

Reactions of Recoiling Silicon Atoms with Phosphine–Diene Mixtures and the Question of Silylene Intermediates†

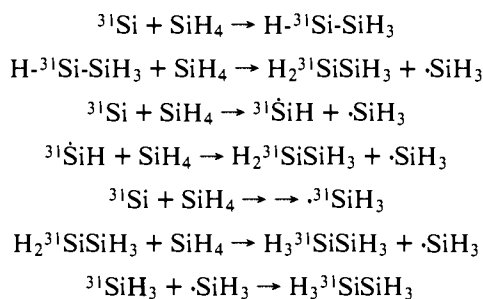
Rong-Juh Hwang and Peter P. Gaspar*

Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130. Received September 9, 1977

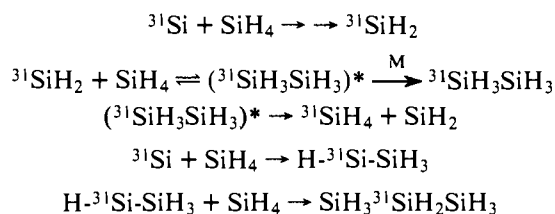
Abstract: Reactions of silicon atoms recoiling from the $^{31}\text{P}(n,p)^{31}\text{Si}$ nuclear transformation in phosphine–butadiene mixtures yield ^{31}Si -1-silacyclopent-3-ene, also obtained in 46% yield from reaction of thermally generated SiH_2 with butadiene, and a product believed to be ^{31}Si -1-silacyclopenta-2,4-diene. The variation of product yields with the composition of $\text{PH}_3\text{-SiH}_4\text{-C}_4\text{H}_6$ recoil reaction mixtures casts doubt on the participation of ground-state singlet silylene $^{31}\text{SiH}_2$ as a reactive intermediate, as does the failure to detect any of the thermal adduct of silylene to cyclopentadiene 1-silacyclohexa-2,4-diene from the reactions of ^{31}Si in $\text{PH}_3\text{-SiH}_4\text{-C}_5\text{H}_6$ mixtures. Alternative mechanisms are considered. Thermally generated Me_2Si does not abstract hydrogen atoms from Me_3SiH , but inserts into the Si–H bond.

Introduction

Previous studies of the reactions of recoiling silicon atoms in mixtures of phosphine and various silanes have been interpreted in terms of reaction schemes in which silylene ($^{31}\text{SiH}_2$) plays a prominent role.^{1–9} Phosphine is the precursor of the recoiling atoms via the $^{31}\text{P}(n,p)^{31}\text{Si}$ nuclear transformation. The major products from the reactions of recoiling silicon atoms with silane, disilane, and trisilane are the next higher homologues disilane, trisilane, and normal and isotetrasilanes, respectively.⁶ These products are also formed in high yield from Si–H insertion reactions of thermally generated silylene.^{10–12} In the case of recoil atom reactions the modest sensitivity of the product yields to the presence of radical scavengers like nitric oxide and ethylene was felt to be in accord with the formation of silylene in high-energy reactions of silicon atoms. This was so since singlet silylene SiH_2 , like CH_2 , was not expected to react preferentially with radical scavengers.^{4,6,9,13,14} The small scavenger effect was also interpreted as ruling out the participation of thermal energy silyl radicals $^{31}\text{SiH}_3$ in the recoil reactions.^{4,6} On this basis the following route to the formation of disilane in the reactions of recoiling silicon atoms with silane was regarded as being improbable:⁶



A reaction scheme incorporating $^{31}\text{SiH}_2$ that rationalizes the formation of silane, disilane, and trisilane from the reactions of recoiling silicon atoms in phosphine–silane mixtures is given below:^{6,46}

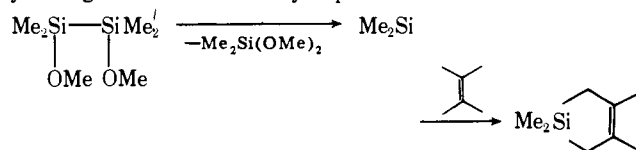


† ERDA Technical Report No. COO-1713-73.

Some important questions remained unanswered, however. In pure phosphine, $^{31}\text{SiH}_4$ is the sole volatile product and is obtained in only ca. 2% yield, while the combined yields from 1:1 phosphine–silane mixtures reach 70%. Does this mean that only a small amount of silylene is produced in pure phosphine? One may ask what are the primary reactions of silicon atoms in the absence of Si–H bonds? Is $^{31}\text{SiH}_2$ still an important intermediate? If $^{31}\text{SiH}_2$ is present, what is its electronic state, and do the reactions of singlet and triplet silylene differ?

To answer these questions and to investigate the formation of silylene in phosphine–silane mixtures, a new silylene trapping agent was required.

Butadiene was chosen as a substrate for silylene reactions⁸ because Atwell and Weyenberg had found that dimethylsilylene undergoes efficient addition to 2,3-dimethylbutadiene, yielding a substituted silacyclopentene.^{15,16}



Tang and co-workers have also employed butadiene as reaction substrate for recoiling silicon atoms. The product ^{31}Si -1,1-difluoro-1-silacyclopent-3-ene from PF_3 –butadiene mixtures was ascribed to $^{31}\text{SiF}_2$ intermediates,¹⁷ both singlet and triplet,^{18–20} although cocondensation of thermally generated SiF_2 and butadiene does not produce it.²¹ From PH_3 –butadiene mixtures ^{31}Si -1-silacyclopent-3-ene was obtained and ascribed to the reactions of $^{31}\text{SiH}_2$,⁷ formed 80% in a triplet state and 20% in the singlet ground state.⁹

To test the assumption that unsubstituted silylene would add to unsubstituted butadiene, silylene was generated by pyrolysis of disilane in the presence of butadiene employing the method of Tebben and Ring.²² Cyclopentadiene was also employed as a silylene substrate, following a report by Chernyshev, Komalenkova, and Bashkurova that addition of dichlorosilylene to cyclopentadiene yields 1,1-dichloro-1-silacyclohexa-2,4-diene.²³

Both butadiene and cyclopentadiene have been employed as substrates for recoiling silicon atoms in mixtures of phosphine and the diene. Competition between silane and these dienes for recoiling silicon atoms has also been investigated in ternary mixtures of phosphine, silane, and the diene.

Experimental Section

Materials. Phosphine (99.5%) was obtained from the Rocky Mountain Research Co.; silane (semiconductor grade) and 1,3-butadiene

tadiene (99%) were obtained from the Matheson Co. These compounds were used without purification. Silacyclopentane was synthesized by the method of West.²⁴ 1-Silacyclopent-2-ene, 1-silacyclopent-3-ene, 3-butenylsilane, and divinylsilane were synthesized according to the methods of Benkeser et al.²⁵ 1,1-Difluoro-1-silacyclopent-2-ene and 1,1-difluoro-1-silacyclopent-3-ene were synthesized by the method of Chao, Moore, and Laane.²⁶ Disilane and *n*-butylsilane were synthesized by a modification²⁷ of the method of Schlesinger et al.²⁸ *cis*- and *trans*-3-butenylsilane were synthesized by the method of Laane²⁹ and Bailey and Pines.³⁰ 1,3-Butadienylsilane was synthesized by a modification²⁷ of the method of Petrov and Sadykh-Zade.³¹ 5-Silaspiro[4.4]nona-2,4-diene was synthesized by the method of Salomon.³²

3-Silyl-1-butene. To 14.4 g (0.6 mol) of Mg turnings under a nitrogen atmosphere was added dropwise 27 g (0.2 mol) of 2-butenyl bromide in 200 mL of dry ether. The resulting Grignard reagent was transferred under nitrogen to a dropping funnel and added dropwise to a vigorously stirred mixture of 500 mL of anhydrous ether and 35.5 g (0.23 mol) of SiCl₄. The resulting mixture was stirred for 5 h. After removal of salts distillation of the filtrate yielded 10 g (30% yield) of 3-trichlorosilyl-1-butene, bp 45–50 °C (26 mm). Reduction of 9.5 g of this compound with LiAlH₄ (2.3 g) in 10 mL of *n*-butyl ether yielded 2.5 g (58% yield) of 3-silyl-1-butene: bp 40–41 °C; NMR (neat) δ 0.88 (CH₃, d, 3 H), 1.6 (CH, m, 1 H), 3.22 (SiH₃, d, 3 H), 4.55 (CH₂, m, 1 H); IR (gas) cm⁻¹ 3040 (m), 2920 (s), 2140 (s), 1620 (m), 1450 (m), 1150 (m), 1050 (m), 920 (s), 850 (m), 730 (m).

