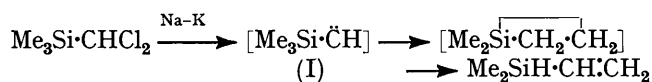


Carbene Chemistry. Part III.¹ Reactions of Diazomethyltrimethylsilane

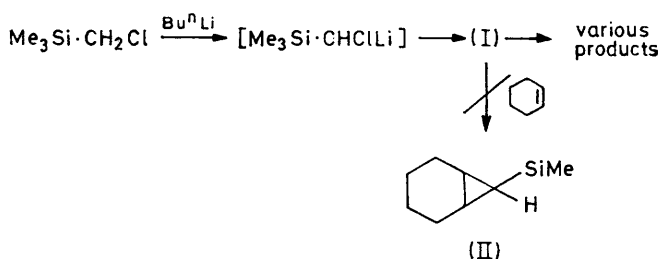
By Robert N. Haszeldine,* David L. Scott, and Anthony E. Tipping, Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Photolysis of diazomethyltrimethylsilane yields nitrogen and trimethylsilylcarbene ($\text{Me}_3\text{Si}\cdot\dot{\text{C}}\text{H}$), which reacts with diazomethyltrimethylsilane, *trans*-but-2-ene, and ethylene to give *trans*-2,2,5,5-tetramethyl-2,5-disilahex-3-ene, *trans*-1,2-dimethyl-3-trimethylsilylcyclopropane, and trimethylsilylcyclopropane, respectively. The carbene does not react with 2,3-dimethylbut-2-ene to form a cyclopropane, but undergoes insertion (i) into the Si-H bond of trimethylsilane to give 2,2,4,4-tetramethyl-2,4-disilapentane, (ii) into a C-H bond of hexamethyldisiloxane to give 2,2,4,4,7,7-hexamethyl-3-oxa-2,4,7-trisilaoctane, and (iii) into the Si-H bond or a C-H bond of 2,2,4,6,6-pentamethyl-3,5-dioxa-2,4,6-trisilaheptane to give 2,2,4,6,6-pentamethyl-4-trimethylsilylmethyl-3,5-dioxa-2,4,6-trisilaheptane and 2,2,4,6,6,9,9-heptamethyl-3,5-dioxa-2,4,6,9-tetrasiladecane, respectively.

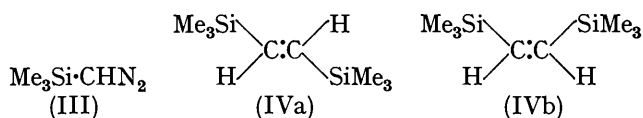
TRIMETHYLSILYLCARBENE (I) is a possible intermediate in the reaction of dichloromethyltrimethylsilane with a mixture of sodium and potassium at 260–280 °C in the gas phase,² and in the reactions of chloromethyl-



trimethylsilane with alkali metals³ and *n*-butyllithium;⁴ an attempt to trap (I) with cyclohexene to afford 7-trimethylsilylnorcaradiene (II) was unsuccessful.⁴



The copper-catalysed decomposition of diazomethyltrimethylsilane (III)^{5,6} in benzene solution in the presence of cyclohexene, however, gave the *anti*-isomer of (II) (65%), the *syn*-isomer of (II) (7%), *trans*-2,2,5,5-tetramethyl-2,5-disilahex-3-ene (IVa) (13%), and the corresponding *cis*-olefin (IVb) (9%).⁶



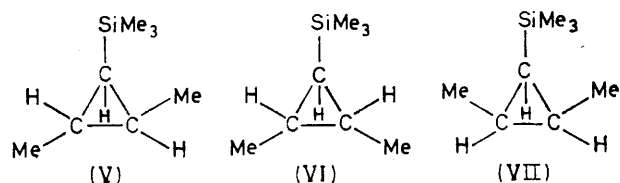
The mercurials $(\text{Me}_3\text{Si}\cdot\text{CCl}_2)_2\text{Hg}$, $(\text{Me}_3\text{Si}\cdot\text{CBr}_2)_2\text{Hg}$, and $(\text{Me}_3\text{Si}\cdot\text{CHBr})_2\text{Hg}$ have been used as precursors of the carbenes, $\text{Me}_3\text{Si}\cdot\dot{\text{C}}\text{Cl}$, $\text{Me}_3\text{Si}\cdot\dot{\text{C}}\text{Br}$, and (I), respectively,⁷ and photochemical decomposition of the diazoacetic ester, $\text{Me}_3\text{Si}\cdot\text{C}(\text{N}_2)\cdot\text{CO}_2\text{Et}$, has been reported⁸ to give the carbene, $\text{Me}_3\text{Si}\cdot\dot{\text{C}}\cdot\text{CO}_2\text{Et}$, which adds to olefins and readily undergoes insertions into C-H bonds.

