and 10% aqueous K_2CO_3 (30 mL), dried (Na_2SO_4), and concentrated in vacuo. Purification was performed as outlined in procedure A.

Data for the Monosilylated Diols 4b–12b. 4b (30% ethyl acetate/hexane): IR (CCl_4) 3610 (sh), 1390, 1360 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.62 (4 H, m), 2.2 (1 H, br s), 0.82 (9 H, s), 0.06 (6 H, s); MS, *m/e* (relative intensity) 119 (10), 75 (100); calcd for $C_4H_{11}O_2Si$ (M – *tert*-butyl) 119.0528, found 119.0516; CIMS, 177 (M + 1).

5b (30% ethyl acetate/hexane): IR (CCl_4) 3615 (sh), 3550 (br), 1392, 1370 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.80 (2 H, t, J = 6.0 Hz), 3.70 (2 H, br t, J = 6.0 Hz), 2.71 (1 H, br s), 1.78 (2 H, pentet, J = 6.0 Hz), 0.84 (9 H, s), 0.06 (6 H, s); MS, *m/e* (relative intensity) 133 (20), 105 (45), 75 (100); calcd for $C_5H_{13}O_2Si$ (M – *tert*-butyl) 133.0685, found 133.0676; CIMS, 191 (M + 1).

6b (40% ethyl acetate/hexane): IR (CCl_4) 3620 (sh), 3500 (br), 1392, 1365 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.80–3.60 (4 H, br m), 2.50 (1 H, br s), 1.78–1.52 (4 H, br m), 0.81 (9 H, s), 0.04 (6 H, s); MS, *m/e* (relative intensity) 147 (8), 105 (47), 75 (100); calcd for $C_6H_{15}O_2Si$ (M – *tert*-butyl) 147.0841, found 147.0835; CIMS, 205 (M + 1).

7b (30% ethyl acetate/hexane): IR (CCl_4) 3640 (sh), 3480 (br), 1390, 1360 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.70–3.52 (4 H, m), 2.61 (1 H, br s), 1.75–1.39 (6 H, m) 0.90 (9 H, s), 0.05 (6 H, s); MS, *m/e* (relative intensity) 161 (7), 105 (50), 75 (100), 69 (77); calcd for $C_7H_{17}O_2Si$ (M – *tert*-butyl) 161.0997, found 161.0952; CIMS, 219 (M + 1).

8b (30% ethyl acetate/hexane): IR (CCl_4) 3615 (sh), 1390, 1360 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.75–3.42 (4 H, br m), 2.25 (1 H, br s), 1.62–1.41 (8 H, br s), 0.80 (9 H, s), 0.04 (6 H, s); MS, *m/e* (relative intensity) 175 (5), 105 (25), 83 (50), 75 (100); calcd for $C_8H_{19}O_2Si$ (M – *tert*-butyl) 175.1154, found 175.1161; CIMS, 233 (M + 1).

9b (25% ethyl acetate/hexane): IR (CCl_4) 3640 (sh), 1390, 1360 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.75–3.55 (4 H, m), 2.10 (1 H, s), 1.60–1.45 (16 H, br s), 0.95 (9 H, s), 0.06 (6 H, s); MS, *m/e* (relative intensity) 231 (8), 105 (35), 75 (100); calcd for $C_{12}H_{27}O_2Si$ (M – *tert*-butyl) 231.1780, found 231.1774; CIMS, 289 (M + 1).

10b (30% ethyl acetate/hexane): IR (CCl_4) 3640 (sh) 3480 (br), 1390, 1360 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.21 (1 H, br d, J = 2.6 Hz), 4.17 (1 H, br d, J = 3.0 Hz), 3.68 (1 H, A of an ABX, dd, J = 10.4, 9.0 Hz), 3.66 (1 H, m), 3.58 (1 H, B of an ABX, dd, J = 10.4, 5.6 Hz), 3.49 (2 H, m, includes OH), 2.07 (2 H, m), 1.63 (2 H, m), 1.42 (2 H, m), 0.81 (9 H, s), 0.02 (6 H, s); MS, *m/e* (relative intensity) 215 (4), 105 (40), 75 (100); calcd for $C_{10}H_{19}O_3Si$ (M – *tert*-butyl) 215.1103, found 215.1093; CIMS, 273 (M + 1).