1-Silyl-3-buten-1-yne. Vinylacetylene (3.5 g, 0.07 mol) was condensed into a tube containing 20 mL of degassed dry benzene. The resulting solution and 100 mL of dry ethyl ether were rapidly poured into a flask which was maintained at -10 to -15 °C under an inert atmosphere and equipped with a reflux condenser maintained at 3 °C. To this reaction mixture was added dropwise 35 mL of a 2 m solution of phenyllithium with vigorous stirring. Then 14.8 g (0.08 mol) of SiCl₄ was added rapidly and stirring was continued for 12 h. After removal of salts distillation of the filtrate yielded 2 g (16%) of 1-trichlorosilyl-3-buten-1-yne, bp 65–70 °C (50 mm). Reduction of this compound with LiAlH₄ in *n*-butyl ether on the vacuum line²⁷ gave 1-silyl-3-buten-1-yne in 40% yield: NMR (neat) δ 5.35 (CH₂=CH, m, 3 H), 3.5 (SiH₃, s, 3 H); IR (gas) cm⁻¹ 3100 (m), 3060 (m), 2970 (s), 2180 (s), 1610 (w), 1490 (m), 1120 (m), 980 (m), 940 (s), 930 (s), 690 (m), 680 (s), 670 (m), 670 (m); mass spectrum (70 eV) *m/e* 82 (parent), 81, 77, 55, 54 (base), 53.

Recoil Atom Reaction Mixtures. Reaction mixtures were prepared using conventional vacuum line techniques previously described⁶ to freeze condensable gases into 6 or 14 mm i.d. \times 9 cm quartz ampules, followed by any noncondensable components. The ampules were sealed with a natural gas-oxygen flame. Recoil losses from 1:1 PH₃-SiH₄ mixtures in the 6-mm ampules have previously been determined to be negligible at 1000 Torr total pressure, 9 \pm 1% at 500 Torr, and 41 \pm 4% at 200 Torr.⁶

Fast Neutron Irradiations. Sets of ampules were rotated to equalize neutron flux during the ca. 45 min irradiations, as previously described.³³ Fast neutrons were produced by an integrated current of 20 μ A h per irradiation of 13 MeV deuterons in the Washington University cyclotron impinging on a beryllium target. The neutron flux at the reaction mixtures was ca. 10⁸ cm⁻² s⁻¹.

Analysis of Recoil Atom Reaction Mixtures. The radio gas chromatographic procedures have been described previously.^{4,6} In the present experiments the windowless flow counter of the Nuclear Chicago Model 4997 digital gas radiochromatography system was replaced by a concentric cylindrical window counter designed by Welch, Withnell, and Wolf,³⁴ and P-10 counting gas was used. The counter was operated at ca. 50 °C with a plateau from ca. 2000 to 2400 V. The window isolating the chromatographic effluent from the counter was a cylinder of 1-mil aluminum foil.

Four different 1/4 in. o.d. aluminum chromatographic columns were employed, the stationary phases supported on 40/50 mesh acid- and base-washed and silanized diatomaceous earth (Anakrom ABS). The stationary phases were SF-96 silicone oil, 20% w/w, 30 ft; diethyl phthalate, 30% w/w, plus DC555 silicone oil 50% w/w, 30 ft; dimethylsulfolane 30% w/w, 40 ft; and SE-30 silicone oil, 20% w/w, 20 ft.

Absolute yield measurements of radioactive products containing ³¹Si were carried out by comparing the total activity per product detected by the flow counter, normalized for the amount of phosphine precursor, with the total activity for the volatile products (silane,

disilane, and trisilane) from 1:1 phosphine-silane mixtures. The absolute product yields from 1:1 phosphine-silane mixtures were determined as previously described³³ by comparing the activities of individual products trapped after chromatographic separation with the total activity induced in a reaction mixture. A liquid scintillation counter was used to measure the activities of the trapped products.

Dose. The total energy deposited in these reaction mixtures during fast neutron irradiation was ca 2 \times 10⁻⁴ eV/molecule as determined by acetylene dosimetry.³⁵

Pyrolysis of Disilane in the Presence of 1,3-Butadiene. The pyrolysis of disilane in the presence of 1,3-butadiene was carried out in a recirculating flow system with a resistance-heated thermolysis zone 8 mm in diameter and 15 cm long. The pyrolysis tube was connected to a peristaltic pump for cycling the reactants through the system and a cold trap employed to condense all products less volatile than the reactants and to fix the vapor pressure of the reactants. A 1-L bulb was located between the cold trap and the peristaltic pump. The reactants were transferred into the cold trap immersed in liquid nitrogen. Then the liquid nitrogen bath was replaced by a slush bath of the desired temperature. The total volume of the apparatus was ca. 1.25 L.

In a typical experiment 1.3 mmol of Si₂H₆ was subjected to pyrolysis in the presence of 6.7 mmol of 1,3-butadiene for 12 h at 375–385 °C with the cold trap maintained at -45 °C. The total pressure of reactants was 120 Torr, and the gas-phase reactant ratio C₄H₆:Si₂H₆ = 5 was confirmed by vapor chromatography before the pyrolysis was started. A small amount of hydrogen was formed. The reaction mixture was separated by trap to trap distillation on the vacuum line. The fraction passing a -78 °C trap contained SiH₄ and Si₂H₆ (1.2 mmol, SiH₄:Si₂H₆ = 9) and excess butadiene. The fraction condensed at -78 °C was 1-silacyclopent-3-ene (0.5 mmol, yield 46%). A trace of trisilane was also found in this fraction. The product was identified from its NMR and IR spectral data, which were in agreement with literature values.²⁵

Pyrolysis of Disilane in the Presence of Cyclopentadiene. The recirculating flow system described above was employed. In a typical experiment 0.67 mmol of disilane was subjected to pyrolysis in the presence of 2.0 mmol of cyclopentadiene for 6 h at 420 °C with the cold trap maintained at -30 °C. The total reactant pressure was 40 Torr and the C₅H₆:Si₂H₆ = 3 ratio was confirmed by vapor chromatography before heating commenced. A small amount of H₂ was produced. The reaction mixture was separated by trap to trap distillation on the vacuum line. The fraction which passed the -78 °C trap and was condensed at -196 °C was SiH₄ and a small amount of Si₂H₆ (0.62 mmol total). The fraction which condensed at -78 °C was 1-silacyclohexa-2,4-diene (0.067 mmol, 11% yield) and excess cyclopentadiene. A trace of trisilane was found in this fraction. The silacyclohexadiene was identified from its spectral data: NMR (neat) δ 1.2 (CH₂, doublet of triplets, *J* = 3, *J'* = 6 Hz, 2 H), 3.7 (SiH₂, t, *J* = 6 Hz, 2 H), 5.4 (CH, m, 3 H), 6.3 (CH, m, 1 H); IR (gas) cm⁻¹ 3030 (s), 2930 (s), 2240 (m), 2150 (s), 1620 (m), 1550 (m), 1400 (w), 950 (s), 850 (s), 830 (s), 700 (m), 620 (m); mass spectrum (70 eV) *m/e* 96 (parent and base), 95, 93, 81, 68, 66, 54, 52; UV λ_{\max} (cyclohexane) 271 nm (ϵ 5280).

Pyrolysis of Hexachlorodisilane in the Presence of Cyclopentadiene. The pyrolysis of hexachlorodisilane in the presence of cyclopentadiene was carried out in a nitrogen flow system at 540 °C. The apparatus consisted of a 22-mm o.d. horizontal Pyrex tube 30 cm in length, packed with 5-mm glass beads contained within a tube furnace. A mixture of 7 mL of freshly distilled cyclopentadiene and 3 mL of hexachlorodisilane was allowed to flow dropwise into the hot zone over a 1.5-h period with a slow stream of nitrogen flowing through the system. A brownish liquid collected in the receiver, which was immersed in a dry ice-acetone cold bath. After the pyrolysis tube was allowed to cool, it was washed with anhydrous ether. Vacuum distillation of the pyrolysate and washings led to the isolation of 1,1-dichloro-1-silacyclohexa-2,4-diene, which was further purified by vapor chromatography on the SE-30 column (oven temperature 130 °C). The product was obtained in 20% yield, and was identified on the basis of NMR, IR, and UV spectral data which match those reported by Benkeser and Cunico.³⁶

LiAlH₄ reduction of this compound in *n*-butyl ether gave a product identical with that obtained from the addition of silylene to cyclopentadiene.

