ether (5 mL). After the addition was complete, the reaction mixture was stirred at room temperature for 1 h and then heated at reflux for 3 h. The excess LAH was decomposed by sequential addition of water (0.1 mL), a 15% NaOH solution (0.1 mL), and water (0.2 mL). After filtration, the ethereal layer was dried over anhydrous sodium sulfate and concentrated to a light, yellow oil. The oil was distilled to provide **16** (120 mg, 90%): bp 110–120 °C (0.3 mmHg); $[\alpha]^{25}_D$ −7.61° (*c* 6.51, EtOH). The ^{1}H NMR spectrum was identical with that of **3a**.

(2*S*,3*S*)-3,4-Epoxy-1,2-*O*-isopropylidenebutane-1,2-diol (17). This compound was prepared in 89% yield from **15**[2] by using the same procedure described for **8**: $[\alpha]_D$ −3.23° (*c* 4.025, EtOH); ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 3, CH_3), 1.41 (s, 3, CH_3), 2.56–2.80 (m, 2), 2.86–3.03 (m, 1), 3.72–4.1 (m, 3). This compound was identical with an authentic sample prepared earlier (see ref 2).

(2*S*,3*S*)-1,3-*O*-Dibenzylbutane-1,2,3-triol (18). The procedure followed was identical with that described for the preparation of **13** by method A: $[\alpha]_D$ +22.6° (*c* 2.55, EtOH); ^{1}H NMR ($CDCl_3$) δ 1.17 (d, 3, *J* = 6 Hz), (d, 1, *J* = 3 Hz), 3.4–3.8 (m, 4), 4.5 (q_{AB}, 2, *J* = 12 Hz), 4.5 (s, 2), 7.25 (s, 10).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.75. Found: C, 75.38; H, 7.70.

(2*S*,3*S*)-1,2-*O*-Isopropylidenebutane-1,2,3-triol (19). This compound was prepared in 91% yield by the same procedure described for **9** and was identical with an authentic sample prepared earlier (see ref 2): $[\alpha]_D$ −11.31 (*c* 3.06, EtOH). The ^{1}H NMR spectrum of **19** was identical with that of **20**.

(2*R*,3*R*)-1,2-*O*-Isopropylidenebutane-1,2,3-triol (20). Compound **9** (14.6 g, 0.1 mol), TPP (39.74 g, 0.15 mol), and benzoic acid were dissolved in dry benzene (200 mL). A solution of DIAD (31.3 g, 0.15 mol) in dry benzene (50 mL) was added dropwise at room temperature. After 20 h, the precipitate was filtered off, and the residue obtained after evaporation was mixed with silica gel (75 g, 60–230 mesh). This mixture was placed on top of a silica gel column and eluted with hexane followed by hexane–ethyl acetate (95:5, v/v) to furnish a crude mixture (22.2 g) of the benzoate and benzoic acid.[11] This mixture was dissolved in methanol (125 mL) and sodium hydroxide (0.144 mol) in water (25 mL) and was stirred at room temperature overnight. Evaporation of the methanol followed by extraction of the residue with ether provided **20** (10.75 g, 74%): $[\alpha]_D$ +11.35° (*c* 2.03, EtOH); ^{1}H NMR ($CDCl_3$) δ 1.13 (d, 3, *J* = 6 Hz), 1.37 (s, 3), 1.42 (s, 3), 2.75 (br s, 1), 3.45–4.2 (m, 4).

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Registry No. **1a**, 50271-42-6; **1b**, 114184-95-1; **2a**, 114184-94-0; **2b**, 114184-96-2; **3a**, 114184-97-3; **3b**, 114184-98-4; **4a**, 114184-99-5; **4b**, 114185-01-2; **5**, 114185-00-1; **6**, 114185-02-3; **7**, 101703-83-7; **8**, 74134-78-4; **9**, 74183-61-2; **10a**, 87604-49-7; **10b**, 114185-03-4; **11**, 87604-55-5; **12**, 114185-04-5; **13**, 114185-05-6; **14**, 114185-07-8; **15**, 91274-05-4; **16**, 114185-09-0; **17**, 93367-10-3; **18**, 114185-10-3; **20**, 74183-62-3; **20** (3-*O*-benzoyl derivative), 114185-11-4; D-isoascorbic acid, 89-65-6; (2*R*,3*S*)-2,3-di-*O*-benzylbutane-1,2,3-triol, 114185-06-7; ethyl (2*S*,3*S*)-2-*O*-benzoyl-3,4-*O*-isopropylidene-2,3,4-trihydroxybutanoate, 114185-08-9.

(11) A small amount of this mixture was purified by silica gel chromatography to give (2*R*,3*R*)-3-*O*-benzoyl-1,2-*O*-isopropylidenebutane-1,2,3-triol: $[\alpha]^{25}_D$ −8.95° (*c* 2.95, EtOH); ^{1}H NMR ($CDCl_3$) δ 1.33 (d, 3, *J* = 6 Hz), 1.37 (s, 3), 1.45 (s, 3), 3.65–4.43 (m, 3), 5.05–5.36 (m, 1), 7.23–7.68 (m, 3), 7.92–8.22 (m, 2). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.19; H, 7.25. Found: C, 67.01; H, 7.16.

(12) Atchely, R. W.; Tolbert, B. M. *Org. Prep. Proc. Int.* **1971**, *3*, 299.

Symmetrical Alkoxysilyl Ethers. A New Class of Alcohol-Protecting Groups. Preparation of *tert*-Butoxydiphenylsilyl Ethers

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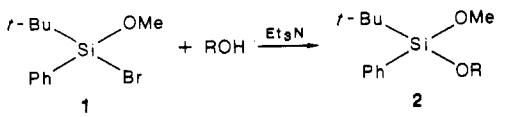
The preparation and evaluation of a new class of alcohol-protecting groups, the alkoxydiphenylsilyl ethers, are described. In particular, *tert*-butoxydiphenylsilyl ethers, which can be formed from primary, secondary, or tertiary alcohols and *tert*-butoxydiphenylsilyl chloride, offer the useful synthetic properties of acid stability and high fluoride reactivity. Opportunities for selective silyl group cleavage are highlighted.

Introduction

Silicon-based methodology for the protection of alcohols has made a major contribution in organic synthesis.[1] The ability to modulate selectivity and reactivity by varying the steric and electronic requirements of the substituents on silicon has been demonstrated by such reagents as *tert*-butyldimethylsilyl chloride[2] and *tert*-butyldiphenylsilyl chloride.[3] This latter compound, for example, can discriminate a primary from a secondary or tertiary alcohol; such discrimination is a consequence of the more demanding steric environment of the *tert*-butyldiphenylsilyl substituent. A consequence of this fact is that, once formed, such silyl ethers are correspondingly more resistant to hydrolysis or fluorolysis.

