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REACTIONS OF HEXAMETHYLSILIRANE WITH PRIMARY AND SECONDARY PHOSPHINES AND WITH CHLOROPHOSPHINES

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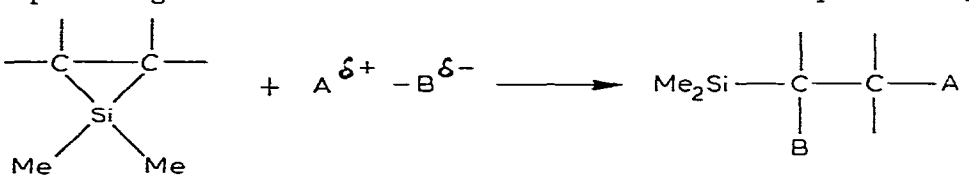
Summary

Secondary phosphines, R_2PH, with R = CH_3, C_6H_5, Me_3Si, cleave the SiC_2 ring of hexamethylsilirane in an exothermic reaction at room temperature to give silylphosphines, $R_2PSiMe_2(CMe_2CHMe_2)$. Methylphosphine reacts similarly. The reaction of the silirane with $RPCl_2$ (R = Me, Et, Ph) proceeds differently, giving Me_2SiCl_2, $Me_2C{=}CMe_2$ and cyclo-$[RP]_5$. With Ph_2PCl, the reaction with the silirane gives $Ph_2P{-}PPh_2$.

Introduction

In previous papers [1], we have reported the preparation of a number of silacyclopropanes (siliranes) and discussed the high reactivity of the saturated SiC_2 ring toward attack by diverse nucleophilic and electrophilic reagents. In general, a polar reagent $A^{\delta+}{-}B^{\delta-}$ reacts with siliranes as shown in eq. 1. Among the



(1)

classes of compounds which react in this manner are water, alcohols and phenols, ammonia, primary and secondary amines, carboxylic acids, hydrogen chloride and other protic acids.

In an extension of our studies of silirane reactivity, we have investigated the reactions of hexamethylsilirane (I) with methylphosphine and several secondary phosphines and with several chlorophosphines.

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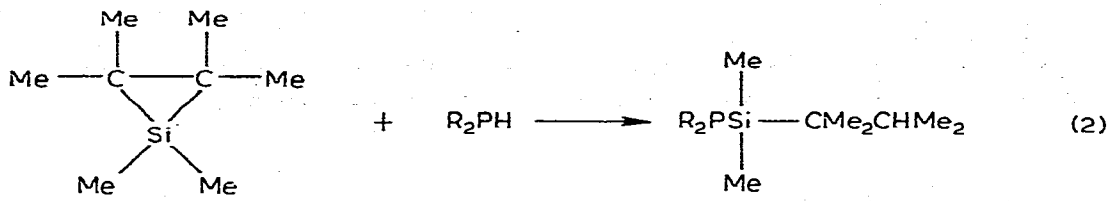
Results and discussion

Diphenylphosphine was found to react exothermally with hexamethylsilirane in pentane solution at room temperature (eq. 2). The product obtained, a very viscous oil, was a silylphosphine (R = Ph), as expected on the basis of the phos-



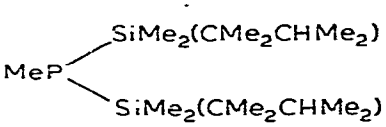
(I) (II) (2)

phorus—hydrogen bond polarity, $P^{\delta-}—H^{\delta+}$ (eq. 1).

Dimethylphosphine and bis(trimethylsilyl)phosphine reacted with hexamethylsilirane in similar fashion to give silylphosphines of type II with R = Me and Me_3Si, respectively. The latter is one of the few unsymmetrically substituted trisilylphosphines known [2]. In contrast to other compounds of this class [3], $(Me_3Si)_2PSiMe_2(CMe_2CHMe_2)$ did not disproportionate on being heated to temperatures as high as 250°C.