In the present work photochemical reactions of (III) with various olefins and two silanes, each containing

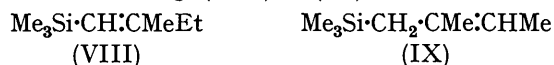
an Si-H bond, have been studied; certain copper(II)-catalysed reactions of (III) have also been carried out.

Reaction of the Diazoalkane (III) with Olefins.—Photochemical reaction of (III) with *trans*-but-2-ene (1:3 molar ratio) gave nitrogen (94%), unchanged *trans*-olefin (80%), *trans*-1,2-dimethyl-3-trimethylsilylcyclopropane (V) (23%), the *trans*-olefin (IVa) (61%), and a polymeric residue.

The cyclopropane (V) was identified by spectroscopic methods. Its ¹H n.m.r. spectrum showed absorptions at τ 8.90 (3H), 9.07 (3H), and 10.0 (12H), assigned to the methyl group *trans* to the SiMe₃ group, the *cis*-methyl group, and a combination of the SiMe₃ group and ring protons, respectively. The *cis*-methyl group would be expected to absorb upfield of the *trans*-methyl group because of shielding of the former by the SiMe₃ group. The presence of two distinct methyl absorptions strongly suggests structure (V). Since g.l.c. showed only one peak it is unlikely that the methyl absorptions are due to the presence of a 1:1 mixture of cyclopropanes (VI) and (VII) formed by non-stereospecific



addition to the olefin. The mass spectrum showed a parent peak at m/e 142 and a base peak at m/e 73 (Me_3Si^+); cyclopropanes of type $\text{RCH}\cdot\text{CH}_2\cdot\text{CH}_2$ (where R = CF_3 , CO_2Me , etc.) invariably show R^+ as the base peak.⁹ These observations, coupled with the observed lack of i.r. absorption in the C:C region, show conclusively that the product does not have an alternative olefinic structure, e.g. (VIII) or (IX).



The olefin (IVa) was identified by comparison of

¹ Part II, J. H. Atherton, R. Fields, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1971, 366.

² P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, 1964, **86**, 1442.

³ J. W. Connolly and G. Urry, *J. Org. Chem.*, 1964, **29**, 619.

⁴ I. A. Dyakonov, I. B. Repinskaya, and G. V. Golodnikov, *Zhur. obshchei Khim.*, 1965, **35**, 199.

⁵ M. F. Lappert and J. Lorberth, *Chem. Comm.*, 1967, 836.

⁶ D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Amer. Chem. Soc.*, 1968, **90**, 1080.

⁷ D. Seyferth and E. M. Hanson, *J. Organometallic Chem.*, 1971, **27**, 19.

⁸ U. Schöllkopf and N. Rieber, *Angew. Chem.*, 1967, **79**, 906;

U. Schöllkopf, D. Hoppe, N. Rieber, and V. Jacobi, *Annalen*, 1969, **730**, 1.

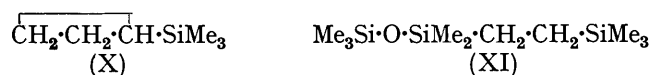
⁹ R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds,' Wiley, London, 1967, p. 102.

its i.r. and n.m.r. spectra with those reported.¹⁰ It is probably formed by reaction of the intermediate carbene (I) with unchanged diazoalkane (III). The *cis*-olefin (IVb) was not detected in the products.

The polymeric residue must be formed from a *ca.* 2 : 1 ratio of olefin and (I), since 84% of (I) formed is accounted for by the products (V) and (IVa) and 89% of the olefin (in excess) is either recovered unchanged or as product (V).

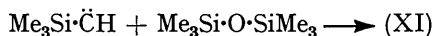
The results are consistent with the formation of the carbene (I) in the singlet state from photochemical decomposition of the diazoalkane (III), since stereospecific addition to *trans*-but-2-ene is observed.

