Trimethylsilyl Derivatives for the Study of Silicate Structures. Part 5.[1] Trimethylsilylation of Dioptase

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The technique of trimethylsilylation developed earlier has been applied to the mineral dioptase $Cu_6Si_6O_{18}\cdot 6H_2O$. The main products are shown to be $Si_6O_{18}(SiMe_3)_{12}$ and $Si_6O_{17}(SiMe_3)_{10}$ by gas–liquid chromatography and mass spectrometry. Three isomers of $Si_6O_{18}(SiMe_3)_{12}$ and three isomers of $Si_6O_{17}(SiMe_3)_{10}$ are observed in the products, depending on the conditions of trimethylsilylation and the type of chromatographic column employed. When HCl is added to the reaction mixture the predominant product is $Si_6O_{17}(SiMe_3)_{10}$ indicating that the ion $[Si_6O_{18}]^{12-}$ is converted mainly into $[Si_6O_{17}]^{10-}$ in an acidic aqueous medium.

THE technique of trimethylsilylation, described in previous papers of this series,[1-4] has been used mainly for the study of discrete silicate ions of relatively low molecular weight. The trimethylsilyl ($SiMe_3$) derivatives of the ions $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, $[Si_3O_{10}]^{8-}$, and $[Si_4O_{12}]^{8-}$ are sufficiently volatile that they may be readily detected by gas–liquid chromatography (g.l.c.) at temperatures up to *ca.* 210 °C. It has recently been shown [5] that the trimethylsilyl derivatives of the higher ions $[Si_4O_{13}]^{10-}$, $[Si_5O_{15}]^{10-}$, $[Si_6O_{17}]^{10-}$, $[Si_7O_{19}]^{10-}$, $[Si_8O_{21}]^{10-}$, and $[Si_9O_{23}]^{10-}$, of charge 10—, may also be identified in chromatograms up to 250 °C. It was the object of the present work to extend these studies to the detection of silicate ions of charge 12—. For this purpose the mineral dioptase H_2CuSiO_4 was chosen for investigation. *X*-Ray crystallographic studies have shown [6-8] that this mineral

[1] Part 4, J. Götz and C. R. Masson, *J.C.S. Dalton*, 1978, 1134.
[2] Part 3, S. K. Sharma, L. S. D. Glasser, and C. R. Masson, *J.C.S. Dalton*, 1973, 1324.
[3] Part 2, J. Götz and C. R. Masson, *J. Chem. Soc.* (*A*), 1971, 686.
[4] Part 1, J. Götz and C. R. Masson, *J. Chem. Soc.* (*A*), 1970, 2683.
[5] C. R. Masson, W. D. Jamieson, and F. Mason in ' Physical Chemistry of Process Metallurgy: The Richardson Conference,' eds. J. H. E. Jeffes and R. J. Tait, Institute of Mining and Metallurgy, London, 1974, p. 223.
[6] N. V. Belov, V. P. Butuzov, and N. I. Golovastikov, *Doklady Akad. Nauk S.S.S.R.*, 1952, **87**, 953.
[7] H. G. Heide, *Naturwiss.*, 1954, **41**, 402.
[8] H. G. Heide, K. Boll-Dornberger, E. Thilo, and E. M. Thilo, *Acta Cryst.*, 1955, **8**, 425.

is a cyclohexasilicate in which the silicate ions are present exclusively as $[Si_6O_{18}]^{12-}$ rings and that the formula is that of a hydrate $Cu_6Si_6O_{18}\cdot 6H_2O$ with the copper atoms and water molecules distributed around the borders of these rings.

Previous work has shown [9] that trimethylsilylation of dioptase and chromatographic analysis of the products yields a large peak which, under the chromatographic conditions employed, emerged from the packed column at 289 °C. Since this was the major product detected it was tentatively ascribed to the trimethylsilyl derivative of the ion $[Si_6O_{18}]^{12-}$. From a study of the retention temperatures of trimethylsilylated silicates of known structure on wall-coated capillary columns Garzo and Hoebbel [10] concluded that the cyclohexasilicate derivative should have a retention temperature of 330 °C and presented evidence that the peak observed at 289 °C corresponded to a mixture of two isomers of the trimethylsilyl derivatives of the bicyclohexasilicate ion $[Si_6O_{17}]^{10-}$. The molecular structures of these isomers have recently been established by ^{29}Si n.m.r. spectroscopy.[11]

EXPERIMENTAL

Trimethylsilylation.—Dioptase (Reneville, Congo Republic), ground to pass 100 mesh, was employed. The purity of the mineral was checked by *X*-ray diffraction. The reaction was allowed to proceed in a tightly capped glass jar (capacity 60 cm^3) which contained a Teflon-coated magnetic stirring bar.

Method (1). Dioptase (0.3 g), hexamethyldisiloxane (9 cm^3), and isopropyl alcohol (1 cm^3) were stirred together at room temperature, chlorotrimethylsilane (2 cm^3) was added, and stirring was continued for *ca.* 17 h. The hexamethyldisiloxane (upper) layer was removed with a micropipette, clarified by centrifugation, and distilled to a column temperature of 98 °C to remove unchanged $SiMe_3Cl$. The residue was stirred with Amberlyst 15 ion-exchange resin (*ca.* 2 g) for various times to complete the trimethylsilylation.

Method (2). Dioptase (0.3 g), hexamethyldisiloxane (9 cm^3), Pr^{i}OH (6 cm^3), distilled water (4 cm^3), and concentrated HCl (37%, 4 cm^3) were stirred together for *ca.* 20 h at room temperature. The hexamethyldisiloxane layer was removed and treated as described for Method (1).

Gas Chromatography.—Both packed and open tubular (capillary) columns were used for analysis of the extracts.

