Addition of Singlet and Triplet Silylene to Buta-1,3-diene†

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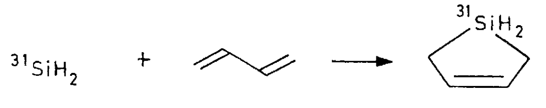
Summary Formation of high-energy silicon atoms by the nuclear recoil technique in the presence of buta-1,3-diene gives rise to silylene consisting of 80% triplet and 20% singlet; both configurations add to buta-1,3-diene to give silacyclopent-3-ene.

The nuclear recoil technique of producing silylene, the silicon analogue of methylene, has been well-established by the extensive work of Gaspar and his co-workers;[1-3] its reactions established thus far include insertion into Si–H[2,4,5] and Si–Si[3] bonds. Substituted silylenes and their silicon atom precursors formed by the thermal vaporization technique have also been shown to undergo Si–H bond insertion.[6]



(1)

However, addition to C=C bonds, which is expected to be a characteristic silylene reaction from consideration of the well-known olefin addition reactions of methylene, has not thus far been unambiguously demonstrated.[1] Here we report the formation of [^{31}Si]silacyclopent-3-ene (SCP*) from the reaction of silylene with buta-1,3-diene as the first observed olefin addition reaction of silylene.

Silicon-31 from the $^{31}P(n,p)^{31}Si$ nuclear transformation[2] was formed using fast neutrons converted from a 16 or 20 MeV deuteron beam at the Texas A&M University Cyclotron Institute. However, since the threshold for the above nuclear reaction is only 2 MeV,[7] we have also succeeded in producing larger amounts of ^{31}Si with neutrons from the Texas A&M University Nuclear Science Center reactor by using an internal cadmium-lined boron sample container to remove thermalized neutrons. Similar results were obtained regardless of the neutron source. Products were analysed by radio-gas chromatography[8] and the identification of SCP* was confirmed by co-injection of authentic samples[9] on four columns (silicone oil, dimethylsulpholane, tri-*o*-tolyl phosphate, and SF-96) with different elution characteristics.

Silicon atoms resulting from the nuclear transformation abstract hydrogen from phosphine [see equations (2) and (3)]. Preliminary measurements, in which relative concentrations of phosphine and buta-1,3-diene were varied, failed to show extensive differences in the normalized specific activity of SCP*.‡ Therefore, reaction (1) is

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‡ Specific activity = activity/Torr ml of PH_3 originally present.

relatively efficient and insensitive to substantial variations in reactant concentrations. However, the addition of nitric oxide as a radical scavenger depressed the SCP* *specific* activity tremendously. A typical scavenger curve consisting of some 30 points shows that the SCP* specific activities decrease rapidly in the 0—4% NO region and remain essentially constant thereafter. Such behaviour shows that nitric oxide is an efficient scavenger for this system. The plateau value attained for the specific activity is 20% of the original unscavenged value. Since nitric oxide effectively removes species having unpaired electrons, this observation then implies that the reacting silylene is 80% triplet and 20% singlet.

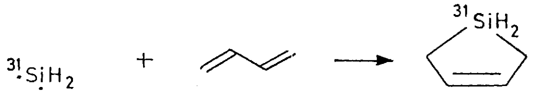
$$^{31}Si + PH_3 \rightarrow {}^{31}SiH + PH_2 \qquad (2)$$

$$^{31}SiH + PH_3 \rightarrow {}^{31}SiH_2 + PH_2 \qquad (3)$$

Besides SCP*, which normally represented 50% or more of the total observed volatile activity, other products obtained include small amounts of $^{31}SiH_4$ and varying amounts of an irreproducible unknown component whose activity seems to be independent of NO concentration but dependent on the condition of the chromatographic column.§ However, the absolute yield of SCP* in unscavenged systems was found to be only *ca.* 0·5% of the total ^{31}Si produced.¶

The 1,4-addition of triplet $^{31}SiH_2$ to buta-1,3-diene is similar to what has been observed for triplet methylene.[10] The apparent 1,4-addition of singlet $^{31}SiH_2$ may be due to consecutive 1,2-addition to give an unstable vinylsilacyclopropane (5) and subsequent isomerization to SCP* (6), a mechanism which has been suggested for similar systems.[11,12] While the isomerization shown in reaction (6) is likely to proceed through a biradical mechanism, we believe that this process is fast and therefore unaffected by the presence of a scavenger.

Finally, it should be borne in mind that the elucidation of the electronic states of silylene is based on the assumption that NO removes triplet but not singlet $^{31}SiH_2$, and that the mechanism for SCP* formation proposed in equations (4) to (6) provides a reasonable, but certainly not unique, scheme for this silylene addition reaction.



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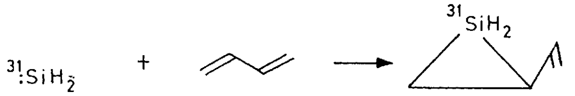

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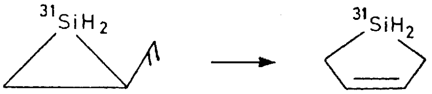

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§ P. P. Gaspar and his co-workers have examined the activities of this unknown component and found them to be several times those of the SCP* (personal communication). However, in our unscavenged systems we have found the carrier-free activities of this component approached the SCP* values only when well-conditioned chromatographic columns were employed.

¶ Samples containing $SiH_4 + PH_3$ and buta-1,3-diene + PH_3 were simultaneously irradiated. Using the $^{31}SiH_4$ and SCP* specific activities from these samples and the absolute yields of $^{31}SiH_4$ from ref. 2 the value of 0·5% was obtained.

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