Scheme I. Preparation of *tert*-Butylmethoxyphenylsilyl Ethers



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With the intent of breaking this steric nexus, we have shown that silyl ethers substituted with a further electron-withdrawing substituent, like an oxygen atom, are readily attacked by fluoride ion. Hence, we prepared the

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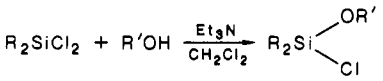
(1) Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley-Interscience: New York, 1981.
(2) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
(3) Hanessian, S.; Lavallée, P. *Can. J. Chem.* **1975**, *53*, 2975.

0022-3263/88/1953-2602$01.50/0

Table I. Preparation of Alkoxy- and (Aryloxy)silyl Chlorides[a]



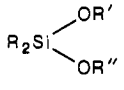
compd	R	R′	yield, %[b]
5	Ph	Me	80
6	Ph	*i*-Pr	82
7	Ph	2,6-$Me_2C_6H_3$	92
8	Ph	*t*-Bu	81[c]
9	Me	2,6-*t*-Bu_2-4-MeC_6H_2	93
10	*t*-Bu	Me	0[c]

[a] Unless otherwise stated, all reactions were carried out at concentrations of 0.10–0.30 M by using 1.0 equiv of ROH and 1.1–1.3 equiv of Et_3N in CH_2Cl_2 at 0 °C to room temperature. [b] Yield of isolated purified product. [c] These reactions were carried out at 0 °C to reflux.

readily available *tert*-butylmethoxyphenylsilyl bromide (*t*-BMPSiBr, 1), which is a versatile reagent for the selective protection of primary alcohols as well as the silylation of secondary and tertiary hydroxyls (Scheme I).[4] The resultant *tert*-butylmethoxyphenylsilyl ethers **2** have useful synthetic applications due to their intrinsic sensitivity to fluoride ion. Such enhanced activity permits, for example, the selective removal of sterically encumbered alkoxysilyl ethers in the preparation of less hindered *tert*-butyldimethylsilyl ethers.[4]

The balance of reactivity and selectivity shown by this class of compounds is a consequence of the collective influence of the *tert*-butyl group, the phenyl group, and the electron-withdrawing methoxy group. While maintaining the essential electronic features of the alkoxysilyl ethers, we have investigated the consequences of modifying the silyl substituents with the aim of identifying a nondiastereotopic version of the previously described *tert*-butylmethoxyphenylsilyl ether **2**.[4] We examined two symmetrical series of structurally related compounds, the alkoxydiaryl- and alkoxydialkylsilyl ethers, with the intention of modulating their reactivity by selecting various alkoxy groups of different steric and electronic requirements. The use of di-*tert*-butyl- and diisopropylsilanes as diol-protecting groups has been studied by Trost[5] and Corey.[6] Extension of this approach to noncyclic systems was not reported.[7]

We report that alkoxysilyl ethers of the general formula **3** offer a broad range of stability and fluoride reactivity. In particular, the *tert*-butoxydiphenylsilyl ethers **4** offer unique advantages as a hydroxyl-protecting group, including hydrolytic stability and enhanced fluoride reactivity, and they can be formed selectively from primary alcohols. Moreover, this group can be selectively cleaved or retained in the presence of other silyl ethers.



3

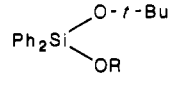


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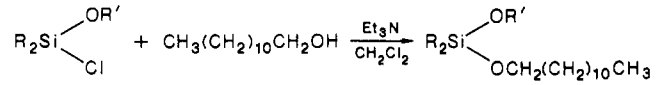
Table II. Preparation of Alkoxysilyl Ethers[a]



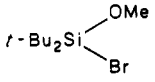
compd	R	R′	yield, %[b]
12	Ph	Me	60[c]
13	Ph	*i*-Pr	88
14	Ph	2,6-$Me_2C_6H_5$	98
15	Ph	*t*-Bu	91
16	Me	2,6-*t*-Bu_2-4-MeC_6H_5	90

[a] All reactions were carried out at concentrations of 0.1 M by using 1.1 equiv of the required silyl chloride and 1.1–1.5 equiv of Et_3N (0.5 h, room temperature). [b] Yield of purified (silica gel chromatography) products. [c] Partial decomposition occurred during purification.

Results and Discussion

Preparation and Stability of Alkoxy- and (Aryloxy)silyl Ethers. 1. Preparation of Alkoxysilyl Ethers. The required alkoxydiphenylsilyl chlorides were readily prepared from the commercially available diphenylsilyl dichloride and the appropriate alcohol (Table I). The alkoxydiphenylsilyl chlorides thus obtained were distillable liquids and could be kept in a desiccator for several months without noticeable decomposition. The only detectable byproducts were small amounts of the corresponding dialkoxysilanes. In general, these impurities did not interfere in subsequent transformations, and hence, further purification was deemed unnecessary.

The (aryloxy)dimethylsilyl chloride **9** was prepared by using a similar procedure and obtained as a white solid.[8] Upon reaction with methanol, the substantially hindered di-*tert*-butylsilyl dichloride did not give useful quantities of the desired methoxysilyl chloride **10**. The analogous bromide derivative, di-*tert*-butylmethoxysilyl bromide (**11**), was prepared by a different route, involving bromination of di-*tert*-butylmethoxysilane.[9]



11

Having the silyl reagents at hand, the dodecanol derivatives were prepared (Table II) in order to evaluate the comparative acid stability and fluoride reactivity of each silyl group.

The alkoxysilyl ethers were obtained by reaction of dodecanol with 1.1–1.3 equiv of the appropriate silyl chloride and 1.5 equiv of triethylamine at room temperature in CH_2Cl_2 as solvent. Excellent yields of the alkoxysilyl ethers resulted in all cases, except for the hydrolytically unstable compound **12**, which partially decomposed during thin-layer chromatography.[10]

In contrast, the reaction of the di-*tert*-butylmethoxysilyl bromide (**11**) with primary alcohols was sluggish under these conditions, requiring the use of 4-(dimethylamino)pyridine and DMF as the reaction solvent. This lack of reactivity limits the general application of this

(4) Guindon, Y.; Fortin, R.; Yoakim, C.; Gillard, J. W. *Tetrahedron Lett.* **1984**, *25*, 4717. Reagent 1 is commercially available from Fluka Chemical Corp. as *tert*-butylmethoxyphenylbromosilane.

