

Preliminary communication

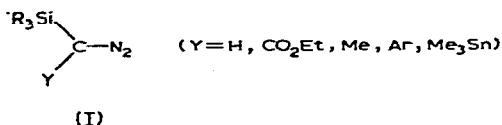
Bis(trimethylsilyl)diazomethane

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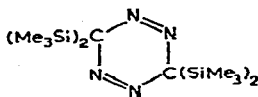
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A large number of triorganosilyldiazoalkanes (I) has been prepared during the



course of the last few years*. Conspicuous in its absence from this list is bis(trimethylsilyl)diazomethane (I, Y = Me₃Si; R = Me) a species of potential interest as a precursor to bis(trimethylsilyl)carbene. In view of the high thermal stability of trimethylsilyldiazomethane², the bis(trimethylsilyl) compound might be expected to be very stable as well. In 1965, Scherer and Schmidt³ reported that reaction of diazomethyl lithium with trimethylchlorosilane gave a volatile, vile-smelling, colorless-to-light yellow liquid, b.p. 75–78° (10 mm), which had the constitution (Me₃Si)₂N₂C on the basis of its total analysis and molecular weight in freezing benzene. However, the available evidence suggested that this product was not bis(trimethylsilyl)diazomethane: its IR spectrum showed no C=C=N absorption in the 2900 to 1500 cm⁻¹ region and it did not react with dilute acids with evolution of nitrogen. Thermally-induced rearrangement (> 120°) of this product to bis(trimethylsilyl)carbo-diimide was observed. In a recent study devoted to Group IV element-substituted diazoalkanes¹, Lappert, Lorberth and Poland reinvestigated the LiCHN₂/Me₃SiCl reaction and confirmed the results of Scherer and Schmidt. In addition, it was claimed that the “(Me₃Si)₂N₂C” produced is monomeric in benzene solution but dimeric in the vapor (by mass spectrometry). On this basis, these authors attempted to rationalize the apparent nonexistence of bis(trimethylsilyl)diazomethane in terms of a less important contribution of “Me₃Si—C^{δ-}—N^{δ-}=N⁺” to the ground state of the molecule (less important than contribution of $\begin{array}{c} \text{SiMe}_3 \\ | \\ \text{Me}_3\text{Si}-\text{C}-\text{N}=\text{N} \end{array}$ the equivalent canonical form in the case of the monomeric tin compound, (Me₃Sn)₂CN₂), leading to a more ready dimerization of the silyl compound to give (presumed) II.

*A complete list of references is given by Lappert *et al.*¹.



(II)

This report, which creates the impression that bis(trimethylsilyl)diazomethane is not capable of existence, prompts us to present our own results which clearly demonstrate the existence of this compound as a stable monomeric species.

Bis(trimethylsilyl)diazomethane was prepared by a reaction sequence in which the preparation and isolation of trimethylsilyldiazomethane by our published procedure² was the first step. This was followed by the metalation of trimethylsilyldiazomethane with *n*-butyllithium in pentane/hexane at -90° to -100° (high speed stirring) and quenching of the intermediate (presumably $\text{Me}_3\text{SiC}(\text{Li})\text{N}_2$) with trimethylchlorosilane. Subsequent work-up consisted of concentration at reduced pressure, filtration and trap-to-trap distillation of the filtrate. The isolation of pure product from the resulting yellow-green solution was complicated by the presence of air-unstable by-products with a pungent odor. It was found that column chromatography (hexane eluent) using alumina washed with triethylamine in ether and reactivated at 180° in short (3" deep, 1.5" diameter) columns several times served to give the pure diazoalkane. A final distillation (80° at 56 mm) gave bis(trimethylsilyl)diazomethane (46% yield) as a pale yellow-green liquid which had a very sweet odor and was stable indefinitely in air. Its IR spectrum (film) showed a very strong band at 2040 cm^{-1} assignable to the $\text{C}=\text{N}=\text{N}$ moiety, and other bands at 2980s, 2900m, 2440w, 1450w, 1405m, 1265(sh), 1250s, 1225s, 970m, 930s, 840vs, 760s, 695m, and 640 m cm^{-1} . Its NMR spectrum (CCl_4) consisted of a singlet at 10.5 Hz downfield from TMS (Varian A60) and its UV spectrum (cyclohexane) showed λ_{max} (ϵ) 359 (13.6), 249 (6320), 228 μ (sh). (Anal. Found: C, 45.14; H, 9.62. $\text{C}_7\text{H}_{18}\text{N}_2\text{Si}_2$ calcd.: C, 45.10; H, 9.73%). The mass spectrum showed a molecular ion at m/e 186*.