11b (25% ethyl acetate/hexane), major isomer[15] (elutes first): IR (CCl_4) 3640, 3480, 1390, 1382, 1361 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (2 H, dd, J = 7.2, 1.5 Hz), 7.19–7.07 (3 H, m), 4.05 (1 H, d, J = 5.6 Hz), 3.77 (1 H, t, J = 10.0 Hz), 3.66–3.49 (4 H, m), 3.12 (1 H, dd, J = 11.1, 5.3 Hz), 2.82 (1 H, td, J = 9.0, 4.2 Hz), 2.41 (1 H, td, J = 11.1, 5.6 Hz), 2.23 (1 H, td, J = 9.0, 5.5 Hz), 1.39 (1 H, dd, J = 11.9, 5.3 Hz), 1.12 (3 H, s), 0.80 (9 H, s) 0.01 (6 H, s); MS, *m/e* (relative intensity) 337 (7), 262 (44), 231 (92), 139 (100), 105 (49), 75 (70); calcd for $C_7H_{25}O_3SiS$ (M – *tert*-butyl) 336.9952, found 336.9941.

11b, minor isomer[15] (elutes second): IR (CCl_4) 3640 (sh), 3475 (br), 1390, 1382, 1361 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (2 H, dd, J = 7.1, 1.5 Hz), 7.30–7.21 (3 H, m), 4.21 (1 H, d, J = 5.5 Hz), 3.87–3.57 (5 H, m), 3.22 (1 H, dd, J = 11.1, 5.2 Hz), 2.88 (1 H, td, J = 9.1, 5.2 Hz), 2.50 (1 H, td, J = 11.8, 5.5 Hz), 2.33 (1 H, td, J = 8.7, 4.6 Hz), 1.50 (1 H, dd, J = 12.5, 5.2 Hz), 1.18 (3 H, s), 0.92 (9 H, s), 0.13 (3 H, s), 0.11 (3 H, s); MS, *m/e* (relative intensity) 376 (12), 337 (4), 253 (61), 231 (66), 75 (100); calcd for $C_{17}H_{25}O_3SiS$ (M – *tert*-butyl) 336.9952, found 336.9939.

12b (cis/trans isomers) (25% ethyl acetate/hexane): 3695 (sh), 3620 (sh), 1380, 1368, 1355 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 3.9–3.4 (2 H, br m), 2.76 (1 H, br s), 1.9–1.4 (8 H, m), 0.90 (9 H, s), 0.02 (6 H, s); MS, *m/e* (relative intensity) 173 (4), 81 (100), 75 (58); calcd for 173.1001, found 173.1021; CIMS, 231 (M + 1).

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Registry No. **4a**, 107-21-1; **4b**, 102229-10-7; **5a**, 504-63-2; **5b**, 73842-99-6; **6a**, 110-63-4; **6b**, 87184-99-4; **7a**, 111-29-5; **7b**, 83067-20-3; **7c**, 77572-86-2; **8a**, 629-11-8; **8b**, 103202-59-1; **9a**, 112-47-0; **9b**, 90934-00-2; **9c**, 103202-64-8; **10a**, 55423-53-5; **10b**, 103202-60-4; **11a**, 103202-58-0; **11b** (major isomer), 103202-61-5; **11b** (minor isomer), 103202-65-9; *cis*-**12a**, 931-71-5; *trans*-**12a**, 6995-79-5; *cis*-**12b**, 103202-62-6; *trans*-**12b**, 103202-63-7; *cis*-**12c**, 103202-66-0; *trans*-**12c**, 103202-67-1; *tert*-butyldimethylsilyl chloride, 18162-48-6.

Facile Anhydride Synthesis Using Trichlorotrifluoroacetone Hydrate

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Several successful methods are available for synthesizing carboxylic acid anhydrides,[1-5] but each of these methods has one or more of the following shortcomings: unstable or special reagents need to be prepared, extra steps are needed to remove side products, or yields are low for some anhydrides.