(5) Trost, B. M.; Caldwell, C. *Tetrahedron Lett.* **1981**, *22*, 499. Trost, B. M.; Caldwell, C. G.; Murayama, E.; Heissler, D. *J. Org. Chem.* **1983**, *48*, 3252.

(6) Corey, E. J.; Hopkins, P. B. *Tetrahedron Lett.* **1982**, *23*, 4871.

(7) The use of 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane for the protection of diols as cyclic silylene acetals has been described. Markiewicz, W. T. *J. Chem. Res. Synop.* **1979**, 24. For a related example, see: Jenner, M. R.; Khan, R. *J. Chem. Soc., Chem. Commun.* **1980**, 50.

(8) Manis, P. A.; Rathke, M. W. *J. Org. Chem.* **1981**, *46*, 5348. See also: Marino, J. P.; Jaen, J. C. *Synth. Commun.* **1983**, *13*, 1057. Kunkel, E.; Reichelt, I.; Reissig, H.-U. *Liebigs Ann. Chem.* **1984**, 802.

(9) Treatment of di-*tert*-butylmethoxysilane with 1.1 equiv of Br_2 at 0 °C in CCl_4 furnished a mixture of **11** and di-*tert*-butylsilyl dibromide. Concentration and fractional distillation [40–42 °C (0.3 Torr)] then gave the silyl bromide **11**: ^1H NMR ($CDCl_3$) δ 1.06 (s, 18 H), 3.60 (s, 3 H).

(10) Unless otherwise stated, new compounds (Tables II–VI) exhibited spectral properties consistent with their assigned structures and gave satisfactory combustion analyses (±0.4%).

Table III. Hydrolytic Stability and Fluoride Reactivity of (Dodecyloxy)silyl Ethers

$$Me(CH_2)_{10}CH_2OR \xrightarrow{A,\ B,\ OR\ C} Me(CH_2)_{10}CH_2OH$$

entry	R	conditions[a]	$t_{1/2}$, h[b]
1	$SiPh_2OMe$ (12)	A (H^+)	0.12
		B (F^-)	<0.03
		C (OH^-)	<0.03
2	$SiPh_2O$-*i*-Pr (13)	A	0.70
		B	<0.03
		C	0.05
3	$SiPh_2O(2,6\text{-}Me_2C_6H_3)$ (14)	A	4.0
		B	0.25
		C	<0.03
4	$SiPh_2O$-*t*-Bu (15)	A	17.5
		B	5.8
		C	5.5
5	$SiMe_2O(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)$ (16)	A	4.0
		B	0.08
		C	0.05
6	SiPh(OMe)-*t*-Bu (17)	A	200
		B	22
		C	45
7	$SiMe_2$-*t*-Bu (18)	A	1.4
		B	140
8	$SiPh_2$-*t*-Bu (19)	A	>200
		B	375
9	Ac (20)	C	0.6

[a] A, 0.1 M in Substrate, 0.01 N $HClO_4$, THF/H_2O (9:1); B, 0.01 M in substrate containing *n*-Bu_4NF (6 equiv), CH_2Cl_2/THF (9:1); C, 0.05 M in substrate containing NaOD (2 equiv), $THF\text{-}D_8/D_2O$ (1:2). All reactions were carried out at room temperature. [b] Determined by 250-MHz ^1H NMR monitoring of the reaction (condition C) or quenched reaction aliquots (conditions A and B).

reagent as an alcohol-protecting group, and thus it was not investigated further.[11]

2. Hydrolytic Stability and Fluoride Reactivity. We have previously shown that the *tert*-butylmethoxyphenylsilyl ethers **2** possessed excellent hydrolytic stability; the synthetic usefulness of such a quality permitted, for example, the selective removal of *tert*-butyldimethylsilyl ethers.[4] Table III summarizes the range of acid sensitivity of the alkoxysilyl ether class, including the previously described *t*-BMPSi group (**17**), relating it to the widely used standard silyl ether protecting groups, *tert*-butyldimethylsilyl ether (**18**) and *tert*-butyldiphenylsilyl ether (**19**).

From the results shown in Table III the groups can be ranked in order of increasing acid stability which in general parallels the increase in steric bulk around the silicon atom (Scheme II). Interestingly, our previously described derivative **17** provided the most stability within the alkoxysilyl ether class. Such stability results from the sterically demanding *tert*-butyl group directly bonded to the silicon atom.[2] Within the alkoxydiphenyl class, the most stable compound was found to be the *tert*-butoxydiphenyl compound **15**, with a synthetically significant order of magnitude increase in stability over *tert*-butyldimethylsilyl ethers.

Scheme II. Comparative Acid Stability of Dodecanol Silyl Ethers

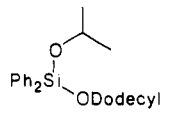
$SiPh_2OMe < SiPh_2O$-*i*-Pr $< SiMe_2$-*t*-Bu $<$
$SiPh_2O(2,6\text{-}Me_2C_6H_3) \approx SiMe_2O(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)$
$< SiPh_2O$-*t*-Bu $<$ Si(OMe)-*t*-BuPh $< SiPh_2$-*t*-Bu

The dodecyl alkoxysilyl ethers were treated with fluoride ion to determine their relative ease of deprotection. As can be seen from Table III, all of alkoxysilyl ethers studied were more sensitive to fluoride ion than the comparable silyl ethers. Compound **12** had a remarkable $10^4\times$ rate enhancement over the corresponding silyl ether **17**; hence, a synthetic application for the silyl reagent **5** may be for the protection of highly hindered alcohols. The relative order of fluoride sensitivity (Scheme III) can be attributed mostly to steric effects within this series. However, the greater electron-withdrawing aryloxy groups in silyl ethers **14** and **16** may contribute to the considerable fluoride sensitivity of these compounds.