For the packed column a Hewlett–Packard model 5 750 gas chromatograph, equipped with flame-ionization detector, was employed. Peak areas were measured with a model 3370-A electronic integrator. The column (6 ft × 0.125 in diameter) was of stainless steel and packed with 3% SE-30 on Chromosorb W, AWDMCS. Helium was used as carrier gas. Operating conditions were: injection-port temperature, 325 °C; flame-detector block temperature, 325 °C; helium flow rate, 66 cm^3 min^{-1}; air flow rate, 375 cm^3 min^{-1}; hydrogen flow rate, 28 cm^3 min^{-1}. The column was cooled to 80 °C prior to injection of the sample. After 4—6 min the temperature was increased at 8° min^{-1} until the final temperature, 270 °C, was reached. The temperature was held constant at the final value for the remainder of the chromatogram. Samples for mass-spectrometric examination were collected in glass capillary tubes with the aid of a modified collection vent similar to that described elsewhere.[12]

For the capillary column a Perkin-Elmer model 910 gas chromatograph, equipped with flame-ionization detector and wall-coated all-glass open-tubular column, was used. The column (25 m × 0.27 mm internal diameter) was coated with OV-101. Helium was used as carrier gas. The operating conditions were: (*a*) isothermal operation, injection-port temperature, 300 °C; flame-detector block temperature, 300 °C; injector carrier-gas pressure, 56 lbf in^{-2}; pre-column flow rate, 60 cm^3 min^{-1}; auxiliary carrier-gas inlet pressure, 30 lbf in^{-2}; make-up gas flow rate, 40 cm^3 min^{-1}; air pressure, 50 lbf in^{-2}; hydrogen pressure, 20 lbf in^{-2}; column temperature, 245 °C; (*b*) programmed operation, injection-port temperature, 280 °C; flame-detector block temperature, 280 °C; injector carrier-gas pressure, 58 lbf in^{-2}; pre-column flow rate, 60 cm^3 min^{-1}; auxiliary carrier-gas inlet pressure, 28 lbf in^{-2}; make-up gas flow rate, 40 cm^3 min^{-1}; air pressure, 50 lbf in^{-2}; hydrogen pressure, 20 lbf in^{-2}; temperature program, 70 °C for 6 min, then 8° min^{-1} to 203 °C, then 2° min^{-1} to 240 °C, then 240 °C for remainder of chromatogram.*

Mass Spectrometry.—Spectra were recorded on a Dupont/CEC model 21-110B mass spectrometer as described elsewhere.[5] Samples (2—15 μg) were admitted so that they sublimed directly into the ionization chamber from a temperature-controlled probe, the temperature of which could be adjusted independently of that of the ionization chamber itself. Mass measurements were determined from photoplates (Ionomet vacuum-deposited silver bromide) using a computer-assisted measurement system.[13] The resolution of the mass spectrometer when scanning was *ca.* 1 200. The resolution was adjusted to be *ca.* 20 000 when spectra were recorded on photoplates.

RESULTS AND DISCUSSION

Figure 1 shows the chromatogram of the product of method (1), after treatment with Amberlyst 15 for 168 h, as obtained by means of the packed column. The mass spectra of the material corresponding to peaks 6 and 9—11 are presented in Figures 2—5.

As shown previously,[5] the most structurally informative ions in the spectra of these trimethylsilyl derivatives are those corresponding to the loss of a methyl radical from the molecular ion. For the material corresponding to peak 6 the $[M - 15]^+$ ion is observed at *m/e* 1 155, corresponding to that predicted for the loss of a methyl group from the compound $Si_6O_{17}(SiMe_3)_{10}$. The peak at *m/e* 1 067 is ascribed to loss of $SiPr^i(OH)$ and/or $SiMe_4$ from the $[M - 15]^+$ ion. The most abundant ion (' base peak ') is $[SiMe_3]^+$ at *m/e* 73. Other prominent peaks occur at *m/e* 147, 207, 221, and 281, and

* Throughout this paper: 1 lbf in^{-2} ≈ (9.8 × 4 536)/6.45 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

[9] J. Götz and C. R. Masson, *Compt. rend. IX Congr. Internat. du Verre*, Versailles, 1971, p. 261.

[10] G. Garzo and D. Hoebbel, *J. Chromatog.*, 1976, **119**, 173.

[11] D. Hoebbel, G. Garzo, G. Engelhardt, H. Jancke, P. Franke, and W. Wieker, *Z. anorg. Chem.*, 1976, **424**, 115.

[12] F. F. H. Wu, J. Götz, W. D. Jamieson, and C. R. Masson, *J. Chromatog.*, 1970, **48**, 515.

[13] W. D. Jamieson and F. G. Mason, 25th Annual Conference on Mass Spectrometry and Allied Topics, Washington, D.C., 29th May—3rd June, 1977, paper WP-39, p. 668.

are attributed to $[Me_3SiOSiMe_2]^+$, $[SiH(OSiMe_3)_2]^+$, $[SiMe(OSiMe_3)_2]^+$, and $[SiH(OSiMe_2)(OSiMe_3)_2]^+$ respectively. The peak at *m/e* 1 095 indicates the presence of a small amount of $Si_5O_{15}(SiMe_3)_{10}$ in the sample {*m/e* for $[Si_5O_{15}(SiMe_2)(SiMe_3)_9]^+$ 1 095}.

