Journal of Organometallic Chemistry, 135 (1977) C37—C44

Preliminary communication

TWO ATOM INSERTIONS INTO THE SILACYCLOPROPANE AND SILACYCLOPROPENE RINGS: MECHANISTIC CONSIDERATIONS

Dietmar Seyferth, Steven C. Vick, Mark L. Shannon,
Thomas F. O. Lim and Don P. Duncan

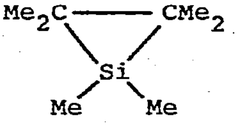
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 (USA)

(Received June 13th, 1977)

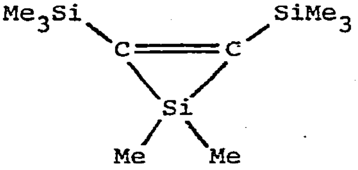
SUMMARY

Novel two atom insertion reactions into the SiC_2 rings of hexamethylsilirane and 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene involving the C=C bonds of styrene and α-methylstyrene, 1,3-butadiene and its 2-methyl and 2,3-dimethyl derivatives, and, in the presence of ultraviolet radiation, of aliphatic aldehydes and ketones, are reported. A radical mechanism is suggested to be operative in these reactions. Also described are novel palladium-catalyzed reactions of the silirene with terminal and internal acetylenes.

In a recent communication we have reported novel two atom insertion reactions into the highly strained and hyperreactive SiC_2 rings of hexamethylsilirane, 1, and 1,1-dimethyl-2,3-bis-

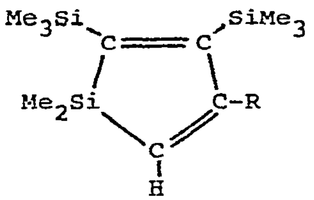


1

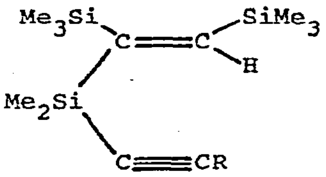


2

(trimethylsilyl)-1-silirene, 2 (1). Such insertion reactions, in which ring expansion to give a five-membered ring occurred, were observed to occur with aryl-substituted and α,β-unsaturated aldehydes and ketones and with phenylacetylene. In an earlier study, similar two-atom insertion of styrene and α-methylstyrene into hexamethylsilirane had been encountered in reactions carried out at 70° (2).* In the reaction of the silirene with phenylacetylene, the five-membered ring compound, 3a, was the minor product; the major product was the acyclic compound 4a (1). Our initial suggestion to rationalize the



3 a, R = Ph
b, R = CMe=CH$_2$
c, R = Me$_3$C



4 a, R = Ph
b, R = CMe=CH$_2$

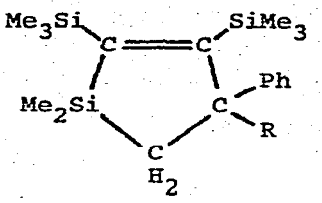
formation of 4a was made in terms of attack of phenylacetylene as a weak acid on the silirene Si-C bond, i.e., electrophilic ring cleavage. However, very little information bearing on the possible mechanism of the two atom insertions was available in these early stages of our investigation.

Further studies have provided some indication that radical intermediates are involved in these reactions. Of particular interest in this connection are the reactions of silirene 2 with styrene, α-methylstyrene and 1,3-dienes.

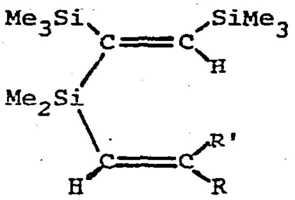
The reaction of the silirene with styrene in benzene solution for 18 hr at 70° gave a mixture of three products, 5a, 6a and 7a, in 40:20:40 ratio, in 87% total yield. A

---

* Hexamethylsilirane also reacted slowly with styrene at room temperature to give two products: Me$_2$(*trans*-PhCH=CH)SiCMe$_2$CHMe$_2$ (6%) and 1,1,2,2,3,3-hexamethyl-4-phenyl-1-silacyclopentane (44%). (Note the change in structure assignment for this cyclization product as compared to that made in ref. 2.)



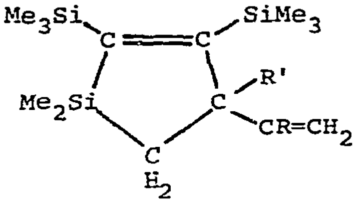
5 a, R = H
b, R = Me



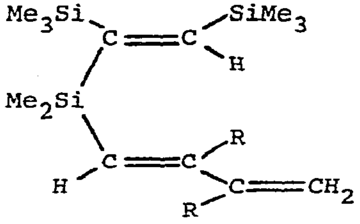
6 a, R = H, R' = Ph
b, R = Me, R' = Ph

7 a, R = Ph, R' = H
b, R = Ph, R' = Me

similar reaction with α methylstyrene resulted in a mixture of 5b, 6b and 7b in 45:25:30 ratio. Reaction of silirene 2 with 1,3-butadiene, 2,3-dimethyl-1,3-butadiene and 2-methyl-1,3-butadiene also took place in benzene solution at 70°, giving both cyclic and acyclic products. The reaction with butadiene produced 8a and 9a in yields of 45% and 20%, respectively, while the reaction with 2,3-dimethyl-1,3-butadiene gave 8b