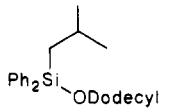
Scheme III. Comparative Fluoride Reactivity of Dodecanol Silyl Ethers

$SiPh_2OMe > SiPh_2O$-*i*-Pr $>$
$SiMe_2O(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2) >$
$SiPh_2O(2,6\text{-}Me_2C_6H_3) > SiPh_2O$-*t*-Bu $>$
Si(OMe)-*t*-BuPh $> SiMe_2$-*t*-Bu $> SiPh_2$-*t*-Bu

The enhanced lability of alkoxysilyl ethers toward nucleophilic species, including the fluoride ion, apparently results from the inherent electrophilicity of the silicon atom in such ethers. This is clearly demonstrated by comparing the fluoride reactivity of the alkoxysilyl ether **13** and its carbon analogue, the silyl ether **21**.[12] The former compound was found to be 2×10^3 times more sensitive to fluoride cleavage. Since the two groups are of similar steric bulk, the higher reactivity of **13** can be attributed to the electron-withdrawing effect of the additional oxygen atom, resulting in a more electrophilic silicon species.[13]



13



21

Within this class of compounds, the diphenylisopropoxysilyl, (e.g., **13**), 2,6-dimethylphenoxydiphenylsilyl (e.g., **14**), and the (2,6-di-*tert*-butyl-4-methylphenoxy)dimethylsilyl (e.g., **15**) groups complement and may offer useful synthetic advantages over the *tert*-butyldimethylsilyl group, especially when fluoride sensitivity is desired. However, this enhanced fluoride sensitivity is mirrored by the sensitivity of such compounds to base (Table II, entries 1–3 and 5 vs 9). The *tert*-butoxydiphenylsilyl group (e.g., **15**) on the other hand, was relatively stable under these conditions being approximately 100-fold more resistant to NaOH in conditions which effect acetate hydrolysis (Table III, entries 4 vs 9). Moreover, this group exhibited the desired (vide supra) acid stability and fluoride reactivity. Thus, the *tert*-butoxydiphenylsilyl group was further investigated in terms of its selectivity for primary alcohols, reactivity toward secondary and tertiary hydroxyls, chemical stability, and opportunity for selective removal.

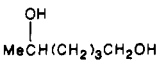
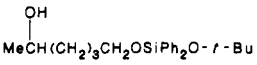
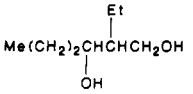
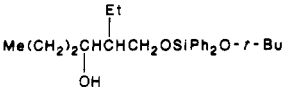
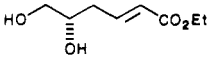
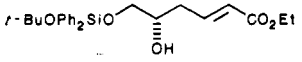
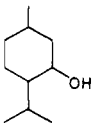
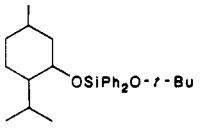
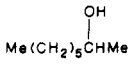
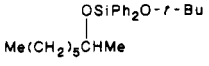
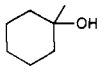
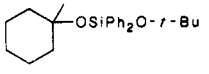
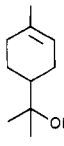
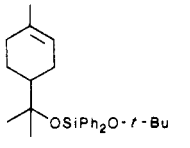
3-*tert*-Butoxydiphenylsilyl Ethers. We have found that primary, secondary, and tertiary alcohols readily react with *tert*-butoxydiphenylsilyl chloride to give the corre-

(11) No reaction was noted (DMF, DMAP) between the silyl bromide **11** and secondary alcohols (e.g., menthol).

(12) Silyl ether **21** was prepared starting from diphenylsilyl dichloride and 1 equiv of isobutylmagnesium bromide (ether, reflux). Reaction of the crude silyl chloride thus obtained with *n*-dodecanol (Et_3N, THF) then afforded **21** as a minor product: ^1H NMR ($CDCl_3$) δ 0.89 (br t, 3 H), 0.96 (d, 6 H, J = 6.0 Hz), 1.18 (d, 2 H, J = 8.5 Hz), 1.20–1.42 (m, 20 H), 1.50–1.65 (m, 2 H), 1.95 (m, 1 H), 3.66 (t, 2 H, J = 7.0 Hz), 7.28–7.42 (m, 6 H), 7.66–7.76 (m, 4 H).

(13) Inductive stabilization of a postulated pentavalent siliconate complex may also contribute to enhanced reactivity. For a more detailed account, see: Sommer, L. H. *Stereochemistry, Mechanism and Silicon*; McGraw Hill: New York, 1985.

Table IV. Preparation of *tert*-Butoxydiphenylsilyl Ethers[a]

entry	alcohol	time, h	product (% yield)[b]
1	 **22**	0.5	 **29** (87)[c]
2	 **23**	1	 **30** (89)
3	 **24**	1	 **31** (86)
4	 **25**	18	 **32** (51)
5	**25**	1	**32** (97)[d]
6	**25**	1	**32** (93)[e]
7	 **26**	1	 **33** (90)[d]
8	 **27**	18	 **34** (89)[f]
9	 **28**	30	 **35** (89)[d,f]

[a] Unless otherwise stated all reactions were initiated at 0 °C by adding 1.1 equiv of *t*-BuOPh$_2$SiCl to a 0.1–0.2 M solution of the alcohol and 1.3 equiv of Et$_3$N and then aged at room temperature for the indicated period. [b] Isolated yield of the purified product. [c] A small amount (4%) of the bisprotected material was also obtained. [d] 0.1 equiv of 4-(dimethylamino)pyridine was included in the reaction mixture. [e] 0.1 equiv of DMF was included. [f] DMF was used as the reaction solvent.

sponding silyl ethers in excellent yield (Table IV). Of particular interest is the utility of this reagent for the selective protection of primary alcohols. For example, treatment of the diol **22** (entry 1) with 1.3 equiv of the silyl chloride (CH_2Cl_2, room temperature, 1 h) resulted in a 87% yield of the monoprotected product **29**. Similar selectivity was noted for 1,3- and 1,2-diols (entries 2 and 3). Under these conditions the reaction of secondary alcohols is slow (entry 4). However, the inclusion of a catalytic amount of DMAP or DMF greatly accelerated the reaction rate and excellent yields of the corresponding secondary silyl ethers resulted (entries 5, 6, and 8). The protection of tertiary alcohols **27** and **28** proceeded smoothly in DMF (entries 8 and 9). This latter result contrasts with the reported conditions necessary for reaction between alcohol **27** and *tert*-butyldimethylsilyl chloride (imidazole, DMF; 3 days, 10% yield).[14]

All of the *tert*-butoxydiphenylsilyl ethers described in Table IV could be cleaved to their parent alcohols in good yield when subjected to hydrolysis (0.1 N HCl/MeOH) or fluoride treatment (*n*-Bu$_4$NF).

The utility of any protecting group in synthesis depends on its compatibility with a range of reagents and reaction conditions. As shown in Table V, the *tert*-butoxydiphenylsilyl ether group was found to be compatible with a wide variety of synthetic transformations. Additions to carbonyl groups can be achieved without loss of the silyl moiety. In the absence of such competition, however, highly reactive nucleophiles such as *n*-BuLi showed reaction at silicon in ethereal solvents (entry 4), affording partial deprotection to the alcohol at −78 °C.[15] It should be noted that the sterically more demanding *tert*-butylmethoxyphenylsilyl group showed somewhat greater stability toward alkyllithium reagents (entries 6 and 7 vs 4).