Here a simple reaction at room temperature forming volatile side products is presented for synthesizing carboxylic acid anhydrides. The key reagent, 1,1,1-trichloro-3,3,3-trifluoroacetone,[6] is commercially available,

(1) Fujisawa, T.; Tajima, K.; Sato, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3529.
(2) Keshavamurthy, K.; Vankar, Y. D.; Dhar, D. N. *Synthesis* **1982**, 506.
(3) Mestres, R.; Palomo, *Synthesis* **1981**, 218.
(4) Cabre-Castellvi, J.; Palomo-Coll, A.; Palomo-Coll, A. L. *Synthesis* **1981**, 616 and references therein.
(5) Kita, Y.; Akai, S.; Yoshigi, M.; Nakajima, H.; Yasuda, H.; Tamuva, Y. *Tetrahedron Lett.* **1984**, *25*, 6027.

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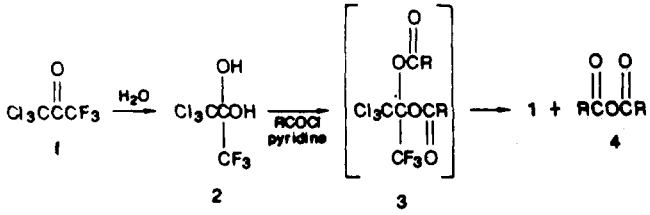
Table I. Preparation of Acid Anhydrides

product [RC(=O)-OC(=O)R],[a] R	yield, %	mp or bp (torr), °C this expt	mp or bp (torr), °C lit.	crystallization solvent
C_6H_5	97	41	42–43[9]	hexane
C_6F_5	97	67	69[10]	hexane
p-ClC_6H_4	89	196	192–193[3,11]	benzene
$C_6H_4CH{=}CH$	91	138	138[1,9]	hexane–acetone
2-naphthyl	89	138	133–134[12]	hexane–acetone
$CH_2{=}C(CH_3)$	93	197–205 (760)	89 (5)[4]	
p-$HO_2CC_6H_5$[b]	80	>360		
succinic	85	118	119–120[9]	chloroform
pivalic	0			

[a] Known compounds were confirmed by MS and also by comparing their IR's with those found in the literature. [b] New Compound: IR (KBr) 3430 (br, OH), 1785 and 1730 (C=O, anhydride), 1210 cm^{-1}; MS, m/z 314 (M^+), 165 ($HOOCC_6H_4COO$), 149 ($C(=O)C_6H_4COOH$), and 104 ($C(=O)C_6H_4$). Anal. Calcd for $C_{16}H_{10}O_7$: C, 61.15; H, 3.21. Found: C, 61.21; H, 3.18. This compound was a white solid and was insoluble in all solvents tested.

the reaction time is short, and several anhydrides are obtained in high yields as summarized in Table I.

The strategy for this reaction is derived from the work of Newallis and Lombardo[7] who prepared and pyrolyzed hemiketal esters from *sym*-dichlorotetrafluoroacetone. Thus we postulate here that trichlorotrifluoroacetone (1) reacts with water to form hydrate[8] 2, which reacts in turn with a carboxylic acid chloride, giving diacyl intermediate 3, which collapses to the desired anhydride 4.



Attempts to isolate 3 by performing the reaction at 0 °C (for R = C_6H_5) were unsuccessful, but the desired product was obtained as usual. Reaction of pivalyl chloride and trichlorotrifluoroacetone hydrate gave no product; instead starting material and pivalic acid were recovered.

Experimental Section

Infrared spectra were taken on Perkin-Elmer Model X99 spectrophotometer and the absorptions are reported in wave numbers (cm^{-1}). Mass spectra were obtained on a Nuclide 12-90-G instrument. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analysis was performed by MultiChem Laboratories. 1,1,1-Trichloro-3,3,3-trifluoroacetone was obtained from Fluka Chemical Co. Toluene, pyridine, and ethyl acetate were obtained from Aldrich Chemical Co.

General Method. Trichlorotrifluoroacetone (10 mmol) and water (10 mmol) were stirred at room temperature for 5 min. Toluene (8 mL) was added followed by a carboxylic acid chloride (20 mmol). Pyridine (20 mmol) was added over 5 min (exothermic reaction). After the reaction mixture was stirred at room temperature under N_2 for 30 min, EtOAc (30 mL) and 5% aqueous HCl (10 mL) were added. The separated organic layer was washed once with 20 mL of water and dried over anhydrous Na_2SO_4. Evaporation of the solvent afforded nearly a pure product, which could be purified by the usual techniques.

