

$n^{25}_D$  1.5822; nmr (CCl<sub>4</sub>)  $\delta$  7.35 (4 H, s, aryl CH), 7.05–7.3 (3 H, m, aryl CH), 2.2 (6 H, s, aryl CH<sub>3</sub>), 0.5 (6 H, s, silyl CH<sub>3</sub>); ir (neat) 1242, 795 cm<sup>-1</sup> (silyl CH<sub>3</sub>).

**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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Received July 6, 1973

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.<sup>1</sup> The mass spectra of trimethylsilyl derivatives frequently exhibit rearrangements explainable by silyl cation attack on an electronegative center.<sup>2</sup> Indicative of the high reactivity of the siliconium center, these rearrangements have been shown to occur both intra- and intermolecularly.<sup>3</sup> We have taken advantage of the latter property by utilizing tetramethylsilane as a reagent gas in chemical ionization mass spectrometry.<sup>4</sup> 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  $(CH_3)_3Si-Si^+(CH_3)_2$  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.<sup>4,5</sup> Because of this demonstrated high reac-

tivity 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.<sup>6</sup>

### 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.<sup>7</sup> 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, etheral 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 5 $\alpha$ -androstan-17 $\beta$ -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*- $\alpha$ -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.

(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).

(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.

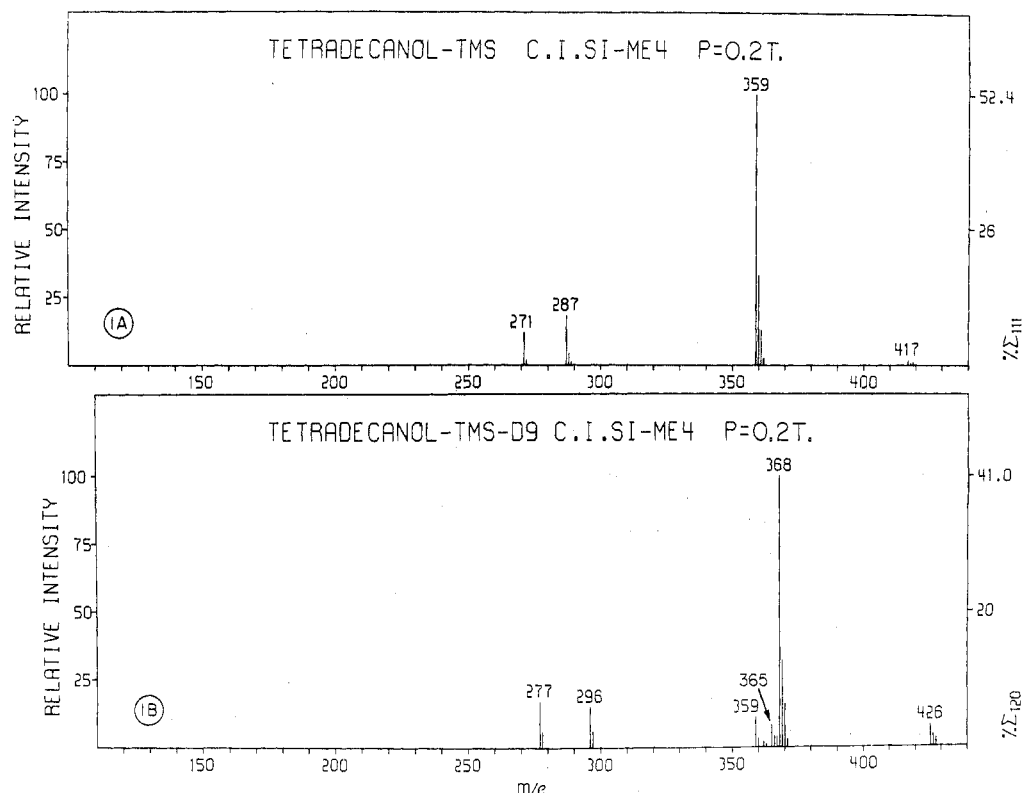
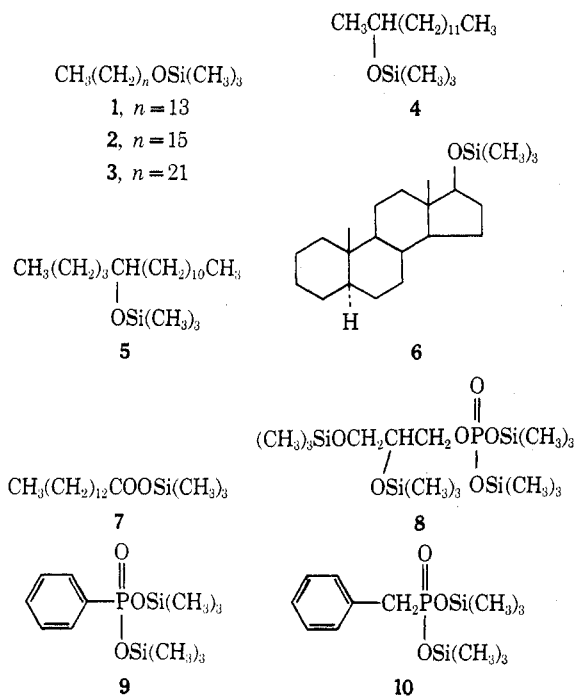


