Esterification of Partially Trimethylsilylated Derivatives of Hemimorphite

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Partial trimethylsilyl derivatives have been prepared from hemimorphite, $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, by direct trimethylsilylation and analysed by means of combined gas–liquid partition chromatography–mass spectrometry. Silanol groups of the hemimorphite which are not trimethylsilylated are esterified by the alcohol used as the organic solvent in the trimethylsilylating reagent.

THE direct trimethylsilylation of silicates reported by Götz and Masson [1,2] is a powerful chemical method for structural studies of some types of silicates. In this method the trimethylsilylating reagent is a mixture of hexamethyldisiloxane, chlorotrimethylsilane, and isopropyl alcohol.

Hemimorphite, $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, is easily decomposed by HCl generated by the reaction of $SiMe_3Cl$ with the water present in hemimorphite [equation (1)].

$$SiMe_3Cl + H_2O \longrightarrow SiMe_3(OH) + HCl \qquad (1)$$

Silanol groups in the acid-decomposed hemimorphite are trimethylsilylated by $SiMe_3Cl$ or trimethylsilanol. The resulting trimethylsilyl derivatives show multiple peaks in gas chromatography because of the presence of incompletely silylated derivatives.[1] However, there have been no studies on the latter derivatives.

The reaction of hemimorphite with a trimethylsilylating reagent containing ethylene glycol in place of Pr^iOH yielded a viscous ' silicate-organic copolymer '[3] as a result of condensation between unsilylated silanol groups and ethylene glycol. The possibility of esterification of ' untrimethylsilylated ' silanol sites ($\equiv$Si–O–H) with the alcohol component of the trimethylsilylating reagent has not been studied. Thus, the purpose of the present study was to investigate the presence of partial trimethylsilyl derivatives from hemimorphite whose residual silanol groups were condensed with methanol or isopropyl alcohol from the trimethylsilylating reagent.

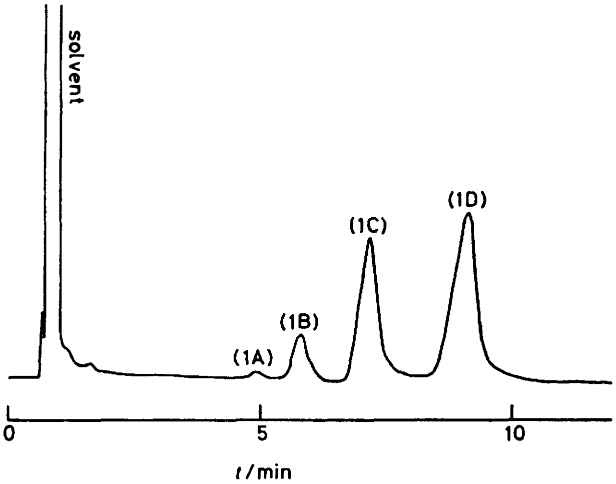

FIGURE 1 Gas chromatogram of trimethylsilyl derivatives from hemimorphite (organic solvent, Pr^iOH)

EXPERIMENTAL

Materials.—Hemimorphite, $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$, from Durango, Mexico, was used. The well developed crystals were hand-picked and ground to pass a 100 mesh sieve. Hexamethyldisiloxane, $Me_3SiOSiMe_3$, was obtained by the hydrolysis of chlorotrimethylsilane followed by a single distillation (100 °C). All of the organic solvents were reagent grade chemicals.

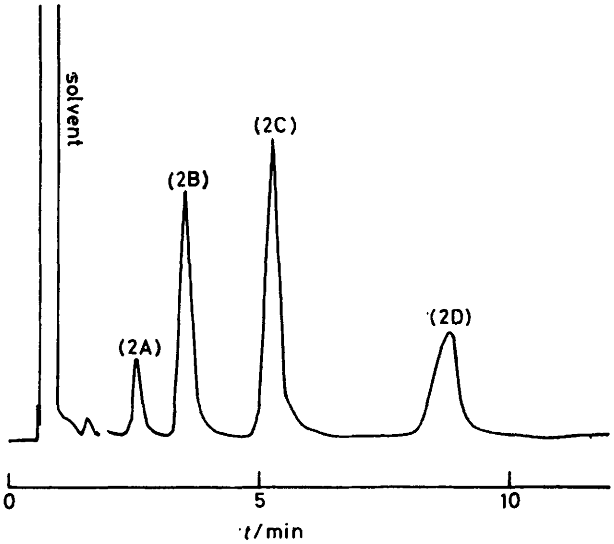

FIGURE 2 Gas chromatogram of trimethylsilyl derivatives from hemimorphite (organic solvent, MeOH)