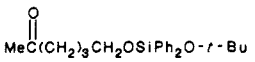
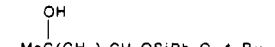
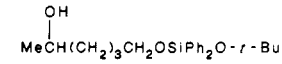
Finally, compatibility to the widely utilized Swern oxidation[16] procedure was demonstrated by the smooth oxidation of **29** to the ketone **36** (Table V, entry 10). Good stability to the chromium-based oxidants, PCC[17] and PDC,[18] was also observed (entries 11 and 12).[19]

4. Selective Deprotections. As with *tert*-butylmethoxyphenylsilyl ethers,[4] the high fluoride reactivity and acid stability of the *tert*-butoxydiphenylsilyl group permits unique opportunities for selective silyl deprotection. Some of the results we have obtained are outlined in Table VI. Primary *tert*-butoxydiphenylsilyl ethers can be cleaved with good selectively using fluoride ion in the presence of

(14) Barton, T. J.; Tulley, C. R. *J. Org. Chem.* **1978**, *43*, 3649.

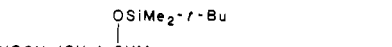
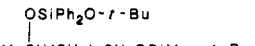
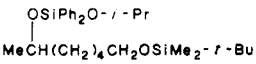
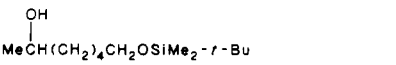
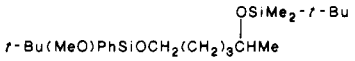
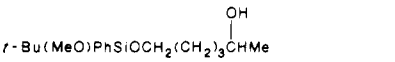
(15) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231.
(16) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.
(17) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, *16*, 2647.
(18) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, *20*, 399.
(19) Such functional stability to chromium-based oxidants would seem a definite advantage in light of the reported sensitivity of other silyl ethers to these reagents. Denmark, S. E.; Hammer, R. P.; Weber, E. J.; Habermas, K. L. *J. Org. Chem.* **1987**, *52*, 165.

Table V. Chemical Compatibility of Alkoxysilyl Ethers

entry	substrate	reagent (conditions)	results (% yield)[b]
1	$Me(CH_2)_{10}CH_2OSiPh_2O$-*t*-Bu (**15**)	$Ph_3P{=}CH_2$ (THF, 25 °C, 3 h)	**15** (90)
2	**15**	EtMgBr (Et_2O, 0 °C, 1 h)	**15** (91)
3	**15**	*t*-BuLi (Et_2O, 0 °C, 1 h)	**15** (90)
4	**15**	*n*-BuLi (Et_2O, −78 °C, 1 h)	**15** (50) + dodecanol (**39**)
5	 **36**	*n*-BuLi (Et_2O, −78 °C, 1 h)	 **37** (89)
6	$Me(CH_2)_{10}CH_2OSiPh(OMe)$-*t*-Bu	*n*-BuLi (THF, −78 °C, 1 h)	**17** (94)
7	**17**	*n*-BuLi (THF, −44 °C, 1 h)	**17** (67)[c]
8	**36**	DIBAl-H (toluene, −78 °C, 1 h)	 **29** (82)
9	**36**	LAH (ether, 0 °C, 1 h)	**29** (79)
10	**29**	Swern oxidation	**36** (83)[d]
11	**15**	PCC (CH_2Cl_2, 25 °C, 2 h)	**15** (87)[e]
12	**15**	PDC (CH_2Cl_2, 25 °C, 24 h)	**15** (79)[f]

[a] Unless otherwise stated 1.1–1.3 equiv of reagent was used at concentrations of 0.1–0.2 M. [b] Yield of isolated purified product. [c] The corresponding *n*-butyldiphenylsilyl ether was also isolated (30%) along with a small amount of dodecanol. [d] DMSO/$(COCl)_2$ in CH_2Cl_2 at −78 °C and then Et_3N, −78 → 25 °C. [e] 2.5 equiv of reagent was used. A small amount (6%) of dodecanal was also isolated. [f] 1.5 equiv of reagent was used. A small amount (9%) of dodecanal was isolated.

Table VI. Selective Removal of Silyl Ethers

entry	substrate	conditions	product (% yield)[a]
1	*t*-$BuOPh_2SiOCH_2(CH_2)_6OSiMe_2$-*t*-Bu (**38**)	*n*-Bu_4NF[b]	$HOCH_2(CH_2)_6CH_2OSiMe_2$-*t*-Bu [**44** (80)[c]]
2	**38**	$HClO_4$[d]	*t*-$BuOPh_2SiOCH_2(CH_2)_6CH_2OH$ [**45** (90)]
3	*t*-$BuOPh_2SiOCH_2(CH_2)_6OSiPh_2$-*t*-Bu (**39**)	*n*-Bu_4NF	$HOCH_2(CH_2)_6CH_2OSiPh_2$-*t*-Bu [**46** (84)]
4	**39**	$HClO_4$	**46** (80)
5	 **40**	*n*-Bu_4NF	 **47** (90)
6	 **41**	*n*-Bu_4NF	mixture of products
7	 **42**	*n*-Bu_4NF	 **48** (89)
8	 **43**	HCl[e]	 **49** (87)

[a] Isolated yields. [b] 3.0 equiv of dry *n*-Bu_4NF (1.0 M in THF) was added to a CH_2Cl_2 solution of substrate (0.033 M) at room temperature. [c] A small amount of diol was also isolated. [d] THF/0.1 N $HClO_4$ (9:1) at 0.1 M. [e] MeOH/0.1 N HCl (9:1) at 0.1 M.

either primary or secondary *tert*-butyldimethylsilyl ethers (entries 1 and 5). Traditionally, silyl ethers are cleaved in THF.[1] The key to the successful transformations listed above is the utilization of CH_2Cl_2 as reaction cosolvent. For example, treatment of the alkoxysilyl ether **38** with 3 equiv of dry tetra-*n*-butylammonium fluoride in CH_2Cl_2–THF (10:1) at room temperature afforded the alcohol **44** in excellent yield. Under these conditions *tert*-butyldiphenylsilyl ethers are essentially inert (entry 3).

Secondary *tert*-butoxydiphenylsilyl ethers showed diminished selectivity with respect to primary *tert*-butyldimethylsilyl ethers (entry 6). However, the highly fluoride-sensitive diphenylisopropoxysilyl group described earlier proved useful for this latter transformation (entry 7). Thus, this group may find useful synthetic application when higher fluoride reactivity is desired.

Under acidic conditions (0.01 N $HClO_4$; THF–H_2O, 9:1) the selective cleavage of a *tert*-butyldimethylsilyl ether in the presence of the *tert*-butylmethoxyphenylsilyl groups is possible (entry 2). The added acid stability of the *tert*-butylmethoxyphenyl version appears to be advantageous in certain cases (entries 2, 8).[20] *tert*-Butyldiphenylsilyl ethers are essentially inert to these reaction conditions (entry 4). Thus a high degree of discrimination between the various silyl groups can be achieved, with the alkoxysilyl ethers described herein complementing the existing repertoire of silyl protecting groups.