Figure 1.—The chemical ionization mass spectra with tetramethylsilane as the reagent gas of (a) the trimethylsilyl derivative of *n*-tetradecanol and (b) the perdeuteriotrimethylsilyl derivative of *n*-tetradecanol.



The  $[\text{M} + 73]^+$  ion ( $m/e$  359, Figure 1a) carries approximately 80% of the total ion current and a further 14% is carried by the  $[\text{M} + 1]^+$  peak at  $m/e$  287. Elimination of either  $\text{CH}_4$  from  $[\text{M} + 1]^+$  or  $\text{Si}(\text{CH}_3)_4$  from  $[\text{M} + 73]^+$  yields the peak at  $m/e$  271 and both processes were indeed confirmed by metastable defocussing. Finally, the peak at  $m/e$  417 corresponds to the  $[\text{M} + 131]^+$  adduct ion. The spectrum (Figure 1b) of the perdeuteriotrimethylsilyl derivative showed the expected nine mass unit shift in the principal ions in agreement with sample analysis by electron impact

mass spectrometry, which had indicated a perdeuteration greater than 99.9%. In addition, however, peaks were observed at  $m/e$  359 and 365 corresponding to exchange of an entire trimethylsilyl group and of a methyl group, respectively. A much smaller peak at  $m/e$  362 indicated exchange of two methyls of the silyl- $d_9$  function. Similar results were obtained with the other primary trimethylsilyl ethers 2 and 3. This exchange was evident in mass spectra recorded at various ion source pressures ranging from 0.045 to 0.400 Torr.

Table I summarizes the types of exchange observed in the chemical ionization mass spectra of compounds 1–10. The numbers in Table I should be taken as qualitative indicators, rather than precise measurements. In all cases where accurate intensity measurements could be made there was definite evidence for exchange of an entire silyl- $d_9$  function in the  $[\text{M} + 1]^+$  and  $[\text{M} + 73]^+$  adduct ions. It is of interest to note that in the spectra of the secondary trimethylsilyloxy derivatives (4–6) there was a marked decrease in the abundance of the  $[\text{M} + 73]^+$  ions, coupled with a sharp increase in the relative intensity of  $[\text{M} + 1]^+$ . The latter ion in the spectra of 4–6 exhibited exchange of an intact silyl- $d_9$  function but no  $d_9$ -methyl exchange. In the spectra of compounds 7–10, which contain more labile silyl functions, there was a measurable exchange of the entire silyl- $d_9$  groups but no detectable silyl methyl scramble with the reagent gas. Progressively decreasing in relative intensity, multiple silyl- $d_9$  exchanges were evident in compounds containing two or more trimethylsilyl groups (8–10).