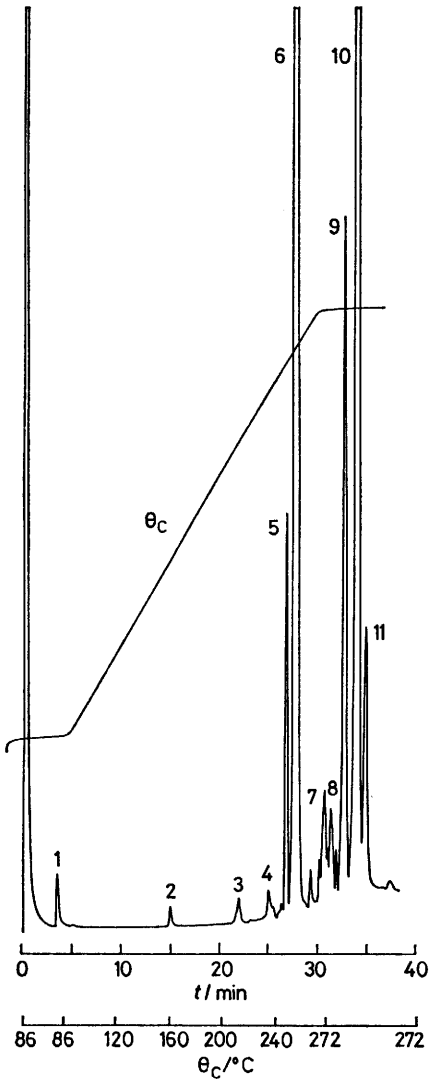


FIGURE 1 Chromatogram of dioptase silylation product using method (1) (Amberlyst treatment for 168 h), with a packed column (SE-30 on Chromosorb W, 6 ft × 0.125 in diameter). Peaks: (1) $SiO_4(SiMe_3)_4$; (2) $Si_2O_7(SiMe_3)_6$; (3) $Si_4O_{12}(SiMe_3)_8 + Si_3O_{10}(SiMe_3)_8$; (5) $Si_6Pr^iO_{17}(SiMe_3)_9$; (6) $Si_5O_{15}(SiMe_3)_{10} + Si_6O_{17}(SiMe_3)_{10}$; (9) $Si_6O_{18}(SiMe_3)_{12}$, isomer (1); (10) $Si_6O_{18}(SiMe_3)_{12}$, isomer (2); (11) $Si_6O_{18}(SiMe_3)_{12}$, isomer (3); (4), (7), and (8) were not identified

The mass spectra of the compounds corresponding to peaks 9—11 are very similar (Figures 3—5). For all the compounds the $[M - 15]^+$ ion occurs at *m/e* 1 317, corresponding to the loss of a methyl radical from the cyclohexasilicate derivative $Si_6O_{18}(SiMe_3)_{12}$. The mass of this ion was determined accurately by photoplate measurements {Found: 1 317.315 7. Calc. for $[Si_6O_{18}(SiMe_2)(SiMe_3)_{11}]^+$: 1 317.314 8}. Peaks 9—11 are therefore attributed to isomers of $Si_6O_{18}(SiMe_3)_{12}$. The main differences in the mass spectra of these three isomers are in the relative intensities of the largest peaks. The peak at *m/e* 1 229 is attributed to loss of $SiPr^i(OH)$ and/or $SiMe_4$ from the $[M - 15]^+$ ion. The most abundant ion is either $[SiMe_3]^+$ at *m/e* 73 or $[Me_3SiOSiMe_2]^+$ at *m/e* 147. Other prominent peaks occur at *m/e* 207, 221, and 281. The small peak at *m/e* 1 155 in the mass spectrum of the material corresponding to peak 9 probably indicates a trace amount of $Si_6O_{17}(SiMe_3)_{10}$ impurity, suggesting incomplete separation on the packed column. Ignoring this peak, the cracking patterns for all the isomers are similar, hence it was not possible to deduce their structures from the mass spectra.

The mass spectrum of the material corresponding to peak 5 showed the $[M - 15]^+$ ion at *m/e* 1 125, consistent with the value predicted for the loss of a methyl radical from the partially trimethylsilylated derivative $Si_6PrO_{17}(SiMe_3)_9$. The mass of this ion was determined accurately by photoplate measurements {Found: 1 125.235 1. Calc. for $[Si_6Pr^iO_{17}(SiMe_2)(SiMe_3)_8]^+$: 1 125.232 6}. Other derivatives of this nature, in which one $SiMe_3$ group is replaced by a Pr^i group, have been reported elsewhere.[5,14] The areas of these peaks in chromatograms generally decrease on prolonged treatment of the extract with Amberlyst 15, a strong acid cation-exchange resin. However, this particular isopropyl derivative appears to be especially stable, and appreciable amounts were present after extended treatment with Amberlyst 15 (see below).

The other peaks in the chromatogram of Figure 1 were identified by their retention times, as established in previous studies. Their identity, and the relative amounts of each product expressed as a percentage of the total peak area (excluding solvent), are presented in the Table. The results show that the $[Si_6O_{18}]^{12-}$ ion in dioptase is not extracted quantitatively as its trimethylsilyl derivative by this procedure but is recovered partly as the bicyclohexasilicate ion $[Si_6O_{17}]^{10-}$. Only very small amounts of derivatives of lower molecular weight were detected in the extract.

Percentage peak areas in chromatograms

Peak number	Derivative [X = $Si(CH_3)_3$]	Method 1 [a]	Method 2 [a]	Method 1 [b]
1	SiO_4X_4	0.5	8.4	0.6
2	$Si_2O_7X_6$	0.2	Trace	0.2
3	$Si_4O_{12}X_8 + Si_3O_{10}X_8$	0.6	3.3	0.4
4	Unknown	0.9	2.0	0.4
5	$Si_6O_{17}X_9(C_3H_7)$	5.9		3.9
6	$Si_5O_{15}X_{10} + Si_6O_{17}X_{10}$	41.3	70.9	41.4
7	Unknown	2.9	Trace	2.2
8	Unknown			
9	$Si_6O_{18}X_{12}$, isomer 1	3.1	9.7	9.6
10	$Si_6O_{18}X_{12}$, isomer 2	35.8	5.6	38.7
11	$Si_6O_{18}X_{12}$, isomer 3	9.0		2.6

[a] 24 hours Amberlyst treatment. [b] 168 hours Amberlyst treatment.

The relative amounts of the various trimethylsilyl derivatives are strongly dependent on the length of time the extract is treated with Amberlyst 15 ion-exchange resin. As in previous studies,[4,15] incompletely tri-

[14] G. Eglinton, J. N. M. Firth, and B. L. Welters, *Chem. Geol.*, 1974, **13**, 125.

[15] C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574.

