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REACTIONS OF SILACYCLOPROPANES WITH 1,2-DIPOLAR REAGENTS: DIAZOMETHANE AND METHYLENETRIMETHYLPHOSPHORANE

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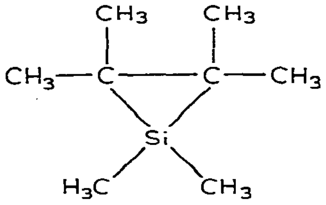
Summary

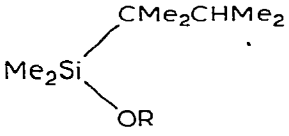
The reaction of diazomethane with hexamethyl-, 1,1,2,2,3-pentamethyl-2-ethyl- and 1,1,2,2,3-pentamethylsilirane in diethyl ether solution resulted in (formal) CH_2 insertion into the SiC_2 ring to give silacyclobutanes as products. The reaction of methylenetrimethylphosphorane with hexamethylsilirane produced a new phosphorus ylide, $Me_2CHCMe_2SiMe_2\bar{C}H\overset{+}{P}Me_3$.

Introduction

The ring silicon—carbon bonds of hexamethylsilacyclopropane (hexamethylsilirane) (I) whose preparation and spectroscopic characterization were reported

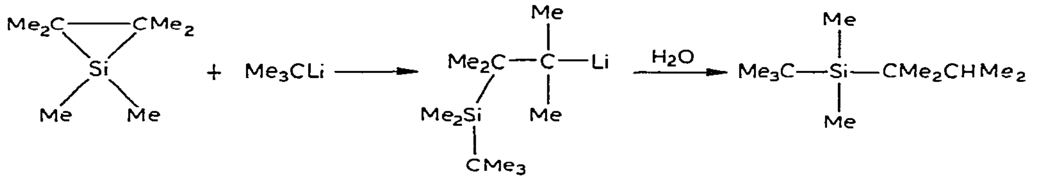


(I)



(II)

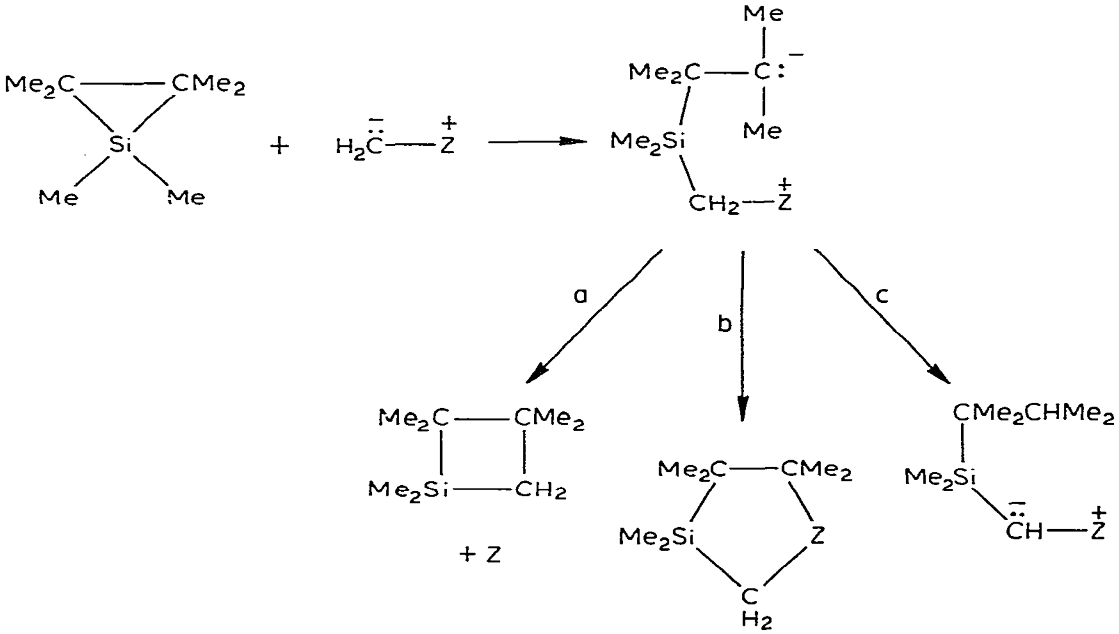
in 1975 [1], are highly reactive as a result of the high ring strain in the silacyclopropane system. Attack at the silicon atom in the SiC_2 ring by nucleophiles is particularly facile [1]. For instance, reactions of I with alcohols are exothermic at room temperature and give acyclic products of type II. Carbon nucleophiles, e.g., organolithium reagents, react with I at —78°C, as shown in eq. 1 [2a].



