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TRIMETHYLSILYL-SUBSTITUTED DIAZOALKANES

I. TRIMETHYLSILYLDIAZOMETHANE

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SUMMARY

Trimethylsilyldiazomethane was prepared by the action of aqueous KOH on *N*-nitroso-*N*-(trimethylsilylmethyl)urea. The spectroscopic properties of this stable, greenish-yellow liquid which can be isolated by gas chromatography are discussed. Its reaction with acetic acid gives the expected $CH_3CO_2CH_2SiMe_3$ in addition to Si–C cleavage products, $CH_3CO_2CH_3$ and $CH_3CO_2SiMe_3$. Products of the 1,3-dipolar addition of Me_3SiCHN_2 to activated olefins were not very stable, and only the adduct with acrylonitrile was isolated as a pure material. Trimethylsilyldiazomethane undergoes Me_3SiCH transfer to olefins, giving trimethylsilyl-substituted cyclopropanes, in the presence of CuCl in benzene, but other products are formed as well. Thus such a reaction with cyclohexene gave *anti*-7-trimethylsilylnorcarane (65%), *syn*-7-trimethylsilylnorcarane (7%), *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylene (9% and 13%, respectively), and an unidentified Me_3SiCH trimer (2.3%).

INTRODUCTION

In connection with our research concerned with silyl-substituted (dihalomethyl)mercury compounds and their application in the generation of silyl-substituted carbenes[1], we became interested in alternative routes to such organosilicon divalent carbon intermediates. Diazoalkanes are well-known sources of carbenes, or, in the presence of appropriate transition metal compounds, of carbenoids. Thus an investigation of silyl-substituted diazoalkanes seemed worth pursuing. In this report we present our results on the synthesis, properties and some reactions of trimethylsilyldiazomethane, $(CH_3)_3SiCHN_2$.

During the course of this study, Lappert and Lorberth[2] prepared (trimethylsilyl)diazomethane via $LiCHN_2$, a procedure which is not the method of choice, and further chemistry of this compound was developed in later work by Lappert and

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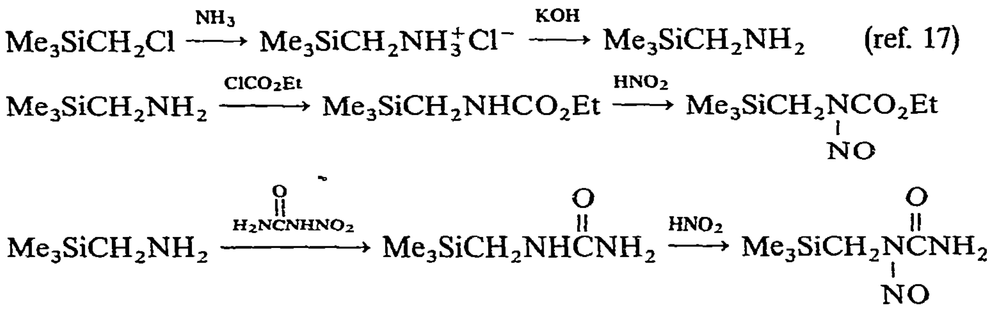
Poland[3-6]. Different syntheses of trimethylsilyldiazomethane have been described since our preliminary communication[7] dealing with this compound, by Mironov and his coworkers[8] and by Schöllkopf *et al.*[9]. Other silyl-substituted diazoalkanes have been prepared, but these were of the type $Me_3SiC(N_2)R$ ($R=CO_2Et$, aryl, etc.)[10-15]. (The field of metal- and metalloid-substituted diazoalkanes has been reviewed[16].)

RESULTS AND DISCUSSION

Preparation and properties of trimethylsilyldiazomethane

Two precursors for trimethylsilyldiazomethane were examined: ethyl *N*-nitroso-*N*-(trimethylsilylmethyl)urethane, $Me_3SiCH_2N(NO)CO_2Et$, and *N*-nitroso-*N*-(trimethylsilylmethyl)urea, $Me_3SiCH_2N(NO)CONH_2$. Their preparation was straightforward and is shown in Scheme 1. The formation of the urea derivative via nitrourea is a clean and simple reaction which affords the silyl-substituted urea in consistently good yield after a particularly convenient work-up, since the only other products are gases. The nitrosation procedure offers no difficulties and results in good yields (70–80%) when performed in small batches (10–12 g) since the reaction is heterogeneous. The preparation of the urethane could be simply effected, but this derivative and the nitrosated product are liquids which require distillation.