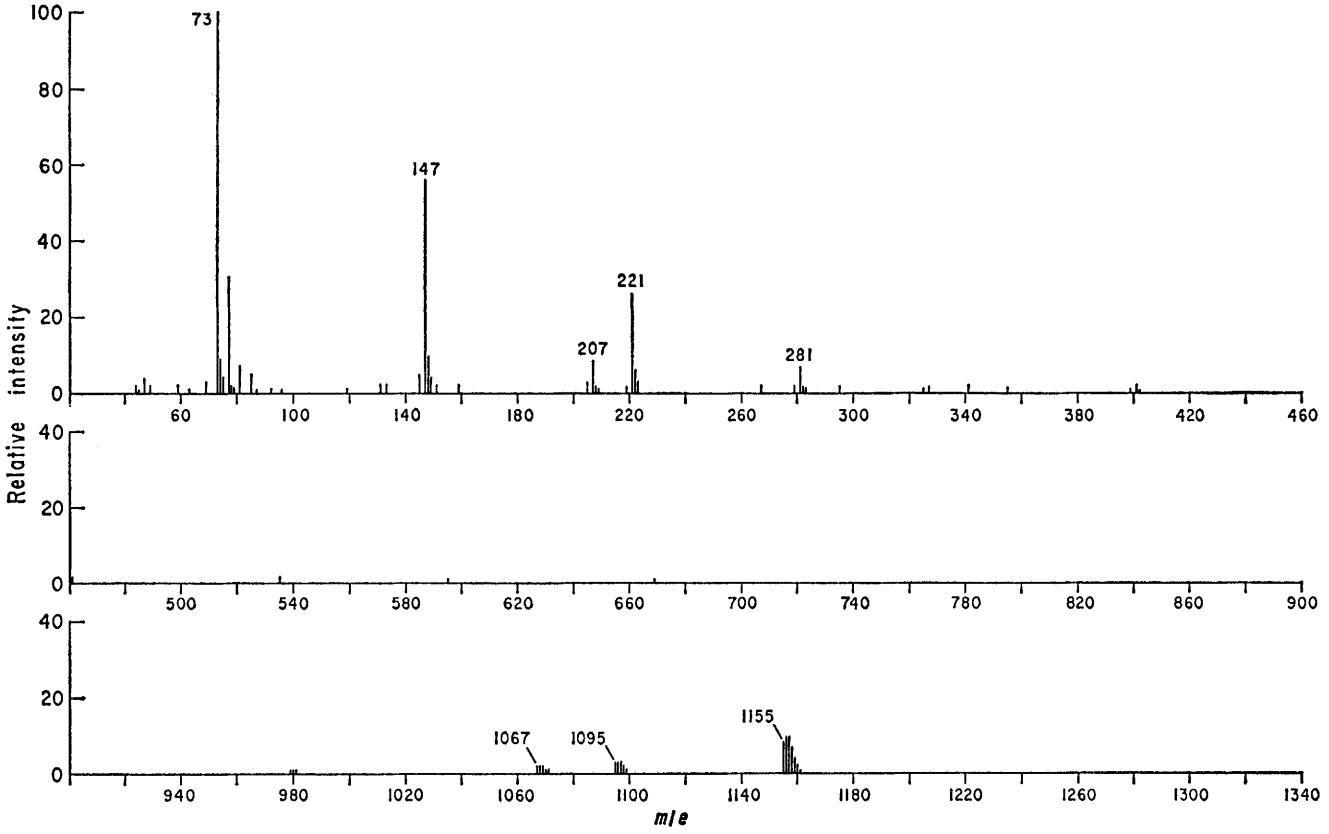


FIGURE 2 70-eV Mass spectrum of $Si_6O_{17}(SiMe_3)_{10} + Si_5O_{15}(SiMe_3)_{10}$ (peak 6, Figure 1)

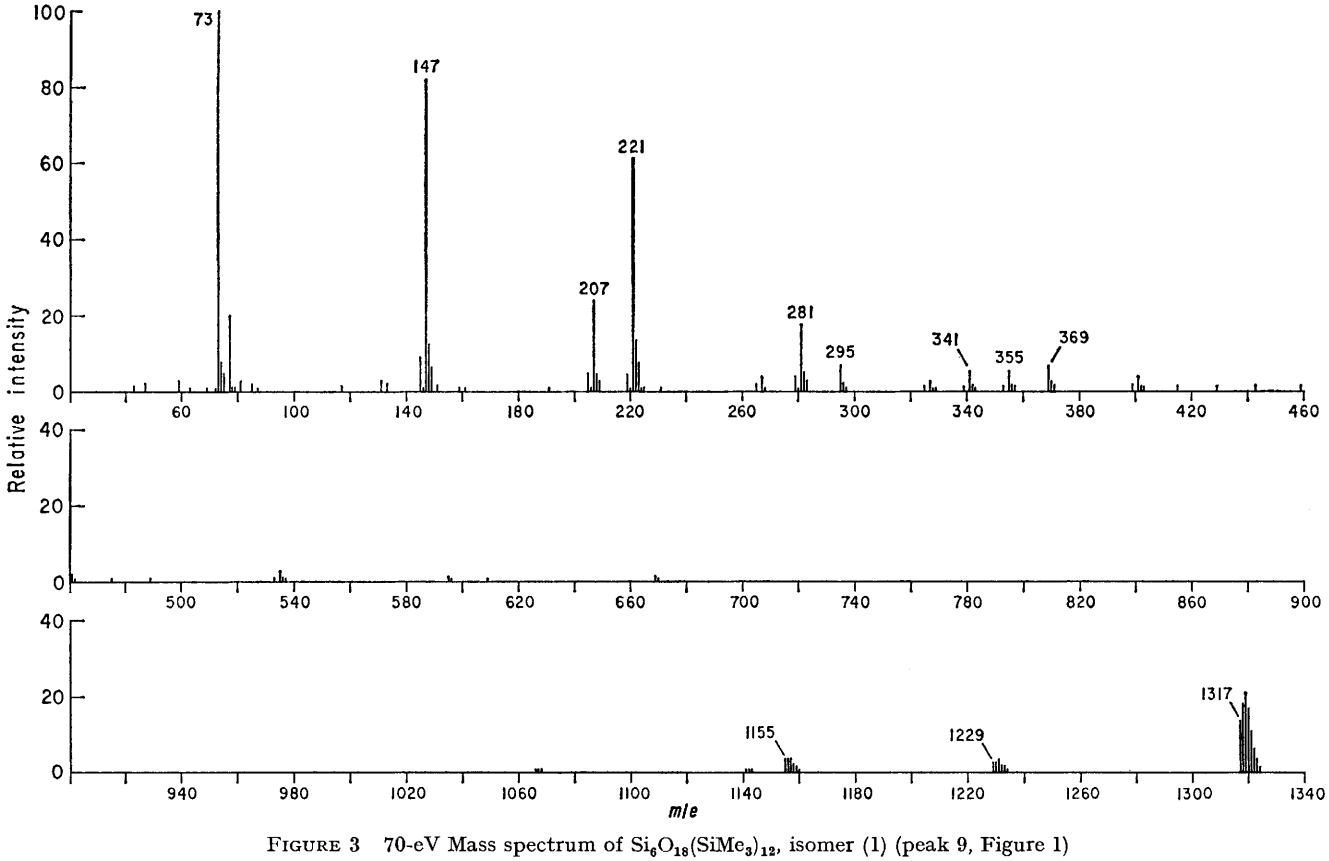


FIGURE 3 70-eV Mass spectrum of $Si_6O_{18}(SiMe_3)_{12}$, isomer (1) (peak 9, Figure 1)