(1)

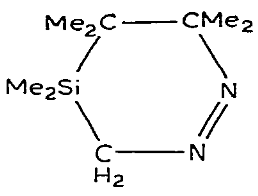
During the course of our investigations of the chemical reactivity of hexamethylsilirane [2] we have investigated reactions of two 1,2-dipolar reagents, diazomethane and methylenetrimethylphosphorane, both of which can react as carbon nucleophiles, with hexamethylsilirane as well as with some other siliranes. Such reactions are of interest since several reaction courses are, in principle, possible after the initial attack at silicon (Scheme 1).

SCHEME 1



Course a is the most likely one for the hexamethylsilirane/diazomethane reaction, although, of course, reaction of diazomethane as a 1,3-dipolar reagent to give III also must be considered. Courses b and c are the most probable in the case of $Me_3\overset{+}{P}—\overset{-}{C}H_2$, with proton transfer to form a new methylenephosphorane derivative (course c) expected to be more favorable. α-Silyl substituents have a strong stabilizing effect on phosphorus ylides [3], which would favor course c, and also, pentaalkylphosphoranes, from the little which is known about this class of compounds, appear to be stable only if the phosphorus atom is part of a homocubyl cage system [4] or the central atom of a spiro system [5].

A study of the reaction of methylenetrimethylphosphorane with hexamethyl-

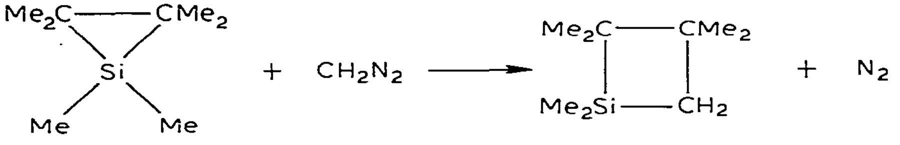


(III)

silirane is of particular interest since this reagent had been found [6] to react readily with the much less reactive silacyclobutanes *.

Results and discussion

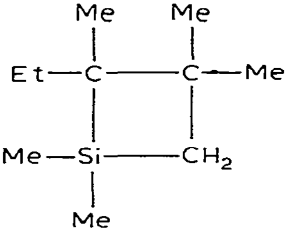
When a THF solution of hexamethylsilirane was added to an excess of diazomethane in diethyl ether solution at 0°C, gas evolution was observed. Subsequent work-up and GLC analysis showed that one major product had been formed in 70% yield. Its combustion analysis and ^{1}H, ^{13}C and ^{29}Si NMR spectra showed it to be 1,1,2,2,3,3-hexamethyl-1-silacyclobutane (IV) (eq. 2).



(IV)

(2)

Such (formal) CH_2 insertion into the saturated SiC_2 ring was found to be of limited scope. Thus 1,1,2,2,3-pentamethyl-2-ethyl-1-silirane [2c] reacted with diazomethane to give a ~2 : 1 mixture of V and VI in 41% total yield, and 1,1,2,2,3-pentamethyl-1-silirane gave a single CH_2 insertion product, VII, in 75% yield. There was no evidence for the formation of the isomeric product, VIII, in which there would be effective CH_2 insertion into the Si—$CHCH_3$ bond of the silirane. This marked preference for effective CH_2 insertion into the more hindered Si—CMe_2 bond of 1,1,2,2,3-pentamethylsilirane was unexpected. More surprising was the fact that the silacyclopropane derived from Me_2Si insertion



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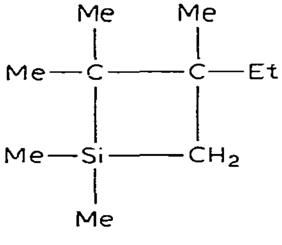

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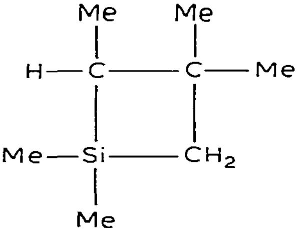

