Organosilicon Compounds. XVIII. Silicon-Containing Dianhydrides

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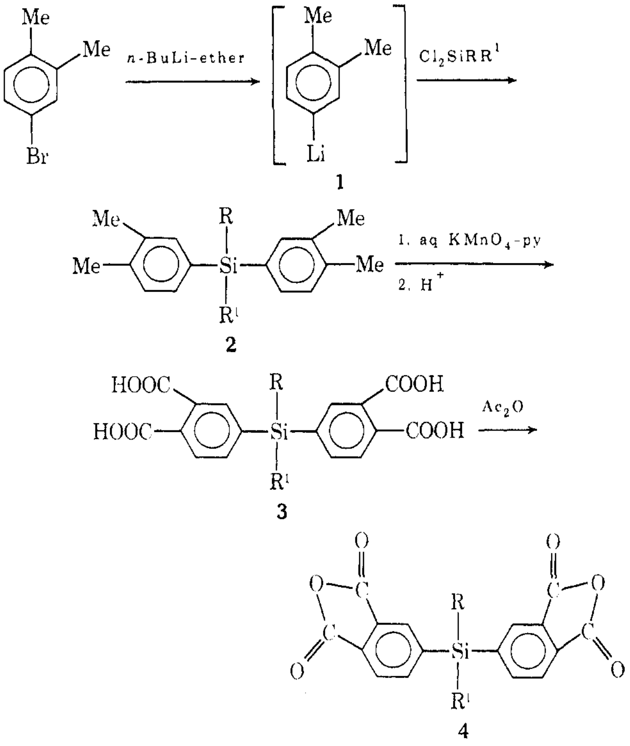
Four new silicon-containing dianhydrides, bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (**4a**), bis(2,3-dicarboxyphenyl)dimethylsilane dianhydride (**6**), 1,4-bis(3,4-dicarboxyphenyldimethylsilyl)benzene dianhydride (**10**), and 1,3-bis(3,4-dicarboxyphenyl)-1,1,3,3-tetramethyldisiloxane dianhydride (**14**), were prepared by aqueous potassium permanganate-pyridine oxidations of corresponding tetramethyl intermediates to form tetracarboxylic acids, which were dehydrated to the dianhydrides.

The number of aromatic dianhydrides suitable for the synthesis of thermally stable polyimides is limited.[1] We have been interested in preparing new silicon-containing polyimide precursors, as methyl- and phenyl-substituted silanes have been reported to provide polymeric materials possessing good thermal and thermooxidative stabilities with good mechanical properties.[2,3] Furthermore, our experience has shown that the incorporation of silicon increases the solubility of polymers in organic solvents. Thus, this work represents an attempt to provide useful silicon-containing polyimide precursors. The synthesis of four new silicon-containing dianhydrides is reported herein.[4]

Results and Discussion

The preparation of **4** (Scheme I) was achieved by first treating *n*-butyllithium with 4-bromo-*o*-xylene *via* halogen–metal interchange to form 4-lithio-*o*-xylene (**1**). Treatment of 2 mol of **1** with 1 mol of the appropriate dichloro disubstituted silane produced the tetramethyl derivative (**2**). Aqueous potassium permanganate–pyridine oxidation of **2a** gave, after neutralization, the tetracarboxylic acid **3a**, which was then dehydrated in refluxing acetic anhydride to the dianhydride **4a**.

SCHEME I



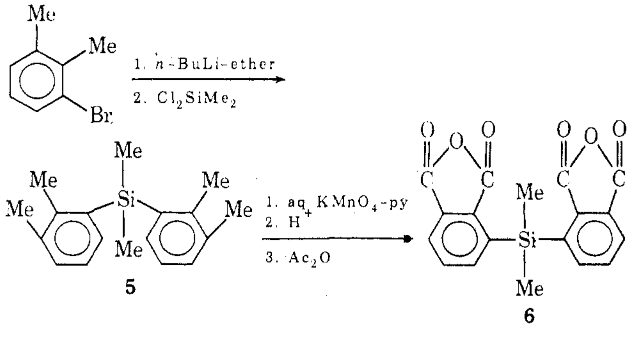
a. R = R^1 = Me
b. R = Me; R^1 = Ph
c. R = R^1 = Ph

This oxidation is unusual in that it represents one of the few reported cases in which a tetramethyl aromatic compound has been completely oxidized to its tetracarboxylic acid with aqueous permanganate.

