Journal of Organometallic Chemistry, 94 (1975) C38—C42
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Preliminary communication

SILYLENE ADDITIONS TO CYCLOPENTADIENE AND 1,3-CYCLOHEXADIENE. EVIDENCE FOR THE ADDITION MECHANISM

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(Received April 7th, 1975)

Summary

Additions of SiH_2, $SiCl_2$ and $Si(CH_3)_2$ to cyclopentadiene and of $Si(CH_3)_2$ to 1,3-cyclohexadiene were carried out by copyrolysis of an appropriate disilane and the diene. All observed products are believed due to 1,2-addition of silylenes forming bicyclic vinylsilacyclopropane derivatives which undergo non-concerted rearrangements.

The addition of silylenes to 1,3-dienes has aroused considerable synthetic and mechanistic interest [1-10]. Recently we ruled out a concerted 1,4-addition mechanism by demonstrating that the reaction is not stereospecific [7]. Our attention next turned to the addition of silylenes to cyclic dienes in the belief that their reaction products would shed light on the detailed reaction mechanism, particularly upon the role of silacyclopropane intermediates.

The two previously reported examples of silylene addition to cyclic dienes present a striking contrast in the finding of a conjugated product by Chernyshev, Komalenkova and Bashkirova [3], while Childs and Weber found only an unconjugated product [8]. Both groups assumed the formation of silacyclopropanes without evidence for such intermediates (Scheme 1).

We have compared the reactions of $Si(CH_3)_2$, SiH_2 and $SiCl_2$ with cyclopentadiene and studied the reaction of $Si(CH_3)_2$ with 1,3-cyclohexadiene. Our results, presented in this communication, as well as the earlier observations, are reconciled in a single mechanistic scheme.

The procedure consisted of copyrolysis in a vacuum flow system at 5 to 50 torr pressure of the silylene precursor $CH_3OSi(CH_3)_2OCH_3$ or Si_2H_6 at 575 °C to 735 °C or 435 °C, respectively, together with a three- to six-fold excess of the diene substrate. Contact time in the hot zone was less than 1 sec. Hexachlorodisilane—diene mixtures were subjected to copyrolysis at 540 °C employing a nitrogen carrier gas and longer contact times as previously described [3]. The un-

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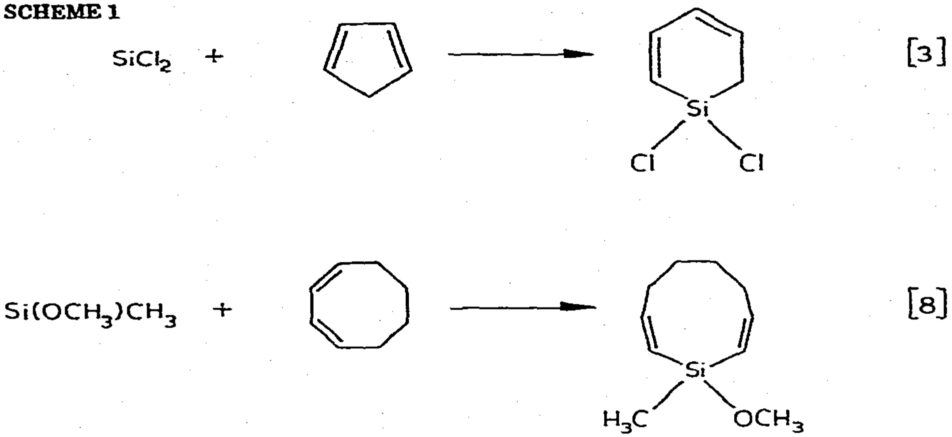
*Technical report No. COO-1713-51.