(VII)

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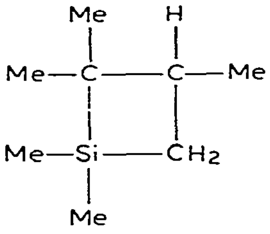
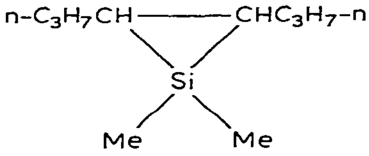
* For a comparison of the reactivity toward selected reagents of a silacyclopropane and 1,1-dimethyl-1-silacyclobutane, see ref. 7.

into *cis*-4-octene, IX, did not appear to react with diazomethane to give a silacyclobutane.

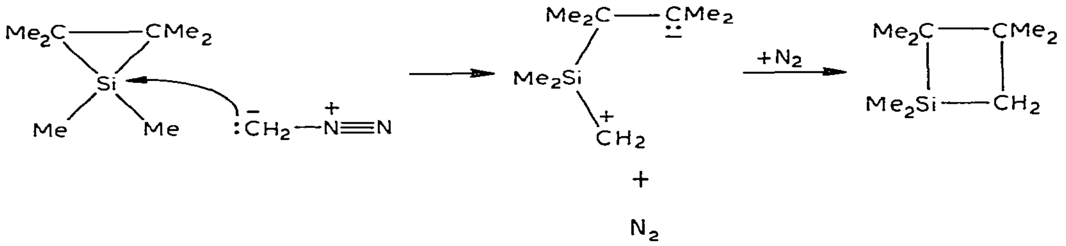


(VIII)



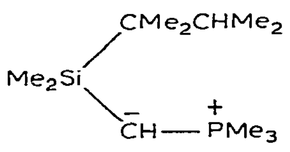
(IX)

While the silacyclobutanes formed in these reactions formally are products of methylene insertion into the respective siliranes, the conditions under which these reactions occurred are not those under which diazomethane releases CH_2. In the present reactions it is probable that the diazomethane molecule is reacting as a carbon nucleophile and that reaction course a is followed:

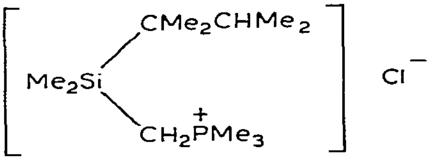


In the case of 1,1,2,2,3-pentamethyl-1-silacyclopropane, ring opening could occur at either Si—C bond. That it is the Si—CMe_2 and not the Si—$CHCH_3$ bond which opens very likely results from the greater steric repulsions in the former.

Successful reaction of methylenetrimethylphosphorane with hexamethylsilirane could be achieved at —78°C in pentane solution. The product, obtained in 78% (distilled) yield, was the α-silyl-substituted methylenephosphorane X, a colorless, air- and moisture-sensitive liquid. Treatment of X with gaseous hydrogen chloride gave the phosphonium salt XI. The 60 MHz proton NMR spectrum of X was too complex to permit an assignment of structure, but more extensive NMR studies (270 MHz ^1H; ^{31}P and $^{31}P\{^1H\}$; ^{13}C and $^{13}C\{^1H\}$) served to define the structure of X unambiguously.

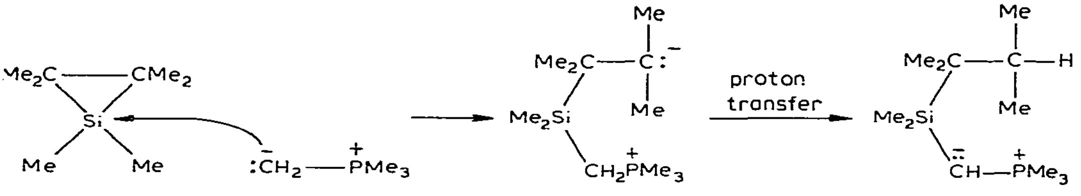


(X)



(XI)

Thus the reaction of methylenetrimethylphosphorane and hexamethylsilirane follows course c:



(XII)

There was no evidence for reaction course b, i.e., ring closure of intermediate XII at phosphorus to give a cyclic pentaalkylphosphorane. Presumably, the large steric factor and the high basicity of the tertiary carbanionic center in XII prevent such ring closure at phosphorus.