The nonthermal nature of the observed group exchanges was confirmed by simulating the ion source conditions (less ionization) in an experiment which in-

TABLE I  
TYPES OF EXCHANGE IN THE  $[M + 1]^+$  AND  $[M + 73]^+$  ADDUCT IONS OF THE PERDEUTERIOTRIMETHYLSILYL ANALOGS OF 1-10<sup>a</sup>

Compd	$[M + 73]$	$[M + 73 - 3]^b$	$[M + 73 - 9]^c$	$[M + 1]$	$[M + 1 - 9]$
1 <sup>d</sup>	100	8	12	14	1
2 <sup>d</sup>	100	9	7	<i>e</i>	<i>e</i>
3 <sup>d</sup>	100	13	9	11	2
4	11		1	100	10
5 <sup>f</sup>	<i>e</i>	<i>e</i>	<i>e</i>	74	3
6 <sup>f</sup>	<i>e</i>	<i>e</i>	<i>e</i>	54	29
7	100		3	7	9
8 <sup>g</sup>	100		24	25	8
9 <sup>g</sup>	100		15	9	1
10 <sup>g</sup>	100		8	6	0.5

<sup>a</sup> All peak intensities normalized to the base peak in the spectrum. The numbers should be treated qualitatively rather than quantitatively. <sup>b</sup> Indicates exchange of one silyl methyl from the perdeuteriotrimethylsilyl derivative. <sup>c</sup> Indicates exchange of the entire silyl-*d*<sub>3</sub> function from the perdeuteriotrimethylsilyl derivative. <sup>d</sup> Exchange of two methyl groups observed in minor amounts. <sup>e</sup> Peak intensities were too low to obtain accurate measurements. <sup>f</sup> Base peak corresponds to elimination of  $(\text{CH}_3)_3\text{SiOH}$  from  $[M + 1]^+$ . <sup>g</sup> Exchange of two silyl-*d*<sub>3</sub> groups observed in the  $M + 73$  adduct ions.

involved heating samples of the perdeuteriotrimethylsilyl derivatives in a closed container in the presence of tetramethylsilane and stainless steel at temperatures ranging from 100 to 120°. The samples were then analyzed by electron impact mass spectrometry, and even after 1 hr at this temperature less than 0.1% exchange of a trimethylsilyl function could be detected. As a comparison it may be noted here that this 1-hr period is obviously orders of magnitude longer than any possible residence time of sample molecules in the ion source. It is thus apparent that the group exchanges summarized in Table I are ionically induced.

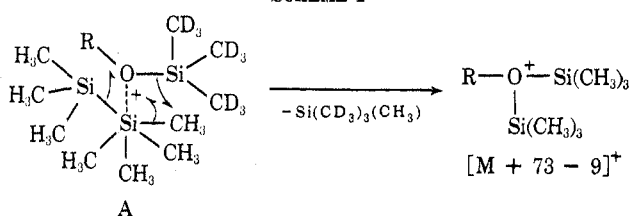
Probably the bulk of the  $[M + 73]^+$  ions are formed by direct addition of the trimethylsilyl cation to the sample molecules. The relatively high pressures used in chemical ionization provide collisional stabilization of the adduct ion. Furthermore, energy dissipation can be effected by equilibration throughout the vibrational modes of the polyatomic systems discussed here. The  $[M + 73]^+$  ion, however, can also be formed by the unimolecular decomposition of activated complexes resulting from the reaction of secondary reagent gas ions with the sample. Metastable defocussing experiments were conducted and indeed confirmed the formation of  $[M + 73]^+$  from adduct ions of the type  $[M + 103]^+$ ,  $[M + 131]^+$ ,  $[M + 145]^+$ , and  $[M + 161]^+$ . This is analogous with the findings of Bursey and coworkers,<sup>8</sup> who studied ion molecule reactions in butanedione utilizing ion cyclotron resonance spectrometry.

In line with this and based on a single collision argument and proper mass balance, a reasonable explanation for the observed exchange would involve participation of the most abundant secondary ion of  $m/e$  161  $[(\text{CH}_3)_7\text{Si}_2]^+$  as shown in Scheme I. The proposed mechanism provides for elimination of tetramethylsilane, a process occurring readily under electron impact in systems possessing adjacent silyl groups as in the case of trimethylsilyl derivatives of phosphates.<sup>9</sup>

(8) M. M. Bursey, T. A. Elwood, M. K. Hoffman, T. A. Lehman, and J. M. Tesarek, *Anal. Chem.*, **42**, 1370 (1970).

(9) D. J. Harvey, M. G. Horning, and P. Vouros, *J. Chem. Soc., Perkin Trans. 1*, 1074 (1972).