We were unable to prepare **3b** or **3c**. In each case a colorless, oily material or a low- and broad-melting solid which resisted purification was isolated. Likewise, we were unable to acquire pure dianhydride from the attempted cyclization of these two crude carboxylic acids. Our contention is that incomplete oxidation of aromatic methyl groups is affording a product mixture which has, to date, defied purification. This tenet was confirmed by the appearance of significant amounts of benzylic protons from unoxidized aromatic methyl groups in the nmr spectra of **3b** and **3c**.

Crude **3b** and **3c** both showed a strong ir siloxane stretch at 1060 and 1050 cm^{-1}, respectively. For this reason the possibility of nucleophilic attack on silicon-aromatic bonds of **3b** and **3c** (but not **3a**) by the OH$^-$ produced during the KMnO$_4$ oxidation has not been ruled out. The mild electron withdrawal of the phenyl substituent would be expected to enhance nucleophilic attack on silicon by polarizing the silicon–phenyl bonds.

SCHEME II



An isomer of **4a** (Scheme II) was produced in a similar fashion. The reaction of 3-bromo-*o*-xylene with *n*-butyllithium in ether, followed by dichlorodimethylsilane, formed bis(2,3-dimethylphenyl)dimethylsilane (**5**), which was oxidized to the tetracarboxylic acid as

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[1] C. E. Sroog, *J. Polym. Sci., Part C*, **16**, 1191 (1967).

[2] R. J. H. Voorhoeve, "Organohalosilanes, Precursors to Silicones," Elsevier, New York, N. Y., 1967, p 288.

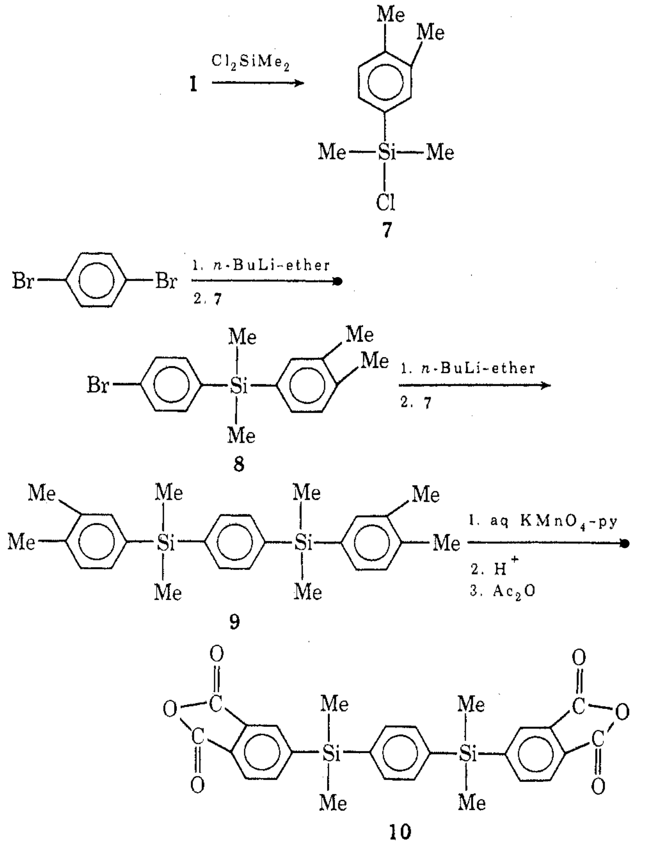
[3] H. N. Kovacs, A. D. Delman, and B. B. Simms, *J. Polym. Sci., Part A-1*, **6**, 2103 (1968).