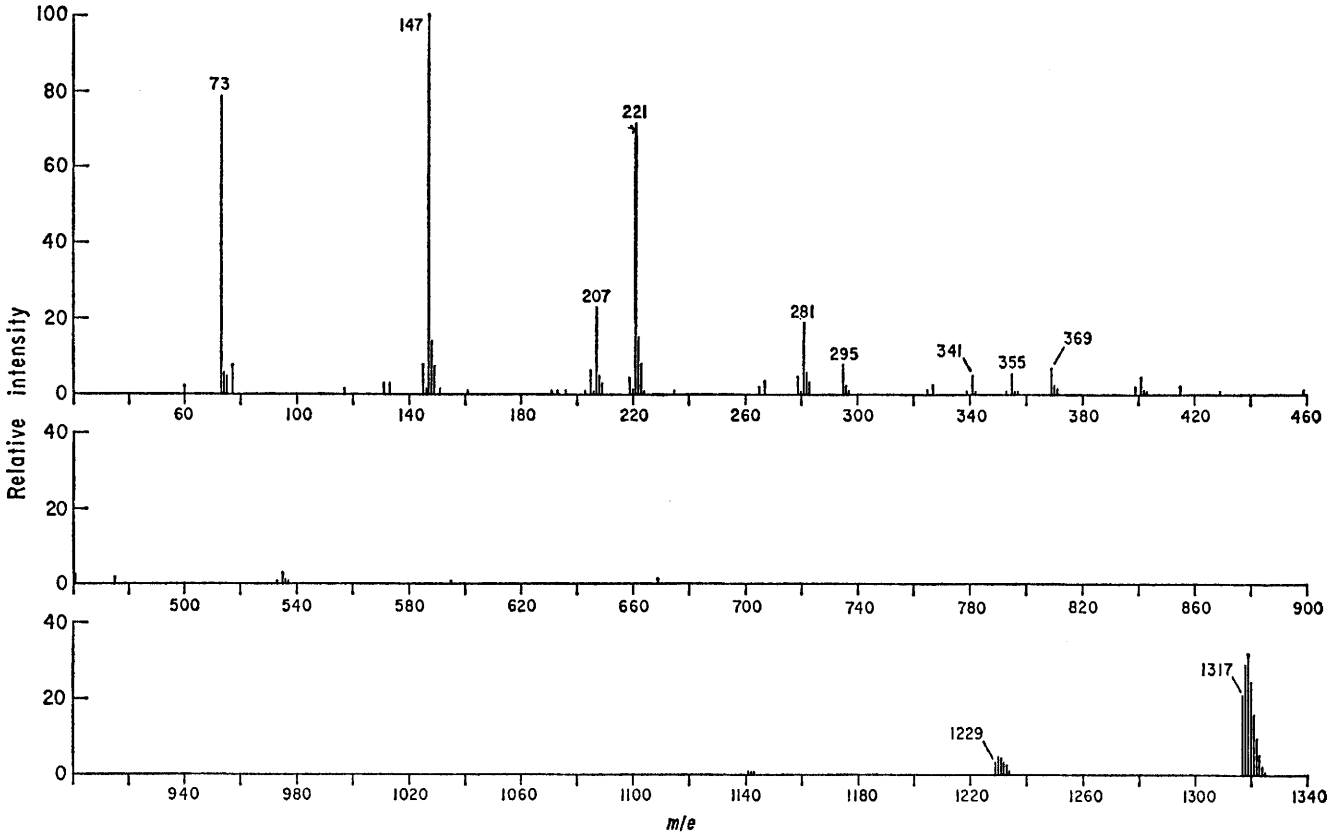


FIGURE 4 70-eV Mass spectrum of $Si_6O_{18}(SiMe_3)_{12}$, isomer 2 (peak 10, Figure 1)