A separate paper [9] describes the reactions of oxygen-nucleophilic 1,2-dipolar reagents, such as dimethyl sulfoxide, pyridine *N*-oxide and trimethylamine *N*-oxide with hexamethylsilirane, as well as with 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene. This silirene also reacts with diazomethane to give the expected silacyclobutene insertion product [10].

Experimental

General comments

All reactions were carried out under dry argon or nitrogen in flame-dried, nitrogen-flushed glassware. Solvents used were rigorously dried, usually by distillation from sodium benzophenone ketyl.

The spectroscopic data were obtained with the following instruments:

IR: Perkin—Elmer Model 457-A grating infrared spectrophotometer; ^{1}H NMR: Varian Associations T-60, Perkin—Elmer R20 (60 MHz) or R22 (90 MHz), Bruker HFX 270 interfaced with a Nicolet Data System (270 MHz); ^{13}C and ^{29}Si NMR: Bruker HFX 90 interfaced with a Digilab FTS/NMR-3 computer; mass spectra: Varian MAT-44, operated at 70 eV.

Solutions of diazomethane in diethyl ether were prepared from *N,N′*-dimethyl-*N,N′*-dinitriosoterephthalamide (70%, with inert filler, du Pont EXR-101) [11]. Methylenetrimethylphosphorane was prepared by the reaction of sodamide with tetramethylphosphonium chloride in THF and was isolated as the pure substance by distillation at reduced pressure [12]. Hexamethylsilirane was prepared by the published procedure [1].

Reactions of siliranes with diazomethane

(a) Hexamethylsilirane. To 9.5 g (0.17 mol) of KOH in 20 ml of water in a 250 ml flask was added 100 ml of diethyl ether. This mixture was cooled to 0°C and 20 ml of 2-(2-ethoxyethoxy)ethanol was added, followed by 6.8 g (19 mmol, 38 meq) of EXR-101. This mixture was allowed to stand, with occasional stirring, for 10 min. The reaction flask then was connected to a distillation apparatus (no ground glass joints), using a 125 ml filter flask with a gas outlet as the receiver. Distillation of the ethereal diazomethane at 50° bath temperature into an ice-cooled receiver was continued (under an argon atmosphere) until the distillate became colorless.

The receiver containing the ethereal diazomethane solution was sealed with a no-air stopper and kept at 0°C. A solution of 1.44 mmol of hexamethylsilirane in 15 ml of tetrahydrofuran then was added dropwise by syringe. Immediate nitrogen evolution was observed. The reaction mixture was allowed to warm slowly to room temperature overnight. It then was warmed gently to remove unreacted diazomethane. The colorless solution which remained was filtered to remove polymethylene and examined by gas chromatography (GLC) (10% DC 200 at 110°C). The single major product (70% yield) which was present was collected by GLC and identified as 1,1,2,2,3,3-hexamethyl-1-silacyclobutane, n_D^{25} 1.4437. (Found: C, 69.41; H, 13.06. $C_9H_{20}Si$ calcd.: C, 69.14; H, 12.89.) ^{1}H NMR ($CCl_4/CHCl_3$) (δ, ppm): 0.26 (s, 6H, Si—CH_3); 0.91 (s, 2H, $SiCH_2$), 0.96 (s, 6H, Si—C—CH_3) and 1.00 (s, 6H, Si—C—C—CH_3). ^{13}C NMR (off resonance proton-decoupled; $CDCl_3$) δ_C (ppm): −1.9 (q, Si—$\underline{C}H_3$), 21.2 (q, Si—C—$\underline{C}H_3$), 26.8 (t, Si—$\underline{C}H_2$), 27.7 (q, Si—C—C—$\underline{C}H_3$), 29.8 (s, Si—$\underline{C}$—CH_3), and 38.9 (s, Si—C—$\underline{C}$—CH_3). ^{29}Si NMR (proton-coupled, $CDCl_3$) δ_{Si} (ppm): 18.5 (m) downfield from tetramethylsilane. (Compare δ_{Si} 18.90 for 1,1-dimethyl-1-silacyclobutane [13].)

(b) 1,1,2,2,3-Pentamethyl-3-ethyl-1-silirane. The title silirane was prepared by the published procedure [2c].