Photochemical reaction of (III) with ethylene (1 : 2 molar ratio) gave nitrogen (95%), unchanged ethylene (82%), trimethylsilylcyclopropane (X) (17%), the *trans*-olefin (IVa) (30%), an unidentified carbene dimer (C₈H₂₀Si₂) (19%), 2,2,4,4,7,7-hexamethyl-3-oxa-2,4,7-trisilaoctane (XI) (3%), and a polymeric residue.



The mass spectrum of (X) showed a parent peak at *m/e* 142 and a base peak at *m/e* 73 (SiMe₃⁺) [cf. the cyclopropane (V)] and the ¹H n.m.r. spectrum consisted of a singlet absorption (Me₃Si) superimposed on a complex absorption (ring CH and CH₂) centred on τ 9.85. The lack of i.r. absorption in the C:C region and absence of vinylic protons as shown by n.m.r. rule out possible alternative olefinic structures.

The other identified product (XI) is considered to arise by insertion of the carbene (I) into a C-H bond of hexamethyldisiloxane, present as an impurity in the reactant diazoalkane (III). It was identified by a



consideration of its i.r., n.m.r., and mass spectra. The i.r. spectrum showed strong absorptions at 1050 (linear Si-O-Si str.), 1250 (Si-C), and 840 cm⁻¹ (Me₃Si). The ¹H n.m.r. spectrum showed absorptions at τ 9.06 (2H, CH₂·SiMe₂·O), 9.46 (2H, CH₂·SiMe₃), and 10.0 (24H, 2SiMe₃ and SiMe₂); the two methylene absorptions appeared as triplets (*J* 8.0 Hz) caused by mutual coupling. The mass spectrum contained a weak peak at *m/e* 175 (Me₃Si·O·SiMe₂·CH₂·CH₂⁺), an intense peak at *m/e* 161 (Me₃Si·O·SiMe₂·CH₂⁺), and the base peak at *m/e* 73 (Me₃Si⁺).

The photochemical reaction of (III) with 2,3-dimethylbut-2-ene did not result in cyclopropane formation. The products, nitrogen (94%), (IVa) (30%), the unknown carbene dimer (30%), and a polymeric oil, indicated that the carbene (I) was formed in the reaction. The reason for the apparent lack of reaction of the carbene (I) with the olefin may be steric hindrance by the four methyl groups to the approach of the carbene to the double bond, allowing other reactions of the

¹⁰ J. Knižek, M. Horak, and V. Chvalovský, *Coll. Czech. Chem. Comm.*, 1963, **28**, 3079; J. Cudlin, J. Schraml, and V. Chvalovský, *ibid.*, 1964, **29**, 1476.

carbene to compete successfully with cyclopropane formation.

Similarly reaction of (III) with tetrafluoroethylene and hexafluoropropene did not result in cyclopropane formation; the products were nitrogen (95%), (IVa) (*ca.* 30%), the unknown carbene dimer (*ca.* 30%), and polymeric material.

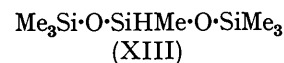
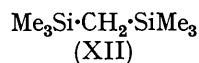
The copper(II) chloride-catalysed reaction of (III) with *trans*-but-2-ene at 0° gave nitrogen, the cyclopropane (V) (13%), the olefin (IVa) (53%), and a polymeric oil. Stereospecific reaction of the diazoalkane to give the cyclopropane (V) was expected under these conditions, because it is reported¹¹ that stereospecific cyclopropane formation takes place in reactions of diazoalkane with *cis*- or *trans*-olefins in the presence of Cu^I or Cu^{II} halides.

However, reaction with 2,3-dimethylbut-2-ene did not result in cyclopropane formation (*cf.* photochemical reaction) and the products were nitrogen, the olefin (IVa) (44%), and a polymeric residue.