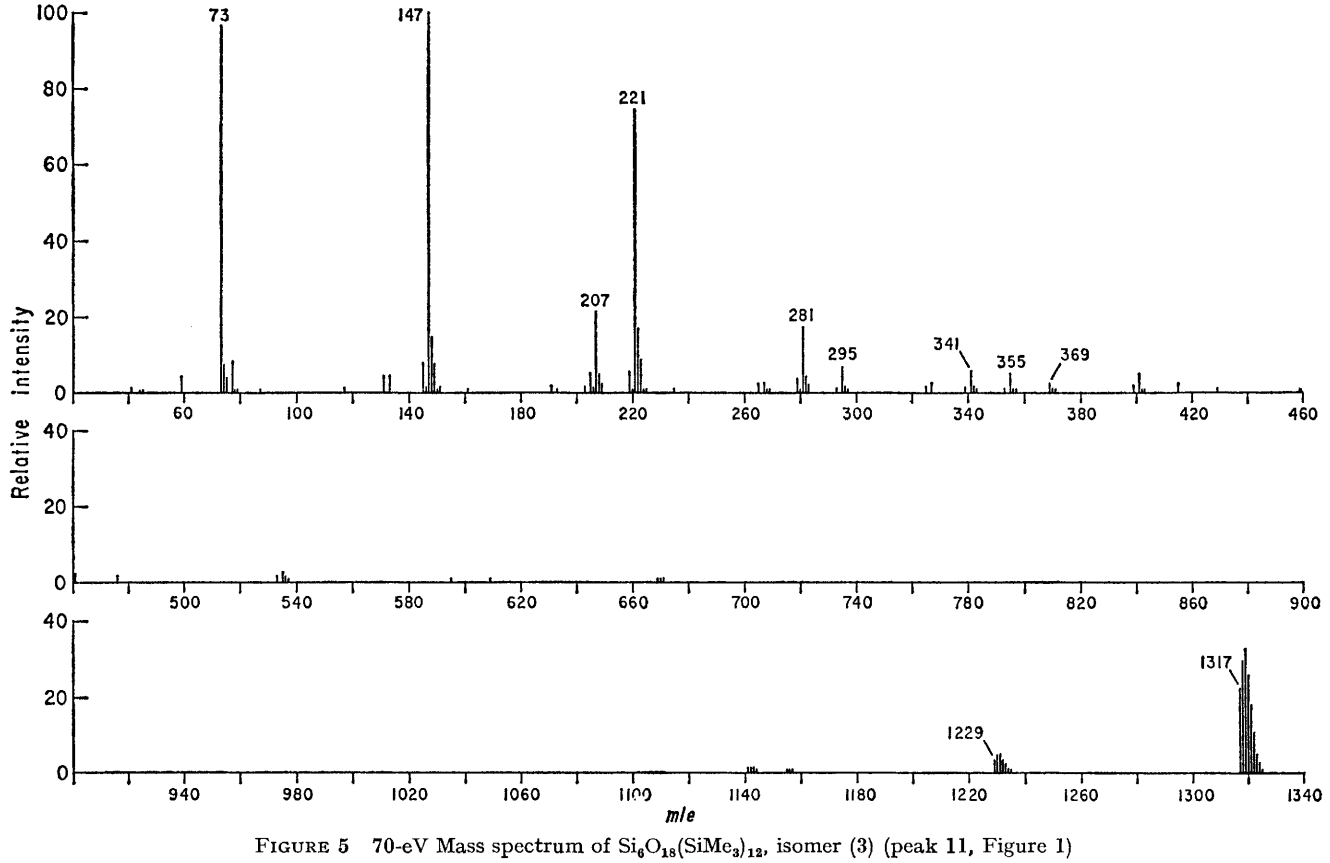


FIGURE 5 70-eV Mass spectrum of $Si_6O_{18}(SiMe_3)_{12}$, isomer (3) (peak 11, Figure 1)

methylsilylated derivatives predominate in the extract before treatment with Amberlyst 15. These have been

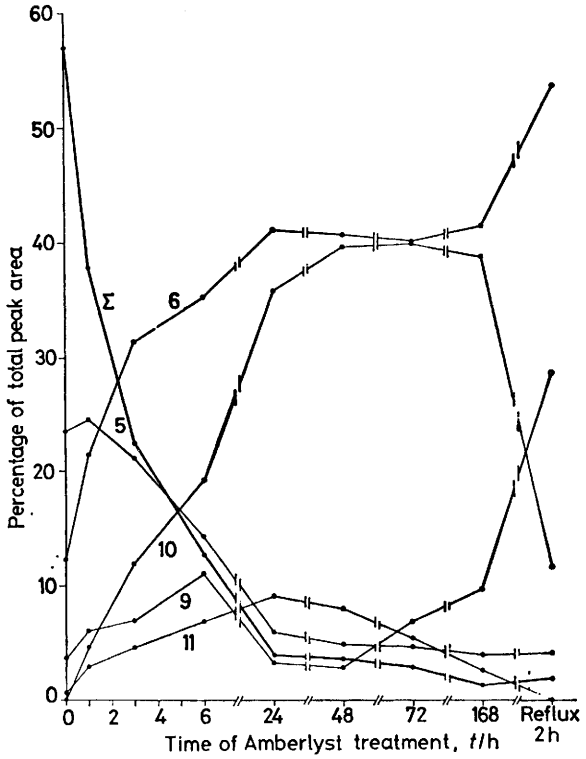


FIGURE 6 Effect of Amberlyst 15 on the dioptase silylation product. Numbers refer to peaks in Figure 1; Σ designates the sum of the peak-area percentages due to unidentified isopropyl and/or hydroxyl derivatives

shown to be hydroxyl and isopropyl derivatives which are gradually converted into their corresponding fully trimethylsilylated derivatives when the extract is stirred with Amberlyst 15 at room temperature. In the case of the more volatile derivatives (derivatives of $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, $[Si_4O_{12}]^{8-}$, and $[Si_3O_{10}]^{8-}$ ions) most of the partially trimethylsilylated derivatives disappear after several hours of treatment with Amberlyst 15. For the higher-molecular-weight derivatives longer treatment with Amberlyst 15 is necessary to complete the trimethylsilylation.

The effect of Amberlyst 15 on the composition of the product of method (1) is shown in Figure 6. Peak-area percentages for the more volatile trimethylsilyl derivatives (of the $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, $[Si_3O_{10}]^{8-}$, and $[Si_4O_{12}]^{8-}$ ions) are not included in Figure 6 for clarity. Derivatives of these ions account for <3% of the total peak area in each case.

Before treatment with Amberlyst 15, unidentified partially trimethylsilylated derivatives [excluding $Si_6Pr^iO_{17}(SiMe_3)_9$, peak 5] accounted for 57% of the total peak area. The sum of the peak-area percentages for these derivatives is designated Σ in Figure 6. After treatment with Amberlyst 15 for 6 h, peaks assigned to these derivatives had decreased to 10.6% of the total peak area, and after 168 h they had diminished to 1.2% of the total peak area. The isopropyl derivative $Si_6Pr^iO_{17}(SiMe_3)_9$ (peak 5) is particularly stable, and significant amounts of it remained after the extract had been in contact with Amberlyst 15 at room temperature for 1 week and then heated under reflux with Amberlyst 15.

Isomer (1) of $Si_6O_{18}(SiMe_3)_{12}$ (peak 9) has a retention time similar to that of an unidentified partially trimethylsilylated derivative, and the two peaks were only partially resolved on the packed column. Peak areas for these two compounds were summed to calculate the peak-area percentages for peak 9 given in Figure 6. During treatment with Amberlyst 15 the two peaks gradually merged into one as the partially trimethylsilylated derivative was converted into another isomer of $Si_6O_{18}(SiMe_3)_{12}$.