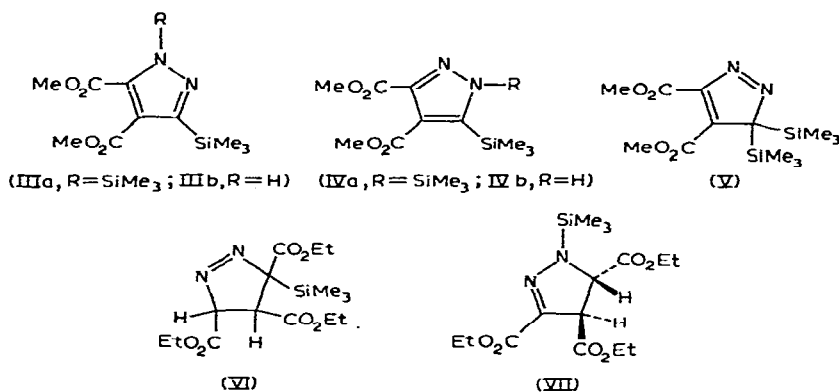
As we had expected, bis(trimethylsilyl)diazomethane is quite stable thermally, surviving essentially undecomposed (98% recovery) after a 7 days heating period in refluxing nonane solution (ca. 151°). In contrast to this high stability when it is pure, this diazoalkane is rearranged to bis(trimethylsilyl)carbodiimide, $\text{Me}_3\text{SiN}=\text{C}=\text{NSiMe}_3$, when it is heated in the presence of suitable "catalysts". Among these are copper(II) sulfate and a by-product (or by-products) formed in the original synthesis. Brominolysis of bis(trimethylsilyl)diazomethane gave the known bis(trimethylsilyl)dibromomethane⁴, the result expected in view of similar reactions of $\text{Me}_3\text{SiC}(\text{N}_2)\text{Ph}$ and $\text{Me}_3\text{SiC}(\text{N}_2)\text{CO}_2\text{Et}$ with bromine giving $\text{Me}_3\text{SiCBr}_2\text{Ph}$ and $\text{Me}_3\text{SiCBr}_2\text{CO}_2\text{Et}$, respectively^{5,6}.

Bis(trimethylsilyl)diazomethane was found to undergo slow protonolysis on treatment with acetic acid in benzene at 50° or with neat propionic acid at room temperature. However, as in the case of trimethylsilyldiazomethane², the protonolysis is complicated by loss of trimethylsilyl groups. The reaction of $(\text{Me}_3\text{Si})_2\text{CN}_2$ (1.39 mmol) with an excess of propionic acid illustrates this point. The products obtained were $\text{C}_2\text{H}_5\text{CO}_2\text{CH}_2\text{SiMe}_3$ (0.51 mmol), $\text{C}_2\text{H}_5\text{CO}_2\text{SiMe}_3$ (2.08 mmol) and $\text{C}_2\text{H}_5\text{CO}_2\text{CH}_3$ (0.81 mmol), as determined by GLC. This represents an accounting of 93% of the Me_3Si

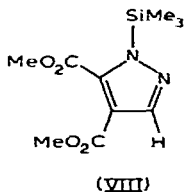
*We are indebted to Drs. E. Hedaya and P.O. Schissel, Union Carbide Research Institute, for this determination.

groups and 95% of the diazomethane carbon atom. It would appear that in the assumed intermediate, $(\text{Me}_3\text{Si})_2\text{CHN}_2^+\text{O}_2\text{C}^-\text{Et}$, carboxylate ion attack at silicon is the only possible process (in contrast to $\text{Me}_3\text{SiCH}_2\text{N}_2^+$, ref. 2) because introducing a second trimethylsilyl group increases the probability of nucleophilic attack at silicon and at the same time decreases the steric accessibility of the diazonium carbon atom. Similar results, only attack at silicon, were obtained with acetic acid.

Bis(trimethylsilyl)diazomethane underwent exothermic reaction with dimethyl acetylenedicarboxylate in the absence of moisture to give a white solid product, m.p. $66-68^\circ$, in 73% yield, which analyzed correctly for $\text{C}_{13}\text{H}_{24}\text{N}_2\text{O}_4\text{Si}_2$ and whose NMR spectrum (CDCl_3) showed two Me_3Si singlets at δ 0.28 and 0.43 ppm and two OCH_3 singlets at δ 3.81 and 3.90 ppm. Recrystallization of this product with no precautions to exclude atmospheric moisture gave a new compound, m.p. $136-137^\circ$, which had only one Me_3Si group ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_4\text{Si}$) and whose NMR spectrum (CCl_4) showed a Me_3Si resonance at δ 0.35 and OCH_3 resonances at 3.83 and 3.93 ppm. In addition, its IR spectrum contained N-H stretching vibrations at 3440w and 3140s (br). On the basis of these results, the isolated product is either IIIa or IVa, and its hydrolysis product then would be either IIIb or IVb, respectively, and thus it is apparent that the initial adduct (V) had rearranged via trimethylsilyl migration. Similar rearrangement processes have been encountered in reactions of $\text{Me}_3\text{SiC}(\text{N}_2)\text{CO}_2\text{Et}$ with dimethyl acetylenedicarboxylate and diethyl fumarate⁷. In the latter case, the initial adduct (VI) also was not isolated and the product obtained was shown to be the *N*-silyl compound VII*.



*In this connection we must question Lappert and Poland's assignment⁸ of structure IIIb to the product (m.p. $78-80^\circ$ dec) of the trimethylsilyldiazomethane/dimethylacetylenedicarboxylate reaction. It seems quite possible that in this case also trimethylsilyl migration would be preferred and that their product actually is the *N*-trimethylsilyl compound VIII.



These several reactions which are characteristic of silyl-substituted diazoalkanes and the spectroscopic properties cited above thus provide strong support for the diazomethane structure of the $(\text{Me}_3\text{Si})_2\text{CN}_2$ species which we have prepared. Bis(trimethylsilyl)diazomethane is very stable thermally and also stable to normal laboratory air when pure. It seems to us that the reaction of diazomethylithium with trimethylchlorosilane should give bis(trimethylsilyl)diazomethane, and we can offer no explanation for the results of previous^{1,3} workers.

Full details of these and other studies dealing with trimethylsilyldiazomethane and bis(trimethylsilyl)diazomethane will be reported in the near future.

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