SCHEME I



Bonding of the pentavalent silicon of the  $m/e$  161 ion with the  $\text{ROSi}(\text{CD}_3)_3$  oxygen can be justified by the ability of silicon to expand its valence shell and participate in bond formation with its 3d orbitals. In this case the silicon with the expanded valence shell in intermediate A (Scheme I) exists in an octahedral  $\text{sp}^2\text{d}^2$  configuration and forms a bond with the oxygen.<sup>10</sup> The proximity of the various methyl groups in intermediate A can induce intramolecular methyl scramble and elimination of  $\text{Si}(\text{CH}_3)_n(\text{CD}_3)_{4-n}$  (where  $n = 1-4$ ) to give peaks at  $[M + 73]^+$ ,  $[M + 73 - 3]^+$ , and  $[M + 73 - 9]^+$  in compounds 1-3 (Table I). An analogous  $[M + 161]^+$  intermediate can also be attained by considering a mechanism based on the direct reaction of the trimethylsilyl cation with a sample molecule. The  $[M + 73]^+$  adduct ion arising from the latter reaction can then collide with a neutral reagent gas molecule to form an  $[M + 161]^+$ -type ion analogous to A, which subsequently undergoes group exchange in the process of fragmenting to  $[M + 73]^+$ . It is not possible from the present data to distinguish between those two or other mechanisms without the employment of ion cyclotron resonance spectrometry, but the metastable defocussing experiments clearly show the participation of at least the  $[M + 161]^+$  intermediate in the exchange process.

An interesting feature may be noted when examining the further loss of tetramethylsilane from the  $[M + 73]^+$  ion to form the fragment ion of  $m/e$  271 in the spectrum of the trimethylsilyl derivative of 1-tetradecanol (Figure 1a). The shift of  $m/e$  271 to  $m/e$  277 in the spectrum of the perdeuteriotrimethylsilyl derivative (Figure 1b) indicates the nonequivalence of the trimethylsilyl groups in the  $[M + 73]^+$  system. Three possible fragmentation pathways are outlined in Scheme II. While the combined routes a and b seem attractive from Scheme I, the lack of any  $m/e$  271 suggests the likelihood of route c. Thus it is apparent that other alternatives must be considered in addition to the normally conceptualized silicon-oxygen bonding as in Scheme I.

**Stereochemical Effects.**—In most ionic organic reactions in solution steric factors have been shown to play a very significant role. Trimethylsilyl reactions in solution have also followed this pattern and thus it seemed reasonable to investigate steric parameters in gas-phase reactions as well. In compounds containing a secondary trimethylsilyloxy function (4-6) we observed virtually no formation of the  $[M + 73]^+$  adduct ion but instead the spectrum was dominated by the  $[M + 1]^+$  peak. This is exemplified by the spectra of the trimethylsilyl derivatives of 1-hexadecanol and 5-hexadecanol shown in Figure 2. The absence of the  $[M + 73]^+$  ion can be rationalized by the increased

(10) J. F. Klebe, *Accounts Chem. Res.*, **3**, 299 (1970).