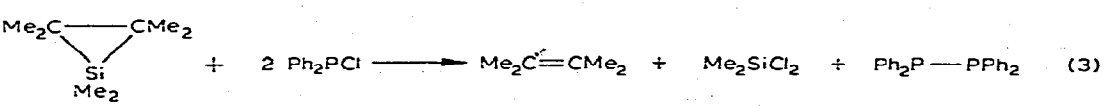
Both 1/1 and 1/2 reactions of methylphosphine with hexamethylsilirane were carried out. The 1/1 reaction, as expected, gave $MeP(H)SiMe_2(CMe_2CHMe_2)$ (III) a liquid which was spontaneously inflammable in air, in 46% yield. Unsymmetrically-substituted secondary silylphosphines of type $Me_3SiPMeH$ are known to undergo thermal disproportionation to give $MePH_2$ and $MeP(SiMe_3)_2$ [4], but compound III appeared to be stable to such decomposition, surviving unchanged purification by gas chromatography at 155°C. Presumably steric hindrance due to the bulky $SiCMe_2CHMe_2$ substituent prevents access to the transition state for the bimolecular disproportionation process.

The 2/1 silirane/methylphosphine reaction proceeded readily at room temperature and produced IV in 92% yield.



(IV)

On the basis of eq. 1, one might expect chlorophosphines, R_2PCl and $RPCl_2$, to react with hexamethylsilirane to give tertiary phosphines of types R_2PCMe_2-CMe_2SiMe_2Cl and $RP(CMe_2CMe_2SiMe_2Cl)_2$, respectively. Such was not the case. The exothermic reaction which occurred between hexamethylsilirane and diphenylchlorophosphine proceeded as shown in eq. 3.



(3)

Tetraphenyldiphosphine was isolated in 92% yield. A similar reaction between equimolar quantities of phenyldichlorophosphine and hexamethylsilirane gave the known pentaphenylcyclopentaphosphine (cyclo-$[PhP]_5$) as the organophosphorus reduction product (78% yield), as well as tetramethylethylene and dimethyldichlorosilane. A reaction of the silirane with methyldichlorophosphine (exothermic at 0°C) gave cyclo-$[MeP]_5$ (36%) and a small amount of cyclo-$[MeP]_6$. Similarly, hexamethylsilirane reacted with ethyldichlorophosphine to produce cyclo-$[EtP]_5$ in 36% yield. In all of these silirane/chlorophosphine reactions $ClMe_2SiCMe_2CHMe_2$ appeared as a by-product. This compound is the HCl cleavage product of hexamethylsilirane, but its provenace is unknown.

Treatment of hexamethylsilirane with phosphorus trichloride in benzene in varying ratios resulted in an exothermic reaction at room temperature. The initially formed product was soluble in benzene, but a yellow solid (which remains unidentified) precipitated from these solutions after they had stood for some time. Dimethyldichlorosilane and tetramethylethylene also were formed. Pentavalent phosphorus dichlorides, e.g., $EtP(S)Cl_2$ and $ClCH_2P(O)Cl_2$, did not react with hexamethylsilirane at room temperature or at 80°C.

The mechanism of these chlorophosphine reactions remains obscure and requires further study. In view of the known radical reactivity of chlorophosphines [5] the observed products could be explained in terms of a radical mechanism.

Experimental

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of dry argon. The standard apparatus consisted of a 100 ml, three-necked, round-bottomed flask which was equipped with a reflux condenser, a gas inlet tube, a no-air stopper and a magnetic stir-bar. All solvents were rigorously dried before use. In general, solvents were removed by trap-to-trap distillation in vacuo into a trap at −196°C.

Because of the unpleasant odors of phosphines and silylphosphines, all operations should be carried out in an efficient hood.

Gas chromatography was used in product isolation and purification (F & M Model 5754 gas chromatograph; 4 ft × 0.25 in. column packed with 25% SE 30 silicone rubber gum on Chromosorb W (column A) or a 6 ft. × 0.25 in., 10% Apiezon L grease column (column B)).

Proton magnetic resonance spectra were recorded using a Varian Associates T60 or a Hitachi—Perkin—Elmer R24B spectrometer and ^{31}P NMR spectra using a Bruker HFX 90 spectrometer interfaced with a Digilab FTS/NMR-3 computer. ^1H chemical shifts are reported in δ units, ppm downfield from tetramethylsilane as internal standard and ^{31}P chemical shifts in ppm relative to 85% H_3PO_4 as external standard. Positive values indicate downfield shifts from the standard.