[4] The polymerization of **4a**, **10**, and other silicon-containing precursors to polyimides was reported: N. J. Johnston and R. A. Jewel, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973, ORPL-169.

before with permanganate and subsequently dehydrated to form the dianhydride **6**.

A dianhydride of higher silicon content was synthesized according to Scheme III. The starting material, chlorodimethyl(3,4-dimethylphenyl)silane (**7**), was prepared by the inverse addition (1:1) of 4-lithio-*o*-xylene to dichlorodimethylsilane at 0°. Although we were unable to purify **7** *via* vacuum distillation for a correct elemental analysis, it was of sufficient purity to be successfully employed in reactions with lithio species. Thus, by the stepwise formation of lithio species from *p*-dibromobenzene, followed by treatment with **7**, a third tetramethyl derivative (**9**) was prepared, which was then oxidized to the tetracarboxylic acid and dehydrated to the dianhydride **10**. The direct synthesis of **9** from *p*-dibromobenzene *via* the *p*-dilithio species led to a low yield (9%) of this material.

SCHEME III



The attempted synthesis of a thiophene-containing tetracarboxylic acid (**15**) *via* a similar aqueous permanganate–pyridine oxidation led to cleavage of the two silicon–thienyl bonds and isolation of the siloxane **13**, which was then dehydrated to the dianhydride **14** (Scheme IV). The cleavage of the silicon–thienyl bonds was not entirely unexpected, in view of the known instability of α-silyl heterocycles to potassium hydroxide solution in refluxing ethanol–dioxane–water.[5] The production of electron-withdrawing carboxylic acid salt groups as the oxidation progressed, no doubt, facilitated this cleavage reaction.[6]

We are continuing our efforts to synthesize silicon-containing dianhydrides, particularly the highly phenylated materials.

Experimental Section

General.—Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. Nmr spectra were determined on a Varian A-60D spectrometer using tetramethylsilane as the internal standard in $\mathrm{CCl_4}$ unless otherwise specified at concentrations of approximately 30% by weight and are reported in parts per million. Microanalysis for silicon was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.; all other analyses were performed by Chemalytics, Inc., Tempe, Ariz.

We have not reported analytical or spectral data on the tetracarboxylic acid, as we were unable in some cases to purify these materials. However, spectral data from the crude materials corresponded in all cases to those of the proposed structures.

Tables I and II contain experimental summaries of the tetramethylsilanes and the dianhydrides. In addition we have included a detailed procedure of typical syntheses.

Bis(3,4-dimethylphenyl)dimethylsilane (**2a**).—To a stirred solution of 4-bromo-*o*-xylene (185.1 g, 1 mol) in anhydrous ether (500 ml) was added *n*-butyllithium (424 ml, 1 mol) 2.36 *M* in hexane dropwise at 0° under nitrogen. After a 5-hr reaction period at ambient temperature, dichlorodimethylsilane (60.6 ml, 0.5 mol) was added dropwise. This solution was allowed to stir overnight before the LiCl was removed by filtration and the ether was removed *in vacuo*. Distillation afforded 90.4 g (68%) of **2a**, bp 120–124° (0.29 mm), which solidified on cooling, mp 51–54°. One recrystallization from ethyl acetate afforded pure **2a**, mp 54–56° (lit.[7] mp 54.5–55.5°).

Bis(3,4-dicarboxyphenyl)dimethylsilane Dianhydride (**4a**).—To a refluxing solution of **2a** (26.8 g, 0.1 mol) in pyridine (400 ml) and water (110 ml) was added $\mathrm{KMnO_4}$ (190 g, 1.2 mol) portionwise to maintain a slow reflux. The solution was then refluxed for 1 hr before methanol (10 ml) was added to destroy any unreacted permanganate. After suction filtration of the $\mathrm{MnO_2}$, followed by washing with boiling water, the pyridine was boiled off, adding water when necessary to prevent boiling to dryness. Acidification with 3 *N* HCl to pH 1 gave 30.2 g of crude tetracarboxylic acid **3a**, which was not recrystallized but cyclicized directly as follows.