SCHEME 1



$$Me_3SiCH_2Cl \xrightarrow{NH_3} Me_3SiCH_2NH_3^+Cl^- \xrightarrow{KOH} Me_3SiCH_2NH_2 \quad \text{(ref. 17)}$$

$$Me_3SiCH_2NH_2 \xrightarrow{ClCO_2Et} Me_3SiCH_2NHCO_2Et \xrightarrow{HNO_2} Me_3SiCH_2\underset{\underset{NO}{|}}{N}CO_2Et$$

$$Me_3SiCH_2NH_2 \xrightarrow{H_2N\overset{\overset{O}{\|}}{C}NHNO_2} Me_3SiCH_2NH\overset{\overset{O}{\|}}{C}NH_2 \xrightarrow{HNO_2} Me_3SiCH_2\underset{\underset{NO}{|}}{N}\overset{\overset{O}{\|}}{C}NH_2$$

Of the two trimethylsilyldiazomethane precursors, the urea compound proved to be the more satisfactory. The aqueous KOH-induced conversion of *N*-nitroso-*N*-(trimethylsilylmethyl)urea to trimethylsilyldiazomethane proceeded smoothly at room temperature or below, but no matter whether the reaction were carried out in various organic solvents or neat, appreciable amounts of hexamethyldisiloxane were produced as a side product. There is no simple chemical method for determining the concentration of trimethylsilyldiazomethane in its solutions. Most chemical reactions of this reagent do not proceed quantitatively or they do not proceed cleanly, varying amounts of Si–C cleavage accompanying the desired reaction. NMR analysis of such reagent solutions could be used to determine the $Me_3SiCHN_2/Me_3SiOSiMe_3$ ratio and GLC yield-determination of the latter after the reaction of interest had been carried out could then be used to obtain the Me_3SiCHN_2 yield. This method, however, is cumbersome and has the flaw that one must assume that the GLC yield-determination represents hexamethyldisiloxane which was all present in the initial solution, an assumption which is not necessarily true in all cases.

As our work in this area progressed, it became clear that trimethylsilyldiazomethane was a very thermally stable compound, and the problem of analysis of solutions containing this reagent was solved when it was found that it survived gas chromatographic analysis and could in fact be collected as the pure compound by GLC. General Electric Co. silicone columns (SE-30 or XF-1150) were found to be satisfactory, with injection port and detection block temperatures of 100° and a column temperature of 35–50°. In a typical preparation of trimethylsilyldiazomethane, GLC yield determination of the solution components showed trimethylsilyldiazomethane and hexamethyldisiloxane to be present in yields of 61 and 17 %, respectively.

Trimethylsilyldiazomethane, as isolated by preparative GLC, was found to be a greenish-yellow liquid, b.p. 96° at 775 mmHg, n_D^{25} 1.4362. It is quite stable neat or in hydrocarbon solution. For instance, it was undecomposed when refluxed in benzene solution for one week. However, it decomposed fairly rapidly when its solution in carbon tetrachloride was exposed to light. This is not surprising in view of the known chemistry of diazomethane[18]. Trimethylsilyldiazomethane was not hydrolyzed by neutral water or by 20 % aqueous potassium hydroxide solution, an observation which indicates that the presence of hexamethyldisiloxane in the reagent solutions is not due to destruction of trimethylsilyldiazomethane by the basic reaction medium. It thus seems likely and reasonable that base-induced Si–C cleavage of the $Me_3SiCH_2N(NO)CONH_2$ intermediate is the source of hexamethyldisiloxane.

Some observations concerning the spectroscopic properties of trimethylsilyldiazomethane merit discussion. The stretching vibration of the diazo group of trimethylsilyldiazomethane (2070 cm^{-1}, pure liquid) is very similar to that of diazomethane (2074 cm^{-1} in solution, 2108 cm^{-1} in the gas phase[19]) and acyl-substituted diazomethanes (2100–2087 cm^{-1})[19]. Alkyl- and aryldiazomethanes, on the other hand, show such absorption at longer wave-length, 2049–2020 cm^{-1} [19]. In diazomethane, the 2108 cm^{-1} band has been assigned to the stretching vibration of the N–N bond[20]. Thus, the shift of the acyl- and silyl-substituted diazomethane stretching frequency to shorter wavelength, compared with the alkyl and aryl derivatives is rationalized by increased contributions of $R\overset{-}{C}H-\overset{+}{N}{\equiv}N$ to the total description of the molecule. In the case of the trimethylsilyl derivative, the increased contribution of this resonance structure can be understood in terms of C→Si p_π–d_π overlap which stabilizes the charge on the carbanionic center adjacent to silicon in much the same way as p_π–p_π overlap stabilizes the carbanionic resonance structure in the α-diazoketones[19] *. Consideration of the NMR spectrum of trimethylsilyldiazomethane leads to a similar interpretation in which such p_π–d_π overlap can again be suggested. Ledwith and Friedrich[21] have compared α-proton chemical shifts in diazomethane and substituted diazomethanes (δ 3.0–5.0 ppm) with proton chemical shifts in various model compounds (olefins, allenes, aldehydes, aldehyde-derived hydrazones). The observed high-field shifts of the resonance position for the α protons of the diazo compounds as compared to the resonance position of the protons in the model compounds (δ 6.0–10.0 ppm) could be explained in terms of shielding effects expected if the

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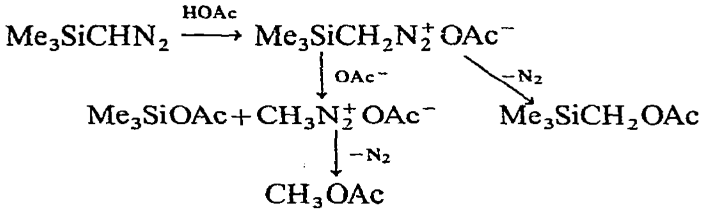
* Lappert *et al.*[5] have reported N=N stretching frequencies for a number of bis(organometal)diazomethanes: $(Me_3Ge)_2CN_2$, 2050; $(Me_3Sn)_2CN_2$, 2000; $(Et_3Sn)_2CN_2$, 1995; $(n\text{-}Bu_3Sn)_2CN_2$, 1995; $(Me_3Pb)_2CN_2$, 1950; $Me_3Si(Me_3Sn)CN_2$, 2022 cm^{-1}. However, a comparison of these values with the corresponding N=N frequency for the monosubstituted Me_3SiCHN_2 may not be very meaningful.