Hexamethylsilirane was prepared as described previously [1c]. The THF solution of this material was concentrated at reduced pressure. The concentration of hexamethylsilirane in the residue was determined by integration of the proton NMR spectrum using toluene as internal standard [1c]. Minor impurities included THF, $Me_2Si(CHMe_2)_2$, $Me_2Si(CMe{=}CH_2)_2$ and $Me_2Si(CHMe_2)(CMe{=}CH_2)$ [1c].

Reaction of hexamethylsilirane with phosphines.

(1) Diphenylphosphine. The standard apparatus was charged (under argon) with 6.17 mmol of hexamethylsilirane and 25 ml of pentane. To this solution was added dropwise by syringe, with stirring at room temperature, 1.15 g (6.17 mmol) of diphenylphosphine [6]. An exothermic reaction resulted. The mixture was stirred at room temperature for 18 h. Subsequently, the pentane was removed at reduced pressure. Distillation of the residue at reduced pressure (short path still head) gave 1.96 g (97% yield) of $Ph_2PSiMe_2(CMe_2CHMe_2)$, b.p. 143°C at 0.01 Torr. The purity of the product was checked by GLC (column A at 250°C). (Found: C, 73.13; H, 8.89. $C_{20}H_{20}PSi$ calcd.: C, 73.13; H, 8.89%.) ^{31}P NMR (C_6H_6): $\delta(^{31}P)$ —59.2 ppm. ^1H NMR (C_6H_6): δ 0.17 (d, J(PSiCH) 3.2 Hz, 6H, $SiMe_2$), 0.84 (s, 6H, CMe_2), 0.86 (d, J 6.2 Hz, $CHMe_2$), 1.78 (septet, J 6.2 Hz, $CHMe_2$), 6.86—7.9 ppm (m, 10H, Ph).

(2) Dimethylphosphine. The standard apparatus was charged with 8.03 mmol of the silirane and 10 ml of benzene and the mixture was cooled with a liquid nitrogen bath. Subsequently, 10.87 mmol of gaseous dimethylphosphine [7] was condensed onto the frozen mixture. The resulting mixture was allowed to warm to room temperature very slowly and then was stirred for 40 h. Trap-to-trap distillation removed solvent and unconverted dimethylphosphine. Vacuum distillation of the residue gave 1.19 g (73%) of $Me_2PSiMe_2(CMe_2CHMe_2)$, b.p. 71°C at 1.0 Torr, 33°C at 0.005 Torr. The product was purified by GLC (column A at 135°C). (Found: C, 58.55; H, 12.10. $C_{10}H_{25}PSi$ calcd.: C, 58.79; H, 12.32%.) ^{31}P NMR (C_6H_6): $\delta(^{31}P)$ —131.4 ppm. ^1H NMR (C_6H_6): δ 0.1 (d, J(PSiCH) 2.5 Hz, 6H, Me_2Si), 0.97 (s, 6H, CMe_2), 0.97 (d, J 6.0 Hz, 6H, $CHMe_2$), 1.03 (d, J(PCH) 2.4 Hz, 6H, Me_2P), 1.73 ppm (septet, J 6.0 Hz, 1H, $CHMe_2$).

(3) Bis(trimethylsilyl)phosphine. The standard apparatus was charged with 12.6 mmol of the silirane and 2.24 g (12.6 mmol) of $(Me_3Si)_2PH$ [8] was added by syringe over a 10 min period. The reaction mixture was stirred at room temperature for 24 h and then was distilled at reduced pressure. After fractions containing 0.105 g of $(Me_3Si)_2PH$ and an unidentified compound had been collected, the expected product, $(Me_3Si)_2PSiMe_2(CMe_2CHMe_2)$, was obtained, 1.99 g (49%), b.p. 97—100°C at 0.005 Torr. Samples for analysis and spectroscopy were obtained by GLC (column B, 210°C). (Found: C, 52.45; H, 11.67. $C_{14}H_{37}PSi_3$ calcd.: C, 52.43; H, 11.63%.) ^{31}P NMR (C_6H_6): $\delta(^{31}P)$ —253.7. ^1H NMR (C_6H_6): δ 0.44 (d, J(PSiCH) 4.2 Hz, 18H, Me_3Si), 0.44 (d, J(PSiCH) 2.4 Hz, 6H, Me_2Si), 1.02 (d, J 6.7 Hz, 6H $CHMe_2$), 1.03 (s, 6H, CMe_2), 1.65 ppm (septet, J 6.7 Hz, 1H, $CHMe_2$).