Crude **3a** (18.2 g) was slowly refluxed for 1 hr with 60 ml of acetic anhydride, taking care to prevent discoloration caused by overheating. Following a vacuum distillation of the solvents, the product was recrystallized from benzene–hexane to afford 9.6 g (45%, based on **2a**) of **4a**, mp 180.5–181°.

Chlorodimethyl(3,4-dimethylphenyl)silane (**7**).—To a solution of 4-bromo-*o*-xylene (80.0 g, 0.43 mol) in anhydrous ether (180 ml) was added dropwise *n*-butyllithium (191 ml, 0.43 mol) 2.25 *M* in hexane at 0° under nitrogen. Following this 3-hr addition period the solution was allowed to warm to ambient temperature for an additional 3-hr period before it was inversely added dropwise to dichlorodimethylsilane (52.4 ml, 0.43 mol). After the usual work-up under anhydrous conditions, distillation afforded 47.6 g (56%) of crude **7**, bp 123–130° (31 mm), $n^{21}\mathrm{D}$ 1.5157. Although this material could not be purified by fractional distillation for a correct elemental analysis, **7** was of sufficient purity to be utilized in the reaction with lithio species (see **8**, **9**, **11**, and **12**): nmr ($\mathrm{CCl_4}$) δ 7.0–7.45 (3 H, m, aryl CH), 2.2 (6 H, s, aryl $\mathrm{CH_3}$), 0.6 (6 H, s, silyl $\mathrm{CH_3}$); ir (neat) 1248, 780 $\mathrm{cm^{-1}}$ (silyl $\mathrm{CH_3}$).

Dimethyl(3,4-dimethylphenyl)(*p*-bromophenyl)silane (**8**).—To a solution of *p*-dibromobenzene (119 g, 0.5 mol) in anhydrous ether (450 ml) at −70° was added *n*-butyllithium (214 ml, 0.5 mol) 2.36 *M* in hexane dropwise. After the solution was stirred at −70° for an additional 6 hr, **7** (100 g, 0.5 mol) was added dropwise and the resultant solution was then allowed to stir overnight at ambient temperature. Following the usual work-up, fractionation afforded 128 g (80%) of **8**: bp 120–124° (0.03 mm);

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(5) R. H. Meen and H. Gilman, *J. Org. Chem.*, **20**, 73 (1955).

(6) V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds," Vol. 1, Academic Press, New York, N. Y., 1965, p 233.

(7) A. V. Topchiev, N. S. Nametkin, C.-L. Gu, and N. A. Leonova, *Dokl. Akad. Nauk SSSR*, 118, 731 (1958); *Chem. Abstr.*, **52**, 11769*i* (1958).