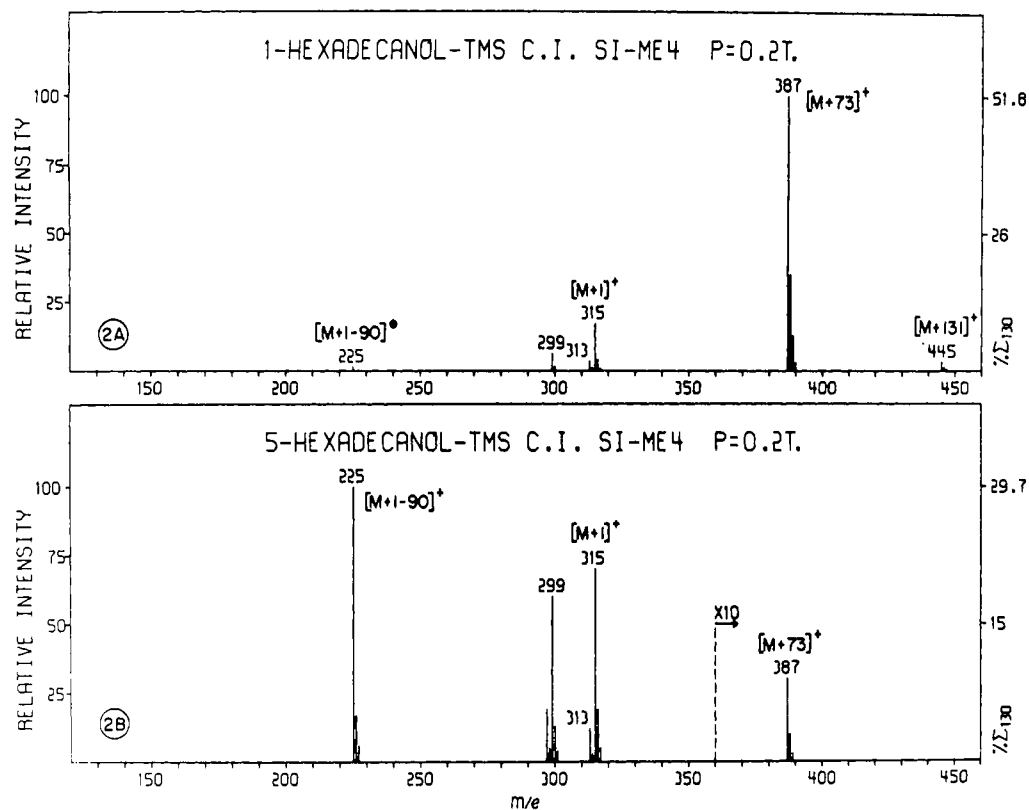
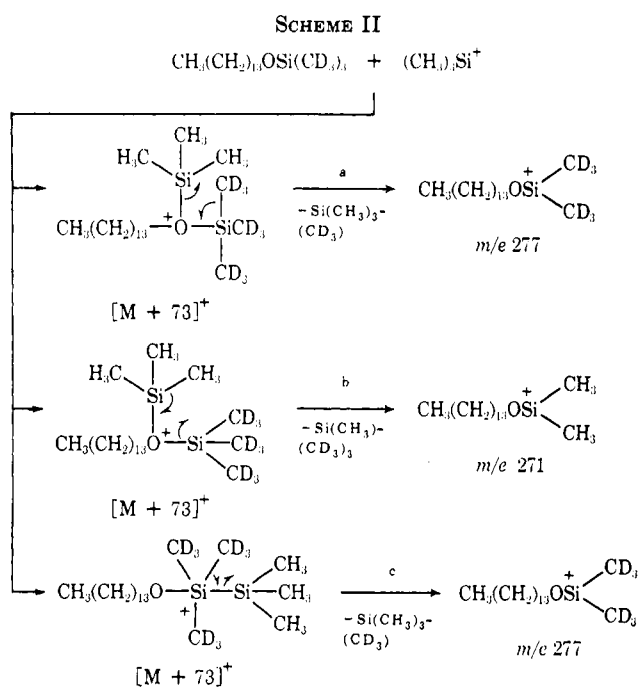


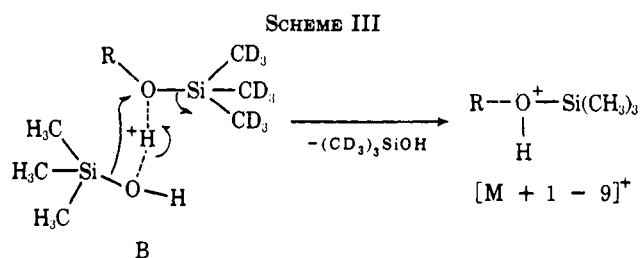
Figure 2.—The chemical ionization mass spectra with tetramethylsilane as the reagent gas of the trimethylsilyl derivative of (a) *n*-hexadecanol and (b) 5-hexadecanol.



steric hindrance, in view of the bulky groups involved in the adduct ion formation. The  $[M + 1 - 90]^+$  peak in the spectrum of the trimethylsilyl derivative of 5-hexadecanol corresponds to elimination of trimethylsilanol from the protonated molecule.