Another reaction was carried out using 6.9 mmol of the silirane and 21.06 mmol of $(Me_3Si)_2PH$ at 70°C for 20 h. Similar work-up gave a 68% recovery of the silylphosphine as well as the expected ring-opening product in 82% yield.

(4) Methylphosphine. (i) 1/1 reactant ratio. A solution of 10.44 mmol of the silirane in 30 ml of pentane was prepared in the standard apparatus and frozen in a liquid nitrogen bath. Subsequently, 12.52 mmol of gaseous methylphosphine [9] was condensed onto this mixture. The resulting mixture was allowed to warm slowly to room temperature and was stirred for 16 h. The unconverted $MePH_2$ and most of the solvent were removed by trap-to-trap distillation. The residue was distilled at reduced pressure to give a fraction, b.p. 116°C at 20 Torr, containing 0.936 g of $MeHPSiMe_2(CMe_2CHMe_2)$ contaminated (by NMR)

with about 7% of $Me_2PSiMe_2(CMe_2CHMe_2)$ and 0.306 g of the bis-adduct IV, b.p. 115—117°C at 0.03 Torr, which contained the components of the first fraction as impurities. The yields of the mono- and bis-adducts were 46 and 14%, respectively, based on the silirane. The mono-adduct was purifed by GLC (column B at 155°C). (Found: C, 57.15; H, 12.37. $C_9H_{23}PSi$ calcd.: C, 56.84; H, 12.09%.) ^{31}P NMR: $\delta(^{31}P)$ —176.6 ppm (d, J(PH) 187 Hz). ^1H NMR (C_6H_6): δ 0.10—0.27 (Me_2Si) *, 0.98 (d, J 6.0 Hz, 6 Hz, $CH\underline{Me}_2$), 1.0 (s, 6H, CMe_2), 1.01 (d of d, J(PCH) 2.0 Hz, 3H, PMe), 1.73 (septet, J 6.0 Hz, 1H, $C\underline{H}Me_2$), 2.13 ppm (d of q, J(HPCH) 7.3 Hz, 1H, PH).

(ii) 2/1 reactant ratio. A similar reaction carried out using 7.9 mmol of the silirane and 3.95 mmol of $MePH_2$ gave 1.21 g (92%) of $MeP[SiMe_2(CMe_2CHMe_2)]_2$, b.p. 113—115°C at 0.03 Torr. The crude product was purified by GLC (column B at 230°C). (Found: C, 60.87; H, 12.45. $C_{17}H_{41}PSi_2$ calcd.: C, 61.44; H, 12.33%.) ^{31}P NMR (C_6H_6): $\delta(^{31}P)$ —202.6 ppm. ^1H NMR (C_6H_6): δ 0.30 (d, J(PSiCH) 2.9 Hz, 12H. $SiMe_2$), 0.98 (s, 12H, CMe_2), 0.98 (d, J 6.5 Hz, 12H, $CH\underline{Me}_2$), 1.18 (d, J(PCH) 2.5 Hz, 3H, MeP), 1.88 (septet, J 6.5 Hz, 1H, $C\underline{H}Me_2$), Mass spectrum: $C_{17}H_{14}{}^{28}Si_2P$ *m/e* found: 332.2485; calcd.: 332.2484.