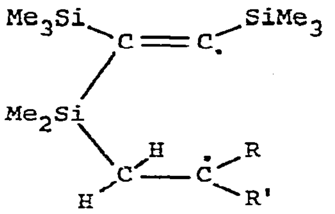
8 a, R = R' = H
b, R = R' = Me
c, R = H; R' = Me
d, R = Me; R' = H



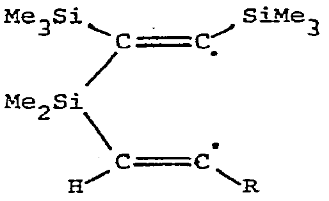
9 a, R = H
b, R = Me

and 9b in yields of 36% and 13%, respectively. 2-Methyl-1,3-butadiene reacted with silirene 2 with complete absence of regioselectivity, giving a 50:50 mixture of 8c and 8d in 48% yield, as well as the two open chain products. Thus, in the case of the two styrenes and the three 1,3-dienes the reactions with the silirene are similar to that observed with phenylacetylene (and with isopropenylacetylene, which later work has shown to give a mixture of 3b (34%) and 4b (66%) after 18 hr at room temperature). The suggestion that it is the acidic C-H bond of the acetylene which is responsible for the production of the acyclic product obviously is not applicable to the reactions of the nonacidic styrenes and 1,3-dienes with the silirene.

An attractive alternative is a radical process, in which a diradical of type 10 is an intermediate. This species, in which



10 (R = H, Me; R' = Ph, CH_2=CH, CMe=CH_2)



11

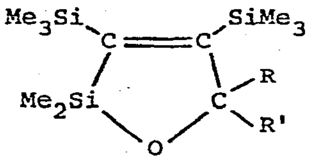
the radical centers are stabilized by phenyl, vinyl or Me_3Si, then can undergo intramolecular coupling to give the silacyclopentene. Or, alternatively, intramolecular hydrogen atom transfer from the CH_2 group adjacent to silicon to the β-radical center of the 1,2-bis(trimethylsilyl)vinyl group can occur, giving the observed acyclic product. The formation of both the trans- and cis-β-styrylsilanes 6 and 7 would be expected if the reaction with the styrenes proceeded via 10. The acetylene insertion reaction then would proceed in similar fashion, with a diradical intermediate of type 11 which could undergo cyclization to form 3 or intramolecular hydrogen transfer to give 4.

Successful two atom aldehyde and ketone carbonyl insertions into 1 and 2 which could be effected at room temperature had been restricted to conjugated carbonyl compounds.*

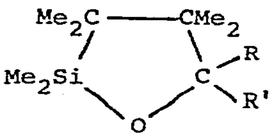
---

* For 2, we had reported such reactions with benzaldehyde and crotonaldehyde in our initial communication (1). In subsequent work, we have effected such room temperature insertion reactions with methyl vinyl ketone, mesityl oxide, acetylacetylene and hexafluoroacetone.

Silirene 2 did react with acetaldehyde and acetone in benzene at 70° to give 1-oxa-2-silacyclopent-3-enes 12a and 12b in yields of 26% and 14%, respectively, after a reaction time of 18 hr, but hexamethylsilirane did not appear to react in this manner with aliphatic ketones under these conditions. However, both 1 and 2 reacted readily with aliphatic aldehydes and ketones in pentane solution upon UV irradiation in a quartz flask. A 2 hr reaction time under these conditions gave 12a in 92% yield and 12b in 73% yield in reactions of 2 with acetaldehyde and acetone, respectively. Other carbonyl compounds which were found to react readily with 2 upon irradiation included cyclopentanone (78% yield of 12, RR' = $(CH_2)_4$), cyclohexanone (73% yield of 12, RR' = $(CH_2)_5$), 2-butanone (57% yield of 12, R = Me, R' = Et), acetylacetone (20% yield of 12, R = Me, R' = $CH_2C(O)CH_3$), isobutyraldehyde (28% yield of 12, R = H, R' = Me_2CH), and pivaldehyde (33% yield of 12, R = H, R' = Me_3C). Ultraviolet irradiation also induces the insertion of propionaldehyde and acetone in pentane solution into hexamethylsilirane to give 13a and 13b in yields of 40% (5 hr) and 34% (4 hr), respectively.