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Registry No. 1, 758-42-9; 4 (R = C_6H_5), 93-97-0; 4 (R = C_6F_5), 15989-99-8; 4 (R = p-ClC_6H_4), 790-41-0; 4 (R = $C_6H_4CH{=}CH$), 538-56-7; 4 (R = 2-napthyl), 20176-11-8; 4 (R = methacryl), 760-93-0; 4 (R = p-$HO_2CC_6H_4$), 18431-45-3; 4 (R = succtine), 108-30-5; 4 (R = pivalic), 1538-75-6; C_6H_5COCl, 100-44-7; C_6F_5COCl, 2251-50-5; p-ClC_6H_4COCl, 122-01-0; $C_6H_4CH{=}CHCOCl$, 102-92-1; $CH_2 = C(CH_3)COCl$, 920-46-7; p-$HO_2CC_6H_4COCl$, 100-20-9; 2-napthoyl chloride, 2243-83-6; succinoyl chloride, 543-20-4; pivaloyl chloride, 3282-30-2.

(6) Other applications of trichlorotrifluoroacetone are its good solvent properties for polymers (Middleton, W. J.; Lindsey, R. V. *J. Am. Chem. Soc.* **1964**, *86*, 4948) and the trifluoroacetylation of amines and amino acids (Panetta, C. A. *Org. Synth.* **1977**, *56*, 122).

(7) Newallis, P.; Lombardo, P. *J. Org. Chem.* **1965**, *30*, 3834.

(8) Halogenated acetones readily form hydrates such as 2: Miller, C. B.; Woolf, C. U.S. Patent 2 870 211, 1959.

(9) *Handbook of Chemistry and Physics*, 64th ed.; CRC: Cleveland, OH, 1983.

(10) Schmeisser, M.; Weidenbruch, M. *Chem. Ber.* **1967**, *100*, 2306.

(11) Allen, C. F.; Kibler, C. J.; McLachlin, D. M.; Wilson, C. V. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 28.

(12) *Handbook of Data on Organic Compounds*; CRC: Boca Raton, FL, 1985.

Calcium and Lithium Reductions of Epoxides in Ethylenediamine. A Comparison Study

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Recently we reported[1,2] that calcium dissolved in ethylenediamine (or in mixtures containing ethylenediamine) is very effective in reducing aromatic ring systems to monoalkenes. In this respect, it resembles the chemistry of lithium dissolved in low molecular weight amines.[3] Furthermore, in the presence of a proton source like *tert*-butyl alcohol, calcium reductions (like lithium) can be stopped at the dihydro stage to give Birch-type products.[4] Thus far we have not reported reduction of functional groups with the calcium–ethylenediamine reagent. Herein we report that the calcium reagent is capable of reducing epoxides to alcohols.

Elegant work by Brown[5] and co-workers has shown that lithium in ethylenediamine can effect facile reductions of labile epoxides. It is a particularly useful procedure in those cases where lithium aluminum hydride reductions are slow or result in rearrangements. In Table I are compared the results obtained with both calcium and lithium reductions of six epoxides. The lithium reductions were carried out exactly as those previously described[5a] except that the amount of epoxide used was somewhat larger. The yields reported in all cased are based on material actually in hand after workup.

The 9,10-epoxyoctahydronaphthalene was prepared from $\Delta^{9,10}$-octalin[6] of 96% purity. Likewise, the 8,9-ep-

(1) Benkeser, R. A.; Kang, J. *J. Org. Chem.* **1979**, *44*, 3737.

(2) (a) Benkeser, R. A.; Belmonte, F. G.; Kang, J. *J. Org. Chem.* **1983**, *48*, 2796. (b) Benkeser, R. A.; Belmonte, F. G.; Yang, M. *Synth. Commun.* **1983**, *13*, 1103.

(3) Benkeser, R. A.; Robinson, R. E.; Sauve, D. M.; Thomas, O. H. *J. Am. Chem. Soc.* **1955**, *77*, 3230.

(4) Benkeser, R. A.; Laugal, J. A.; Rappa, A. *Tetrahedron Lett.* **1984**, *25*, 2089.

(5) (a) Brown, H. C.; Ikegami, S.; Kawakami, J. H. *J. Org. Chem.* **1970**, *35*, 3243. (b) Brown, H. C.; Ikegami, S.; Kawakami, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 6914.

0022-3263/86/1951-3391$01.50/0