Pyrolysis of Dimethoxytetramethyldisilane in the Presence of Trimethylsilane. Thermal decomposition of 1,2-dimethoxy-1,1,2,2-te-

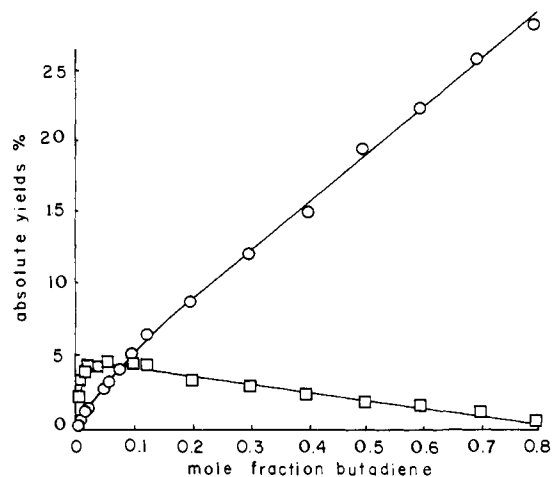


Figure 1. Product yields from reactions of recoiling silicon atoms in phosphine–butadiene mixtures, total pressure 1000 Torr: □, $^{31}\text{SiC}_4\text{H}_8$ (1-silacyclopent-3-ene); ○, $^{31}\text{SiC}_4\text{H}_6$.

tramethylidisilane was carried out by flash vacuum pyrolysis³⁷ in a one-pass flow system at low pressure. The hot zone was an electrically heated quartz tube 10 mm i.d. \times 12 cm. A Y-inlet arrangement allowed the disilane vapor to flow into the hot zone at a rate that was nearly independent of the flow rate of added substrate. Products were condensed in a U-trap immersed in liquid N_2 immediately (within 2 cm) after leaving the hot zone. The vapor pressure of disilane immediately above the hot zone was less than 100 μm . In one experiment 400 mg of dimethoxytetramethylidisilane was pyrolyzed at 650 $^\circ\text{C}$ in the presence of a sixfold excess of trimethylsilane over a period of 2 h. The residence time within the hot zone was less than 1 s. The reaction mixture was separated by trap to trap distillation followed by vapor chromatography. About 50% of the starting disilane was decomposed in the pyrolysis. The only reaction product detected in addition to dimethyldimethoxysilane and traces of dimethylsilylene dimers³⁸ was pentamethylidisilane, formed in 11% yield based on the $\text{Me}_2\text{Si}(\text{OMe})_2$ produced. The pentamethylidisilane was identified from its infrared and mass spectra, which were in accord with literature values.³⁹

Results



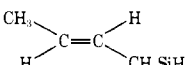
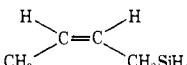



Phosphine–Butadiene Mixtures. Fast-neutron irradiation of phosphine–butadiene mixtures produces two major products, one of which was identified as [^{31}Si]-1-silacyclopent-3-ene by comparison of its retention time on three different gas chromatographic columns (SF-96 silicone oil, diethyl phthalate–DC-555 silicone oil, and dimethylsulfolane) with that of an authentic sample. To the other major product the structure [^{31}Si]-1-silacyclopenta-2,4-diene, an unknown compound, has been assigned on the basis of the following evidence.

1. This product contains carbon, hydrogen, and silicon, but not phosphorus, as indicated by its formation in $9 \pm 5\%$ yield from reactions of silicon atoms produced by the $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$ nuclear transformation in 1:1 silane–butadiene mixtures. The other products from silane–butadiene mixtures and their absolute yields follow: [^{31}Si]-1-silacyclopent-3-ene, $0.6 \pm 0.2\%$; silane ($^{31}\text{SiH}_4$) and disilane ($\text{H}_3^{31}\text{SiSiH}_3$) in combined yield of $12 \pm 1\%$; and trisilane, $1.2 \pm 0.2\%$. Silane, disilane, and trisilane are also formed from reactions of recoiling silicon atoms in pure silane.

2. The chromatographic behavior of this product suggests that it contains four carbon atoms. It has been compared chromatographically with the accessible SiC_4H_n ($n = 6, 8, 10, 12$) compounds, and it is not identical with any of them as indicated by the retention times given in Table I.

3. An empirical formula $^{31}\text{SiC}_4\text{H}_6$ is indicated by its formation in nearly identical $20 \pm 3\%$ yields from 1:1 phos-

Table I. Vapor Chromatographic Retention Times for the Major Products from Fast-Neutron Irradiations of Phosphine–Butadiene Mixtures and a Comparison with Authentic Compounds

	SF-96 ^{a,d}	DEPSO ^{b,d}	DMS ^{c,d}	
			A	B
Radioactive Products				
$^{31}\text{SiH}_2$  (tentative structure)	31	51	23	28
$^{31}\text{SiH}_2$ 	48	64	21	26
Authentic Compounds				
$\text{CH}_3\text{CHCH}=\text{CH}_2$ SiH_3	19	20	7.5	
$(\text{CH}_2=\text{CH})_2\text{SiH}_2$		24	9	
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{SiH}_3$	24	27.5	9.5	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$	26.5			
	27.5	33		
	29.5	37		
$\text{CH}_2=\text{CHCH}=\text{CHSiH}_3$	26	42.5		
$\text{CH}_2=\text{CHC}\equiv\text{CSiH}_3$	29		32	
			19	
	48	64	21	26
	48		24	29.5

^a Flow rate data: SF-96 60 mL/min (25 $^\circ\text{C}$). ^b Flow rate data: DEPSO 80 mL/min (50 $^\circ\text{C}$). ^c Flow rate data: DMS A, 100 mL/min (25 $^\circ\text{C}$); B, 80 mL/min (25 $^\circ\text{C}$). ^d Retention times in minutes.

phine–butadiene and 1:1 trifluorophosphine–butadiene mixtures. The other major product from $\text{PF}_3\text{-C}_4\text{H}_6$ mixtures is [^{31}Si]-1,1-difluoro-1-silacyclopent-3-ene formed in $9 \pm 3\%$ yield,⁸ and has been detected previously by Tang et al.¹⁷ Since acquisition of hydrogen from hydrocarbons by recoiling silicon atoms has never been observed, the formation of this new product in undiminished yield from a system containing no labile hydrogens implies that the product is an adduct of silicon atoms and butadiene with no additional hydrogen. The same product is formed in 3% yield as the only volatile product from a 1:1 mixture of trimethylphosphine and butadiene, another system without labile hydrogens.

Two alternative SiC_4H_6 structures, $\text{SiH}_3\text{CH}=\text{CHC}\equiv\text{CH}$ and $\text{CH}_2=\text{C}(\text{SiH}_3)\text{C}\equiv\text{CH}$, have not been excluded. Possible mechanisms for the formation of silacyclopentadiene will be presented in the Discussion section.

The dependence of the major product yields from the reactions of recoiling silicon atoms in phosphine–butadiene mixtures upon the composition of the reaction mixture at constant total pressure (1000 Torr) is shown in Figure 1. While the product believed to be silacyclopentadiene increases in yield monotonically with increasing mole fraction of butadiene, the yield of silacyclopentene goes through a maximum at low butadiene concentration. Tang found no variation in silacyclopentadiene yield with phosphine–butadiene ratio.⁷

Radioactive silane ($^{31}\text{SiH}_4$) is a minor product obtained in yields of less than 2% from all $\text{PH}_3\text{-C}_4\text{H}_6$ mixtures.

Addition of a radical scavenger (nitric oxide) to 1:1 $\text{PH}_3\text{-C}_4\text{H}_6$ mixtures before neutron irradiation left the yield of $^{31}\text{SiC}_4\text{H}_6$ product unchanged at $22 \pm 1\%$ but caused a decrease of ca. 40% in the yield of silacyclopentene. The yields of $^{31}\text{SiC}_4\text{H}_8$ were 0% NO, 2.7%; 1.0% NO, 2.5%; 2.0% NO,

Table II. Variation of Major Products Yields with the Amount of Butadiene Added to 1:1 Phosphine-Silane Mixtures

reactants, Torr			% of C ₄ H ₆	absolute yields of products, % ^a			
PH ₃	SiH ₄	C ₄ H ₆		³¹ SiH ₄ + ³¹ SiSiH ₆	³¹ SiSi ₂ H ₈	³¹ SiH ₂	³¹ SiH ₂
500	500	0	0	61 (100)	6.5 (100)	0	0
500	500	5	0.49	55 (91)	5.9 (90)	0.49	0.64
500	500	10	0.99	53 (88)	5.8 (90)	0.69	0.84
500	500	20	2.0	50 (83)	5.3 (82)	1.1	1.0
500	500	30	2.9	38 (62)	4.6 (71)	1.9	1.3
500	500	50	4.8	38 (62)	4.7 (72)	3.0	1.5
500	500	100	9.1	31 (51)	3.4 (52)	3.0	1.2
500	500	200	17	24 (39)	2.5 (39)	5.7	1.5
500	500	300	23	19 (32)	2.5 (38)	7.8	1.4
500	500	400	28	15 (24)	2.2 (34)	10	1.4
500	500	500	33	12 (20)	1.4 (22)	11	1.1
500	500	600	38	11 (18)	1.0 (16)	13	1.1
500	500	800	44	1.3 (14)	0.88 (14)	15	0.69
500	500	1000	50	.61 (10)	0.64 (10)	16	0.44

^a Probable errors are $\pm 10\%$ for all yields except those less than 2%, which are $\pm 20\%$. The numbers in parentheses are yields relative to that of 1:1 PH₃-SiH₄.