Conclusion

In summary, the alkoxydiphenylsilyl ethers studied possess a broad range of hydrolytic stability and fluoride sensitivity. In particular, the *tert*-butoxydiphenylsilyl group most closely resembles the *tert*-butylmethoxyphenylsilyl ethers previously described offering both acid stability and fluoride reactivity. Furthermore, the symmetry of the molecule avoids diastereoisomeric separation or NMR signal doubling occasionally seen with this latter reagent. Moreover, *tert*-butoxydiphenylsilyl chloride allows for the selective protection of primary alcohols in addition to reactivity toward tertiary alcohols. Thus, this

(20) Treatment of compound **39** with 0.01 N $HClO_4$ resulted in a mixture of products.

reagent should find many useful applications in organic synthesis for alcohol protection especially when fluoride sensitivity is desirable.

Experimental Section

General Methods. Distillation temperatures are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 681 spectrophotometer. Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a Bruker AM 250 (250 MHz) spectrometer. Either tetramethylsilane or chloroform (δ 7.26) was used as the reference. Elemental analyses were performed by Galbraith Laboratories Inc. (Knoxville, TN).

Crude products were purified by flash chromatography using 230–400 mesh silica gel (E. Merck). The purity of known compounds was ascertained by TLC using commercial silica gel plates (E. Merck, Kieselgel 60F 254) and by spectral means (IR, ^{1}H NMR).

Glassware and syringes were dried in an oven (120 °C) prior to use. Methylene chloride, DMSO, and triethylamine were distilled from CaH_2 and stored over 4-Å molecular sieves. MeOH and *i*-PrOH were distilled from Na prior to use. Dry ether was obtained by distillation from Na/benzophenone. DMF (anhydrous) and THF (anhydrous), *t*-BuOH, 2,6-dimethylphenol, 2,6-di-*tert*-butyl-4-methylphenol, diphenyldichlorosilane, and dimethyldichlorosilane were obtained from the Aldrich Chemical Co. and used without further purification. Anhydrous *n*-Bu_4NF was prepared by azeotropic drying (PhH) of *n*-$Bu_4NF{\cdot}3H_2O$ (Aldrich).

Representative Procedure for the Preparation of Silyl Chlorides 5–8. Preparation of *tert*-Butoxydiphenylsilyl Chloride (8). To a cold (0 °C), stirred mixture of diphenylsilyl dichloride (50 mmol) and triethylamine (55 mmol) in 200 mL of dry methylene chloride, under nitrogen, was added a solution of *tert*-butyl alcohol (50 mmol) in the same solvent (20 mL). The reaction mixture was then stirred at room temperature for 6 h and heated to reflux for 36 h. The reaction mixture was then cooled to room temperature and concentrated under reduced pressure. The resultant thick oil was dissolved in a 1:1 ether–hexane mixture (200 mL), suction filtered, and reconcentrated to afford an oil, which was purified by distillation through a 20-cm Vigreux column [130–145 °C (0.5 Torr)] to give the desired product as a pale yellow oil (81%): IR (neat) 3065, 1590, 1365, and 1055 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 9 H), 7.33–7.48 (m, 6 H) 7.64–7.74 (m, 4 H).

Representative Procedures for the Preparation of Alkoxy- and (Aryloxy)diphenylsilyl Ethers. (a) Preparation of *n*-Dodecyl *tert*-Butoxydiphenylsilyl Ether (15). To a cold (0 °C), stirred solution of *n*-dodecanol (1.0 mmol) and triethylamine (1.3 mmol) in 5.0 mL of dry methylene chloride was added *tert*-butoxydiphenylsilyl chloride (298 μL, 1.1 mmol). The cooling bath was then removed and the resultant mixture stirred at room temperature. After 30 min saturated aqueous sodium bicarbonate and ether were added. The organic layer was separated, washed with water and brine, and dried over $MgSO_4$. Filtration and concentration gave a pale yellow oil, which was purified by flash chromatography on silica gel (eluant, hexane–ethyl acetate, 98:2) to give pure silyl ether **15** (91%): IR (neat) 3071 (C=CH), 1592 (C=C), 1365 (CH of *t*-Bu) and 1050 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83–0.94 (br t, 3 H), 1.20–1.36 (m, 18 H), 1.29 (s, 9 H), 1.50–1.64 (m, 2 H), 3.72 (t, 2 H, J = 6.5 Hz), 7.28–7.42 (m, 6 H), 7.59–7.70 (m, 4 H). Anal. Calcd for $C_{28}H_{44}O_2Si$: C, 76.30; H, 10.06. Found: C, 76.27; H, 9.97.

(b) Preparation of 2-Octyl *tert*-Butoxydiphenylsilyl Ether (33). To a cold (0 °C), stirred solution of 2-octanol (2.0 mmol) and triethylamine (2.6 mmol) in 10 mL of dry methylene chloride were sequentially added *tert*-butoxydiphenylsilyl chloride (597 μL, 2.2 mmol) and 4-(dimethylamino)pyridine (24 mg, 0.2 mmol). The mixture was then allowed to warm to room temperature and stirred for an additional period of 1 h. Quenching with saturated aqueous sodium bicarbonate and normal workup (as above) gave, after flash chromatography on silica gel (eluant, hexane–methylene chloride, 92:8), pure silyl ether **33** (90%): IR (neat) 3070, 1591, 1365, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (*t*, 3 H, J = 6.5 Hz), 1.15 (d, 3 H, J = 6.0 Hz), 1.18–1.45 (m, 8 H), 1.28 (s, 9 H), 1.48–1.61 (m, 2 H), 3.97 (m, 1 H), 7.28–7.42 (m, 6 H), 7.60–7.69 (m, 4 H). Anal. Calcd for $C_{24}H_{36}O_2Si$: C, 74.94; H, 9.43. Found: C, 74.81; H, 9.37.

(c) Preparation of 1-Methylcyclohexyl *tert*-Butoxydiphenylsilyl Ether (34). A solution of 1-methylcyclohexanol (**27**) (2.0 mmol) and triethylamine (2 mmol) in 10 mL of dry DMF was treated with *tert*-butyoxydiphenylsilyl chloride (597 μL, 2.2 mmol). The resultant mixture was then stirred at room temperature for 18 h. Quenching and workup (as above) gave, after flash chromatography on silica gel (eluant, hexane–methylene chloride 92:8), pure silyl ether **34** (89%): IR (neat) 3065, 1590, 1364, and 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16–1.87 (unresolved m, 10 H), 1.22 (s, 3 H), 1.26 (s, 9 H), 7.28–7.41 (m, 6 H), 7.64–7.68 (m, 4 H). Anal. Calcd for $C_{23}H_{32}O_2Si$: C, 74.95; H, 8.75. Found: C, 75.07; H, 8.81.