SCHEME 1



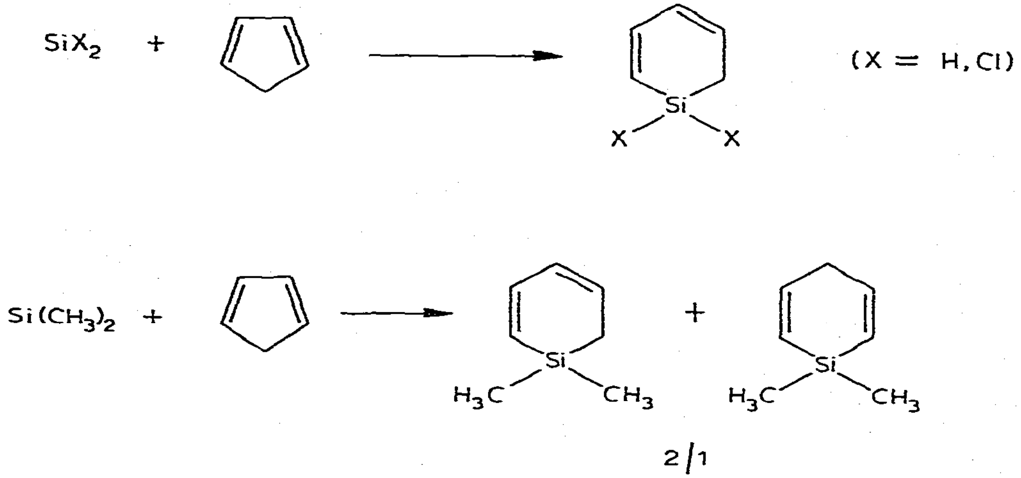
symmetrical thermolysis of disilanes to silylenes is well documented [11-13].

$$Y{-}SiX_2{-}SiX_2{-}Y \rightarrow SiX_2 + SiX_2Y_2$$

While addition of SiH_2 as well as of $SiCl_2$ to cyclopentadiene gives rise exclusively to the conjugated 1-sila-2,4-cyclohexadiene, addition of $Si(CH_3)_2$ gives both the 2,4- and 2,5-isomers* (Scheme 2). These products were identified and unambiguously characterized by their spectroscopic properties. Nuclear magnetic resonance, mass spectroscopy, infrared and ultraviolet spectroscopy were all utilized to examine samples purified by gas chromatography. Spectroscopic data for 1,1-dichloro-1-sila-2,4-cyclohexadiene were identical with those reported by Benkeser and Cunico [14]. Reduction of this compound with lithium aluminum hydride gave a product identical with the SiH_2 adduct.

The product ratio from $Si(CH_3)_2$ addition to cyclopentadiene remained constant, 2.1 ± 0.2, over three temperatures spanning 150 °C. This suggests a

SCHEME 2



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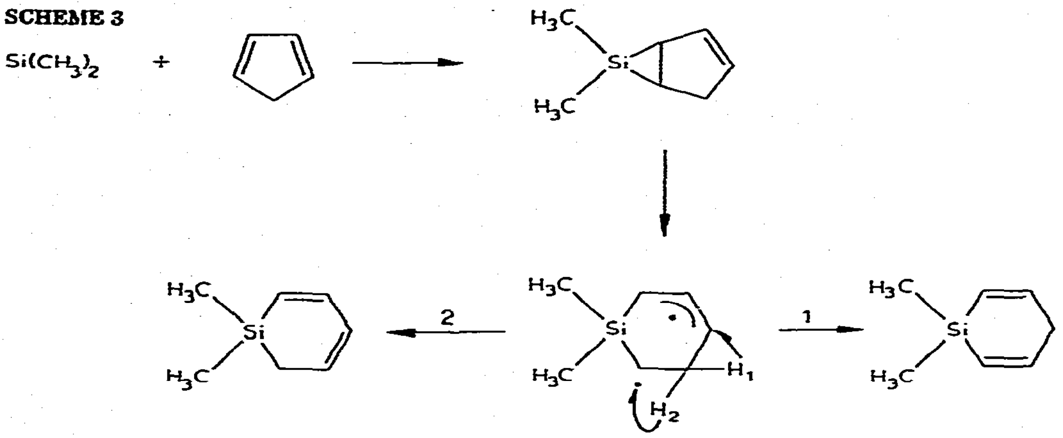
*Yields were: from SiH_2 10%. from $SiCl_2$ 40%; from $Si(CH_3)_2$ 50% (combined).

common intermediate followed in the reaction sequence by branching steps with similar temperature dependences, perhaps due to low activation energies. Such a mechanism, including the formation of a silacyclopropane intermediate which rearranges to the final products via a diradical, is shown in Scheme 3.

