Reactions of Recoiling Silicon Atoms with Phosphine and Butadiene, and the Addition of Silylene to Butadiene†

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Summary Silicon atoms recoiling from the $^{31}P(n,p)^{31}Si$ nuclear transformation in gaseous mixtures of phosphine and buta-1,3-diene give a low yield of [^{31}Si]-1-silacyclopent-3-ene and a $^{31}SiC_4H_6$ compound believed to be [^{31}Si]-1-silacylopenta-2,4-diene; the formation of some silylene from phosphine is indicated, and silylene is found to add in high yield to butadiene.

In recent years we have studied the mechanisms of the reactions of silicon atoms recoiling from the nuclear transformation $^{31}P(n,p)^{31}Si$ in gaseous phosphine–silane mixtures.[1] Silylene $^{31}SiH_2$, believed to be the most important intermediate species, undergoes insertion into silicon–hydrogen bonds.‡ To define the path for the formation of silylene it is important to determine the extent to which it is formed from phosphine in the absence of silane. To this end a new trapping reagent is required. Phosphine itself is ineffective.[2]

We report here our preliminary findings on the reactions of butadiene and phosphine with recoiling silicon atoms and also the reaction of butadiene with silylene.[3]

Fast-neutron irradiation of gaseous phosphine–butadiene mixtures leads to the incorporation of recoiling ^{31}Si atoms in two major and several minor products. Reaction mixtures were analysed by conventional radio-gas-chromatographic techniques.[1] The Figure shows the absolute yields of the major products plotted as a function of the mole fraction of butadiene. At low concentrations of butadiene, [^{31}Si]-1-silacyclopent-3-ene is the major product, identified by comparison of its retention time with that of authentic samples[4] on three different chromatographic columns.

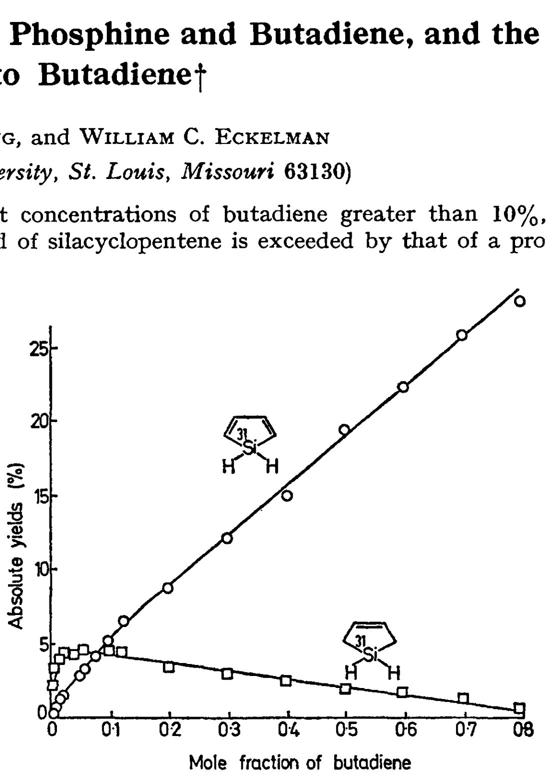

Figure. Variation of major product yields from fast-neutron irradiation of phosphine–butadiene mixtures (1000 Torr) with variation in composition.

At concentrations of butadiene greater than 10%, the yield of silacyclopentene is exceeded by that of a product to which the structure [^{31}Si]-1-silacyclopenta-2,4-diene is tentatively assigned on the basis of the following evidence.

i. This product contains carbon, hydrogen, and silicon but *no* phosphorus, as indicated by its formation through reactions in silane–butadiene mixtures of silicon atoms from

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‡ Absolute yields from 1 : 1 phosphine–silane mixtures at 1000 Torr are: $^{31}SiH_4$ 13 ± 2%, $^{31}SiSiH_6$ 48 ± 5%, and $^{31}SiSi_2H_8$ 7 ± 2%.

the ^{30}Si(n,γ)^{31}Si nuclear transformation. ii. Its chromatographic behaviour suggests that it is an organosilicon compound containing four carbon atoms. iii. An empirical formula ${}^{31}SiC_4H_6$ is indicated by its formation in nearly identical ($20 \pm 3\%$) yields from 1:1 phosphine–butadiene and 1:1 trifluorophosphine–butadiene mixtures. In the latter system there is no indication of hydrogen-abstraction by silicon, the other major product, 1,1-difluoro[^{31}Si]-1-silacyclopent-3-ene, being formed in $9 \pm 3\%$ yield by fluorine abstraction.[5] iv. Formation by a direct reaction of silicon atoms with butadiene, in agreement with an empirical formula ${}^{31}SiC_4H_6$, is indicated by the monotonic increase in yield with increasing butadiene concentration, while the yield of 1-silacyclopent-3-ene passes through a maximum.§ A competition for recoiling silicon atoms between phosphine and butadiene will produce the observed variation of product yields if butadiene reacts to form ${}^{31}SiC_4H_6$ while the reaction with phosphine forms ${}^{31}SiH_2$, which reacts with butadiene to give 1-silacyclopent-3-ene. [reactions (1)—(3)]. If other reactions of ^{31}Si and ${}^{31}SiH_2$