Trimethylsilylation.—Trimethylsilylation of hemimorphite was carried out according to the direct method of Götz and Masson.[1] However, the amounts of reactants used (hemimorphite, 0.25 g; $SiMe_3Cl$, 2.5 cm^3; hexamethyldisiloxane, 4.5 cm^3; and organic solvent, 0.5 cm^3) were half those described previously. The organic solvents were methanol, isopropyl alcohol, acetone, and ethyl methyl ketone. The crude products were not treated with Amberlyst 15.

Analytical Procedures.—The trimethylsilylated derivatives were analysed by means of gas–liquid partition chromatography (g.l.p.c.). Chromatographic conditions were as follows: Shimadzu GC–2C; stainless-steel column (length 2.25 m, internal diameter 3 mm) packed with SE–30 5% Shimalite W (60—80 mesh); oven temperature 160 °C, injection temperature 260 °C; carrier gas (hydrogen) flow rate 20 cm^3 min^{-1}.

Combined g.l.p.c.–mass spectrometric studies were conducted with a Hitachi M–52 gas chromatograph–mass spectrometer using an ionizing energy of 20 eV.† The ion-

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† Throughout this paper: 1 eV $\approx$ 1.60 $\times$ 10^{-19} J.

source block was maintained at 200 °C and the molecular separator at 260 °C. The g.l.p.c. column consisted of coiled glass (length 2 m, internal diameter 3 mm) packed with 5% OV-17. The column was operated isothermally. The carrier gas was helium (0.4 kg cm^{-2}).

The 100-MHz ^{1}H n.m.r. spectra were recorded with a JEOL JNM PS-100 spectrometer using CCl_4 as solvent and tetramethylsilane as standard. Infrared spectra were obtained in CCl_4 solution with a Shimadzu IR-400 spectrometer.

RESULTS AND DISCUSSION

The yields of the trimethylsilylated derivatives were 0.13 g (in case of methanol as solvent) and 0.15 g (isopropyl alcohol). Figure 1 shows the chromatogram of the trimethylsilylated product obtained by the reaction between hemimorphite and the trimethylsilylating reagent containing Pr^{i}OH. Multiple peaks were recorded, which agreed with the data from Götz and Masson.[1] The chromatogram in the case of MeOH is shown in Figure 2. Multiple peaks were also found here, but at relatively lower retention times except for the peak due to the fully silylated dimeric derivative. These findings indicate that the nature of the partial trimethylsilyl derivatives differed with the alcohol used in the trimethylsilylating reagent.

Mass Spectra of the Components separated by G.L.C.—The trimethylsilylated products were analysed by means of combined gas chromatography–mass spectrometry.