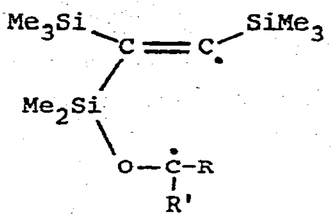


12 a, R = H, R' = Me
b, R = R' = Me



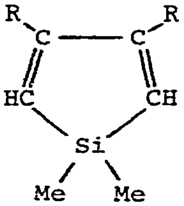
13 a, R = H, R' = Et
b, R = R' = Me

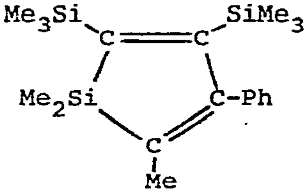
It seems reasonable to suggest that the active species in these reactions is the carbonyl compound in the excited (n,π^* triplet) state. This would explain why irradiation of the aliphatic carbonyl compounds is required: their n,π^* triplet state is much less accessible. One may then view these carbonyl compound SiC_2 ring insertion reactions as mechanistically akin to the formation of oxetanes by cycloaddition of carbonyl compounds to simple alkenes, dienes and acetylenes upon irradiation (3). A diradical intermediate, 14, for these reactions may then be discussed, but most certainly, further experiments are required to secure this mechanism.



14

While the present evidence favors a radical mechanism for these two atom insertions into the SiC_2 cyclics, there are other reactions of silirene 2 with acetylenes and 1,3 dienes which are catalyzed by $(Ph_3P)_2PdCl_2$. We have reported the reaction of 2 with phenylacetylene which proceeds exothermally in the presence of the palladium catalyst to give the silacyclopentadiene 15a (1). This appears to be



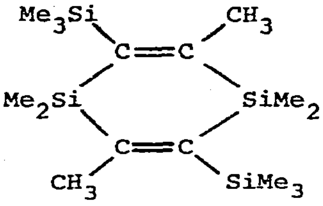


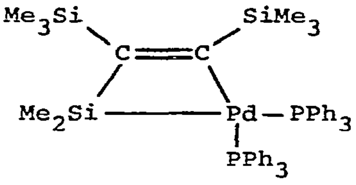
15 a, R = Ph
b, R = $CMe{=}CH_2$
c, R = Me_3C

16

a general reaction with terminal acetylenes. We found silirene 2 to react with isopropenylacetylene to give 15b (42%) and with tert-butylacetylene to give 15c (22%), in addition to a 30% yield of the two atom insertion product 3c.

The disubstituted acetylenes which we have examined have shown two different kinds of behavior. Methyl(phenyl)acetylene did not react with silirene 2 in benzene, either at room temperature or at 70°. It did react at room temperature in the presence of a catalytic amount of $(Ph_3P)_2PdCl_2$ to give 16. (or its isomer with the methyl and phenyl groups interchanged). On the other hand, the reaction of methyl(trimethylsilyl)acetylene with the silirene (18 hr at 75° in benzene, palladium catalyst) resulted in formation of 17 as the major product. The course of the reaction of silirene 2 with 2,3-dimethyl-1,3-butadiene also was changed when it was carried out at 75° in the presence of $(Ph_3P)_2PdCl_2$. In addition to the two atom insertion product, 9b (26% yield), there was obtained the Me_2Si addition product to the diene, 1,1,3,4-tetramethyl-1-silacyclopent-3-ene in 21% yield. Further studies will be required in order to obtain an understanding of the mechanism of these palladium-catalyzed processes. However, the key step in all is very likely the formation of an insertion product of type 18 after initial reduction of the $(Ph_3P)_2PdCl_2$ to a Pd(0) species. The formation of 16 then merely requires insertion of the acetylene into the Pd-Si or Pd-C bond, and subsequent extrusion of $(Ph_3P)_2Pd$. The formation of 15 and 17 would require release of $Me_3SiC{\equiv}CSiMe_3$ from 18 to give a dimethylsilylene-palladium complex [$Me_2SiPd(PPh_3)_2$ or an oligomer?] followed by reactions of this species with the external acetylene.


17


18

We were prompted to report these results at this time by the recent publications of two Japanese groups (4,5) on the chemistry of photochemically generated 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene. Both groups reported limited examples of two atom insertions of ketones into this silirene and of palladium-catalyzed reactions of this silirene with acetylenes. Our work in this area is continuing.

Acknowledgments. The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC (Grant AF-AFOSR-76-2917) for generous support of this work, and to Union Carbide Corp. for gifts of chemicals.

References

1. D. Seyferth, D. P. Duncan and S. C. Vick, J. Organometal. Chem., 125 (1977) C5
2. D. Seyferth and D. C. Annarelli, J. Organometal. Chem., 117 (1976) C51

3. J. A. Bartrop and J. D. Coyle, "Excited States in Organic Chemistry", John Wiley & Sons, New York/London, 1975, pp. 208-212.

4. (a) M. Ishikawa, T. Fuchikami and M. Kumada, J. Amer. Chem. Soc., 99, (1977) 247; (b) M. Ishikawa, T. Fuchikami and M. Kumada, J. Chem. Soc., Chem. Comm. (1977) 352

5. H. Sakurai, Y. Kamiyama and Y. Nakadaira, J. Amer. Chem. Soc., 99 (1977) 3879