Comparative Stability and Reactivity (Table III) Studies of Silyl Ethers.[21] In general the hydrolysis and fluorolysis reactions employed in this study obeyed simple first-order rate laws and a plot of ln (% completion) vs time afforded $t_{1/2}$. **(A) Acid Hydrolysis.** A solution of the appropriate silyl ether (0.3 mmol) in 2.7 mL of tetrahydrofuran was treated with 0.1 N $HClO_4$ (0.3 mL) at room temperature. The appearance of dodecanol with time was then monitored by ^{1}H NMR analysis ($CDCl_3$ or Ph-d_6) of quenched (basic alumina, activity I; eluant ether) reaction aliquots. **(B) Fluoride Reactivity.** A solution of the silyl ether (0.1 mmol) in 9.4 mL of methylene chloride was treated with a 1.0 M solution of *n*-Bu_4NF (0.6 mL) at room temperature. Reaction aliquots were quenched by dilution with ether followed by aqueous workup. The formation of dodecanol was then determined as outlined above. **(C) Base Hydrolysis.** A stirred solution of the silyl ether (0.1 mmol) in 0.67 mL of THF-d_8 was treated at room temperature with 0.15 M NaOD (1.33 mL) in D_2O. The reaction was then monitored directly by ^{1}H NMR.

Representative Procedures for the General Removal of *tert*-Butoxydiphenylsilyl Ethers. (a) Acid Hydrolysis of *tert*-Butoxydiphenylsilyl Ether 15. To a stirred solution of the silyl ether **15** (1.0 mmol) in 9.0 mL methanol was added 1.0 mL of 0.1 N HCl. After 2 h at room temperature saturated aqueous sodium bicarbonate and ether were added. The organic layer was separated, washed with water and brine, and dried over $MgSO_4$. Concentration followed by flash chromatography on silica gel (eluant, hexane–ethyl acetate, 9:1) gave after distillation [air bath temperature, 135–145 °C (20 Torr)] pure dodecanol (91%). This material exhibited spectral properties (IR, ^{1}H, NMR) identical with those of commercially available material.

(b) Fluoride-Mediated Cleavage of *tert*-Butoxydiphenylsilyl Ether 15. To a stirred solution of the silyl ether **15** (0.5 mmol) in 1.5 mL of tetrahydrofuran was added a 1.0 M solution of tetra-*n*-butylammonium fluoride (1.5 mmol) in the same solvent. After 0.5 h ether was added and the mixture washed with water (2×) and brine. Drying ($MgSO_4$) followed by concentration and flash chromatography on silica gel (eluant, hexane–ethyl acetate, 9:1) gave pure dodecanol (95%). This material exhibited spectral properties (IR, ^{1}H NMR) identical with those of commercially available material.

Representative Procedure for the Selective Removal of *tert*-Butoxy- and Isopropoxydiphenylsilyl Ethers. (a) Cleavage of *tert*-Butoxydiphenylsilyl Ether 38. To a stirred solution of the silyl ether **38** (1.0 mmol) in 30 mL of dry methylene chloride, under nitrogen, was added a 1.0 M solution of dry tetra-*n*-butylammonium fluoride (3 mmol) in tetrahydrofuran. After 8 h at room temperature the reaction mixture was diluted with ethyl acetate, washed with water (2×) and brine and dried over $MgSO_4$. Concentration gave a yellow oil, which was purified by flash chromatography on silica gel. Elution of the column with a 9:1 hexane–ethyl acetate mixture gave the silyl alcohol **44** (80%). This material exhibited spectral properties identical with those previously prepared.[22]

Further elution of the column with a 3:7 hexane–ethyl acetate mixture gave pure 1,8-octanediol (4%).

(b) Cleavage of *tert*-Butoxydiphenylsilyl Ether 39. To a stirred solution of the bis(silyl ether) **39** (0.5 mmol) in 4.5 mL of tetrahyrofuran was added 0.5 mL of 0.1 N $HClO_4$. After 8 h

(21) These studies were undertaken to ascertain relative stabilities and do not represent an indepth kinetic analysis.

(22) Guindon, Y.; Yoakim, C.; Morton, H. E. *J. Org. Chem.* **1984**, *49*, 3912.

at room temperature saturated aqueous sodium bicarbonate and ether were added. The organic layer was separated, washed with water and brine, and dried over $MgSO_4$. Concentration followed by flash chromatography (eluant, hexane–ethyl acetate, 9:1) gave the alcohol **46** (80%): IR (neat) 3630, 1589, and 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 9 H), 1.23–1.45 (m, 8 H), 1.42 (broad s, 1 H, exchangeable with D_2O), 1.50–1.63 (m, 4 H), 3.64 (t, 2 H, J = 6.5 Hz), 3.65 (t, 2 H, J = 6.5 Hz), 7.34–7.46 (m, 6 H), 7.64–7.70 (m, 4 H). Anal. Calcd for $C_{24}H_{36}O_2Si$: C, 74.94; H, 9.46. Found: C, 74.76; H, 9.62.

Selective Removal of *tert*-Butyldimethylsilyl Ether 38. A solution of the bis(silyl ether) **38** (0.5 mmol) in 4.5 mL tetrahydrofuran was treated with 0.1 N $HClO_4$ (0.5 mL) and stirred at room temperature for 24 h. Normal workup gave after flash chromatography (eluant, hexane–ethyl acetate, 9:1) pure alcohol **45**: ^1H NMR ($CDCl_3$) δ 1.21–1.38 (m, 9 H), 1.28 (s, 9 H), 1.47–1.63 (m, 4 H), 3.61 (t, 2 H, J = 6.5 Hz), 3.71 (t, 2 H, J = 6.5 Hz), 7.28–7.42 (m, 6 H), 7.61–7.66 (m, 4 H). Anal. Calcd for $C_{24}H_{36}O_3Si$: C, 71.95; H, 9.06. Found: C, 71.84; H, 9.01.