SCHEME IV

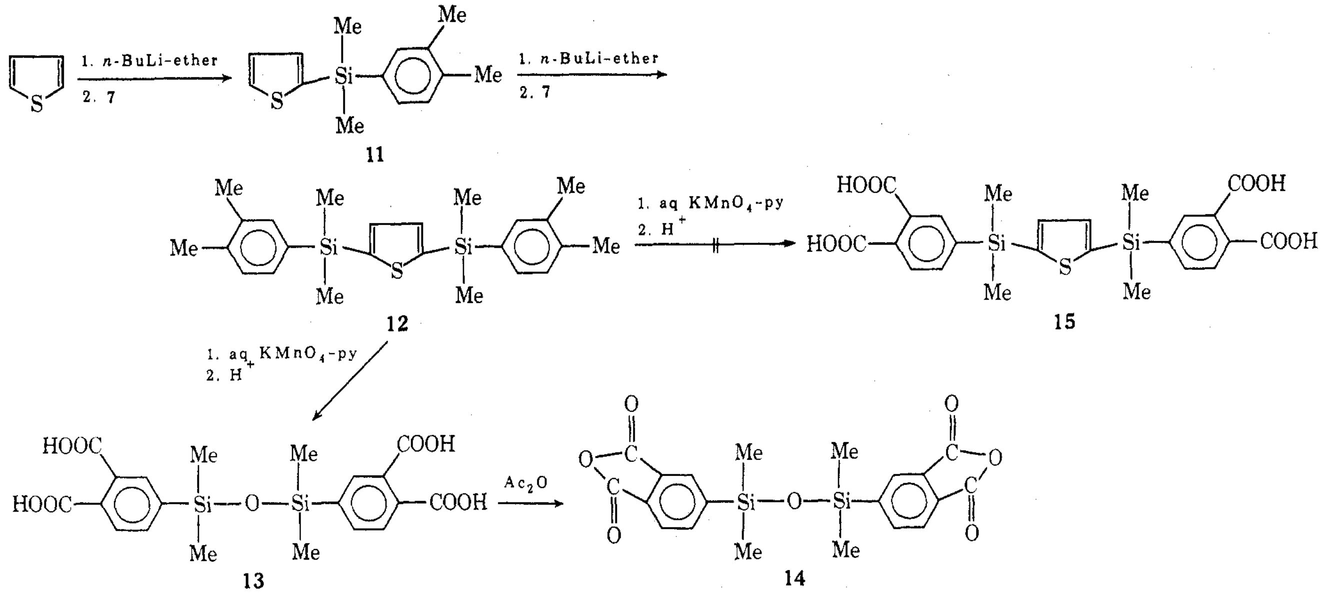

TABLE I[d]

EXPERIMENTAL SUMMARY OF ALKYL ARYL SILANES

Compd	Yield, %	Mp, °C	Bp, °C (mm)	$n^{27}D$	Nmr, δ (assignment)	Ir, cm^{-1} (assignment)
2a	68	54–56[e]			6.9–7.35 (6 H, m, aryl CH), 2.15 (12 H, s, aryl CH_3), 0.45 (6 H, s, silyl CH_3)	1260, 805 (silyl CH_3)[b]
2b	55	50.5–54.5			6.9–7.65 (11 H, m, aryl CH), 2.25 (12 H, s, aryl CH_3), 0.75 (3 H, s, silyl CH_3)	1420, 1088, 695 (silyl phenyl), 1240, 774 (silyl CH_3)[c]
2c	61	100–102			6.65–8.0 (16 H, m, aryl CH), 2.2 (12 H, s, aryl CH_3)	1422, 1098, 698, (silyl phenyl)[c]
5	29		106 (0.005)	1.5645	6.9–7.55 (6 H, m, aryl CH), 2.25 (12 H, s, aryl CH_3), 0.55 (6 H, s, silyl CH_3)	1249, 811 (center of multiplet, silyl CH_3)[b]
9	61	88–89			7.4 (4 H, s, aryl CH), 6.9–7.35 (6 H, m, aryl CH), 2.2 (12 H, s, aryl CH_3), 0.5 (12 H, s, silyl CH_3)	1240, 803 (silyl CH_3)[c]
11	36		107 (0.04)	1.5651	6.9–7.55 (6 H, m, aryl CH), 2.2 (6 H, s, aryl CH_3), 0.5 (6 H, s, silyl CH_3)	1254, 805 (silyl CH_3)[b]
12	77	57.5–58			6.95–7.4[a] (8 H, m, aryl CH), 2.25 (12 H, s, aryl CH_3) 0.55 (12 H, s, silyl CH_3)	1245, 796 (silyl CH_3)[c]

[a] DMSO-d_6. [b] Neat. [c] KBr. [d] Satisfactory analytical data for carbon and hydrogen were reported for all compounds listed in the table except **2a**, which is known. [e] Reference 7.