The high relative abundance and, for that matter, even the presence of the intense  $[M + 1]^+$  peak was somewhat puzzling, since sample protonation from the reagent gas ions would require transfer of a methyl hydrogen or possibly of a methylene hydrogen in the case of  $m/e$

131. It is much more likely that the majority of the  $[M + 1]^+$  ions are formed through participation of water impurities present in the system. Reaction of  $(\text{CH}_3)_3\text{Si}^+$  with water yields protonated trimethylsilanol,  $[(\text{CH}_3)_3\text{SiOH}_2]^+$ , which reacts as a Brønsted acid with the sample to give  $[M + 1]^+$ . This hypothesis is supported by the presence of a strong peak at  $m/e$  91 in the spectrum of the reagent gas. It was further confirmed by an experiment in which we introduced  $\text{D}_2\text{O}$  vapor into the system and correlated the ratio of  $[M + \text{H}]^+$  and  $[M + \text{D}]^+$  to that of  $[(\text{CH}_3)_3\text{SiOH}_2]^+$  ( $m/e$  91) and  $[(\text{CH}_3)_3\text{SiOD}_2]^+$  ( $m/e$  93). When the bulky alkyl siliconium ions are unable to react with sterically hindered heteroatoms, protonation from  $[(\text{CH}_3)_3\text{SiOH}_2]^+$  becomes predominant (Scheme III). Intermediate B seems to be of sufficient lifetime



to allow a trimethylsilyl scramble *via* elimination of the stable perdeuteriotrimethylsilanol as shown in Scheme III.

In spite of the low energy release upon protonation by  $[(\text{CH}_3)_3\text{SiOH}_2]^+$  the difference in the steric environment between the primary and secondary trimethylsilyloxy isomers 2 and 4 is sufficient to produce significantly different amounts of fragmentation of the  $[M +$

1]<sup>+</sup> ion. By contrast the methane chemical ionization mass spectra of both isomers are very similar, with the base peak occurring at  $[M + 1 - 90]^+$ . On the other hand the isobutane chemical ionization spectra of **2** and **4** were not informative because of the poor reactivity of the reagent.

### Conclusions

The examples presented above provide new evidence about functional group interactions during ionic vapor-phase reactions of alkyl siliconium ions. The vapor-phase reaction of these ions with sample molecules containing a trimethylsilyl function results in exchange of methyl groups as well as the entire trimethylsilyl group. The extent of intermolecular exchange of either the methyl groups or the entire trimethylsilyl function is in part determined by the acidity of the trimethylsilyl derivative. This indicates that a finite lifetime is probably required for the postulated intermediates to effect methyl group scramble. Recognition of ionically induced trimethylsilyl group exchanges such as the ones reported here is important in analytical studies of trimethylsilyl derivatives, since in the spectra of the latter compounds much of the structural information is carried by ions containing the silyl function. The data presented also point out that stereochemical factors play a significant role in vapor-phase reactions. Unlike proton transfer reactions from  $\text{NH}_4^+$  or  $\text{CH}_5^+$ ,

which are generally not sterically "sensitive", chemical ionization studies with alkyl siliconium ions may provide important information about stereochemical requirements in vapor-phase ionic reactions.

### Experimental Section

Chemical ionization mass spectra were obtained with a modified CEC 21-110B mass spectrometer.<sup>11</sup> All spectra were recorded at ion source pressures of 0.2 Torr, temperatures of 100–135°, a repeller field of 10 V/cm, and ion-accelerating voltage of 8 kV. The total filament emission current was 100  $\mu\text{A}$  and the electron energy was 400 V. The ion beam was focussed for maximum secondary ion intensity at  $m/e$  161. The principal ions in the spectrum of tetramethylsilane at ion source pressure of 0.2 Torr and temperature of 125° occurred at  $m/e$  73 (75%  $\Sigma_{40}$ ), 131 (2.5%  $\Sigma_{40}$ ), 145 (<1%  $\Sigma_{40}$ ), and 161 (18%  $\Sigma_{40}$ ). Trimethylsilyl derivatives of the compounds investigated were prepared according to established procedures.<sup>12</sup> The samples were introduced into the ion source *via* the standard solid probe inlet of the mass spectrometer.

**Acknowledgment.**—Financial support by the National Institutes of Health (GM-13901, GM-16216, and GM-02055) is gratefully acknowledged.

**Registry No.**—1, 6221-89-2; 2, 6221-90-5; 3, 42449-18-3; 4, 42449-19-4; 5, 42449-20-7; 6, 7604-82-2; 7, 18603-17-3; 8, 29881-28-5; 9, 42449-24-1; 10, 18406-56-9.