Chemical Compatibility: Preparation of *tert*-Butoxydiphenylsilyl Ether 37 from Diol 22. (a) Selective Silylation of Diol 22. Following the representative procedure outlined above a mixture of 1,5-hexanediol (16.8 mmol) and triethylamine (25.1 mmol) in 87 mL of dry methylene chloride, under nitrogen, was treated at 0 °C with *tert*-butoxydiphenylsilyl chloride (22.7 mmol). The cooling bath was removed and the resulting mixture stirred for an additional period of 20 h and then quenched with saturated aqueous sodium bicarbonate. Normal workup (ether) gave after flash chromatography (eluant, hexane–ethyl acetate, 8:2) the monosilyl alcohol **29** (82%): IR (neat) 3360, 3068, 1591, 1365, and 1051 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (d, 3 H, J = 7.5 Hz), 1.21 (s, 9 H), 1.40–1.50 (m, 4 H), 1.52–1.66 (m, 2 H), 3.70–3.81 (m, 1 H), 3.75 (t, 2 H, J = 6.0 Hz), 7.29–7.43 (m, 6 H), 7.62–7.68 (m, 4 H). Anal. Calcd for $C_{22}H_{32}O_3Si$: C, 70.92; H, 8.66. Found: C, 70.61; H, 8.71.

(b) Oxidation of Alcohol 29. A cold (−78 °C) stirred solution of oxalyl chloride (6.0 mmol) in 10 mL of dry methylene chloride, under nitrogen, was treated with a solution of DMSO (7.0 mmol) in 2 mL of the same solvent. After 10 min a solution of alcohol **29** (4.7 mmol) in 6 mL of dry methylene chloride was added dropwise and the reaction mixture aged for 50 min. Triethylamine (14.0 mmol) was then added and the resultant mixture allowed to warm to room temperature. After 1 h water and ether were added. The organic layer was separated and washed with 10% aqueous sodium hydrogen sulfate, water, and brine. Drying ($MgSO_4$) and concentration gave a yellow oil, which was purified by flash chromatography (eluant, hexane–ethyl acetate, 85:15) to yield ketone **36** (83%): IR (neat) 3055, 1710, 1583, 1367, and 1042 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 (s, 9 H), 1.54–1.72 (m, 4 H), 2.10 (s, 3 H), 2.42 (br t, 2 H, J = 7.0 Hz), 3.73 (t, 2 H, J = 6.0 Hz), 7.29–7.42 (m, 6 H), 7.61–7.66 (m, 4 H). Anal. Calcd for $C_{22}H_{30}O_3Si$: C, 71.31; H, 8.16. Found: C, 70.32; H, 8.12.

(c) Butyllithium Addition of Ketone 36. A cold (−78 °C) stirred solution of ketone **36** (0.3 mmol) in 1.6 mL dry ether was treated with a 1.6 M solution of butyllithium (0.24 mL) in hexanes. After 1 h the reaction mixture was quenched with saturated aqueous ammonium chloride and diluted with ether. The ether layer was separated, washed with water and brine, and dried over sodium sulfate. Concentration followed by purification (silica gel, 9:1 hexane–ethyl acetate) gave the tertiary alcohol **37**: IR (neat) 3350, 3058, 1365, and 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86–0.94 (br t, 3 H), 1.12 (s, 3 H), 1.20–1.48 (m, 9 H), 1.31 (s, 9 H), 1.50–1.70, (m, 4 H), 3.70–3.78 (br t, 2 H), 7.29–7.42 (m, 6 H), 7.6–7.69 (m, 4 H).[23]

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Registry No. **5**, 53668-78-3; **6**, 114058-14-9; **7**, 114058-15-0; **8**, 17922-24-6; **9**, 90101-29-4; **11**, 114058-16-1; **12**, 114058-17-2; **13**, 114058-18-3; **14**, 114058-19-4; **15**, 114058-20-7; **16**, 114058-21-8; **17**, 94124-59-1; **18**, 114058-22-9; **19**, 114058-23-0; **20**, 112-66-3; **21**, 114058-24-1; **22**, 928-40-5; **23**, 94-96-2; **24**, 96720-08-0; **25**, 1490-04-6; **26**, 123-96-6; **27**, 590-67-0; **28**, 98-55-5; **29**, 114058-25-2; **30**, 114094-30-3; **31**, 114058-26-3; **32**, 114058-27-4; **33**, 114058-28-5; **34**, 114058-29-6; **35**, 114058-30-9; **36**, 114058-31-0; **37**, 114058-32-1; **38**, 114058-33-2; **39**, 114058-34-3; **40**, 114058-35-4; **41**, 114058-36-5; **42**, 114058-37-6; **43**, 94124-43-3; **44**, 91898-32-7; **45**, 114058-38-7; **46**, 94124-45-5; **47**, 114058-39-8; **48**, 114058-40-1; **49**, 94124-47-7; Ph_2SiCl_2, 80-10-4; t-Bu_2SiCl_2, 18395-90-9; MeOH, 67-56-1; i-PrOH, 67-63-0; 2,6-$Me_2C_6H_3OH$, 576-26-1; t-BuOH, 75-65-0; Me_2SiCl_2, 75-78-5; $CH_3(CH_2)_{11}OH$, 112-53-8; HSi(Bu-t)$_2$(OMe), 56310-21-5; t-Bu_2SiBr_2, 94403-14-2; i-BuMgBr, 926-62-5; (i-Bu)Si(Ph)$_2$Cl, 81851-76-5; 2,6-di-*tert*-butyl-4-methylphenol, 128-37-0.

(23) This compound was not submitted for elemental analysis.

Organic Disulfides and Related Substances. 49. Preparation of Cyclic Thiosulfinates and Reactions with Thiols[1]

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The four stereoisomers of 1,2-dithiane-4,5-diol 1-oxide were prepared by oxidizing the corresponding dithianes with H_2O_2 in MeOH/H_2O by using tungstic acid as a catalyst, MnO_2 to destroy excess H_2O_2, and chromatography to separate products. These cyclic thiosulfinates (**8**, **9**, **12**, and **13**), together with 1,4-dihydro-2,3-benzodithin 2-oxide (**2**), were converted to bisunsymmetrical disulfides, $R^a(SSR^b)_2$ with *p*-toluenethiol and 3-mercaptopropanediol as models respectively for arene- and alkanethiols. 1,5-Dihydro-2,3,4-benzotrithiepin 2-oxide (**5**) gave the disulfide trisulfides **6a** and **6b**, $R^a(SSR^b)(SSSR^b)$, with these thiols but **6a** and **6b** were quite unstable. Mass spectra are discussed; tetramethylene sulfone may provide a useful matrix for both positive- and negative-ion FAB spectra of organosulfur compounds.

Relatively little attention has been given to thiosulfinates, RS(O)SR.[2] In particular, reactions of thiosulfinates with thiols seem to have been studied preparatively in a fairly general way only by Schöberl and Gräfje[3]

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