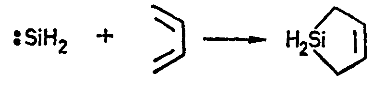
$$ {}^{31}Si + PH_3 \xrightarrow{k_1} {}^{31}SiH_2 \qquad (1)$$

$$ {}^{31}Si + C_4H_6 \xrightarrow{k_2} {}^{31}SiC_4H_6 \qquad (2)$$

$$ {}^{31}SiH_2 + C_4H_6 \xrightarrow{k_3} \text{1-silacyclopent-3-ene} \qquad (3)$$

are assumed to give involatile material, and reaction (3) is faster than other reactions of ${}^{31}SiH_2$, the yield ratio, 1-silacyclopent-3-ene/${}^{31}SiC_4H_6$ will be given by $k_1[PH_3]/k_2[C_4H_6]$. The yield ratio is a linear function of the substrate ratio with $k_1/k_2 = ca.\ 0{\cdot}1$. v. While 1-silacyclopenta-2,4-diene has not been prepared,[4] its stability is indicated by the stability of 1,1-dimethyl-1-silacyclopenta-2,4-diene.[6] vi. Other ^{31}Si-C_4H_6 structures such as ${}^{31}SiH_3$–C≡C–CH=CH$_2$ and ${}^{31}SiH_3$–CH=CH–C≡CH, while not excluded, require more extensive rearrangement for their formation than [^{31}Si]-1-silacyclopenta-2,4-diene.

The formation of a product in a single reactive collision followed by intramolecular rearrangement, rather than in a complex reaction sequence, provides a mechanistic tool which will greatly simplify the study of silicon atom reactions.



To prove that 1-silacyclopent-3-ene is the product of a silylene reaction[7] and that the reaction of silylene with butadiene does *not* produce the product we have identified as 1-silacyclopenta-2,4-diene, we treated silylene with butadiene, using the pyrolysis of disilane in a circulating flow system as the silylene source.[8] 1-Silacyclopent-3-ene (40% yield) was the only carbon-containing product from the copyrolysis of a 1:10 disilane–butadiene mixture at 375°.[9]

The low yield of [^{31}Si]-1-silacyclopent-3-ene from the recoil system implies that only a small amount of silylene is formed from the reactions of recoiling silicon atoms with phosphine, or that the silylene formed is principally in an electronic state which does not undergo efficient addition to butadiene.

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§ Tang *et al.* (ref. 3) report that the yield of [^{31}Si]-1-silacyclopent-3-ene is *ca.* 0·5%, independent of substrate concentrations. The variation in yield shown in the Figure is significant, however, and reaches 4·5% in our experiments.

[1] P. P. Gaspar, P. Markusch, J. D. Holten, III, and J. J. Frost, *J. Phys. Chem.*, 1972, **76**, 1352 and references therein.

[2] M. D. Sefcik and M. A. Ring, *J. Amer. Chem. Soc.*, 1973, **95**, 5168.

[3] The reaction of silicon atoms with butadiene has recently been reported by G. P. Gennaro, Y.-Y. Su, O. F. Zeck, S. H. Daniel, and Y.-N. Tang, *J.C.S. Chem. Comm.*, 1973, 637, to involve the addition of silylene.

[4] R. A. Benkeser, Y. Naga, J. L. Noe, R. E. Cunico, and P. H. Gund, *J. Amer. Chem. Soc.*, 1964, **86**, 2446.

[5] Y.-N. Tang, G. P. Gennaro, and Y.-Y. Su, *J. Amer. Chem. Soc.*, 1972, **94**, 4355. These workers reported 1,1-difluoro[^{31}Si]-1-silacyclopent-3-ene as the predominant product, constituting >95% of the observed volatile products.

[6] J. Goubeau, T. Kalmar, and H. Hofmann, *Annalen*, 1962, **659**, 39.

[7] In addition to the suggestions by Tang *et al.* that ${}^{31}SiH_2$ (ref.3) and ${}^{31}SiF_2$ (ref. 5) add to butadiene, formation of 1,1,3,4-tetramethyl-1-silacyclopent-3-ene from dimethylsilylene and 2,3-dimethylbutadiene has been reported: W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, 1968, **90**, 3438.

[8] E. M. Tebben and M. A. Ring, *Inorg. Chem.*, 1969, **8**, 1787; P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *ibid.*, 1970, **9**, 1068.

[9] The copyrolysis of disilane and butadiene has also been studied by M. A. Ring and R. L. Jenkins, who obtain similar results (personal communication).