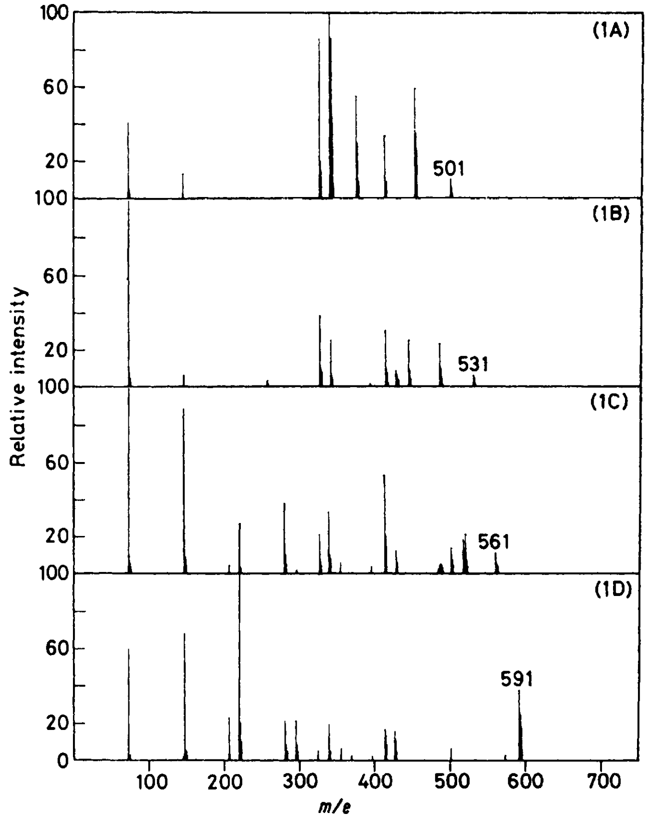


FIGURE 3 Mass spectra (20 eV) of the labelled components in Figure 1

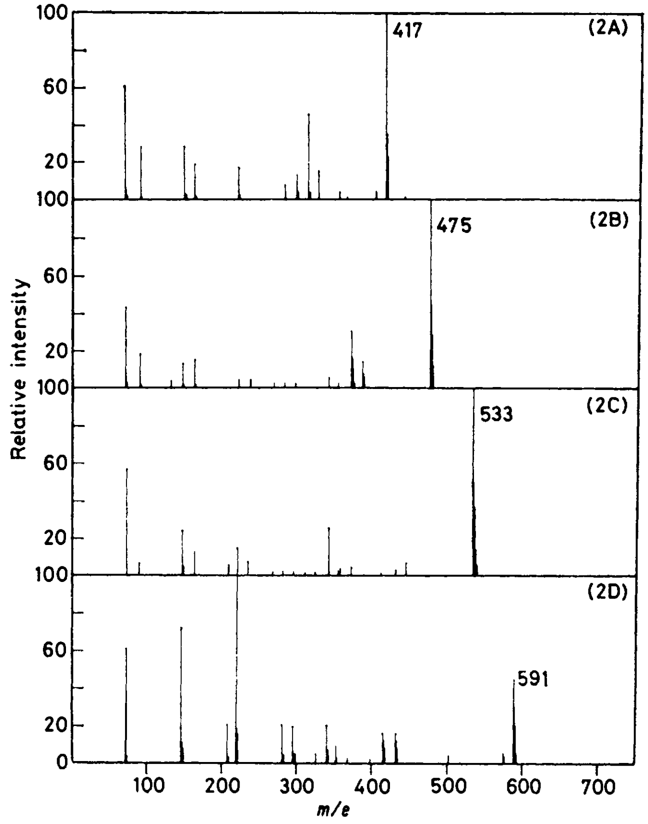


FIGURE 4 Mass spectra (20 eV) of the labelled components in Figure 2

Mass spectra of the components separated by g.l.c. are given in Figures 3 (Pr^{i}OH) and 4 (MeOH). The fragments at *m/e* 73 and 147 were found in almost all the spectra and they are due to $[SiMe_3]^+$ and $[Me_3SiOSiMe_2]^+$, respectively.[4]

The spectrum of species (1D) was identical with that of (2D). It was apparent that the largest peak at *m/e* 591 was due to $[Si_2O_7(SiMe_3)_6 - Me]^+$. Although the molecular-ion peaks could not be found for these derivatives, the fragment peaks at $[M - 15]^+$ were pronounced and were significant for the structure determination. Similar phenomena have been reported by Wu *et al.*[4] From peak (1D) to (1A), the largest $M - 15$ peaks between *m/e* 591 and 501 were each separated by 30 mass numbers ($SiMe_3 - CHMe_2 = 30$). A similar trend between *m/e* 591 and 417 but with a separation of 58 mass numbers ($SiMe_3 - Me = 58$) was observed in the spectra from (2D) to (2A). These results suggest that the components of (1A), (1B), and (1C) are tri-, di-, and mono-isopropyl-substituted trimethylsilyl derivatives, respectively, and that similar methyl-substituted trimethylsilyl derivatives correspond to the components from (2A) to (2C). The structural formulae and molecular weights are summarized in the Scheme. Although tetra- and penta-alkyl-substituted partial trimethylsilylated derivatives could not be detected under the present reaction conditions, the preparation of their derivatives may be possible and they will appear at