$R\bar{C}H-\overset{+}{N}\equiv N$ form is the major contributor to the resonance description of the molecules. However, separation of such effects from possible diamagnetic anisotropy effects of the diazo group was not possible. The chemical shifts of the vinyl protons in *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylene (δ 6.76 and 6.59 ppm, respectively) are considerably less shielded than the α proton of (trimethylsilyl)diazomethane [δ 2.64 (neat), 2.23 ppm in benzene], and here also one may invoke the predominance of the contribution of the $Me_3Si\bar{C}H-\overset{+}{N}\equiv N$ resonance form. The UV spectrum of (trimethylsilyl)diazomethane (hexane solution) showed λ_{max} [nm (log ε)] 238(4.00), 402(1.36), 412(1.30), infl.

Reactions of trimethylsilyldiazomethane

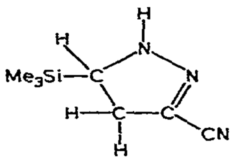
As expected, trimethylsilyldiazomethane reacts with carboxylic acids, but such reactions are complicated by trimethylsilyl cleavage reactions. Thus a reaction with water-free acetic acid in benzene solution at room temperature gave not only the expected $CH_3CO_2CH_2SiMe_3$, but also equimolar quantities of methyl acetate and trimethylsilyl acetate. The ratio of trimethylsilylmethyl acetate to trimethylsilyl acetate obtained increased with reaction temperature, being 0.7 at 0°, 1.0 at 25°, and 1.45 at 40°; the ratio of trimethylsilyl acetate to methyl acetate was about 1 at all temperatures. These results may be understood in terms of Scheme 2. The suggestion that the (trimethylsilyl)methyldiazonium ion undergoes Si–C cleavage as shown to give the methyldiazonium ion finds precedent in the report[22] that nitrosation of (trimethylsilylmethyl)amine with nitrous acid results in cleavage of the trimethylsilyl group.

SCHEME 2



$$\begin{tikzcd}
\mathrm{Me_3SiCHN_2} \arrow[r, "\mathrm{HOAc}"] & \mathrm{Me_3SiCH_2N_2^+OAc^-} \arrow[d, "\mathrm{OAc^-}"] \arrow[dr, "-\mathrm{N_2}"] & \\
 & \mathrm{Me_3SiOAc+CH_3N_2^+OAc^-} \arrow[d, "-\mathrm{N_2}"] & \mathrm{Me_3SiCH_2OAc} \\
 & \mathrm{CH_3OAc} &
\end{tikzcd}$$

Trimethylsilyldiazomethane undergoes 1,3-dipolar addition reactions with a number of activated olefins, but only in the case of acrylonitrile could a pure product be isolated. Even this adduct, assigned the structure (I) on the basis of its IR and NMR



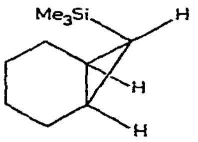
(I)

spectra, was extemely unstable to hydrolysis by atmospheric moisture. In contrast to the rapid reaction observed with acrylonitrile, diethyl maleate reacted only slowly with trimethylsilyldiazomethane, but the product could not be isolated in analytical purity. Ethyl cinnamate reacted with Me_3SiCHN_2 during several weeks in the dark, but the product was a white, insoluble, apparently polymeric solid. Maleic anhydride and trimethylsilyldiazomethane gave an intractable purple solid under a variety of conditions. In view of these results, we did not continue our investigations of this aspect of the reactivity of trimethylsilyldiazomethane. However, we note that Lappert and Poland[6] have prepared adducts of trimethylsilyldiazomethane with dipolarophiles such as di-*p*-tolylcarbodiimide, dimethyl acetylenedicarboxylate and methacrylonitrile.

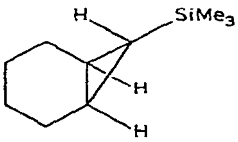
Our further investigations of trimethylsilyldiazomethane focused on its application as a divalent carbon transfer agent. Copper-catalyzed decomposition of diazoalkanes is well-known and when carried out in the presence of olefins it has the advantage of producing cyclopropanes to the exclusion of C–H insertion products with high stereoselectivity[23]. In contrast, photolysis of diazoalkanes in the presence of olefins gives C–H insertion products in substantial quantity, and the cyclopropanes are produced in a less stereoselective manner. Accordingly, we examined the stability of trimethylsilyldiazomethane in the presence of copper bronze and copper(I) chloride.