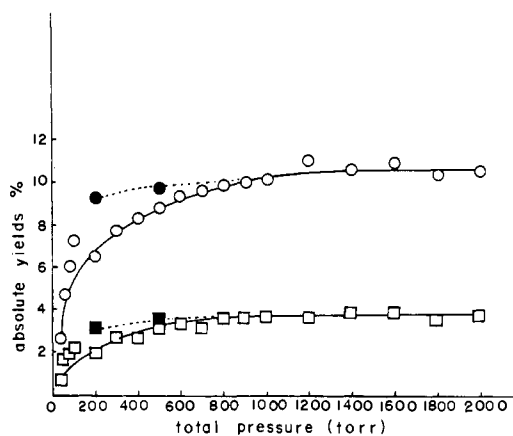


Figure 2. Variation of product yields from reactions of recoiling silicon atoms in 3:1 phosphine-butadiene mixtures with pressure. Black points include corrections for recoil loss between 200 and 1000 Torr: ■, □, ³¹SiC₄H₈ (1-silacyclopent-3-ene); ●, ○, ³¹SiC₄H₆.

1.1%; 2.9 NO, 1.6%; 3.8% NO, 2.1%; 4.8% NO, 1.6%; 9.1% NO, 1.6%; 13.0% NO, 1.5%.

In a moderator experiment with varying total pressure, neon was added to 3:1 PH₃-C₄H₆ mixtures, the phosphine and butadiene pressures being held constant at 750 and 250 Torr, respectively. The yield of silacyclopentene was found to decline slightly with increasing mole fraction neon moderator from 3.8% with no neon to 3.3% at 55% neon. The yield of ³¹SiC₄H₆ was found to increase: 0% Ne, 9.7%; 9% Ne, 9.6%; 17% Ne, 9.7%; 29% Ne, 11%; 38% Ne, 12%; 44% Ne, 13%; 55% Ne, 14%. Tang has found a somewhat more pronounced decrease in the yield of silacyclopentene with increasing neon concentration.⁹

The pressure dependence of the major product yields was investigated over the range 40–2000 Torr at 3:1 constant ratio of phosphine to butadiene. No change in yields with increase in pressure was detected above 800 Torr. Only a modest decrease in the yields of both major products was noted until pressures below 200 Torr were reached. The data are presented in Figure 2. At lower pressures recoil losses even in 14 mm i.d. ampules become quite large, and a quantitative assessment of the extent of unimolecular decomposition of product molecules at low pressures cannot be made at this time without an accurate assessment of the recoil loss.

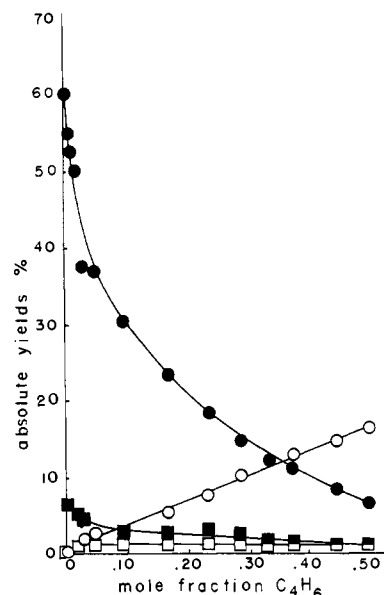





Figure 3. Variation of product yields from reactions of recoiling silicon atoms in 1:1 phosphine-silane mixtures (500 Torr each) with concentration of added butadiene: □, ³¹SiC₄H₈ (1-silacyclopent-3-ene), ○, ³¹SiC₄H₆; ■, ³¹SiSi₂H₈; ●, ³¹SiH₄ + H₃³¹SiH₃.

Phosphine-Silane-Butadiene Mixtures. Two series of experiments were carried out in which phosphine, silane, and butadiene were allowed to compete for recoiling silicon atoms and for the reactive intermediates derived from them. Various amounts of butadiene were added to 1:1 PH₃-SiH₄ mixtures, the ratio of butadiene to silane varying from 0 to 2. The product yields are given in Table II and Figure 3. Silane was added to 1:1 PH₃-C₄H₆ mixtures, the ratio of silane to butadiene varying from 0 to 2. The data from these experiments are presented in Table III. With the addition of butadiene to PH₃-SiH₄ mixtures, the yields of the major products obtained in the absence of butadiene decreased to the same extent in relative terms, i.e., when normalized to the yields in the absence of butadiene. Likewise the normalized yields of the two major products from the reactions of recoiling silicon atoms in PH₃-C₄H₆ mixtures declined equally with the addition of silane. All the volatile products observed from the binary phosphine-silane and phosphine-butadiene mixtures were found in the ternary mixtures.

Table III. Variation of Major Product Yields with the Amount of Nonradioactive Silane Added to 1:1 Phosphine-Butadiene Mixtures

reactant, Torr			% of SiH ₄	absolute yields of products, % ^a					
PH ₃	C ₄ H ₆	SiH ₄		³¹ SiH ₄ + ³¹ SiSiH ₆	³¹ SiSi ₂ H ₈	³¹ SiH ₂ 	³¹ SiH ₂ 	³¹ SiH ₂ 	
500	500	0	0	0	0	22 (100)	2.8 (100)	0.13	
500	500	100	9.1	3.2	0	21 (93)	2.4 (85)	0.12	
500	500	200	17	6.7	0.39	19 (83)	2.2 (76)	0.12	
500	500	300	23	10	1.4	17 (78)	2.0 (72)	0.12	
500	500	400	29	13	1.9	15 (65)	1.8 (62)	0.12	
500	500	500	33	16	2.4	14 (61)	1.7 (61)	0.13	
500	500	535	35	17	2.5	13 (58)	1.6 (57)	0.12	
500	500	600	37	18	2.7	12 (56)	1.5 (53)	0.12	
500	500	800	44	22	3.6	11 (50)	1.4 (49)	0.12	
500	500	1000	50	24	4.2	9.4 (42)	1.1 (39)	0.12	

^a Probable errors are $\pm 10\%$ for all yields except those less than 2%, which are $\pm 20\%$. The numbers in parentheses are yields relative to that of 1:1 PH₃-C₄H₆.

Phosphine-Silane-Cyclopentadiene Mixtures. Various amounts of cyclopentadiene were added to 1:1 mixtures of PH₃ and SiH₄ prior to fast-neutron irradiation. In addition to radioactive silane, disilane, and trisilane, two unidentified radioactive products were observed at retention times of 20 and 61 min, respectively (SF-96 column, 80 °C, He flow rate 80 mL/min) compared to a retention time of 28.5 min for the addition product of thermally generated silylene and cyclopentadiene, 1-silacyclohexa-2,4-diene (vide infra). The product yields are given in Table IV. When phosphine-cyclopentadiene mixtures without silane present are irradiated with fast neutrons, the only volatile product observed is silane formed in ca. 2% yield.

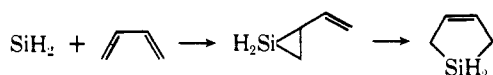
Addition of Thermally Generated Silylene to Butadiene. To determine whether the products from the reactions of recoiling silicon atoms in phosphine-butadiene mixtures could be due to silylene intermediates, the addition of thermally generated silylene from disilane pyrolysis to butadiene was carried out. A 46% yield of 1-silacyclopent-3-ene was obtained. No product corresponding to the recoil reaction product ³¹SiC₄H₆ believed to be silacyclopentadiene was detected.

Addition of Thermally Generated Silylene to Cyclopentadiene. Pyrolysis of disilane in the presence of cyclopentadiene yielded 1-silacyclohexa-2,4-diene in 11% yield based on disilane consumed. This product was not found in recoil experiments (vide supra).

Discussion

Products from Phosphine-Butadiene Mixtures and the Mechanism Including Silylene Intermediates. The reactions of recoiling silicon atoms in gaseous phosphine-butadiene mixtures lead to the formation of two major products in addition to small quantities of silane. [³¹Si]-1-silacyclopent-3-ene has been definitely identified by comparison of the retention time of the radioactive product with that of authentic samples on several widely varying gas chromatographic columns (Table I). The other product has been assigned the empirical formula ³¹SiC₄H₆ on the basis of the argument presented above.