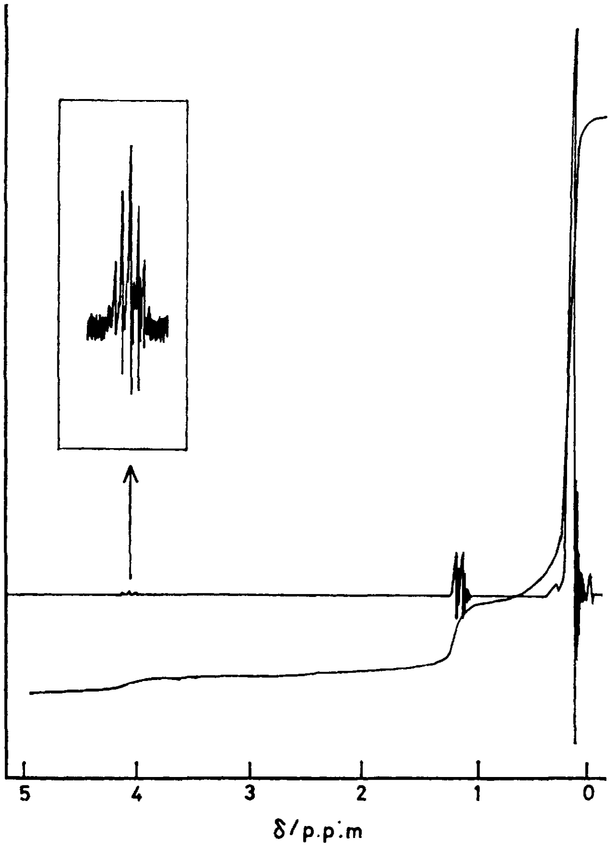


FIGURE 5 Hydrogen-1 n.m.r. spectrum of component (1C)

lower retention times and in lower yields on a gas chromatogram.

Identification of the Component (1C) *obtained by Preparative Thin-layer Chromatography* (*T.L.C.*).—The crude trimethylsilyl products in the case of $\mathrm{Pr^iOH}$ were separated by t.l.c. The chromatographic conditions were as reported by Hoebbel and Wieker.[5] Component (1C) was obtained by preparative t.l.c. and its purity was checked by g.l.c. [Components (1A) and (1B) could not be obtained by preparative t.l.c. because they remained near the starting point in t.l.c.] The 100-MHz ^{1}H n.m.r. spectrum of this component is shown in Figure 5. Proton signals attributed to CH_3 in $SiMe_3$ (δ 0.12), CH_3 in $CHMe_2$ (1.16), and CH in $CHMe_2$ (4.10) p.p.m. were apparent and the integrated values indicated that the proton ratio of these signals was *ca.* 45 : 6 : 1. Figure 6 shows the i.r. spectra of (1C) and (1D). Both of the spectra showed absorption bands due to trimethylsilyl groups [2 960 and 2 890 cm^{-1}, $\nu(CH_3)$; 1 410 and 1 255 cm^{-1}, $\delta(CH_3)$; 1 070 cm^{-1}, ν(Si–O–Si)]. In the i.r. spectrum of (1C), bands due to $\delta(CH_3)$ arising from $CHMe_2$ were also found at 1 370 and 1 380 cm^{-1}, indicating the presence of isopropyl groups. The C (37.5%) and H (9.3%) contents of (1C) were in good agreement with the theoretical values (C, 37.5; H, 9.1%) for mono-alkyl-substituted $\mathrm{Si_2Pr^iO_7(SiMe_3)_5}$.

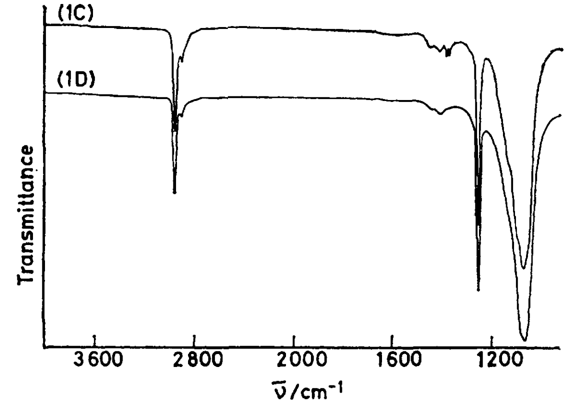


FIGURE 6 Infrared spectra of components (1C) and (1D)