No nitrogen appeared to be evolved when a benzene solution of trimethylsilyldiazomethane was heated at 50° in the presence of copper bronze. On the other hand, copper(I) chloride caused a rapid evolution of nitrogen in an exothermic reaction which required external cooling. An examination of the CuCl-catalyzed decomposition of Me_3SiCHN_2 in benzene at 0° using a $Me_3SiCHN_2/CuCl$ ratio of 11.5 showed the products of the decomposition reaction to be trimethylchlorosilane (10% yield), *trans*-1,2-bis(trimethylsilyl)ethylene (47%) and *cis*-1,2-bis(trimethylsilyl)ethylene (16%). A decrease in the diazo compound/CuCl ratio to 1.5 gave these products in yields of 14, 59 and 28%, respectively. A fourth product was present in very low yield. This also was found as a minor product in various $Me_3SiCHN_2/CuCl$/olefin reactions and was identified as a trimer of the Me_3SiCH moiety.

Decomposition of trimethylsilyldiazomethane by copper(I) chloride in the presence of cyclohexene proceeded rapidly at 0° and Me_3SiCH transfer to the olefin occurred in good yield. In a reaction in which a 1.2 ratio of Me_3SiCHN_2 to CuCl and a considerable excess of olefin were used, the following products were isolated and characterized: *trans*-1,2-bis(trimethylsilyl)ethylene (13%), *cis*-1,2-bis(trimethylsilyl)ethylene (9%), *anti*-7-trimethylsilylnorcarane (III) (65%), *syn*-7-trimethylsilylnorcarane (II) (7%) and a compound with analysis and molecular weight corresponding to $(Me_3SiCH)_3$ (2.3%). The bis(trimethylsilyl)ethylene isomers are known compounds[24], but they were fully characterized spectroscopically and by analysis in this study. Structural assignments for the *syn* and *anti* isomers [(II) and (III)] were based



(II)

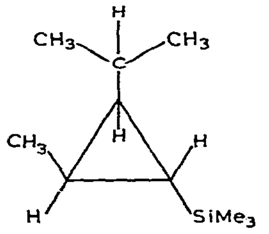


(III)

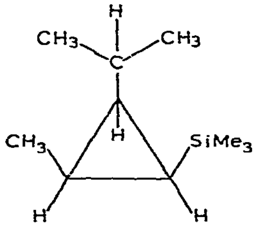
on a consideration of their NMR spectra. In the spectrum of the *anti* isomer (III), the trimethylsilyl protons appeared as a singlet at δ −0.09 ppm and the cyclopropyl proton *gem* to the trimethylsilyl group as a triplet at δ −0.69 ppm (J 7 Hz). For the *syn* isomer (II), these resonances were seen at δ 0.12 and -0.41 (t, J 10 Hz). Previous work has established that in norcarane derivatives the 7-proton *syn* to the tetramethylene bridge is more highly shielded than is the *anti* proton, and furthermore, that the magnitude of *cis* spin–spin coupling between vicinal protons in cyclopropanes is greater than is *trans* coupling[25]. The structure of the "trimer" remains unknown.

A more detailed study of the reaction of trimethylsilyldiazomethane with cyclohexene was made. A reaction carried out at 0° with a 10/1 $Me_3SiCHN_2/CuCl$ ratio gave *anti*- and *syn*-7-trimethylsilylnorcarane in yields of 67% and 5%, respectively, and *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylene in yields of 6.5% and 15%. A change in the $Me_3SiCHN_2/CuCl$ ratio to 1/1 caused no significant change in product yields or distribution (71% and 6% yields for the norcaranes and 7% and 16% for the olefin isomers). When copper(II) sulfate was used in place of CuCl, with $Me_3SiCHN_2/CuSO_4$ ratio of 10, in a reaction carried out at 50° for 24 h, the product yields were much lower, and the 1,2-bis(trimethylsilyl)ethylene isomers exceeded the 7-trimethylsilylnorcarane by about a factor of 2.5 in yield. Moreover, only the *anti* isomer was present in the reaction mixture. When copper(II) acetylacetonate was examined as catalyst ($Me_3SiCHN_2/Cu(acac)_2 = 10$, 42 h at 50°), the yields of the 1,2-bis(trimethylsilyl)ethylene isomers and of *anti*-7-trimethylsilylnorcarane were about equal; The *syn* isomer was present only in trace quantity.

The CuCl-catalyzed reaction of trimethylsilyldiazomethane with *cis*-4-methyl-2-pentene gave two isomeric cyclopropanes in yields of 18% and 5%, and these were assigned structures (IV) and (V), respectively, on the basis of their NMR spectral properties. In addition, *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylene were present in yields of 8% and 34%, respectively. A CuCl-catalyzed reaction of trimethylsilyldiazomethane with tetramethylethylene gave these olefins in yields of 10% and 24%, respectively, in addition to the expected 1,1,2,2-tetramethyl-3-trimethylsilylcyclopropane (13%).