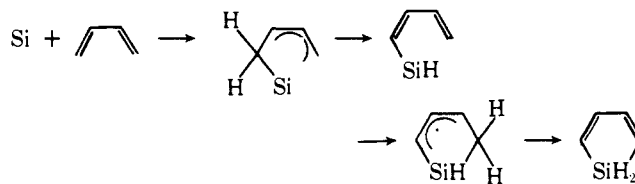
The structures of the products and the variation of product yields with the phosphine-butadiene substrate ratio can be accommodated by a reaction scheme in which silicon atoms and silylenes are important product-forming intermediates. Evidence has previously been presented for the formation of silacyclopentenes as rearrangement products of 1,2-addition products of silylenes to 1,3-dienes.^{16,40}

**Table IV.** Variation of Major Product Yields with the Amount of Cyclopentadiene Added to 1:1 Phosphine-Silane Mixtures

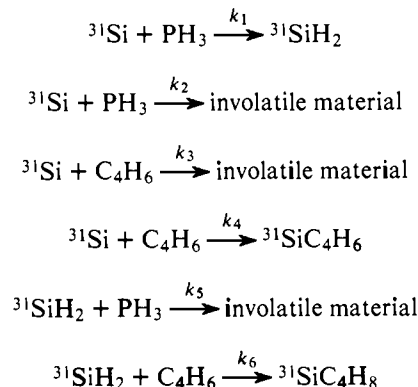
reactants, Torr				absolute yields of products, % ^{a,b}			
PH ₃	SiH ₄	C ₅ H ₆	% of C ₅ H ₆	³¹ SiH ₄ + ³¹ SiSiH ₆	³¹ SiSi ₂ H ₈	U ₁ ^{c,d}	U ₂ ^{c,d}
500	500	0	0	57 (100)	11 (100)	0	0
500	500	20	2.0	49 (87)	8.9 (84)	0	3.7
500	500	50	4.8	40 (70)	7.1 (68)	0.7	4.0
500	500	100	9.1	34 (59)	6.5 (62)	0.3	4.5
500	500	200	17	24 (42)	4.7 (44)	0.3	4.3
500	500	300	23	19 (34)	3.6 (33)	0.5	2.0
500	500	350	26	17 (31)	3.1 (29)	0.6	0

^a Probable errors are $\pm 10\%$ for all yields except those less than 2%, which are $\pm 20\%$. ^b The numbers in parentheses are the relative yields compared to that for 1:1 PH₃-SiH₄. ^c U₁ and U₂ are unknown products. ^d Retention times of U₁ and U₂ are 20 and 61 min, respectively (column SF-96, 80 mL/min, 80 °C), compared to 28.5 min for 1-sila-2,4-cyclohexadiene.

A reasonable mechanism can also be written for the formation of silacyclopentadiene from the reactions of silicon atoms with butadiene:



The following kinetic scheme may be considered:



Here phosphine and butadiene compete for recoiling silicon atoms whose reaction with butadiene produces (presumably after rearrangement) the $^{31}\text{SiC}_4\text{H}_6$ product believed to be silacyclopentadiene. Since this product requires only the collision of silicon atoms and butadiene, its yield increases monotonically with butadiene concentration. This reaction scheme leads to a maximum to the yield of $^{31}\text{SiC}_4\text{H}_8$, since with increasing butadiene concentration less silylene is produced, but some butadiene is required to capture $^{31}\text{SiH}_2$ if silacyclopentene is to be produced.

The data can be fitted quantitatively as well as qualitatively to this reaction scheme. This is shown by the linearity of product yield functions when plotted against substrate concentration functions. These relationships can be derived from the reaction scheme above.

Equating the absolute product yields with the ratios of the rate of formation of each product to the rate of formation of all products, a steady-state approximation for the concentration of $^{31}\text{SiH}_2$ leads to the following expressions:

yield of $^{31}\text{SiC}_4\text{H}_8 =$

$$\frac{k_1 k_6 [\text{C}_4\text{H}_6] [\text{PH}_3]}{\{k_5 [\text{PH}_3] + k_6 [\text{C}_4\text{H}_6]\} \{ (k_1 + k_2) [\text{PH}_3] + (k_3 + k_4) [\text{C}_4\text{H}_6] \}}$$

$$\text{yield of } ^{31}\text{SiC}_4\text{H}_6 = \frac{k_4 [\text{C}_4\text{H}_6]}{(k_1 + k_2) [\text{PH}_3] + (k_3 + k_4) [\text{C}_4\text{H}_6]}$$

For the binary $\text{PH}_3\text{-C}_4\text{H}_6$ mixtures the yield of $^{31}\text{SiC}_4\text{H}_6$ can be rewritten in terms of the mole fraction of butadiene:

$$\text{yield of } ^{31}\text{SiC}_4\text{H}_6 = \frac{k_4 [\text{C}_4\text{H}_6]}{k_1 + k_2 + (k_3 + k_4 - k_1 - k_2) [\text{C}_4\text{H}_6]}$$

This is a linear function of the butadiene mole fraction if $k_1 + k_2 \gg (k_3 + k_4 - k_1 - k_2) [\text{C}_4\text{H}_6]$. Figure 1 indicates that the yield of $^{31}\text{SiC}_4\text{H}_6$ is a nearly linear function of the mole fraction of butadiene in $\text{PH}_3\text{-C}_4\text{H}_6$ mixtures.

From the expressions above for the yields of the two major products in terms of the reaction scheme assumed, a linear relationship can be derived between the yield ratio and the substrate ratio:

$$\begin{aligned} \frac{\text{yield } ^{31}\text{SiC}_4\text{H}_8}{\text{yield } ^{31}\text{SiC}_4\text{H}_6} &= \frac{k_1 k_6 [\text{PH}_3]}{k_4 (k_5 [\text{PH}_3] + k_6 [\text{C}_4\text{H}_6])} \\ &= \frac{k_1 [\text{PH}_3]}{k_4 [\text{C}_4\text{H}_6]} \quad \text{if } k_6 [\text{C}_4\text{H}_6] \gg k_5 [\text{PH}_3] \end{aligned}$$

Figure 4 indicates that the yield ratio is indeed a linear function of the substrate ratio for $\text{PH}_3:\text{C}_4\text{H}_6 < 10$. The slope of this plot is 0.097.

Relative rate constants for the postulated reaction scheme can be deduced from the variation of product yields with substrate concentrations. One may obtain an estimate of k_1/k_4 from the slope of Figure 4, $k_1/(k_3 + k_4)$ from the slope (or intercept) of a plot of yield ($^{31}\text{SiC}_4\text{H}_8$) vs. $1/[\text{C}_4\text{H}_6]$ at high concentrations of butadiene, and $k_4/(k_1 + k_2)$ from the slope of yield ($^{31}\text{SiC}_4\text{H}_6$) vs. $[\text{C}_4\text{H}_6]$ shown in Figure 1. Thus a ratio of rate constants for the reactions of recoiling silicon atoms in phosphine-butadiene mixtures can be derived for this reaction scheme: $k_1:k_2:k_3:k_4 = 1:30:18:10$. A ratio of rate constants for the reactions of $^{31}\text{SiH}_2$, $k_6:k_5 = 25$, can be derived from the estimate for $k_1:k_2$ given above, and the slope and intercept of a plot of yield ($^{31}\text{SiC}_4\text{H}_8$) vs. $1/[\text{PH}_3]$ at low concentrations of butadiene.

In terms of this reaction scheme then, the yield of silacyclopentene is low even at its maximum because relatively little silylene ($^{31}\text{SiH}_2$) is formed in phosphine-butadiene mixtures, the reactions of recoiling silicon atoms with phosphine being much more likely to produce involatile material than silylene.

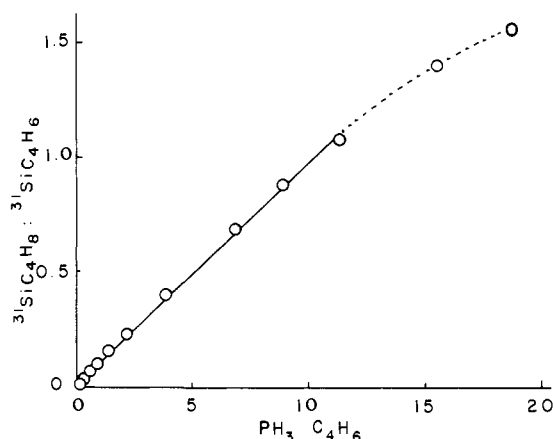


Figure 4. Variation of product yield ratio from reactions of recoiling silicon atoms in phosphine-butadiene mixtures with substrate ratio.