Hexamethylsilirane was prepared in THF and then the solution was concentrate at reduced pressure. A 1.02 g aliquot of the concentrate, found by NMR to contain 6.05 mmol of hexamethylsilirane, and 5.9 g (60 mmol) of 2,3-dimethyl-2-pentene (Chemical Samples Co.) were charged under argon into a 50 ml three-necked flask which was equipped with a magnetic stir-bar, a reflux condenser topped with an argon inlet, a glass stopper and a rubber septum. The mixture was stirred and heated at 70°C under argon for 15 h. Subsequently, a 0.6754 g aliquot (10.5% of the reaction mixture) was treated with 0.5 ml (12 mmol) of absolute methanol. GLC analysis showed that the expected 3-(3,4-dimethylpentyl)dimethylmethoxysilane, n_D^{25} 1.4394 (lit. [9] n_D^{25} 1.4395), had been formed in 68% yield. This indicates that the title silirane had been formed in ~70—75% yield in the Me_2Si transfer reaction.

The remainder of the silirane solution was added dropwise, under argon at 0°C, to a large excess of ethereal diazomethane. Work-up as in (a) followed. GLC analysis (10% DC 710 at 30°C) showed the presence of two closely spaced product peaks in 63/37 ratio (41% total yield). The product mixture was collected by GLC, n_D^{25} 1.4548, and analyzed. (Found: C, 70.55; H, 13.24. $C_{10}H_{22}Si$ calcd.: C, 70.50; H, 13.02.)

A small quantity of each isomer was collected by GLC for NMR and mass spectral analyses. The major isomer was assigned structure V on the basis of its mass spectrum which showed a large fragment ion with *m/e* corresponding to $[Me_2Si{=}CMeEt]^+$. Similarly, the identification of the minor isomer as VI is based on the occurence of a major fragment ion in its mass spectrum assignable to $[Me_2Si{=}CMe_2]^+$.

Major isomer, V. ^{1}H NMR ($CCl_4/CHCl_3$) (δ, ppm): 0.13 (s, 3H, $SiCH_3$), 0.25 (3, 3H, $SiCH_3$), 0.76 (t, *J* 7.5 Hz, 3H, CH_3 of Et), 0.83 (broad s, 2H, $SiCH_2$), 0.95 (s, 3H, CCH_3), 0.97 (s, 3H, CCH_3), 1.03 (s, 3H, CCH_3) and 1.25 (q, *J* 7.5 Hz, 2H, CH_2 of Et). Mass spectrum, *m/e* (rel. intensity): 171 (M^+ + 1, 0.14), 170 (M^+, 0.6), 115 (8), 114 ($Me_2Si{=}CMeEt^+$, 65), 100 (13), 99 (100), 73 (44), 72

(23), 59 (36), 58 (13), 55 (13), 45 (11), 44 (8), 43 (24), 41 (15) and 39 (8).

Minor isomer, VI. ^{1}H NMR ($CCl_4/CHCl_3$) (δ, ppm): 0.18 (s, 3H, $SiCH_3$), 0.29 (s, 3H, $SiCH_3$), 0.82 (t, J 7.5 Hz, 3H, CH_3 of Et), 0.46—0.86 (m, 2H, $SiCH_2$), 0.98 (s, 3H, CCH_3), 1.01 (s, 3H, CCH_3), 1.06 (s, 3H, CCH_3) and 1.31 (q, J 7.5 Hz, 2H, CH_2 of Et). Mass spectrum, m/e (rel. intensity): 171 (M^+ + 1, 0.6), 170 (M^+, 3), 127 (6), 114 (15), 101 (18), 100 ($Me_2Si{=}CMe_2^+$, 100), 99 (37), 86 (10), 85 (82), 84 (9), 83 (9), 74 (7), 73 (59), 72 (49), 71 (8), 69 (7), 60 (8), 59 (79), 58 (57), 57 (11), 56 (6), 55 (31), 53 (10), 45 (27), 44 (23), 43 (65), 42 (15), 41 (41) and 39 (22).