TABLE II[e]

EXPERIMENTAL SUMMARY OF SILICON-CONTAINING DIANHYDRIDES

Compd	Yield, %[a]	Mp, °C	Nmr, δ (assignment)	Ir,[d] cm^{-1} (assignment)
4a	45	180.5–181	8.05–8.15[b] (6 H, m, aryl CH), 0.8 (6 H, s, silyl CH_3)	1855 and 1765 (anhydride carbonyl), 1240 and 803 (silyl CH_3)
6	19	181.5–182	8.05–8.2[b] (6 H, m, aryl CH), 0.8 (6 H, s, silyl CH_3)	1855 and 1760 (anhydride carbonyl), 1240 and 810 (silyl CH_3)
10	35	199–200.5	7.95–8.35[c] (6 H, m, aryl CH), 7.7 (4 H, s, aryl CH), 0.7 (12 H, s, silyl CH_3)	1845 and 1770 (anhydride carbonyl), 1240 and 790 (silyl CH_3)
14	21	137–138	7.9–8.35[b] (6 H, m, aryl CH), 0.5 (12 H, s, silyl CH_3)	1850 and 1780 (anhydride carbonyl), 1250 and 795 (silyl CH_3), 1088 (siloxane)

[a] Based on the tetramethyl derivative. [b] $CDCl_3$–TMS. [c] Acetone-d_6–TMS. [d] KBr pellet. [e] Satisfactory analytical data for carbon and hydrogen were reported for all compounds listed in the table; in addition **4a** and **14** checked for silicon and **14** contained no sulfur.

$n^{26}{}_D$ 1.5822; nmr (CCl_4) δ 7.35 (4 H, s, aryl CH), 7.05–7.3 (3 H, m, aryl CH), 2.2 (6 H, s, aryl CH_3), 0.5 (6 H, s, silyl CH_3); ir (neat) 1242, 795 cm^{-1} (silyl CH_3).

Acknowledgment.—We gratefully acknowledge the advice and encouragement of Drs. Norman Johnston and Vernon Bell of NASA, Langley Research Center, Hampton, Va. We are particularly grateful to NASA for making this investigation possible *via* NASA Grant 25-005-005-008. We also express appreciation to Dr. W. H. Daudt, Dow Corning Corp., for the organosilicon reagents.

Registry No.—**2a**, 18057-66-4; **2b**, 42297-15-4; **2c**, 42297-16-5; **3a**, 42297-17-6; **4a**, 42297-18-7; **5**, 42297-19-8; **6**, 42297-20-1; **7**, 42297-21-2; **8**, 42297-22-3; **9**, 42297-23-4; **10**, 42297-24-5; **11**, 42297-25-6; **12**, 42297-26-7; **13**, 42297-27-8; **14**, 42297-28-9; 4-bromo-*o*-xylene, 583-71-1; dichlorodimethylsilane, 75-78-5; dichloromethylphenylsilane, 149-74-6; dichlorodiphenylsilane, 80-10-4; 3-bromo-*o*-xylene, 576-23-8; *p*-dibromobenzene, 106-37-6; thiophene, 110-02-1.

Reactions of Alkyl Siliconium Ions under Chemical Ionization Conditions

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The chemical ionization mass spectra of the trimethylsilyl derivatives of various types of compounds have been determined in tetramethylsilane reagent gas. Data are presented showing the occurrence of intermolecular exchange reactions between sample trimethylsilyl groups and reagent gas ions, and involving part or all of the sample trimethylsilyl moiety. The extent of interaction between reagent siliconium ions and sample molecules is strongly influenced by steric effects.

In recent years there has been a growing interest in the chemistry of organosilicon compounds as applied to biochemistry and analytical organic chemistry. Most of this interest stems from the technique of trimethylsilylation, *i.e.*, replacement of labile hydrogens in organic compounds with trimethylsilyl groups for the purpose of application in gas chromatography–mass spectrometry.[1] The mass spectra of trimethylsilyl derivatives frequently exhibit rearrangements explainable by silyl cation attack on an electronegative center.[2] Indicative of the high reactivity of the siliconium center, these rearrangements have been shown to occur both intra- and intermolecularly.[3] We have taken advantage of the latter property by utilizing tetramethylsilane as a reagent gas in chemical ionization mass spectrometry.[4] Siliconium ions were produced at high pressures (0.1–0.5 Torr) from this gas and the resulting chemical ionization mass spectra were usually characterized by the predominance of the $[M + 73]^+$ adduct ions. This corresponds to the addition of a trimethylsiliconium ion $[(CH_3)_3Si]^+$. Other abundant adduct ions have also been observed at $[M + 131]^+$ and $[M + 145]^+$ corresponding to the addition of $(CH_3)_3$-Si–$Si^+(CH_3)_2$ and $(CH_3)_3Si$–$Si^+(CH_3)_2(CH_2)$, respectively.

