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Preliminary communication

NOVEL TWO ATOM INSERTIONS INTO THE SILACYCLOPROPANE AND SILACYCLOPROPENE RINGS

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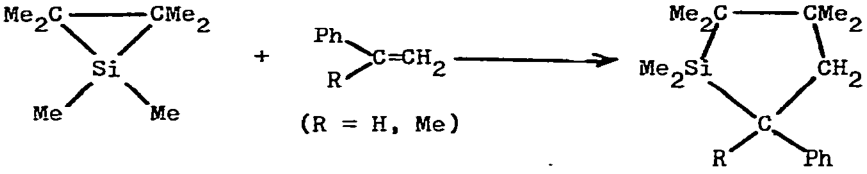
Summary

The reactions of hexamethylsilirane and 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene with aromatic and α,β-unsaturated aldehydes and ketones gave insertion products having the 1-sila-2-oxacyclopentane and 1-sila-2-oxacyclopent-4-ene structures, respectively. Benzaldehyde methylimine reacted with hexamethylsilirane in similar fashion, giving 1,1,2,4,4,5,5-heptamethyl-3-phenyl-1-sila-2-azacyclopentane. Reactions of the silirane and silirene with phenylacetylene gave both ring insertion and ring opening products. 1,1-Dimethyl-3,4-diphenyl-1-silacyclopentadiene was formed in the reaction of the silirene with an excess of phenylacetylene in the presence of a catalytic quantity of bis(triphenylphosphine)palladium dichloride.

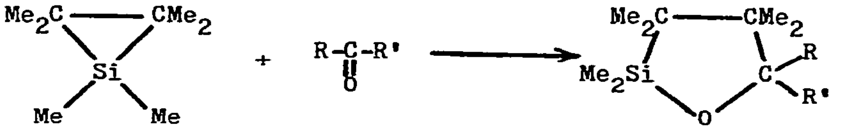
Hexamethylsilirane transfers Me_2Si to other olefins at 70°, giving new silacyclopropanes, but it reacts differently with phenyl-substituted olefins such as styrene and α-methylstyrene


(1)

in which the $\cdot SiMe_2CMe_2CMe_2\cdot$ diradical is intercepted by the olefin. (A molecular mechanism, however, is by no means excluded).

In an investigation of the possible scope of such novel "two atom" insertions into SiC_2 ring compounds, we have examined the reactions of aldehydes, ketones, an imine and a terminal acetylene with hexamethylsilirane, as well as some similar reactions with the recently reported[2] 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene.

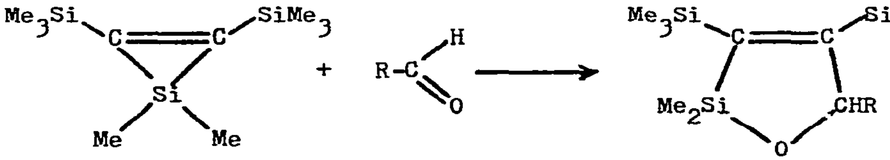
Hexamethylsilirane was found to react at room temperature with aromatic and α,β-unsaturated aldehydes and ketones to give the 1-sila-2-oxacyclopentane system (eq. 2). In a typical reaction, 3 mmol of acetophenone was added, under argon, to 2.76 mmol of hexamethylsilirane (HMS) in THF in a 50 ml three-necked flask equipped with a no-air rubber stopper, argon outlet and magnetic stir-bar. The resulting solution was stirred at room temperature for 12 hr. Subsequent GLC analysis showed the presence of a single major component (60% yield). The product, a liquid, $n^{25}D$ 1.5158, was isolated by GLC and characterized. (Found: C, 73.05; H, 9.97. $C_{16}H_{26}OSi$ calcd.: C, 73.22; H, 9.99%). NMR (CCl_4/CH_2Cl_2): δ 0.24 and 0.29 (s, 3H each, CH_3-Si), 0.4, 0.84, 0.99, 1.14 (s, 3H each, CH_3 of $-CMe_2CMe_2-$ unit), 1.54 (s, 3H, CH_3CPh) and 7.18 ppm [illegible]


I

(2)

found to occur with PhCH=O, $Ph_2C=O$, $Me_2C=CH(CH_3)C=O$ and $CH_3CH=CH$-CH=O, but not with $C_2H_5CH=O$ and $Me_3CCH=O$, at least under these conditions. The product derived from crotonaldehyde (I, R = $CH_3CH=CH$, R' = H) had a ^1H NMR spectrum which showed the presence of the $CH_3CH=CH$ group, clearly demonstrating that 1,2, not 1,4, addition had occurred, and its mass spectrum (70 eV) showed the molecular ion at m/e 212 and no higher species, confirming that the five-membered ring was in hand.