(IV)



It would be of interest to extend this study to other olefins in order to assess the effect of olefin structure and of the nature of the substituents on the C=C bond on olefin reactivity toward the $Me_3SiCHN_2/CuCl$ system, but such an extension of scope is not possible at the present time. This study has indicated that trimethylsilyldiazomethane can be a useful Me_3SiCH transfer agent, and an improved synthesis developed more recently by Schöllkopf *et al.*[9] should enhance its utility.

It is of interest to mention two other potential Me_3SiCH transfer reagents developed in these laboratories: $(Me_3SiCHBr)_2Hg$[1] and $(Me_3SiCHI)_2Hg$[26]. The first of these was found to be much too stable to show useful transfer reactivity. The latter, in combination with one molar equivalent of diphenylmercury, reacted with cyclohexene (148° for 7 days) to give *trans*-1,2-bis(trimethylsilyl)ethylene (29 %) and *anti*-7-trimethylsilylnorcarane (10 %) as the only products. The similarity in trends in stereoselectivity to those observed in the Me_3SiCHN_2/CuCl system is noteworthy.

EXPERIMENTAL

General comments

IR spectra were measured using Perkin–Elmer 237B or 337 grating infrared spectrophotometers, NMR spectra using a Varian Associates A60 or T60 spectrometer. Chemical shifts are given in δ units (ppm) downfield from TMS. Gas chromatography was used extensively to determine yields and to isolate samples of products. F&M 700, 720 and 5754 gas chromatographs were used. The internal standard procedure for yield determination was used.

Preparation of trimethylsilyldiazomethane precursors

(1). *N-Nitroso-N-(trimethylsilylmethyl)urea.* (Trimethylsilylmethyl)amine[17] (75 g, 0.73 mol) was dissolved in 600 ml of 95 % ethanol in a one liter flask equipped with a reflux condensor and a stirrer and 88 g (0.84 mol) of nitrourea[27] was added in one portion. A mildly exothermic reaction commenced and the clear solution was alternately stirred magnetically and shaken over a steam bath so as to maintain rapid gas evolution and reflux. After vigorous gas evolution had ceased, the solution was heated at reflux on the steam bath for 1 h. The solvent was removed at reduced pressure and the residue taken up in benzene. Upon partial concentration of the benzene solution, a small amount of precipitate formed which was filtered. The solution was concentrated further to cause crystallization of *N*-(trimethylsilylmethyl)urea. Several more crops were collected from the mother liquor. The combined product was dried to give 86 g (81 %). The product (white needles) had m.p. 113–114° after recrystallization from benzene. IR (Nujol mull): 3440 s, 3360 s, 3255 m, 1650 s, 1605 s, 1550 s, 1250 s and 850 s cm^{-1}.

Since the nitrosation reaction is heterogeneous, it is best carried out in small (12 g) batches in the following manner. Concentrated H_2SO_4 (6.4 g) and about 15 g of ice were combined in a one-liter beaker cooled in a methanol-ice bath. The 12 g of $Me_3SiCH_2NHCONH_2$ was finely powdered and mixed with 7.2 g of sodium nitrite and enough ice and water to make a cold slurry. This then was added in one portion to the cold acid solution. The mixture was stirred vigorously at first, then periodically for 20 min with continued cooling. Seven such reaction mixtures (86 g, 0.59 mol total, of the urea derivative) were successively collected on a Buchner funnel, washed with water and pressed dry. The damp solid was dissolved in benzene and the residual water removed by pipet. The solution was concentrated by rotary evaporation and the product crystallized. Temperatures above 55° were avoided to minimize thermolysis. Several crops were successively collected from the mother liquor to give a total yield of *N*-nitroso-*N*-(trimethylsilylmethyl)urea of 71.6 g (70 %), m.p. 94–96°. Recrystallization from benzene gave pure material, m.p. 95.5–96°. (Found: C, 34.29; H, 7.45; N, 24.25; Si, 15.90. $C_5H_{13}N_3O_2Si$ calcd.: C, 34.27; H, 7.53; N, 23.98; Si, 16.00 %.) The pale yellow plates showed the following IR spectrum (in CCl_4): 3540 m, 3485 m, 3420 m, 2955 m, 1745 vs, 1560 m, 1480 s, 1395 s, 1248 s, 1187 m, 1010 s, 865, 852 vs (doublet), 690 m cm^{-1}.

(2). *Ethyl N-nitroso-N-(trimethylsilylmethyl)urethane.* A 500 ml round-bottomed, three-necked flask was equipped with a mechanical stirrer, Claisen adapter, thermometer and two addition funnels and charged with 40 g (0.4 mol) of (trimethylsilylmethyl)amine in 100 ml of diethyl ether. The solution was cooled to 0° and 43.3 g (0.4 mol) of $ClCO_2Et$ was added dropwise with vigorous stirring. After about one half of the addition was completed, the simultaneous addition of a solution of 24 g of NaOH in 36 ml of water was started, at such a rate that the temperature of the reaction mixture did not exceed 0°. The reaction mixture was stirred for 15 min and then treated with water to dissolve the precipitated NaCl. The aqueous phase was separated, extracted with ether and the combined ether solution and extracts were dried over anhydrous potassium carbonate. The ether was removed and the residue distilled to give 54 g (80%) of ethyl *N*-(trimethylsilylmethyl)urethane, b.p. 81–82° (3 mmHg), n_D^{25} 1.4401. (Found: C, 48.27; H, 9.87; N, 8.18. $C_7H_{17}NO_2Si$ calcd.: C, 47.95; H, 9.78; N, 7.99%.)