That silylene does undergo efficient addition to butadiene was verified by pyrolysis of disilane in the presence of butadiene,⁴¹ which gave a 46% yield of 1-silacyclopent-3-ene. No other adduct was obtained, and this is in accord with the scheme written above in which the $^{31}\text{SiC}_4\text{H}_6$ product is not derived from a silylene intermediate, but $^{31}\text{SiC}_4\text{H}_8$ is a silylene product.

Competition between Silane and Butadiene and the Question of Silylene Intermediates. The variation of product yields with the composition of ternary mixtures of phosphine, silane, and butadiene was studied as a test for silylene formation in the reactions of recoiling silicon atoms.

The high total yield of volatile radioactive products, ca. 70%, obtained from the reactions of recoiling silicon atoms in phosphine-silane mixtures, has been attributed to the formation of silylene and silylsilylene intermediates $^{31}\text{SiH}_2$ and $\text{H}^{31}\text{SiSiH}_3$.⁶ Therefore addition of butadiene to phosphine-silane mixtures prior to fast-neutron bombardment should lead to the trapping of these silylenes. Conversely, addition of silane to phosphine-butadiene mixtures should enhance the formation of silylene intermediates.

It was found (Table II and Figure 3) that addition of butadiene to 1:1 $\text{PH}_3\text{-SiH}_4$ mixtures causes a decrease in the yields of radioactive silane, disilane, and trisilane. The decreases in yields, expressed as a fraction of the yield in the absence of butadiene, are nearly identical for all three silanes. In the presence of butadiene, $^{31}\text{SiC}_4\text{H}_6$ and $^{31}\text{SiC}_4\text{H}_8$ are formed, but it is striking that the decrease in absolute yields of $^{31}\text{SiH}_4$, $\text{H}_3^{31}\text{SiSiH}_3$, and $^{31}\text{SiSi}_2\text{H}_8$ is much greater than the yields of $^{31}\text{SiC}_4\text{H}_6$ and $^{31}\text{SiC}_4\text{H}_8$. The total yield of volatile radioactive products decreases from 67 to 24% when the mole fraction of butadiene is increased from 0 to 0.5.

When silane was added to 1:1 phosphine-butadiene mixtures, the yields of $^{31}\text{SiC}_4\text{H}_6$ and $^{31}\text{SiC}_4\text{H}_8$ both decreased uniformly when normalized to the yields in the absence of silane.

It may thus be inferred that butadiene and silane compete for common intermediates and that a common precursor for all the major products is trapped by silane and butadiene. This common precursor *cannot* be $^{31}\text{SiH}_2$, since this species has not been invoked in the formation of trisilane or $^{31}\text{SiC}_4\text{H}_6$. If, however, the competition is for a species such as ^{31}Si atoms themselves, which could initiate reactions in which silylene is formed, then the question remains open whether $^{31}\text{SiH}_2$ is an intermediate in these recoil reactions.

Let us see what can be inferred from a reaction scheme which includes the formation of silylene. For phosphine-silane-butadiene mixtures the following sequence of reactions can be written:

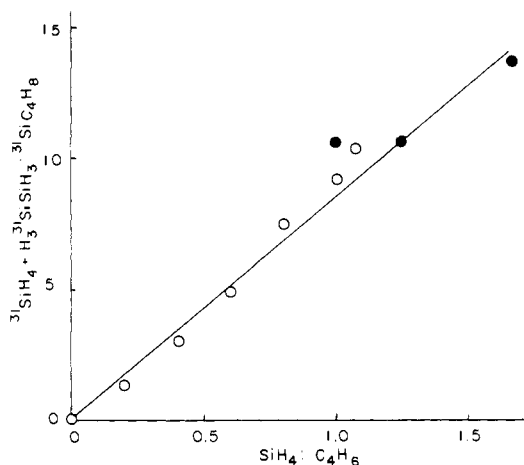


Figure 5. Variation of product yield ratio from reactions of recoiling silicon atoms in phosphine-silane-butadiene mixtures with silane-butadiene ratios between 0 and 1.8: O, addition of SiH₄ to 1:1 PH₃-C₄H₆ mixtures; ●, C₄H₆ added to 1:1 PH₃-SiH₄ mixtures.

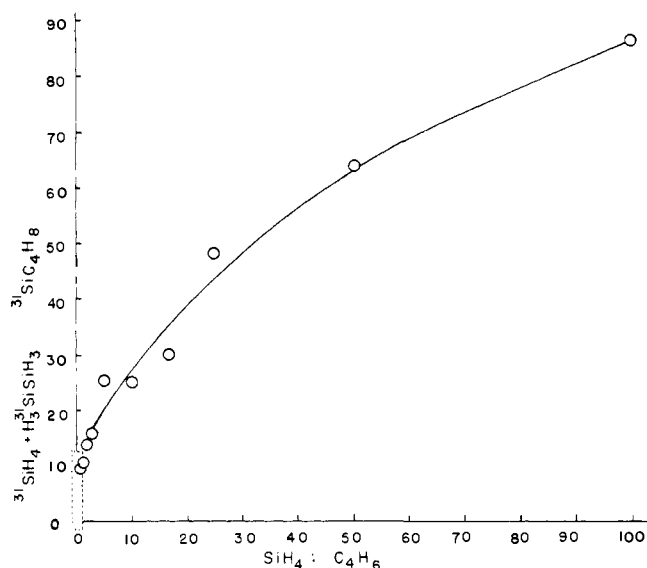
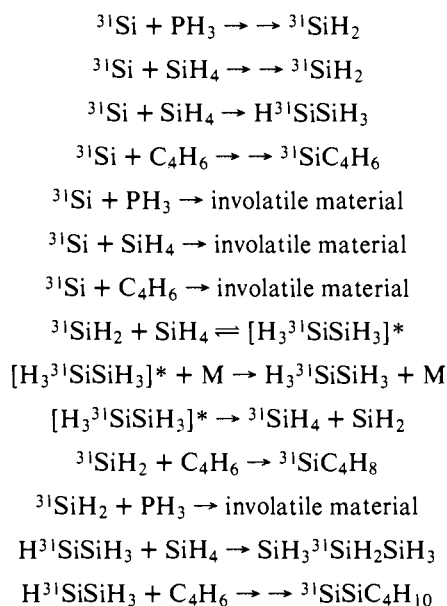
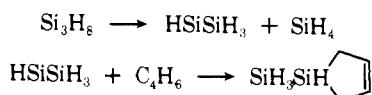


Figure 6. Variation of product yield ratio from reactions of recoiling silicon atoms in phosphine-silane-butadiene mixtures with silane-butadiene ratios between 0 and 100, C₄H₆ added to 1:1 PH₃-SiH₄ mixtures. The dotted rectangle at the origin represents the range of Figure 5.



According to this scheme silane and butadiene compete for ³¹Si, ³¹SiH₂, and H³¹SiSiH₃. One can reconcile with this model the observation that addition of butadiene to phosphine-silane mixtures causes an identical decline in the relative yields of ³¹SiH₄, H³¹SiSiH₃, and ³¹SiSi₂H₈ if either of the following conditions prevails: 1. Butadiene competes successfully with silane for silicon atoms but cannot compete effectively for ³¹SiH₂ and H³¹SiSiH₃. 2. The relative reactivity of SiH₄ and C₄H₆ is the same toward ³¹Si, ³¹SiH₂, and H³¹SiSiH₃.

The latter condition is possible but unlikely. The former condition is precluded for the electronic state of silylene formed in thermal reactions by the observed efficiency of silylene addition to butadiene. Silylsilylene has also been found by Ring to add to butadiene,⁴¹ but the resulting product has not thus far been observed in recoil experiments.



The reaction scheme above which attributes the silane, disilane, and silacyclopentene products to the reactions of ³¹SiH₂ intermediates requires the yield ratio [³¹SiH₄ +

H³¹SiSiH₃]:[³¹SiC₄H₆] to be a linear function of the silane-butadiene ratio, with the slope equal to the relative reactivity of silane and butadiene toward ³¹SiH₂. Figure 5 reveals such a linear relationship for low SiH₄:C₄H₆ ratios whose slope indicates that silane is nine times as reactive as butadiene toward the product-forming intermediate. Figure 6 reveals a fall-off from a linear relationship at high ratios of silane to butadiene. Previous studies of the relative rates of reaction of thermally generated silylene lead to an estimate for the relative reactivity of silane and butadiene at 385 °C of 1.2.⁴²

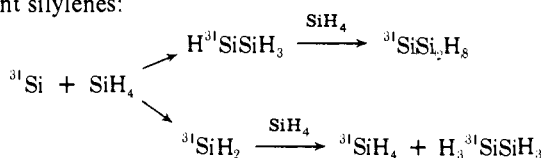
In the reaction scheme above, addition of silane to phosphine-butadiene mixtures should cause a decrease in the yield of ³¹SiC₄H₆ if silane can compete with butadiene for the recoiling silicon atoms. Upon addition of silane the amount of ³¹SiH₂ formed should, however, increase. Therefore a decrease in the yield of ³¹SiC₄H₆ due to increased trapping of ³¹SiH₂ by silane in competition with butadiene should be partially offset by the enhanced formation of ³¹SiH₂ with addition of silane. Thus the scheme above predicts that the decrease in the yield of ³¹SiC₄H₆ with increasing silane addition to PH₃-C₄H₆ mixtures should *not* equal the decrease in yield of ³¹SiC₄H₆. For these two products to decrease in yield equally with increasing silane concentration, a fortuitous cancellation must occur: the relative selectivity of ³¹SiH₂ toward silane and butadiene must be sufficiently greater (in favor of silane) than the selectivity of ³¹Si, to just compensate for the circumstance that in the formation of ³¹SiC₄H₆ there are two stages at which competition between silane and butadiene can occur, while there is only one stage in the formation of ³¹SiC₄H₈ at which competition (for ³¹Si) can occur between silane and butadiene.