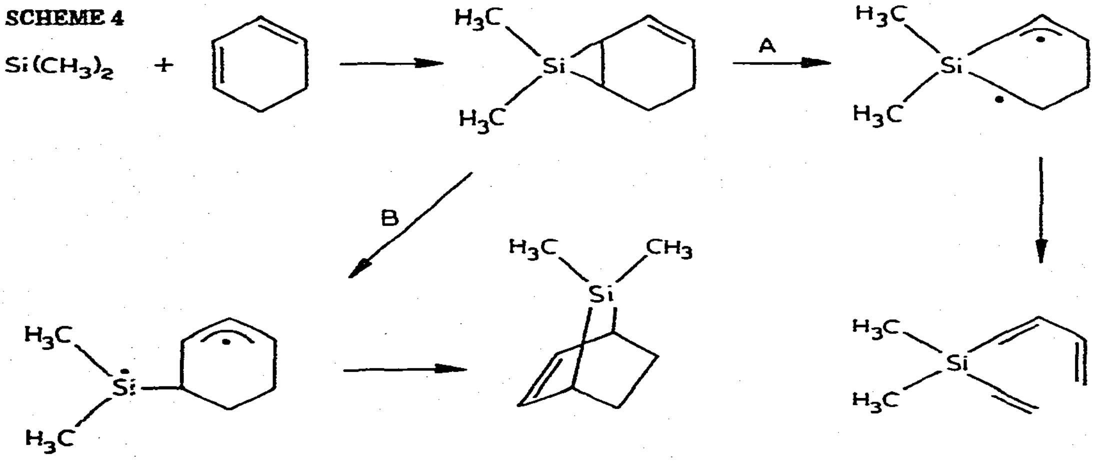
SCHEME 3



A similar diradical mechanism has been proposed for the thermal rearrangement of the all-carbon analog for the bicyclic silacyclopropane above, bicyclo-[3.1.0]hex-2-ene [15, 16]. Formation of silacyclopropanes by addition of silylenes to monoolefins and dienes has recently been indicated by methanol trapping experiments [10, 17], and the isolation of silacyclopropanes (but not from silylene addition) has been effected [18-20].

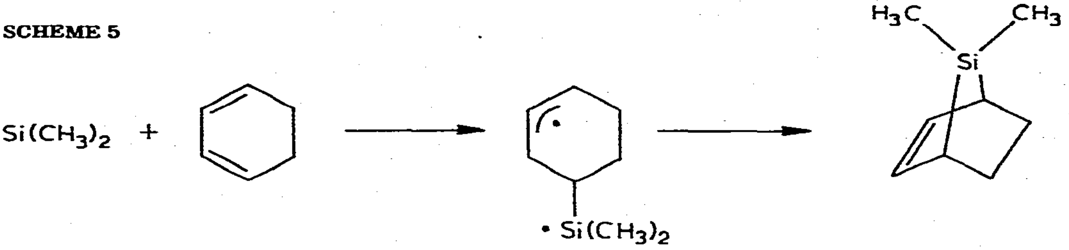
We offer as compelling evidence for the intermediacy of a silacyclopropane upon addition of Si(CH$_3$)$_2$ to a diene, the formation of 3,3-dimethyl-3-sila-1,4,6-heptatriene (10% yield) from the addition of Si(CH$_3$)$_2$ to 1,3-cyclohexadiene. This product also was identified from its spectra. Particularly characteristic was the olefinic region of the NMR spectrum, identical with superimposed spectra of vinyltrimethylsilane and 1-silyl-1,3-butadiene. The other isolated product, also formed in 10% yield, was 7,7-dimethyl-7-silanorbornene, also characterized by its spectra. The mechanism of Scheme 4 is proposed.

SCHEME 4



It is noteworthy that in the all-carbon system, bicyclo[4.1.0]hept-2-ene, analogous to the bicyclic silacyclopropane in Scheme 4, pyrolysis leads to exclusive cleavage to a bond external to the six-membered ring, as in process B above [21]. We attribute the ability of process A to compete with process B to the exceptionally strained carbon—carbon bond of a bicyclic silacyclopropane. It seems clear that the silaheptatriene product must arise via the silacyclopropane intermediate shown. It seems possible, however, that the silanorbornene could arise directly via an initial diradical adduct (Scheme 5).

SCHEME 5



That the initial adduct of silylenes and 1,3-dienes may be a diradical (which can close to a silacyclopropane) is suggested by the observation that 1,3-cyclohexadiene is much more reactive toward $Si(CH_3)_2$ than is 1,4-cyclohexadiene.