A one-liter three-necked flask was equipped with a thermometer, a gas exit tube and a dropping funnel whose delivery tube extended to the bottom of the flask and then charged with 25 g (0.14 mol) of ethyl *N*-nitroso-*N*-(trimethylsilylmethyl)-urethane in 100 ml of ether and 44.5 g (0.65 mol) of sodium nitrite in 100 ml of water and 45 g of ice. A 35% nitric acid solution was prepared from 43 g of 70% HNO_3 and 43 g of ice and this cold acid solution was added slowly through the dropping funnel, taking care that the reaction temperature did not exceed 10°. The aqueous phase and then the organic phase became blue-green and some gas evolution was observed. The reaction vessel was shaken occasionally and left to stand for 2 h at 10–15° after the addition of acid had been completed. The organic layer was washed with water and sodium bicarbonate solution and dried. Removal of ether was followed by distillation of the residue to give 26.4 g (90%) of the title compound, b.p. 70° (1.5 mmHg), n_D^{25} 1.4475. (Found: C, 41.43; H, 7.85; N, 13.68. $C_7H_{16}N_2O_3Si$ calcd.: C, 41.14; H, 7.89; N, 13.71%.) IR: absorption due to N–NO at 1485, 1460 and 1050 cm^{-1}, ν(C=O) at 1730 cm^{-1}, absorption due to Me_3Si at 1240, 850 and 760 cm^{-1}.

Preparation of trimethylsilyldiazomethane from N-nitroso-N-(trimethylsilylmethyl)-urea

Trimethylsilyldiazomethane has been generated in a variety of solvents: benzene, cyclohexane, decalin, pentane, diethyl ether, di-n-butyl ether and carbon tetrachloride. The following typical preparation was carried out in pentane.

The nitrosourea derivative (29.3 g, 0.17 mol) was suspended in 125 ml of pentane in a 500 ml flask which was connected to a −78° trap. Potassium hydroxide (60 ml of 20 weight % solution) was added all at once to the flask which had been cooled in an ice bath, with vigorous magnetic stirring. The heterogeneous system was stirred vigorously for 90 min while it was maintained at room temperature or below by external cooling. The organic layer was washed with three 50 ml portions of water, combined with the contents of the cold trap and dried over anhydrous sodium sulfate. The dry pentane solution was stored in the cold over fresh Na_2SO_4.

Such solutions can be assayed quantitatively, or the diazo compound can be isolated by gas chromatography. A detector and injector temperature of about 100° and any boiling point column at 35–50° were found to be quite suitable conditions. For example, the above solution was analyzed on a 6 ft. × $\frac{1}{4}$ in., 20% General Electric

Co. XF-1112 column using n-octane as a standard and, using the calculated response factors, was found to have 0.90 mmol of Me_3SiCHN_2 and 0.15 mmol of $Me_3SiOSiMe_3$ per gram of the 120 g of solution, for a yield of the diazo compound of 64%, with an 86% accounting of the trimethylsilyl groups charged.

Trimethylsilyldiazomethane may also be generated as the neat liquid. The following procedure was used. Two g of the nitrosourea derivative (1.14 mmol) was added slowly in small portions to a 10 ml one-neck flask which contained 4 ml of a rapidly stirred solution of 20% aqueous KOH. An ice bath was used to maintain the reaction mixture at room temperature or below as the pale yellow flakes of the nitrosourea compound were converted slowly to a greenish-yellow liquid. After 45 min, the KOH layer was separated with a pipet, the product was washed once with water and then the organic layer was pipetted into a test tube. The small amount of water carried over was allowed to settle and then the diazo compound was transferred to a tared test tube; yield, 0.91 g (70%). The crude Me_3SiCHN_2 showed bands at 2070 (N=N) and 1065 (SiOSi) cm^{-1}, indicating that it was contaminated with hexamethyldisiloxane. Pure Me_3SiCHN_2 was isolated by GLC (5 ft. columns using either 20% General Electric Co. SE-30 or 15% General Electric Co. XF-1150 on Chromosorb P at 35°). The pure material had n_D^{25} 1.4362. (Found: C, 42.06; H, 8.65; N, 24.44. $C_4H_{10}N_2Si$ calcd.: C, 42.06; H, 8.82; N, 24.52%.) NMR (neat): δ 2.64 (s, 1H, CHN_2) and 0.20 ppm (s, 9H, Me_3Si) (internal *p*-dioxane standard). IR (neat): 2975 s, 2070 s, 1419 m, 1270 s (broad), 1168 m, 1025 m, 860 s (broad), 768 s, 715 s cm^{-1}. The UV spectrum is given in the discussion section.