In addition to completing the trimethylsilylation reaction, treatment with Amberlyst 15 interconverted isomers of $Si_6O_{18}(SiMe_3)_{12}$. After prolonged treatment,

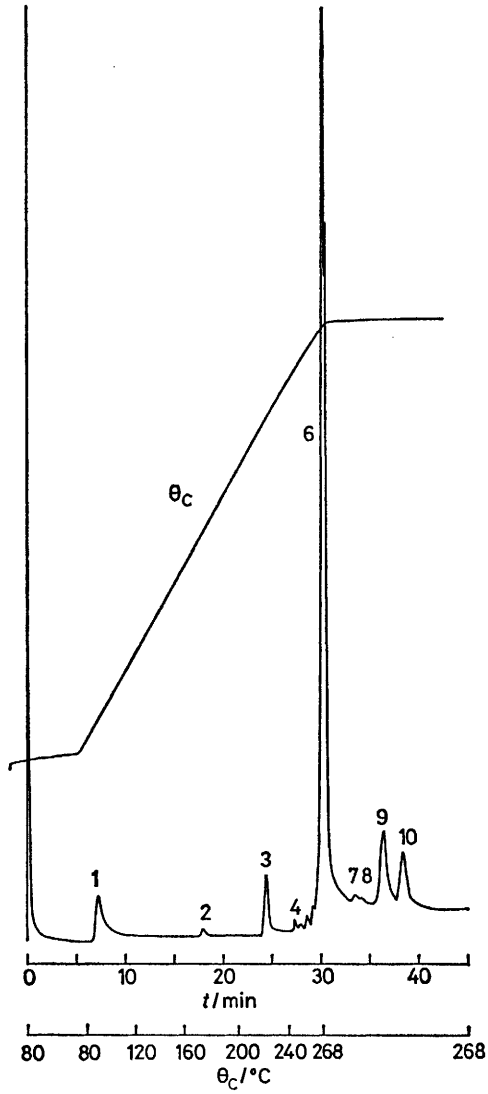


FIGURE 7 Chromatogram of dioptase silylation product using method (2), with a packed column. Peaks as in Figure 1

when most of the partially trimethylsilylated derivatives had disappeared, the relative amount of $Si_6O_{18}(SiMe_3)_{12}$, isomer (3) (peak 11), decreased and the relative amount of isomer (1) (peak 9) increased as the solution remained in contact with Amberlyst 15 at room temperature. Refluxing the solution with Amberlyst 15 changed the pattern considerably, resulting in the breakdown of $Si_6O_{18}(SiMe_3)_{12}$ isomers (2) and (3) (peaks 10 and 11), with a corresponding increase in the relative amounts of isomer (1) and $Si_6O_{17}(SiMe_3)_{10}$ (peaks 9 and 6).

The chromatogram of the products obtained by method (2), which is similar to the original method of Lentz,[15] is shown in Figure 7. Peak areas for this chromatogram are included in the Table. It is noted that addition of HCl further increases the relative yield of the $[Si_6O_{17}]^{10-}$ derivative to 71% of the total peak area and also leads to an increase in the proportion of lower-molecular-weight derivatives. This is accompanied by a corresponding decrease in the yield of the $[Si_6O_{18}]^{12-}$ derivative.

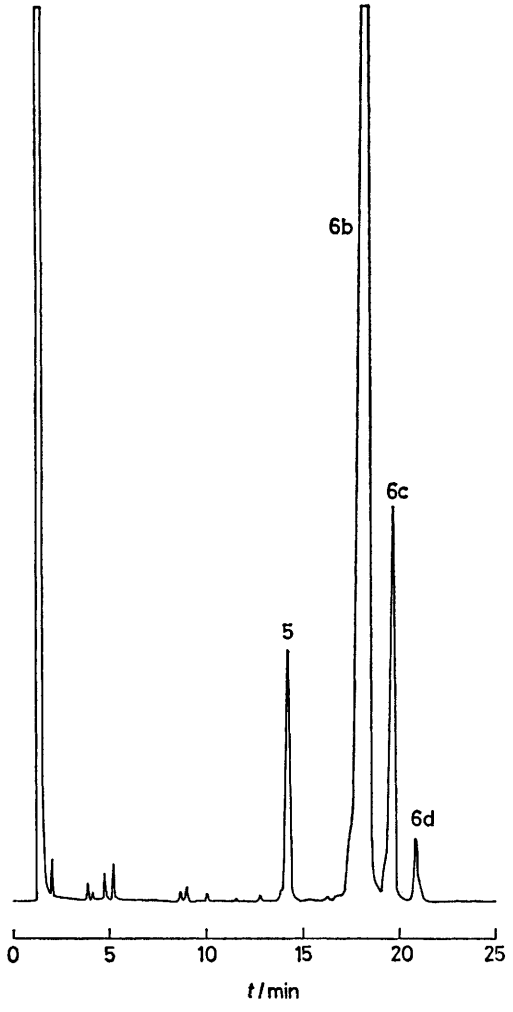


FIGURE 8 Chromatogram of dioptase silylation product using method (1) with a 25-m glass capillary column coated with OV-101. Temperature, 245 °C. Peaks: (5) $Si_6Pr^iO_{17}(SiMe_3)_9$; (6b) $Si_5O_{15}(SiMe_3)_{10}$ + $Si_6O_{17}(SiMe_3)_{10}$; (6c), (6d) isomers of $Si_6O_{17}(SiMe_3)_{10}$

The chromatogram in Figure 7 suggests that the peak due to the $[Si_6O_{17}]^{10-}$ derivative (peak 6) is not single but