In our preliminary experiments we were able to obtain chemical ionization mass spectra in tetramethylsilane using microgram quantities of a variety of organic compounds, including steroids and prostaglandins.[4,5] Because of this demonstrated high reactivity of the siliconium ion there exists a good possibility for application to the analysis of biological compounds. In view of the fact that the vapor-phase analysis of many such compounds is conducted with their trimethylsilyl derivatives, it seemed logical to acquire some additional information about any interaction between sample trimethylsilyl groups and alkylsiliconium ions from the reagent, especially since considerable structural information is carried by ions containing the trimethylsilyl moiety.[6]

Results and Discussion

The extent of interaction between the reagent gas and sample is indicated not only by adduct ion formation, but also by the occurrence of silyl group exchange between the reagent gas and the trimethylsilyl group of the sample. Assessment of this interaction was made by using perdeuteriotrimethylsilyl derivatives of the sample.[7] The lability of the sample trimethylsilyl group possibly influences the amount and type of interaction, and as a consequence we investigated the reactions of two general types of trimethylsilyl groups, ethereal and the more labile acidic group. Compounds chosen from the first category included the perdeuteriotrimethylsilyl and/or trimethylsilyl derivatives of *n*-tetradecanol (**1**), *n*-hexadecanol (**2**), *n*-docosanol (**3**), 2-tetradecanol (**4**), 5-hexadecanol (**5**), and 5α-androstan-17β-ol (**6**). Compounds **1–3** contained a primary trimethylsilyloxy function whereas **4–6** had a secondary trimethylsilyloxy group. Compounds in the second category included the derivatives of *n*-tetradecanoic acid (**7**), L-α-glycerophosphate (**8**), phenylphosphonic acid (**9**), and benzylphosphonic acid (**10**).

Exchange Reactions.—Figure 1 shows the chemical ionization mass spectra of the trimethylsilyl derivative of *n*-tetradecanol (**1**, Figure 1a) and of its perdeuteriotrimethylsilyl analog (Figure 1b), obtained in tetramethylsilane reagent gas under similar conditions.

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[1] A. E. Pierce, "Silylation of Organic Compounds," Pierce Chemical Co., Rockford, Ill., 1968.

[2] See, for example, (a) J. Diekman, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, **34**, 3147 (1969); (b) W. P. Weber, R. A. Felix, and A. K. Willard, *J. Amer. Chem. Soc.*, **91**, 6544 (1969); (c) P. D. Woodgate, R. T. Gray, and C. Djerassi, *Org. Mass Spectrom.*, **4**, 257 (1970); (d) E. White, S. Tsuboyama, and J. A. McCloskey, *J. Amer. Chem. Soc.*, **93**, 6340 (1971); (e) W. P. Weber, R. A. Felix, A. K. Willard, and H. G. Boettger, *J. Org. Chem.*, **36**, 4060 (1971), and references cited therein.

[3] (a) D. J. Harvey, M. G. Horning, and P. Vouros, *Chem. Commun.*, 898 (1970); (b) D. J. Harvey, M. G. Horning, and P. Vouros, *Anal. Lett.*, **3**, 489 (1970).

[4] T. J Odiorne, D. J. Harvey, and P. Vouros, *J. Phys. Chem.*, **76**, 3217 (1972).

[5] D. M. Desiderio, B. S. Middleditch, and P. Vouros, *Chim. Chron.*, in press.

[6] J. Diekman and C. Djerassi, *J. Org. Chem.*, **32**, 1005 (1967).

[7] J. A. McCloskey, R. N. Stillwell, and A. M. Lawson, *Anal. Chem.*, **40**, 233 (1968).