Reaction of trimethylsilyldiazomethane with acetic acid

Ten ml of a benzene solution about 0.1 *M* in Me_3SiCHN_2 in a 50 ml flask equipped with a magnetic stirring unit, a drying tube and an addition funnel was treated slowly at 0° with a solution of 1 ml of glacial acetic acid in 3 ml of benzene. All reagents used were dried; the acetic acid was distilled from acetic anhydride. The reaction mixture was stirred for 30 min after the color of the diazo compound had been discharged. GLC analysis of the reaction mixture (15% XF-1150 at 120°) showed the presence of hexamethyldisiloxane, methyl acetate (49%, based on the diazo compound), trimethylsilyl acetate (49%, based on the diazo compound) and trimethylsilylmethyl acetate (36%, based on the diazo compound). These products were identified by comparison of their GLC retention times and IR spectra with those of authentic samples. A sample of trimethylsilylmethyl acetate was prepared by reaction of Me_3SiCH_2OH (30 mmol) with acetic acid (60 mmol) in the presence of 1.8 ml of conc. H_2SO_4 at 120° for 4 h; n_D^{25} 1.4057; lit.[28] n_D^{25} 1.4060. Trimethylsilyl acetate was prepared by reaction of sodium acetate with trimethylchlorosilane in refluxing diethyl ether[29].

Reaction of trimethylsilyldiazomethane with acrylonitrile

Ten mmol of freshly distilled acrylonitrile was charged into a flame-dried 25 ml flask equipped with a rubber septum and a magnetic stirring bar and 10 ml of ca. 1 *M* Me_3SiCHN_2 in decalin was added by syringe in one portion. The flask was covered and stirred for 30 min, after which time the Me_3SiCHN_2 color had been discharged. Crystallization was induced by cooling in a n-propyl alcohol/ice bath. (All further manipulations were carried out in a glove bag under nitrogen in the presence of P_4O_{10} because of the instability of the product to atmospheric moisture). The white needles were collected on a Büchner funnel, washed several times with cyclohexane and dried in a stream of nitrogen to give 1.21 g (73 %) of crude adduct. Three recrystallizations from benzene/cyclohexane gave pure product, m.p. 55.4–57.6°. (Found: C, 50.04; H, 8.00; N, 24.94. $C_7H_{13}N_3Si$ calcd.: C, 50.26; H, 7.83; N, 25.12%.) NMR (in CCl_4): 0.0 (s, 9H, Me_3Si), 2.6 (m, 2H) and 6.15 ppm (broad s, 1H, N–H). IR (in CCl_4): 3400 and 3350 s (N–H), 2963 s, 2905 m, 2840 (sh), 2815 m, 2215 s (N≡C), 1676 w, 1630 w, 1540 s, 1440 m, 1405 m, 1385 m, 1305 w, 1280 s, 1265 (sh), 1252 s, 1190 m, 1080 m, 1030 s, 980 s, 915 m, 860 vs, 700 m cm^{-1}.

Reactions of trimethylsilyldiazomethane with olefins

A CuCl-catalyzed reaction of trimethylsilyldiazomethane with cyclohexene is described as an example of the procedure used.

A 25 ml round-bottom flask was flame dried, purged with dry nitrogen and capped with a rubber septum. A syringe needle inserted through the septum connected to a bubbler so that the rate of nitrogen evolution during the reaction could be monitored. The flask was charged with 0.5 g (5.05 mmol) of CuCl and 3.82 ml of dry cyclohexene. Using a syringe, 8 ml of a benzene solution containing 6.12 mmol of Me_3SiCHN_2 and 2 mmol of hexamethyldisiloxane was added dropwise with occasional cooling in an ice bath. About 10 min after the completion of the addition, the evolution of nitrogen appeared to cease. The reaction mixture was stirred for 1 h, during which time the color of the catalyst changed from black to light tan.

The mixture was trap-to-trap distilled *in vacuo* (pot temperature to 170°) to give a nearly colorless distillate. GLC analysis of the distillate (5 ft. 20% GE SE-30 on Chromosorb P at 83° and 15% GE XF-1150 on Chromosorb P) showed the presence of the following (in order of their elution on the SE-30 column): *trans*-1,2-bis(trimethylsilyl)ethylene (13%); *cis*-1,2-bis(trimethylsilyl)ethylene (9%); *anti*-7-trimethylsilylnorcarane (65%); *syn*-7-trimethylsilylnorcarane (7%); $(Me_3SiCH)_3$ (2.3%). Samples of the products were isolated by GLC and characterized.

1,2-*Bis*(*trimethylsilyl*)*ethylene.* (*a*). *trans-Isomer.* n_D^{25} 1.4262; lit.[24] n_D^{25} 1.4272. (Found: C, 55.15; H, 11.22. $C_8H_{20}Si_2$ calcd.: C, 55.65; H, 11.68%.) IR (CCl_4): 2965 s, 2900 m, 1407 m, 1297 m, 1245 s (doublet), 1172 s, 1011 s, 849 s, 710, 691 m (doublet) cm^{-1}. NMR (CCl_4): δ 0.11 (s, 9H, Me_3Si) and 6.59 ppm (s, 1H, =CH); lit.[24] 0.06 and 6.55 ppm. (*b*). *cis-Isomer.* n_D^{25} 1.4361; lit.[24] n_D^{25} 1.4365. (Found: C, 55.66; H, 11.45. $C_8H_{20}Si_2$ calcd.: C, 55.65; H, 11.68%.) IR (CCl_4): 2965 s, 2908 s, 2843 m, 1410 m, 1261 s(sh), 1247 s, 852 s, 691 m cm^{-1}. NMR (CCl_4): δ 0.19 (s, 9H, Me_3Si) and 6.76 ppm (s, 1H, =CH); lit.[24] 0.14 and 6.68 ppm.