From both of these liquid-phase reactions the dimer (C₈H₂₀Si₂) (contrast photochemical reaction with 2,3-dimethylbut-2-ene) and the *cis*-olefin (IVb) were not detected in the products. The copper(I)-catalysed reaction of cyclohexene with the diazoalkane (III) also does not yield the unidentified dimer, but it does result in the formation of the olefins (IVa and b).⁶

Reaction of the Diazoalkane (III) with Silanes.—Gas-phase photochemical reaction of (III) with trimethylsilane (1 : 2 molar ratio) gave nitrogen (98%), unchanged silane (98%), (IVa) (52%), the unidentified carbene dimer (12%), and a polymeric oil. Similarly, thermal reaction [150 °C (5 h) then 200 °C (3 h)] of (III) with trimethylsilane (1 : 4 molar ratio) gave nitrogen (98%), unchanged silane (85%), a mixture containing *ca.* 20 components (g.l.c.), and polymeric material.

However, liquid-phase photochemical reaction of (III) with trimethylsilane (1 : 18 molar ratio) gave nitrogen (93%), unchanged silane (95%), unchanged (III) (45%), 2,2,4,4-tetramethyl-2,4-disilapentane (XII) (66%), and polymeric material. Thus under liquid-phase photochemical conditions insertion of the carbene (I) into the Si-H bond of trimethylsilane competes successfully with other reactions of the carbene to give (IVa) and the unidentified dimer (C₈H₂₀Si₂).



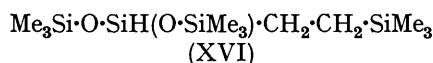
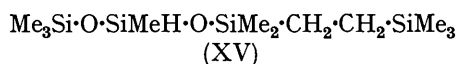
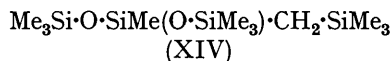
Although there are nine C-H bonds in trimethylsilane and only one Si-H bond, reaction apparently takes place exclusively at the Si-H bond; similarly reaction of the carbene CHF₂·CF with trimethylsilane results in exclusive Si-H insertion.¹²

The liquid-phase photochemical reaction of (III) with 2,2,4,6,6-pentamethyl-3,5-dioxa-2,4,6-trisilaheptane (XIII) (1 : 10 molar ratio), gave nitrogen (80%),

¹¹ W. Kirmse and M. Kapps, *Angew. Chem. Internat. Edn.*, 1965, **4**, 691.

¹² R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *Chem. Comm.*, 1969, 1364.

an azeotropic mixture of unchanged (III) (*ca.* 20%) and unchanged (XIII), and a higher-boiling mixture; g.l.c. gave a mixture of the two major components. Analytical results for this mixture were as expected for 1:1 adducts of carbene (I) and the silane (XIII), and n.m.r. spectroscopy suggested that the major product was 2,2,4,6,6-pentamethyl-4-trimethylsilylmethyl-3,5-dioxa-2,4,6-trisilaheptane (XIV) (7%) and the minor product was 2,2,4,6,6,9,9-heptamethyl-3,5-dioxa-2,4,6,9-tetrasiladecane (XV) (3.5%) [SiH (q) absorption *ca.* 1/90 total CH absorption], formed by insertion of the carbene (I) into the Si-H and a C-H bond of (XIII), respectively. Since the Si-H n.m.r. absorption ap-



peared as a quartet the C-H insertion product must be (XV) and not (XVI); in the latter the Si-H absorption would be expected to be a triplet.

In this reaction the ratio of rates of insertion of (I) into the Si-H bond and into a primary C-H bond (21 present) is *ca.* 40:1. However, this ratio must be viewed with caution because of the low isolated yield of the mixture of (XIV) and (XV).

EXPERIMENTAL

Techniques used were as described previously.¹³ Photochemical reactions were carried out using a Hanovia S500 medium-pressure u.v. lamp *ca.* 15 cm from the reaction tubes. Separation of products by g.l.c. was effected with a Pye model 105 instrument and columns packed with Celite impregnated with Silicone MS550 oil or Kel-F 10 oil (30% by weight). Diazomethyltrimethylsilane was prepared from chloromethyltrimethylsilane⁶ using certain modifications described previously.¹³ The diazoalkane so prepared contained hexamethyldisiloxane (usually 2–5%), and in the majority of the reactions the impurity was merely an inert diluent. The amounts of reactant diazoalkane have been calculated with allowance for the hexamethyldisiloxane impurity present.