Reactions of hexamethylsilirane with chlorophosphines

(1) Diphenylchlorophosphine. The standard apparatus was charged with a solution of 9.96 mmol of the silirane in 15 ml of benzene and a solution of 2.19 g (9.96 mmol) of diphenylchlorophosphine (Strem Chemicals, Inc.) in 10 ml of benzene was added dropwise with stirring. An exothermic reaction commenced, and subsequently, the mixture was stirred at room temperature for 12 h. Removal of volatiles ($Me_2C{=}CMe_2$, Me_2SiCl_2 and $Me_2ClSiCMe_2CHMe_2$, by GLC and IR and/or NMR) left a white solid residue, m.p. 117°C after several washings with pentane. Recrystallization from benzene/petroleum ether gave pure tetraphenyldiphosphine, m.p. 119—121°C (lit. [10] m.p. 121—122°C), $\delta(^{31}P)$ (C_6H_6) —15.03 ppm (lit. [11] —15.2 ppm). The product yield was 1.7 g (92%).

(2) Phenyldichlorophosphine. The phosphine (0.5 g, 2.8 mmol, Strem Chemicals, Inc.) was added by syringe over a 30 min period at room temperature with stirring to a solution of 5.6 mmol of the silirane in 5 ml of benzene, resulting in an exothermic reaction. The mixture was stirred at room temperature for 24 h. At this time, a ^1H NMR spectrum of the solution showed that about half of the silirane still was present. Therefore, another 2.8 mmol of $PhPCl_2$ was added. After this mixture had been stirred for 3 h, trap-to-trap distillation was used to remove volatiles ($Me_2C{=}CMe_2$, Me_2SiCl_2, $Me_2ClSiCMe_2CHMe_2$, as before). The residue was dissolved in a benzene/pentane mixture. After 3 days, 0.473 g (78%) of colorless crystals of cyclo-$[PhP]_5$, m.p. 149—152°C (lit. [12] m.p. 151—152°C), $\delta(^{31}P)$ (C_6H_6): —5.0 ppm (lit. [13] —4.6 and [14] —5.0 ppm), were separated.

(3) Methyldichlorophosphine. The phosphine (0.67 g, 5.73 mmol, Strem Chemicals, Inc.) was added slowly with stirring by syringe to a solution of 5.74 mmol of the silirane in 10 ml of benzene at 0°C. The initially exothermic

* Spectrum of higher order because of the high field quartet of the $PHCH_3$ group [4].

reaction was followed by stirring at room temperature for 14 h.

Some of the volatiles (solvent, $Me_2C{=}CMe_2$, Me_2SiCl_2, $Me_2ClSiCMe_2CHMe_2$, the latter in 23% yield) were removed by trap-to-trap distillation and identified as in previous experiments. The residue was examined by GLC (column B at 120°C and then at 250°C). At 250°C, cyclo-$[MeP]_5$ was collected ($\delta(^{31}P)$ (C_6H_6) 16.4 ppm; lit. [14] 18 ppm; mass spectrum: molecular ion, *m/e* 230; calcd. 230). Yield determination (column B, 230°C, hexadecane) indicated the presence of 0.41 mmol (36%). GLC also showed a small amount of cyclo-$[MeP]_6$ to be present. A solid by-rpduct could not be identified.

(4) Ethyldichlorophosphine. The procedure used in the reaction of $PhPCl_2$ was applied in the reaction of 3.91 mmol of the silirane with0.512 g (3.91 mmol) (Strem Chemicals, Inc.) in 5 ml of benzene at room temperature for 14 h. An initial exotherm was observed. Trap-to-trap distillation gave the same volatiles: $Me_2C{=}CMe_2$, Me_2SiCl_2 and $Me_2ClSiCMe_2CHMe_2$ (8%). The residue was examined by GLC (column B, 260°C) and cyclo-$[EtP]_5$ was collected ($\delta(^{31}P)$ (C_6H_5) 15.1 ppm; lit. [14,15] 15.7 ppm; mass spectrum: molecular ion *m/e* 300; calcd. 300). GLC yield determination showed 0.28 mmol (36%) of cyclo-$[EtP]_5$ to be present. An unidentified by-rpoduct, which had the same GLC retention time as that obtained in the $MePCl_2$ reaction, also was isolated.

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