The simplest interpretation of the variation of product yields with substrate concentrations from phosphine-silane-butadiene mixtures is that there is a kinetically important intermediate in the reactions of recoiling silicon atoms and butadiene, in addition to silicon atoms, that is the precursor of both observed products. The ratio of ³¹SiC₄H₆ and ³¹SiC₄H₈ formed from this intermediate seems to be independent of the amount of silane present but does depend on the ratio of phosphine to butadiene. This is evident from the close resemblance of the yield vs. mole fraction of butadiene curves obtained when the butadiene concentration is varied in PH₃-

C₄H₆ (Figure 1) and in PH₃-SiH₄-C₄H₆ (Figure 3) mixtures. When the ratio of the yields of ³¹SiC₄H₈ and ³¹SiC₄H₆ is plotted against the PH₃:C₄H₆ ratio, the plot is linear in the presence of silane with a slope, 0.082, similar to that found in the absence of silane, 0.097. Thus the kinetically important intermediate in the reactions of recoiling silicon atoms with butadiene does not react with silane to form either ³¹SiC₄H₆ or ³¹SiC₄H₈.

This is a deduction of some interest since the addition of nitric oxide to 1:1 phosphine-butadiene mixtures prior to neutron bombardment *does* change the product ratio, reducing the yield of ³¹SiC₄H₈ by ca. 40% while the yield of ³¹SiC₄H₆ is unaffected. This suggests that there is a scavengeable intermediate along the reaction path that leads to ³¹SiC₄H₈. If, however, ³¹SiC₄H₆ and ³¹SiC₄H₈ share a common precursor, then the scavengeable precursor of ³¹SiC₄H₈ must follow the nonscavengeable common precursor.

If recoiling silicon atoms react with silane to form two different silylenes:

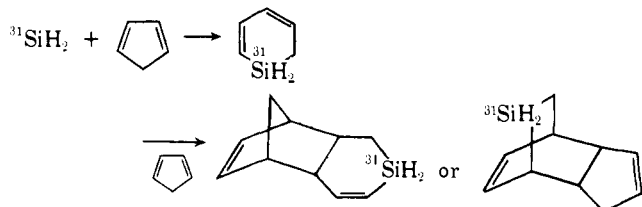


we would expect that the reactivity of H³¹SiSiH₃ and ³¹SiH₂ toward butadiene would differ sufficiently that competition for the two silylenes from added butadiene would cause the ratio of yields for trisilane, and silane plus disilane, to depend on the amount of butadiene present, but this is not the case.

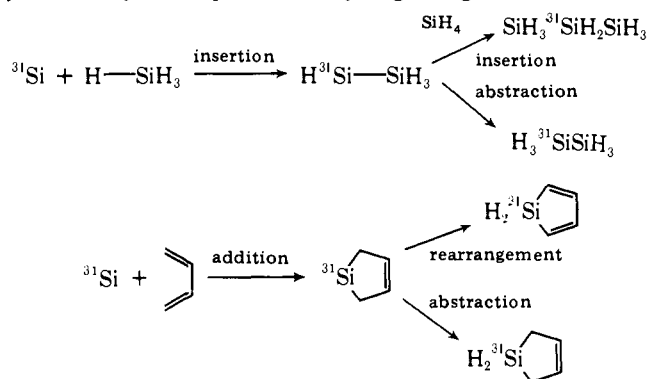
Phosphine-Silane-Cyclopentadiene Mixtures and the Absence of Silylene Adduct. The experiments in which cyclopentadiene was added to phosphine-silane reaction mixtures prior to fast-neutron irradiation provide data that cast doubt on the intervention of singlet ³¹SiH₂, and in this case the argument is less complex.

Cyclopentadiene is another substrate whose reactions with thermally generated singlet silylene have been explored. The only product found was 1-silacyclohexa-2,4-diene, obtained in 11% yield from pyrolysis of disilane in the presence of excess cyclopentadiene. Addition of various amounts of cyclopentadiene to 1:1 phosphine-silane mixtures prior to fast-neutron irradiation led to a decrease in the yields of the products—silane, disilane, trisilane—obtained in the absence of cyclopentadiene, but none of the silylene adduct [³¹Si]-1-silacyclohexa-2,4-diene was detected. Two new products were found whose structures have not been determined but whose chromatographic retention times indicated that they incorporated one and two cyclopentadiene molecules, respectively. Their yields did not exceed 0.7 and 4.5%, respectively, although the sum of the silane yields was reduced from 67 to 21% when the mole fraction of cyclopentadiene reached 0.26.

This result throws doubt on the intermediacy of ³¹SiH₂ but does not absolutely exclude it. If cyclopentadiene were quite reactive toward recoiling silicon atoms, but much *less* reactive than silane toward ³¹SiH₂, then the results could be reconciled with the intermediacy of silylene. It could also be argued that the heavier of the two unknown recoil reaction products formed in the presence of cyclopentadiene is actually a Diels-Alder adduct of the silylene adduct with excess cyclopentadiene. However, this product was not found under the thermal reaction conditions.



Alternative Mechanisms. Are there viable alternatives to ³¹SiH₂ as an important reactive intermediate in the recoil experiments? In the reaction schemes which postulate the formation of silylene as a product of the primary reactions of recoiling silicon atoms, hydrogen acquisition leading to the formation of ³¹SiH₂ is followed by addition or insertion as product-forming steps. All the products attributed to the reactions of ³¹SiH₂ can also be rationalized by invoking addition or insertion as primary reactions of recoiling silicon atoms followed by the acquisition of hydrogen, e.g.:



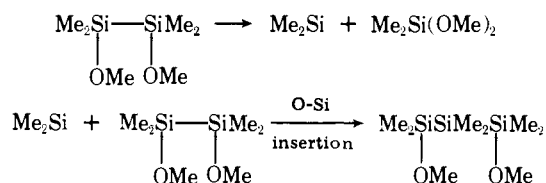
Schemes such as these are capable of quantitatively fitting the product yield data to a set of relative rate constants.⁴³ Here a common intermediate is invoked that leads to the formation of silane, disilane, and trisilane from the reactions of silicon atoms with silane, and another common intermediate is postulated that leads to the formation of ³¹SiC₄H₆ (silacyclopentadiene?) and ³¹SiC₄H₈ (1-silacyclopent-3-ene) from the reactions of recoiling silicon atoms and butadiene. Thus the equal decrease in the yields of silane, disilane, and trisilane upon the addition of butadiene to phosphine-silane mixtures can be simply explained by competition of silane and butadiene for one precursor, rather than the two postulated in the silylene mechanism. Again, the similar decrease in the normalized yields of ³¹SiC₄H₆ and ³¹SiC₄H₈ when silane is added to phosphine-butadiene mixtures can be explained by the competition of silane and butadiene for one intermediate, i,

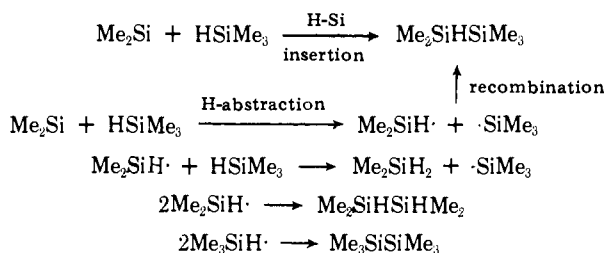


rather than two, ³¹Si and ³¹SiH₂.

A disadvantage of mechanisms in which divalent intermediates formed from the primary reactions of recoiling silicon atoms are transformed into chemically stable products by hydrogen acquisition reactions is that these mechanisms require hydrogen abstraction by an intermediate silylene to be a facile process. This has not been found by other workers, and we failed in an attempt to demonstrate it.