anti-7-Trimethylsilylnorcarane. n_D^{25} 1.4561. (Found: C, 71.41; H, 11.77. $C_{10}H_{20}Si$ calcd.: C, 71.34; H, 11.97%.) IR (CCl_4): 3003 s, 2933 s, 2866 s, 1450 m, 1403 m, 1259 s(sh), 1246 s, 1232 m(sh), 1140 m, 1086 and 1078 m (doublet), 998 and 983 s (doublet), 938 m, 917 s, 850 s, 700 and 687 m (doublet) cm^{-1}. NMR (CCl_4): δ −0.69 (t, 1H, J 7.0 Hz), −0.09 (s, 9H, Me_3Si), 0.79, 1.25, 1.73 (m, 10H total).

syn-7-Trimethylsilylnorcarane. n_D^{25} 1.4734. (Found: C, 71.55; H, 12.01. $C_{10}H_{20}Si$ calcd.: C, 71.34; H, 11.97%.) IR (CCl_4): 3000 s 2940 s, 2857 s, 1447 m, 1401 m, 1387 m, 1294 m, 1254 s(sh), 1244 s, 987 m, 971 s, 941 m, 904 s, 841 s, 682 m cm^{-1}. NMR (CCl_4): δ −0.41 (t, 1H, J 10.0 Hz), 0.12 (s, 9H, Me_3Si) and 1.25 and 1.68 (m, 10H total).

Me_3SiCH trimer. n_D^{25} 1.4465. (Found: C, 55.56; H, 11.45; mass spectrometric parent ion *m/e* 259. $C_{12}H_{30}Si_3$ calcd.: C, 55.65; H, 11.68 %.) IR (CCl_4): 2962 s, 2898 m, 2837 m, 1586 s, 1412 m, 1262 s(sh), 1245 s, 1118 m, 1037 s, 990 m, 860 s, 711 m, 686 m cm^{-1}. This "trimer" also is a minor product when Me_3SiCHN_2 is decomposed by reaction with CuCl in the absence of an olefinic substrate.

The other Me_3SiCHN_2/olefin reactions were carried out in similar manner. The reaction of the diazo compound with *cis*-4-methyl-2-pentene in the presence of CuCl gave two new cyclopropanes.

(cis, trans)-1-Methyl-2-isopropyl-3-trimethylsilylcyclopropane (IV). 18 % yield, n_D^{25} 1.4153. (Found: C, 70.06; H, 12.79. $C_{10}H_{22}Si$ calcd.: C, 70.50; H, 13.02 %.) IR (CCl_4): 3157 w(sh), 2960 s, 2903 s, 2877 s, 1470 s, 1418 m, 1388 m, 1367 m, 1292 m, 1253 s, 1187 m, 1167 m, 1095 m, 1078 s, 1014 m, 990 s, 972 m, 944 s, 855 s, 708 and 693 m (doublet) cm^{-1}. NMR (CCl_4): δ -0.10 (s, 9H), 0.10 (s, 1H) and 1.00 ppm (m, 12H).

all cis-1-Methyl-2-isopropyl-3-trimethylsilylcyclopropane (V). 5 % yield, n_D^{25} 1.4385. (Found: C, 70.57; H, 13.08. $C_{10}H_{22}Si$ calcd.: C, 70.50; H, 13.02 %.) IR (CCl_4): 3150 w(sh), 2965 s, 2775 s(sh), 1466 and 1455 m (doublet), 1406 m, 1384 m, 1370 m, 1286 and 1279 m (doublet), 1248 s, 1071 m, 1014 w, 975 m, 940 m, 875 s, 833 s, 682 m cm^{-1}. NMR (CCl_4): δ 0.0 (s, 9H, Me_3Si), 0.83 ppm (m, 13H).

The reaction of Me_3SiCHN_2/CuCl with tetramethylethylene (6.0/6.0 and 60.4 mmol used) gave 1,1,2,2-tetramethyl-3-trimethylsilylcyclopropane in 13 % yield. (Found: C, 70.76; H, 13.41. $C_{10}H_{22}Si$ calcd.: C, 70.50; H, 13.02 %.) IR (CCl_4): 3110 w, 2950 s, 2735 m, 1467 s, 1453 s, 1408 and 1397 m (doublet), 1375 s, 1254 s(sh), 1243 s, 1183 m, 1138 s, 1117 s, 1034 m, 947 m, 916 s, 853 s cm^{-1}. NMR (CCl_4): δ -1.91 (s, 1H, Me_3SiCH), 0.04 (s, 9H, Me_3Si) and 1.15 and 1.10 (s, total 12H). Also produced were *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylene in yields of 10 % and 24 % respectively.

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