Reactions of Diazomethyltrimethylsilane.—(a) *With trans-but-2-ene.* A mixture of the diazoalkane (1.75 g, 15.4 mmol) and *trans-but-2-ene* (2.51 g, 44.0 mmol), sealed in a silica tube (*ca.* 250 ml) and irradiated (60 h), gave (i) nitrogen (0.40 g, 14.3 mmol, 94%; *M*, 28); (ii) unchanged *trans-but-2-ene* (1.92 g, 35.4 mmol, 80% recovered) (Found: *M*, 56. Calc. for C₄H₈: *M*, 56); (iii) a mixture (1.29 g) of two components which were separated by g.l.c. (8 m Kel-F at 100 °C) and identified as *trans-1,2-dimethyl-3-trimethylsilylcyclopropane* (0.51 g, 3.51 mmol, 23%) (Found: C, 67.9; H, 13.0. C₈H₁₈Si requires C, 67.6; H, 12.7%), b.p. 138–140 °C; ν_{max} 3000m (C-H str.), 1475w, 1430w, 1380w, 1250s (Si-C str.), 1080w, 950m, 920m, 848vs (Me₃Si), 832vs, 753m, and 635m cm⁻¹; *m/e* 142 (15%, *M*⁺), 86 (10%, C₄H₁₀Si⁺), 73 (100%, Me₂Si⁺), 58 (7%, Me₂Si⁺), 56 (4%, C₄H₈⁺), 54 (4%, C₄H₆⁺), 45 (15%, CH₃⁺SiH₂⁺), and 43 (5%, MeSi⁺), τ 10.0 (12H, complex, SiMe₃

and CH), 9.07 (3H, s, Me), and 8.90 (3H, s, Me); and *trans-2,2,5,5-tetramethyl-2,5-disilohex-3-ene* (0.78 g, 4.56 mmol, 61%) (Found: C, 56.1; H, 11.5. Calc. for C₈H₂₀Si₂: C, 55.8; H, 11.6%), b.p. 144–146 °C (lit.,¹⁰ 145.5 °C), the i.r. and n.m.r. spectra of which were identical with those reported;¹⁰ and (iv) a brown polymeric oil (0.2 g) which was not investigated further.

(b) *With trans-but-2-ene in the presence of copper(II) chloride.* The diazoalkane (1.75 g, 15.4 mmol), slowly added to a stirred mixture of *trans-but-2-ene* (2.28 g, 40.1 mmol) and copper(II) chloride (0.2 g) at 0 °C, gave (i) nitrogen; (ii) unchanged *trans-but-2-ene* (2.01 g, 35.1 mmol, 88% recovered); (iii) a mixture (1.03 g), separated by g.l.c. (as before) into its two components, *trans-1,2-dimethyl-3-trimethylsilylcyclopropane* (0.31 g, 2.10 mmol, 13%) and *trans-2,2,5,5-tetramethyl-2,5-disilohex-3-ene* (0.72 g, 4.10 mmol, 53%); and (iv) non-volatile material (0.35 g) which was not examined further.