(c) 1,1,2,2,3-Pentamethyl-1-silirane. To a THF solution (1.277 g total) containing 4.57 mmol of hexamethylsilirane was added 5.0 ml (47 mmol) of 2-methyl-2-butene (Aldrich) and this mixture was heated at 70°C and stirred under argon for 15 h. Treatment of a 10% aliquot of the reaction mixture with 75 μl (1.9 mmol) of absolute methanol gave a mixture of both of the expected ring-opening products, n_D^{25} 1.4169, 2-(2-methylbutyl)dimethylmethoxysilane, $CH_3CH_2C(CH_3)_2SiMe_2OMe$ (XIII) and 2-(3-methylbutyl)dimethyldimethoxysilane, $(CH_3)_2CHCH(CH_3)SiMe_2OMe$ (XIV), in 2/1 ratio, in 80% combined yield (by GLC, 10% DC 200 at 90°C). (Found (isomer mixture): C, 60.14; H, 12.63. $C_8H_{20}OSi$ calcd.: C, 59.93; H, 12.57.) ^{1}H NMR (isomer mixture, $CCl_4/CHCl_3$) (δ, ppm): 0.05 (s, $SiCH_3$, XIII), 0.09 (s, $SiCH_3$, XIV) (total integration 6H), 0.87 (s, $C(CH_3)_2$, XIII), 0.89—1.00 (m, all other CH_3) (total integration 9H), 1.08—1.43 (m, CH, and CH_2) (total integration 2H), 3.39 (s, OCH_3, XIII) and 3.41 (s, OCH_3, XIV) (total integration 3H). The structure of the major product was assigned as XIII on the basis of the NMR spectrum of the mixture. The singlet at δ 0.87 ppm ($C(CH_3)_2$ of XIII) was found to be in a 1/1 ratio with the larger of the two ($Si(CH_3)_2$ peaks by NMR integration.

The remainder of the pentamethylsilirane solution was added dropwise by syringe to a large excess of ethereal diazomethane, under argon at 0°C. Work-up as in (a) gave a product solution which GLC (10% Apiezon L at 90°C) showed to contain a single major product (75% yield) which was collected and identified as 1,1,2,2,3-pentamethyl-1-silacyclobutane, n_D^{25} 1.4324. (Found: C, 67.26; H, 12.75. $C_8H_{18}Si$ calcd.: C, 67.52; H, 12.75.) ^{1}H NMR (90 MHz, $CS_2/CHCl_3$) (δ, ppm): 0.33 (s, 6H, $SiCH_3$), 0.98 (d, J 6.3 Hz, 3H, $CHC\underline{H}_3$), 1.03 (s, 3H, CCH_3), 1.17 (s, 3H, CCH_3). ^{1}H NMR (270 MHz; $CS_2/CHCl_3$): 0.33 (s, 6H, $SiCH_3$), 0.945 (d, J 3.4 Hz, 1H, methylene CH), 1.005 (d, J 7.1 Hz, 3H, $CHC\underline{H}_3$), 1.025 (d, J 3.4 Hz, 1H, methylene CH), 1.03—1.10 (m, 1H, methine CH), 1.08 (s, 3H, CCH_3) and 1.20 (s, 3H, CCH_3). ^{13}C NMR (off-resonance proton-decoupled $CDCl_3$) (δ_C, ppm) —2.3 (q, $SiCH_3$), 1.6 (q, $SiCH_3$), 10.4 (q, $CH\underline{C}H_3$), 14.2 (q, CCH_3), 22.7 (q, CCH_3), 26.9 (d, $\underline{C}HCH_3$), 28.6 (t, CH_2), 34.5 (s, CMe_2). Mass spectrum, m/e (rel. intensity): 143 (M^+ + 1, 0.6), 142 (M^+, 3), 114 (8), 100 (6), 99 (10), 87 (21), 86 ($Me_2Si{=}CHCH_3^+$, 57), 85 (13), 73 (35), 72 (37), 71 (11), 70 (5), 60 (8), 59 (43), 58 (100), 57 (14), 56 (6), 55 (12), 53 (7), 45 (18), 44 (23), 43 (46), 42 (13), 41 (18), 40 (6) and 39 (12).

(d) 1,1-Dimethyl-2,3-di-n-propyl-1-silirane. A mixture of 4.05 mmol of hexamethylsilirane in 1.0 ml of THF and 2.24 g (20 mmol) of *cis*-4-octene (Aldrich) was stirred and heated under argon at 70°C for 15 h. Treatment of a 0.72 g aliquot (23% of the solution) with 0.75 ml (18 mmol) of absolute methanol gave the expected [2c] ring-opening product, 4-octyldimethylmethoxysilane,

n_D^{25} 1.4263, lit. [2c] n_D^{25} 1.4260, in 58% yield.