1,1-Dimethyl-2,3-bis(trimethylsilyl)-1-silirene reacted *exothermally* with benzaldehyde in benzene solution. After the reaction mixture had been stirred under nitrogen for 12 hr at room temperature, GLC analysis showed the formation of a single product, mp 61-62°, in 77% yield, whose combustion analysis and IR and NMR spectra showed it to be the two-atom insertion product (eq. 3, II, R = Ph). A similar reaction with crotonaldehyde gave II (R = MeCH=CH) in 93% yield as a liquid, $n^{25}D$ 1.4870. The mass spectrum of this product showed the molecular ion at m/e 298, thus demonstrating that the five-membered ring had been formed.



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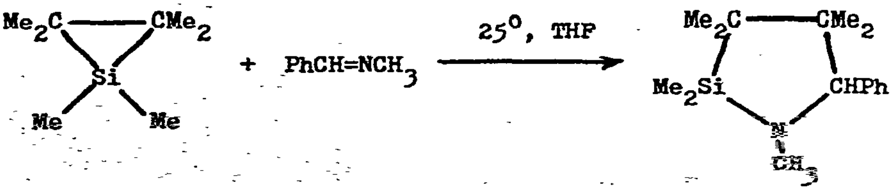
II

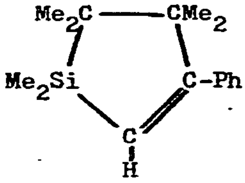
The reaction of HMS with benzaldehyde methylimine showed that the C=N bond also could be inserted into the SiC_2 ring (eq. 4).



(4)

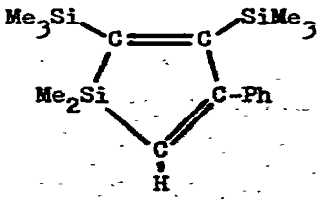
Of special interest were the reactions of the silacyclopropane and the silacyclopropene with phenylacetylene. In addition to its reactive C≡C bond, this substrate has another potential site of reactivity, its weakly acidic C-H bond. In our previous studies we had found that the silacyclopropane ring is very reactive toward weakly acidic substrates,[3,4] and the same is true for the silacyclopropene ring.[2] Thus it was by no means clear how these SiC_2 ring compounds would react with phenylacetylene.

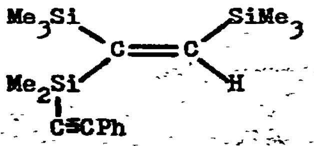
Hexamethylsilirane and phenylacetylene (in 1:1 molar ratio) in THF solution reacted during 12 hr at room temperature to give both the ring insertion and the ring opening products, III and IV, in yields of 47% and 20%, respectively. The ^1H NMR spectrum of III showed a vinyl proton signal as a singlet at δ 5.64 ppm, while no resonance due to a vinylic proton was apparent in the NMR spectrum of IV. Compound III, a liquid, $n^{25}D$ 1.5281, and IV, a liquid, $n^{25}D$ 1.5248, could be separated by GLC. The reaction of phenylacetylene with 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silirene also gave both possible products, V and VI, in 30:70 ratio (75% combined yield) after a reaction time of 18



III

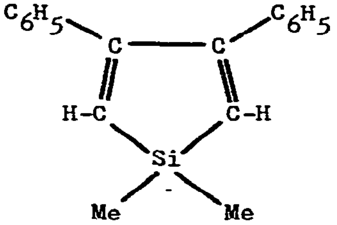
IV





VI

hr at room temperature. GLC columns on which clean separation of III and IV was possible could not effect a separation of V and VI. However, the presence of two vinyl proton resonances in the ^1H NMR spectrum of the product mixture (at δ 5.89 ppm, due to V, and at 7.58, due to VI) in integrated ratios of 30:70 gave clear indication that both products were present. In another experiment the reaction of the silacyclopropene with 9 molar equivalents of phenylacetylene was carried out in benzene in the presence of 1 mol % of $(Ph_3P)_2PdCl_2$. An exotherm was observed immediately upon addition of the silacyclopropene to the acetylene/catalyst solution. After 1 hr at room temperature, GLC analysis showed the presence of a single major product (73% yield) which was collected as a solid, mp 98-99°, and identified as VII (^1H NMR, in CCl_4,CH_2Cl_2: δ 0.37 (s, 6H, $Si-CH_3$), 6.1 (s, 2H, vinyl H) and 6.72 (broad s, 10H, C_6H_5). The other likely structural



VII

possibility, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene, is a known compound with mp 132-133° and a different NMR spectrum.[5]

The reactions described in this communication show that silacyclopropanes and silacyclopropenes can be useful building blocks for more complicated organosilicon structures and we are searching for further "two atom" insertion reactions in order to extend the utility of this approach. At this time we have no evidence concerning the mechanisms of these processes and this question will receive our future attention. The formation of VII in the $(Ph_3P)_2PdCl_2$-catalyzed reaction of the silirene with phenyltion metal-catalyzed conversions of the silirene as well as of the silirane. The preparation of stable transition metal complexes derived from these SiC_2 ring systems is an interesting possibility which is under active investigation.

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