(11) (a) J. H. Futrell and L. H. Wojcik, *Rev. Sci. Instrum.*, **42**, 244 (1971); (b) I. Djidic, D. M. Desiderio, M. S. Wilson, P. F. Crain, and J. A. McCloskey, *Anal. Chem.*, **43**, 1877 (1971).

(12) E. M. Chambaz and E. C. Horning, *Anal. Biochem.*, **30**, 7 (1969).

## Synthesis, Structure, and Conformation of 10,15-Dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-trimethyl-5H-tribenzo[*a,d,g*]cyclononene and Its Tripropyl Analog

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Received July 3, 1973

Acid-catalyzed condensation of 6-hydroxymethyl-4-methylguaiaicol produced a new cyclic trimer similar to cyclotrimeratrylene (CTV). Its structure was determined by proton magnetic resonance spectroscopy and mass spectrometry to be 10,15-dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-trimethyl-5H-tribenzo[*a,d,g*]cyclononene (**3**). In contrast to CTV, neither **3** nor its triacetate **3a** adopt rigid "crown" conformations normal for compounds of this type; nor do they form inclusion complexes. Similar properties were exhibited by the tripropyl analog, 10,15-dihydro-1,6,11-trihydroxy-2,7,12-trimethoxy-4,9,14-tripropyl-5H-tribenzo[*a,d,g*]cyclononene (**4**) and its triacetate **4a**.

Although originally described as a dimer<sup>1</sup> and subsequently as a hexamer,<sup>2</sup> the condensation product of veratrole with formaldehyde under acid conditions, with the general formula  $(\text{C}_9\text{H}_{10}\text{O}_2)_n$ , has been shown by Lindsey,<sup>3</sup> Erdtman, *et al.*,<sup>4</sup> and others<sup>5–8</sup> to be in fact a trimer ( $n = 3$ ). The trivial name for this trimer, cyclotrimeratrylene (CTV), was coined by Lindsey.<sup>3</sup>

- (1) G. M. Robinson, *J. Chem. Soc.*, **107**, 267 (1915).
- (2) A. Oliverio and C. Casinovi, *Ann. Chim. (Rome)*, **42**, 168 (1952); **46**, 926 (1956).
- (3) A. S. Lindsey, *J. Chem. Soc.*, 1685 (1965); *Chem. Ind. (London)*, 823 (1963).
- (4) H. Erdtman, F. Haglid, and R. Ryhage, *Acta Chem. Scand.*, **18**, 1249 (1964).
- (5) R. C. Cookson, B. Halton, and I. D. R. Stevens, *J. Chem. Soc. B*, 767 (1968); N. K. Anand, R. C. Cookson, B. Halton, and I. D. R. Stevens, *J. Amer. Chem. Soc.*, **88**, 370 (1966).
- (6) B. Miller and B. D. Gesner, *Tetrahedron Lett.*, No. **38**, 3351 (1965).
- (7) T. Sato and K. Uno, *J. Chem. Soc., Chem. Commun.*, 579 (1972); *J. Chem. Soc., Perkin Trans. 1*, 895 (1973).
- (8) A. Goldup, A. B. Morrison, and W. G. Smith, *J. Chem. Soc.*, 3864 (1965).

The stereochemistry of this tribenzocyclononene system has been investigated by several groups.<sup>3–8</sup> On the basis of pmr spectra, CTV adopts a rigid "crown" conformation. This is also the most stable conformation for cyclononatriene,<sup>9</sup> although here interconversion between two equivalent "crown" conformations occurs at room temperature. However, unlike cyclononatriene, CTV does not show any tendency to invert its conformation, even at 200°. <sup>5,6</sup> CTV forms clathrate complexes with a large number of organic compounds<sup>10</sup> suggesting that this molecule must adopt a rigid non-planar conformation.

An alternative conformation proposed in the literature is a flexible "saddle" form, which would be ex-

- (9) P. Radlick and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 344 (1963); K. G. Untch and R. J. Kurland, *ibid.*, **85**, 346 (1963).
- (10) V. Gaglioti, A. M. Liquori, N. Galo, E. Giglio, and M. Scrocco, *J. Inorg. Nucl. Chem.*, **8**, 572 (1958).