(c) *With ethylene.* A mixture of the diazoalkane (1.75 g, 15.4 mmol) and ethylene (0.99 g, 32.3 mmol), sealed in a silica ampoule (*ca.* 250 ml) and irradiated (72 h), gave (i) nitrogen (0.41 g, 14.6 mmol, 95%; *M*, 28); (ii) unchanged ethylene (0.81 g, 26.3 mmol, 82% recovered); (iii) a mixture (1.09 g) which was separated by g.l.c. (as before) into its four components identified as *trimethylsilylcyclopropane* (0.32 g, 2.63 mmol, 17%) (Found: C, 62.9; H, 12.6. C₆H₁₄Si requires C, 63.1; H, 12.3%), b.p. 69–70 °C; ν_{max} 2995m (C-H str.), 1480m, 1220m (SiMe₃), 1014m, 1002w, 900w, 840s (Me₃Si), 783s, 760m, and 672s cm⁻¹; *m/e* 114 (15%, *M*⁺), 100 [10%, (*M* - CH₂)⁺], 86 (8%, CHSiMe₃⁺), 73 (100%, Me₂Si⁺), 59 (7%, Me₂SiH⁺), 45 (4%, MeSiH₂⁺), 43 (10%, MeSi⁺) and 41 (7%, C₃H₅⁺); τ 9.85 (complex); 2,2,4,4,7,7-hexamethyl-3-oxa-2,4,7-trisilaoctane (0.10 g, 0.40 mmol, 3%) (Found: C, 48.2; H, 11.0. C₁₀H₂₈OSi₃ requires C, 48.4; H, 11.3%), b.p. 188–190 °C; ν_{max} 2920m and 2900w (C-H str.), 1400w, 1250s (Si-C str.), 1050s (Si-O-Si str.), 1010w, 955w, 840s (Me₃Si), 805m, 780m, 750w, and 690w cm⁻¹; *m/e* 219 [6%, (*M* - C₂H₅)⁺], 161 (50%, C₆H₁₇OSi₂⁺), 148 (13%, C₅H₁₅OSi₂⁺), 132 (50%, C₄H₁₂OSi₂⁺), 131 (25%, C₄H₁₁OSi₂⁺), 119 (13%, C₃H₁₀OSi₂⁺), 75 (25%, C₂H₇OSi⁺), and 73 (100%, Me₃Si⁺); τ 9.06 (2H, t, CH₂, *J* 8.0 Hz), 9.46 (2H, t, CH₂), and 10.0 (24H, s, SiMe₃ and SiMe₂); *trans-2,2,5,5-tetramethyl-2,5-disilohex-3-ene* (0.42 g, 2.37 mmol, 30%); and an unidentified trimethylsilyl carbene dimer (0.25 g, 14.5 mmol, 19%) (Found: C, 55.5; H, 11.3. Calc. for C₆H₂₀Si₂: C, 55.8; H, 11.6%); and (iv) a brown polymeric residue (0.3 g).

(d) *With 2,3-dimethylbut-2-ene.* A mixture of the diazoalkane (1.75 g, 15.4 mmol) and the olefin (1.98 g, 23.8 mmol), sealed in a silica ampoule (*ca.* 250 ml) and irradiated (72 h), gave (i) nitrogen (0.40 g, 14.3 mmol, 94%; *M*, 28); (ii) unchanged olefin (1.85 g, 22.0 mmol, 93% recovered); (iii) a mixture of *trans-2,2,5,5-tetramethyl-2,5-disilohex-3-ene* (0.39 g, 2.29 mmol, 30%) and the unidentified trimethylsilyl carbene dimer (0.38 g, 2.28 mmol, 30%); and (iv) a brown polymeric residue (0.7 g).

(e) *With 2,3-dimethylbut-2-ene in the presence of copper(II) chloride.* The diazoalkane (1.75 g, 15.4 mmol), slowly added to a stirred mixture of the olefin (3.00 g, 36.0 mmol) and copper(II) chloride (0.2 g) at 20 °C, evolved nitrogen and gave (i) unchanged olefin (2.91 g, 34.0 mmol, 96% recovered); (ii) *trans-2,2,5,5-tetramethyl-2,5-disilohex-3-*

¹³ J. C. Crossman, R. N. Haszeldine, and A. E. Tipping, *J.C.S. Dalton*, 1973, 483.

ene (0.67 g, 3.89 mmol, 44%); and (iii) a black tar (*ca.* 0.8 g).

(f) *With fluoro-olefins.* A mixture of the diazoalkane (1.75 g, 15.4 mmol) and tetrafluoroethylene (1.54 g, 15.4 mmol), sealed in a silica ampoule (*ca.* 250 ml) and irradiated (120 h), gave (i) nitrogen (0.41 g, 14.6 mmol, 95%); (ii) unchanged olefin (1.53 g, 15.3 mmol, 99% recovered); (iii) a mixture (0.71 g) of *trans*-2,2,5,5-tetramethyl-2,5-disilahex-3-ene (0.40 g, 2.30 mmol, 31%) and the unidentified trimethylsilyl carbene dimer (0.31 g, 1.86 mmol, 24%); and (iv) a brown polymeric residue (0.47 g).

A reaction with hexafluoropropene under the same conditions and with the same molar ratio of reactants gave (i) nitrogen (95%); (ii) unchanged hexafluoropropene (99% recovered); (iii) *trans*-2,2,5,5-tetramethyl-2,5-disilahex-3-ene (33%); (iv) the unidentified trimethylsilyl carbene dimer (24%); and (v) a brown polymeric residue.