We chose a reaction system in which hydrogen abstraction products would not be observed as by-products of silylene generation. In our experiments dimethoxytetramethyldisilane was subjected to pyrolysis in the presence of excess trimethylsilane. The decomposition of dimethoxytetramethyldisilane gives dimethylsilylene and dimethoxydimethylsilane.¹⁵ Since the latter compound is not among the products awaited from hydrogen abstraction by the dimethylsilylene, a sensitive test for this process was afforded. The following reactions were anticipated:

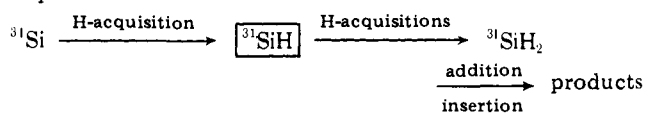




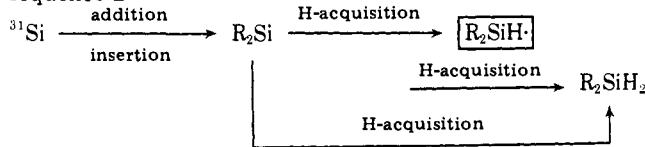
Pentamethyldisilane (11% yield) was found as well as $\text{Me}_2\text{Si}(\text{OMe})_2$ as reaction products, but no dimethylsilane, tetramethyldisilane, or hexamethyldisilane were detected. Thus it may be inferred that all the pentamethyldisilane was formed by direct insertion of dimethylsilylene into the Si-H bond of trimethylsilane, and no evidence for hydrogen abstraction by this silylene was obtained.

A further disadvantage of a mechanism which postulates hydrogen acquisition as occurring in the later stages of a multistep reaction sequence initiated by recoiling silicon atoms is that the rather small decreases in product yields (<50%) caused by the presence of free-radical scavengers^{3,5,8} require careful consideration. If hydrogen acquisition is a primary reaction of a recoiling atom (sequence 1 below) then the reaction may occur at high energy and may be efficient enough to be insensitive to low scavenger concentrations even if scavengeable intermediates (indicated by boxes below) are produced.

sequence 1

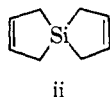


sequence 2



If a scavengeable intermediate is produced late in a multistep reaction sequence, it is likely to occur at lower energy, and then an insensitivity to scavenging action must be explained by low selectivity toward the scavenger or high reactivity. In light of our present knowledge silyl radicals $\text{R}_3\text{Si}\cdot$ still seem unlikely to be important reactive intermediates in the recoil systems, as they would be expected to be readily scavenged by olefins and nitric oxide,⁴⁴ and the recoil reaction products are not those expected from the reactions of silyl radicals with olefins and dienes.

An attempt to demonstrate the intermediacy of the cyclic silylene through its further reactions was also unsuccessful. The spiro compound ii



was synthesized according to Salomon³² and was employed as a carrier for the products from recoiling silicon atoms in phosphine-butadiene mixtures. No radioactive spiro compound was found, however, indicating that if this cyclic silylene is formed in the recoil reaction, its rearrangement and other reactions are more rapid than its addition to butadiene.

Conclusion

Comparison of the reactions of recoiling silicon atoms with those of thermally generated silylene, employing butadiene and cyclopentadiene as reaction substrates, leads to the conclusion that singlet silylene is not an important intermediate in the

recoil systems. This conclusion is supported by the following observations: (1) Addition of butadiene to phosphine-silane mixtures prior to neutron irradiation causes a large decrease in the yields of products previously attributed to the reactions of ${}^{31}\text{SiH}_2 + \text{SiH}_4$ but only a small amount of 1-silacyclopent-3-ene, the adduct of thermally generated silylene and butadiene, was formed. (2) Addition of cyclopentadiene to phosphine-silane mixtures prior to neutron irradiation causes a decrease in the products attributed to reactions of silylene with silane, but none of the adduct of thermally generated silylene to cyclopentadiene, 1-silacyclohexa-2,4-diene, was observed.

Both these findings can be reconciled with a ${}^{31}\text{SiH}_2$ intermediate if the diene substrate is more reactive than silane toward ${}^{31}\text{Si}$, but silane is more reactive than the diene toward ${}^{31}\text{SiH}_2$. Silane must be four to ten times as reactive as butadiene toward silylene for the yields from phosphine-silane-butadiene mixtures to be reconciled with a reaction scheme in which ${}^{31}\text{SiH}_2$ is the precursor of the disilane and silacyclopentene products. Thermally generated silylene has been estimated to be only 1.3 times as reactive toward silane as toward butadiene. Even if silylene were produced in the same electronic state in the thermal and recoil experiments, differences in temperature and in the kinetic and internal energy of the silylene at reaction could cause differences in reactivity.

It has been suggested by Tang and co-workers that silylene formed from the reactions of recoiling silicon atoms in phosphine-butadiene mixtures is principally (80%) in a triplet electronic state.⁹ If this is the case then the difference in behavior between the intermediates in the reactions of recoiling silicon atoms and thermally generated silylene could be attributed to the difference in electronic state.

We have considered other mechanisms for the recoil reaction system in which the hydrogen acquisition steps follow addition and insertion reactions of the recoiling atoms, but conclusive evidence in their favor has not been obtained.

It has been shown by the experiments reported in this paper that ${}^{31}\text{SiH}_4$, $\text{H}_3{}^{31}\text{SiSiH}_3$, and ${}^{31}\text{SiSi}_2\text{H}_8$ have a common precursor. Therefore we must abandon our previous suggestion that recoiling silicon ions ${}^{31}\text{Si}^+$ might be precursors of radioactive trisilane but not of silane and disilane.⁴⁵ If, as seems likely, the precursor of silane and disilane is neutral, then so is the precursor of trisilane.

We must conclude that the intermediates in the reactions of recoiling silicon atoms differ in their behavior from any reactive silicon species which has thus far been generated by thermal means. This provides further incentive for two kinds of experiments: (1) recoil experiments in which reactive intermediates are deprived of electronic excitation and excess kinetic energy by the presence of very high concentrations of inert rare gas moderators in order to facilitate comparison with thermally generated species; (2) further studies of thermally generated species like free silicon atoms, SiH , SiH_3SiH , and $:\text{SiH}_2$.

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(Polystyrylbipyridine)(tetracarbonyl)tungsten. An Active, Reusable Heterogeneous Catalyst for Metathesis of Internal Olefins

Seizo Tamagaki, Roger J. Card, and Douglas C. Neckers*

Contribution from the Department of Chemistry, Bowling Green State University,
Bowling Green, Ohio 43403. Received December 1, 1977

Abstract: (Polystyrylbipyridine)(tetracarbonyl)tungsten is prepared from the reaction of polystyrylbipyridine and tungsten hexacarbonyl in refluxing xylene. This material is an active cocatalyst for the metathesis of internal olefins. Ethylaluminum dichloride is required as a cocatalyst. Greater than 90% conversion of 2-pentene to a 1:2:1 ratio of 2-butene, 2-pentene, and 3-hexene can be obtained in less than 40 min at room temperature. The catalyst can be easily recovered from the reaction solution and reused. Oxygen has a dramatic rate-increasing effect on the metathesis. The most effective catalysts have a W/bipyridine ratio close to unity. (Polystyrylbipyridine)(tetracarbonyl)molybdenum, (polystyryl(diphenylphosphine)(pentacarbonyl)tungsten, (bipyridine)(tetracarbonyl)tungsten, and (triphenylphosphine)(pentacarbonyl)tungsten were also prepared. The polymer bound catalysts are at least an order of magnitude more active than the analogous nonpolymer bound species. The tungsten compounds are more active than the molybdenum compound. And the polymer-bipyridine-tungsten system is more active than the polymer-phosphine-tungsten system.

Introduction

The pioneering work of Merrifield demonstrated many of the advantages inherent in the use of a polymer bound reagent in polypeptide synthesis.¹ Interest and activity in this area have grown dramatically over the past few years and immobilized enzymes, photosensitizers, organic reagents, and transition metal reagents and catalysts are frequently reported.²⁻⁴

Polymer based organotransition metal catalysts offer several significant advantages in synthetic and industrial chemistry.

Of these, the ease of purification of the reaction product(s) and the ease of recovery and reuse of the catalyst are most important. As part of our continuing interest in the development and use of polymer bound reagents,⁵⁻¹¹ we have reported that polystyrylbipyridine¹² is a generally useful support for the preparation of heterogeneous catalysts for such processes as the hydrogenation of alkenes and alkadienes^{13,14} and the isomerization of strained hydrocarbons.¹⁵ This report describes the use of polystyrylbipyridine in the preparation of a heterogeneous catalyst for olefin metathesis.

Since the initial report of olefin metathesis by Banks and