Finally, we suggest an explanation for the exclusive isolation of the conjugated 2,4-silacyclohexadiene from addition of SiH_2 to cyclopentadiene. Again guidance comes from the all-carbon system, where facile 1,4-elimination of molecular hydrogen from 1,4-cyclohexadiene has been demonstrated [15]. Thus the absence of 1-sila-2,5-cyclohexadiene as an observed product from flow pyrolyses with brief contact times may be due to the secondary decomposition of the unconjugated silacyclohexadiene with loss of H_2. Experiments on the trapping of the expected silabenzene product are underway.

Since the contact time for the reaction of $SiCl_2$ with cyclopentadiene is much longer than that for SiH_2, and since concerted loss of HCl from a silacyclohexadiene should be less facile than loss of H_2, the absence of the unconjugated 1,1-dichloro-1-sila-2,5-cyclohexadiene as an observed product may be due to other secondary reactions. That elimination of methane is more difficult than that of hydrogen would explain the survival of 1,1-dimethyl-1-sila-2,5-cyclohexadiene.

On the basis of the present as well as the earlier results we favor as the mechanism for silylene addition to 1,3-dienes an initial 1,2-addition forming a silacyclopropane which undergoes non-concerted rearrangement to products. The relative amount of C—Si and C—C bond cleavage upon rearrangement of the silacyclopropane seems to depend on whether it is fused into a bicyclic system, and, if so, upon the size of the other ring.

Acknowledgment

We thank Mr. Maurizio Speranza for stimulating discussions, and Dr. Michael D. Sefcik for both theoretical and practical assistance. This work was supported by the United States Energy Research and Development Administration.

References

1 W.H. Atwell and D.R. Weyenberg, J. Amer. Chem. Soc., 90 (1968) 3438; Angew. Chem., Intern. Ed., 8 (1969) 469.
2 Y.-N. Tang, G.P. Gennaro and Y.Y. Su, J. Amer. Chem. Soc., 94 (1972) 4355.
3 E.A. Chernyshev, N.G. Komalenkova and S.A. Bashkirova, Dokl. Akad. Nauk SSSR, 205 (1972) 868.
4 G.P. Gennaro, Y.Y. Su, O.F. Zeck, S.H. Daniel and Y.-N. Tang, Chem. Commun., (1973) 637.
5 P.P. Gaspar, R.-J. Hwang and W.C. Eckelman, Chem. Commun., (1974) 242.
6 O.F. Zeck, Y.Y. Su, G.P. Gennaro and Y.-N. Tang, J. Amer. Chem. Soc., 96 (1974) 5967.
7 P.P. Gaspar and R.-J. Hwang, J. Amer. Chem. Soc., 96 (1974) 6198.
8 M.E. Childs and W.P. Weber, Tetrahedron Lett., (1974) 4033.
9 R.L. Jenkins, R.A. Kedrowski, L.E. Elliott, D.C. Tappen and M.A. Ring, J. Organometal. Chem., 86 (1975) 347.
10 M. Ishikawa, F. Ohi and M. Kumada, J. Organometal. Chem., 86 (1975) C23.
11 E.M. Tebben and M.A. Ring, Inorg. Chem., 8 (1969) 1787.
12 P. Estacio, M.D. Sefcik, E.K. Chan and M.A. Ring, Inorg. Chem., 9 (1970) 1068.
13 M. Bowrey and J.H. Purnell, Proc. Roy. Soc., Ser. A., 321 (1971) 341.
14 R.A. Benkeser and R.F. Cunico, J. Organometal. Chem., 4 (1965) 284.
15 R.J. Ellis and H.M. Frey, J. Chem. Soc. (A), (1966) 553.
16 R.S. Cooke and U.H. Andrews, J. Org. Chem., 38 (1973) 2725.
17 M. Ishikawa and M. Kumada, J. Organometal. Chem., 81 (1974) C3.
18 R.L. Lambert, Jr. and D. Seyferth, J. Amer. Chem. Soc., 94 (1972) 9246.
19 D. Seyferth, C.K. Haas and D.C. Annarelli, J. Organometal. Chem., 56 (1973) C7.
20 Y. Nakadaira, S. Kanouchi and H. Sakurai, J. Amer. Chem. Soc., 96 (1974) 5623.
21 V.A. Mironov, A.D. Fedorovich, E.M. Mil'vitskaya, O.Ya. Korner and A.A. Akhrem, Doklady Akad. Nauk SSSR, 203 (1972) 347.