(g) *With trimethylsilane.* (i) A mixture of the diazoalkane (1.75 g, 15.4 mmol) and trimethylsilane (2.28 g, 30.8 mmol), sealed in a silica ampoule (*ca.* 250 ml) and irradiated (100 h), gave (i) nitrogen (0.42 g, 15.0 mmol, 98%); (ii) unchanged trimethylsilane (2.25 g, 30.4 mmol, 98% recovered); (iii) a mixture (0.84 g) of *trans*-2,2,5,5-tetramethyl-2,5-disilahex-3-ene (0.69 g, 4.08 mmol, 52%) and the unidentified trimethylsilyl carbene dimer (0.15 g, 1.42 mmol, 12%); and (iv) a brown oil (*ca.* 0.4 g; *M*, 426).

(ii) A mixture of the diazoalkane (0.50 g, 4.39 mmol) and trimethylsilane (1.48 g, 20.0 mmol), sealed in a Pyrex bulb (5 l) and heated at 150 °C (5 h) and then at 200 °C (3 h), gave (i) nitrogen (0.12 g, 4.31 mmol, 98%); (ii) unchanged trimethylsilane (1.26 g, 17.0 mmol, 85% recovered); (iii) a higher-boiling fraction (0.4 g) which was shown by g.l.c. (10 m Silicone at 100 °C) to contain *ca.* twenty components; and (iv) a small amount of a white polymeric solid which coated the inside of the bulb.

(iii) A mixture of the diazoalkane (2.00 g, 17.5 mmol) and trimethylsilane (22.0 g, 300 mmol) was sealed in a silica ampoule (*ca.* 250 ml) and the liquid phase was ir-

radiated (5 h). The reaction gave (i) nitrogen (0.25 g, 8.90 mmol, 93%); (ii) unchanged trimethylsilane (21.1 g, 284 mmol, 95% recovered); (iii) a mixture (1.90 g) which was separated by g.l.c. (4 m Silicone at 100 °C) into its two components identified as unchanged diazoalkane (0.90 g, 7.91 mmol, 45% recovered) and 2,2,4,4-tetramethyl-2,4-disilapentane (1.0 g, 6.3 mmol, 66%) (Found: C, 52.0; H, 12.4. Calc. for C₇H₂₀Si₂: C, 52.2; H, 12.5%), b.p. 131–133 °C (lit.¹⁴ 132 °C), the i.r. spectrum of which was identical with that reported;¹⁴ and (iv) a polymeric residue (*ca.* 0.7 g).

(h) *With 2,2,4,6,6-pentamethyl-3,5-dioxo-2,4,6-trisilaheptane.* A mixture of the diazoalkane (2.00 g, 17.5 mmol) and the trisilaheptane (40.0 g, 180 mmol) was sealed in a silica ampoule (*ca.* 250 ml) and the liquid phase was irradiated (10 h). The reaction gave nitrogen (0.39 g, 14.0 mmol, 80%) and a higher-boiling mixture (41.5 g) which was distilled (20 cm column) to yield an azeotrope (*ca.* 39.5 g) of unchanged diazoalkane and unchanged trisilaheptane, b.p. 138–140 °C, and a distillation residue (1.0 g) which when separated by g.l.c. (10 m Silicone at 135 °C) gave a mixture (0.51 g, 1.62 mmol, 10%) (Found: C, 43.0; H, 10.5. Calc. for C₁₁H₃₂O₂Si₄: C, 42.8; H, 10.4%) of 2,2,4,6,6-pentamethyl-4-(trimethylsilyl)methyl-3,5-dioxo-2,4,7-trisilaheptane and 2,2,4,6,6,9,9-heptamethyl-3,5-dioxo-2,4,6,9-tetrasiladecane, present in the ratio *ca.* 2 : 1 (n.m.r.); ν_{\max} . 3000m (C–H str.), 2195m, 1456w, 1380s, 1250s (Me₃Si), 1040s and 1025s (Si–O–Si str.), 920m, 885m, 840s (Me₃Si), 753m, and 690w cm⁻¹; τ 5.21 (q, intensity 1, MeSiH), and *ca.* 10.05 (complex, intensity 90, CH₂ and Me); several minor components with longer g.l.c. retention times were also present in the residue.

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¹⁴ G. Fritz, H. Butil, J. Grobe, F. Aulinger, and W. Reeving, *Z. anorg. Chem.*, 1961, **312**, 201.