The remainder of the silirane solution was added at 0°C, dropwise by syringe, to an ethereal diazomethane solution (from 19 mmol of EXR-101). Immediate separation of a large amount of white solid was observed. Subsequent addition of methanol (0.5 ml) to the reaction mixture produced no exotherm. The reaction mixture was filtered. GLC examination (10% DC 710 at 100°C) showed that no major product was present. Several minor products were present, but NMR analysis showed that none of them contained propyl groups. 4-Octyldimethylmethoxysilane was absent.

Reaction of hexamethylsilirane with methylenetrimethylphosphorane

Methylenetrimethylphosphorane, 1.52 g (16.9 mmol) was dissolved in 20 ml of pentane under a purified nitrogen atmosphere and this solution was cooled to −78°C. To the resulting fine precipitate of the ylide was added slowly, dropwise, 2.66 g (18.6 mmol) of hexamethylsilirane in 70 ml of pentane. The reaction mixture was stirred while it warmed slowly to room temperature. After 2 h, the solvent was removed at 60 mmHg, further volatiles at 5 mmHg. Distillation of the residue at 75°C/0.1 mmHg gave 3.06 g (78%) of phosphorane X. (Found: C, 61.92; H, 12.64. $C_{12}H_{29}PSi$ calcd.: C, 62.01; H, 12.58.) The product, which was unchanged after it had been heated at reflux at atmospheric pressure for 3 h, was a colorless, air- and moisture-sensitive liquid. ^1H NMR (270 MHz; C_6D_6, 35°C, TMS ext): (δ, ppm): −0.93 (d, J(HCP) 9.0 Hz, 1H, CHP), −0.02 (s, 6H, Me_2Si), 0.67 (d, J(HCP) 12.5 Hz, 9H, PCH_3), 0.81 (s, 6H, CCH_3), 0.87 (d, 6H, $CH(C\underline{H}_3)_2$), 1.73 ppm (sept, J(HCCH) 7.2 Hz, 1H, CH); (^{31}P decoupled): s, s, s, s, d, sept. ^{13}C NMR (C_6D_6, 35°C. TMS ext.) (δ_C, ppm): −2.5 (dd, J(PC) 90.0 Hz, PCH), 2.1 (q, Me_2Si), 19.3 (q, $C\underline{C}H_3$); 20.0 (dq, J(PC) 58 Hz, PCH_3), 21.3 (q, $\underline{C}H_3CH$), 24.6 (d, J(PCSiC) 5.0 Hz, CSi) and 34.7 ppm (d, $\underline{C}HMe_2$); (proton decoupled): d, s, d, d, s, s. ^{31}P NMR (C_6D_6, 35°C, H_3PO_4 ext) (δ, ppm): −1.52 (d dec, $J(H_3CP)$ 12.0, J(HCP) 9.0 Hz; (proton-decoupled): s. IR (neat liquid, KBr) (cm^{-1}): $\nu(P{=}C)$ 1155. Mass spectrum (20 eV), m/e (rel. intensity): 233 (M^+ + 1, 12), 218 ($[M - CH_3]^+$, 9), 148, 147 ($[M - C_2Me_4]^+$, 100).

The phosphonium chloride XI was prepared by dissolving 0.46 g (2.18 mmol) of ylide X in 10 ml of THF at 0°C and bubbling dry HCl gas through this solution for 2 min. The precipitated salt was filtered, washed with 2 ml of pentane and vacuum-dried. The white, hygroscopic powder had m.p. 122°C and was obtained in 96% yield. (Found: C, 53.63; H, 11.18; Si, 10.4. $C_{12}H_{30}ClPSi$ calcd.: C, 53.60; H, 11.25; Si, 10.44.) ^1H NMR (D_2O, 35°C, TMS ext) (δ, ppm): 0.58 (s, $SiCH_3$), 1.20 (d, J(HCCH) 6.5 Hz, $CHC\underline{H}_3$), 1.21 (s, CCH_3), 1.98 (d, J(PCH) 20.2 Hz, PCH_2), 1.70—2.38 (m), 2.20 (d, J(PCH) 14.0 Hz, PCH_3).

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