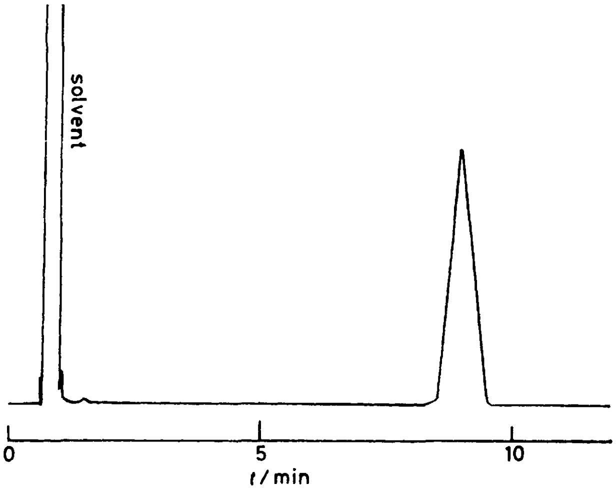
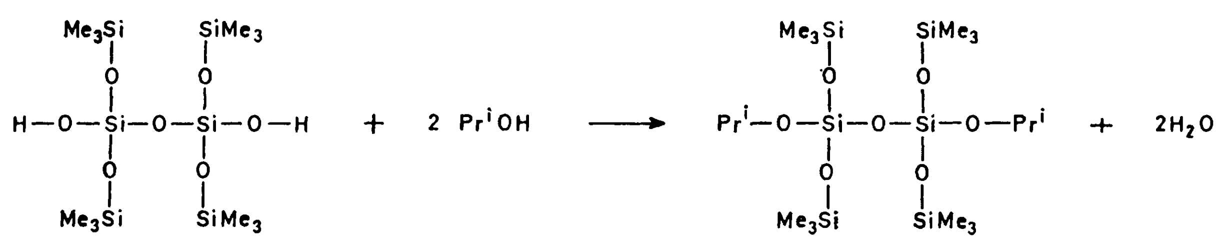


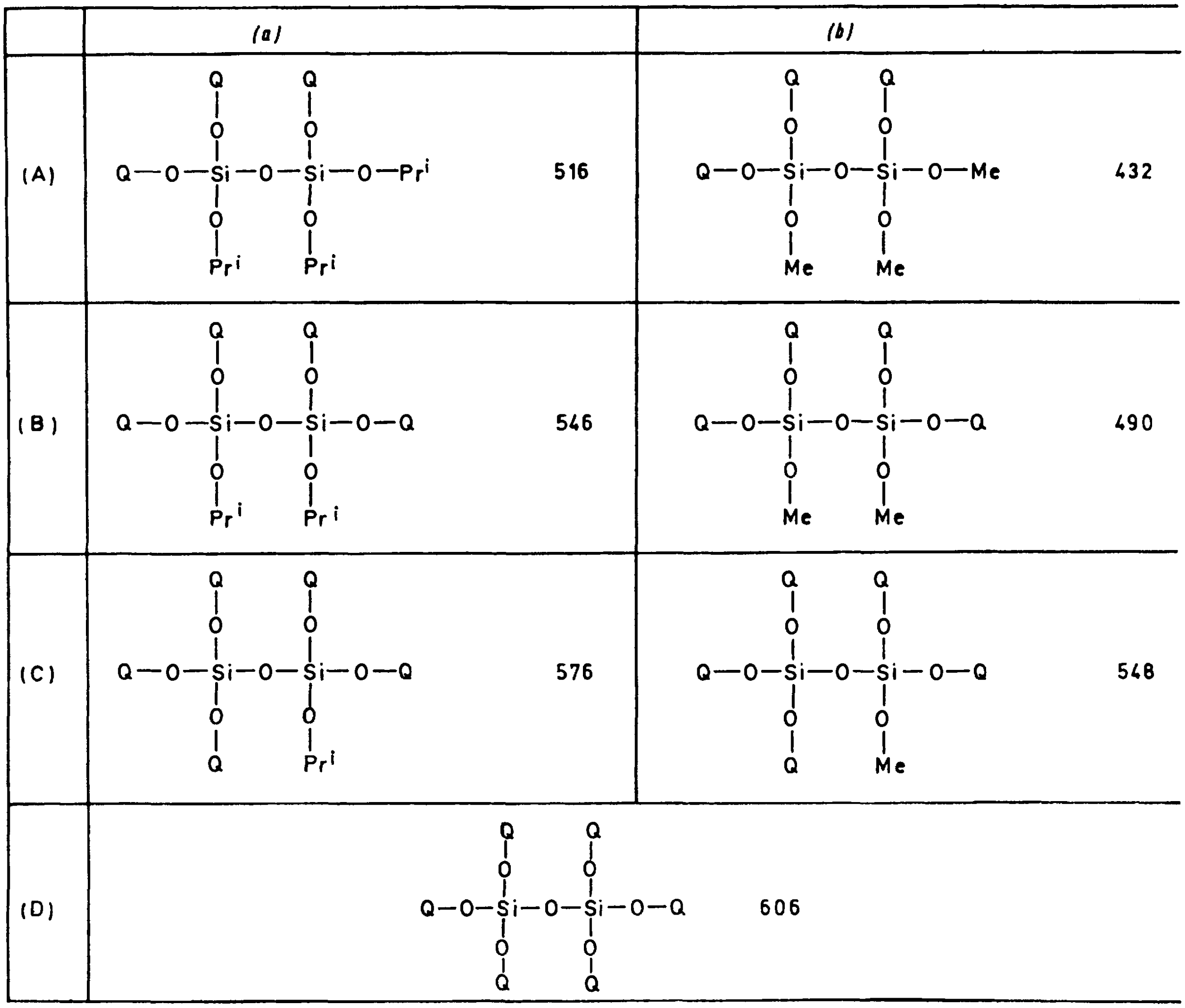
FIGURE 7 Gas chromatogram of trimethylsilyl derivatives from hemimorphite (organic solvent, acetone)