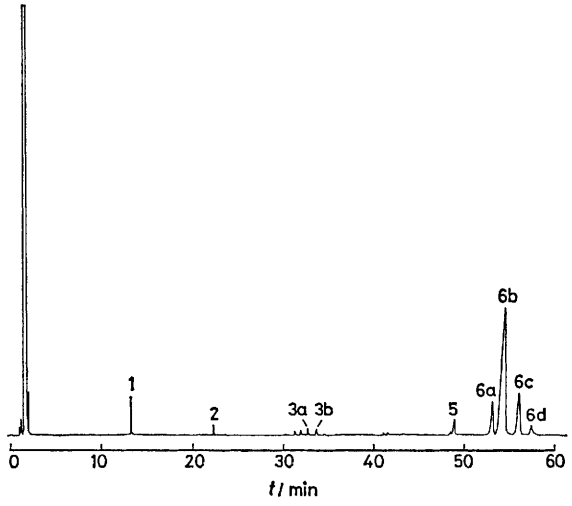


FIGURE 9 Chromatogram of dioptase silylation product using method (1). Column: 25-m glass capillary coated with OV-101. Temperature program: 70 °C for 6 min, 8° min^{-1} to 203 °C, 2° min^{-1} to 240 °C, then held at 240 °C until end of chromatogram. Peaks as in Figure 1 except: (3a) $Si_4O_{12}(SiMe_3)_8$; (3b) $Si_3O_{10}(SiMe_3)_8$; (6a) $Si_5O_{15}(SiMe_3)_{10}$; (6b), (6c), and (6d) isomers of $Si_6O_{17}(SiMe_3)_{10}$

contains at least two components which are partially resolved on the packed column. This peak could be resolved into three components on the glass capillary column with isothermal operation. The isothermal chromatogram at 245 °C for the product of method (1) is shown in Figure 8 and indicates clearly the presence of three separate peaks, designated 6b, 6c, and 6d, for this derivative. Comparison with the chromatogram of the dioptase silylation product published by Garzo and Hoebbel [10] confirms their conclusion that peaks 6b and 6c are due to isomers of the $[Si_6O_{17}]^{10-}$ derivative. The third main peak observed by these workers and tentatively ascribed to a third isomer of the $[Si_6O_{17}]^{10-}$ derivative has a retention time similar to that of $Si_6Pr^iO_{17}(SiMe_3)_9$ (peak 5).

Further resolution of peak 6 was accomplished by temperature-programmed operation of the capillary column. This chromatogram is illustrated in Figure 9 and shows that peak 6 may be resolved into four components, designated 6a, 6b, 6c, and 6d, by this procedure. To confirm that peak 6 separates into four components a sample of this material was collected from the packed column, dissolved in a small amount of pure hexamethyldisiloxane, and injected on to the capillary column with temperature-programmed operation. The resulting chromatogram (Figure 10) clearly shows that peak 6 contains at least four components. Recent studies in this laboratory have shown that $Si_5O_{15}(SiMe_3)_{10}$ is one of the products of trimethylsilylation of PbF_2–PbO–SiO_2 glass. Chromatograms of mixtures of extracts from the trimethylsilylation of dioptase and of PbF_2–PbO–SiO_2 glass have enabled us to assign peak 6a

as $Si_5O_{15}(SiMe_3)_{10}$. Peaks 6b, 6c, and 6d are therefore assigned as isomers of $Si_6O_{17}(SiMe_3)_{10}$.

The derivatives of the $[Si_6O_{18}]^{12-}$ ion were not detected using the glass capillary column due to temperature limitations imposed by the use of OV-101 as wall coating.

It is clear from these results that the presence of water and HCl in the reaction mixture leads to an increase in the relative yields of by-products from the trimethylsilylation of dioptase, and that the most important structural rearrangement which occurs in acidic aqueous medium is conversion of the cyclic ion $[Si_6O_{18}]^{12-}$ into the bicyclic ion $[Si_6O_{17}]^{10-}$. The most direct mechanism by

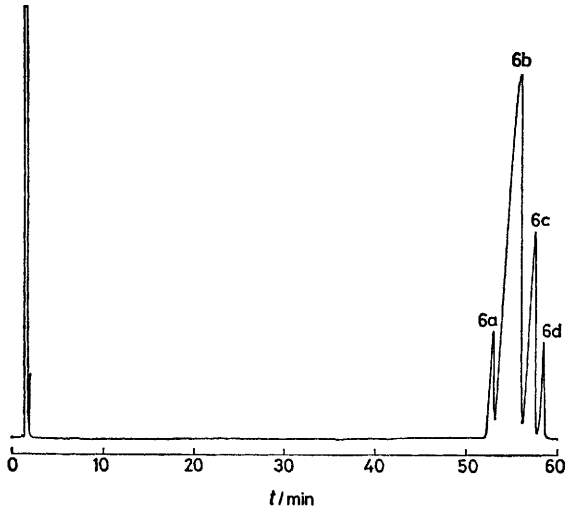
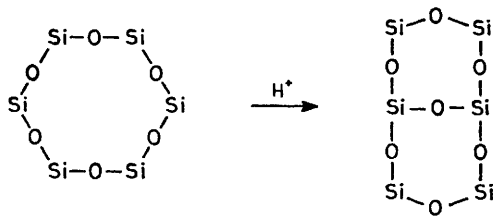


FIGURE 10 Chromatogram of material corresponding to peak 6 (Figure 1) collected from the packed column and redissolved in hexamethyldisiloxane. Details of conditions and peaks as in Figure 9

which this can occur is an acid-catalysed self-condensation to yield a biplanar double-ring structure in which the Si–O–Si bond angles are only slightly altered. It is probable that this represents the structure of the main isomer, peak 6b, in Figures 9 and 10. The presence of additional isomers in the extracts suggests that other



side reactions, associated with hydrolytic cleavage of skeletal Si–O–Si bonds, must also occur to some extent.

Conclusions.—Trimethylsilylation of dioptase under the conditions of method (1) results in the formation of two main products, $Si_6O_{18}(SiMe_3)_{12}$ and $Si_6O_{17}(SiMe_3)_{10}$. Gas chromatograms of the reaction product have shown that three isomers of both derivatives are present. Acidification of the reaction medium results in a marked decrease in the yield of $Si_6O_{18}(SiMe_3)_{12}$ and an increase in the yield of $Si_6O_{17}(SiMe_3)_{10}$. Based on the present results, it is now apparent that the main peak in the chromatogram of the dioptase trimethylsilylation product reported by Götz and Masson [9] was due to $Si_6O_{17}(SiMe_3)_{10}$. This conclusion was also reported by Hoebbel and his co-workers,[10,11] who found that the main products of trimethylsilylation of dioptase under their reaction conditions were two isomers of $Si_6O_{17}(SiMe_3)_{10}$. The fact that the previous workers found no $Si_6O_{18}(SiMe_3)_{12}$ in their product may possibly be due to the more acidic reaction conditions they employed.

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