From the results described above it can be concluded that the partial trimethylsilyl products contained one, two, and three alkyl groups formed from the esterification of silanol groups which had not been trimethylsilylated, and the reaction may be expressed as in equation (2).



$$\mathrm{H{-}O{-}Si(OSiMe_3)_2{-}O{-}Si(OSiMe_3)_2{-}O{-}H} + 2\,\mathrm{Pr^iOH} \longrightarrow \mathrm{Pr^i{-}O{-}Si(OSiMe_3)_2{-}O{-}Si(OSiMe_3)_2{-}O{-}Pr^i} + 2\mathrm{H_2O} \qquad (2)$$

Acetone or Ethyl Methyl Ketone as the Organic Component of the Trimethylsilylating Reagent.—Figure 7



SCHEME Structural formulae and molecular weights of partial trimethylsilyl derivatives from hemimorphite. Organic component: (*a*) Pr^iOH, (*b*) MeOH. Q = $SiMe_3$

shows the gas chromatogram of the trimethylsilyl derivatives obtained by the reaction of hemimorphite with a trimethylsilylating reagent containing acetone or MeCOEt as the organic solvent. Only a singlet peak due to $Si_2O_7(SiMe_3)_6$ could be detected in addition to a very small amount of a monomeric derivative. The yields of the trimethylsilyl derivatives in the cases of acetone and MeCOEt were 0.11 and 0.17 g, respectively, comparable to the yields obtained by the use of MeOH or Pr^iOH. If the reaction is quantitative, 0.31 g of the derivative (*M* 606) should be obtained from 0.25 g of hemimorphite (*M* 481.6). Therefore, the yields were roughly 35—55%, in accord with the presence of unsilylated solid in the reaction mixture. (The reaction residue is removed by filtration before separation of the upper organic layer.[1]) The absence of the partial trimethylsilyl derivatives in the products may be easily explained by the fact that esterification of silanol groups with ketones is impossible whereas with an alcohol the reaction proceeds.

Therefore, it has been demonstrated that the conversion of the pyrosilicate mineral hemimorphite into its trimethylsilyl derivative can be completed by the direct trimethylsilylation method, without the need for treatment with Amberlyst 15,[1,2,6] when a simple ketone is used as the organic component of the trimethylsilylating reagent.

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