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REACTION OF SILYLENE WITH ALLENES: ALKYLIDENESILACYCLOPROPANE AND SILATRIMETHYLENEMETHANE

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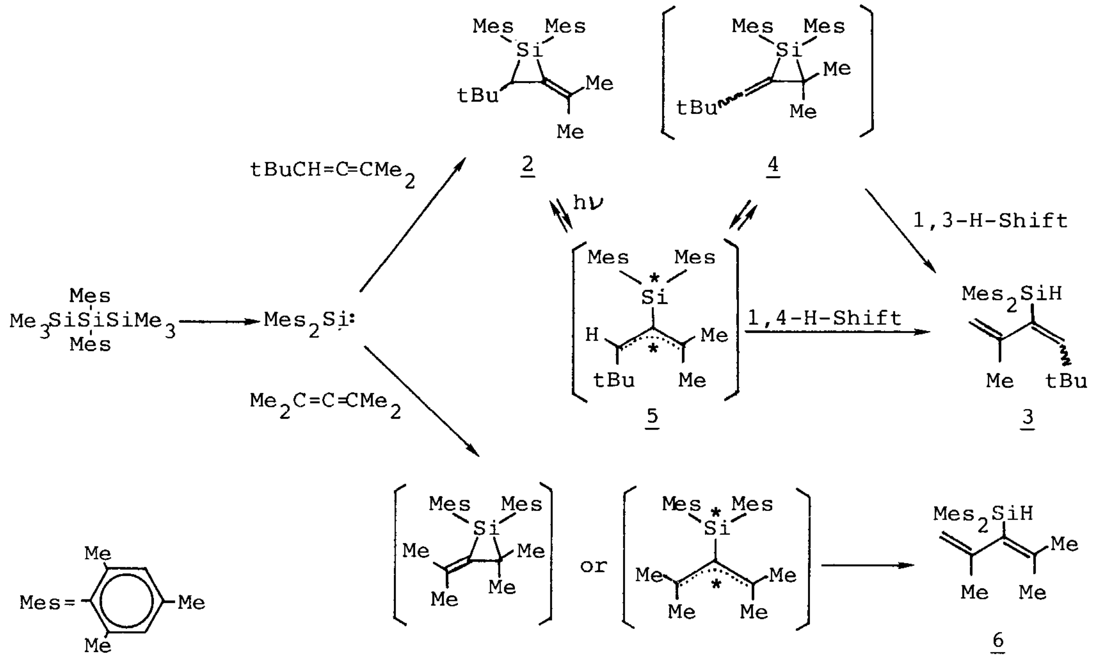
Summary; Reaction of photogenerated dimesitylsilylene with tert-butyldimethylallene and tert-butylallene yielded the corresponding alkylidenesilacyclopropanes. Its photochemical behavior and some reactions with nucleophiles are described.

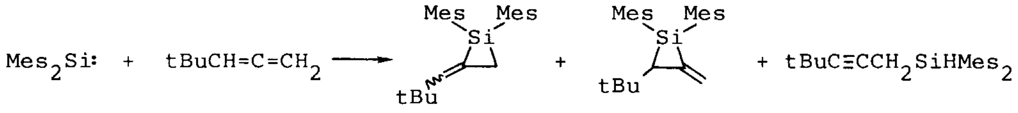
Because of the unique properties resulting from high strain energy, the studies of silicon-containing three-membered ring compounds have been fruitful in recent silicon chemistry.$^{1)}$ Alkylidenesilacyclopropanes are specially suited targets for such strained silicon compounds, because of the unique structural and mechanistic features of trimethylenemethane silicon analogue species. However, the isolation of alkylidenesilacyclopropane has not been reported so far as we know.$^{2)}$ Direct method of alkylidenesilacyclopropane formation by a reaction of silylene with allene appears to be most suitable, and we present here our preliminary results toward the synthesis and some reactions of alkylidenesilacyclopropanes.

Irradiation of cyclohexane solution of 2,2-dimesitylhexamethyltrisilane 1 (1 mmol) with excess amount of tert-butyldimethylallene was carried out with low pressure mercury lamp for 5.5 hr. The products were separated by preparative GLC(10% SE-30 on Uniport B). Two major products, compound 2 and 3 were obtained in 36 and 7% yields respectively, with 23% of remained trisilane, and characterized by spectroscopic data.$^{3)}$ Alkylidenesilacyclopropane 4 has not been isolated from the reaction mixture. Although alkylidenesilacyclopropane 2 was found to be thermally stable and inert to methanol owing to the protection by bulky substituents, it undergoes photochemically to compound 3. Photolysis of 2 in cyclohexane with low pressure mercury lamp gave 3 in 42% yield. These results suggest the intermediacy of silatrimethylenemethane 5 in the course of the procedure to 3. Absence of 4 is explained by the rapid isomerization to 3 with 1,4-hydrogen shift of 5 or direct 1,3-hydrogen shift to give 3.$^{4)}$ Photoisomerization of 2 is also interpreted by the mechanism via 5 or isomerization to 4 via 5 followed by hydrogen shift as described above. Alternatively, direct addition of silylene generates 5 at first step to give 2 and 3. A similar phenomenon was observed in the reaction with tetramethylallene, in which product 6 was isolated in 27% yield without any isolation of alkylidenesilacyclopropane.

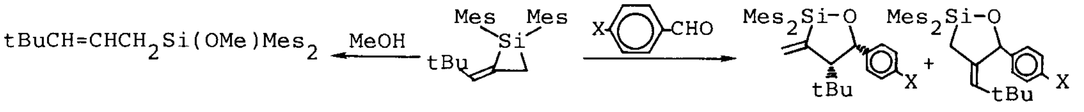


Irradiation of cyclohexane solution of 1 (1 mmol) with excess amount of tert-butylallene for 14 hr gave a mixture of three isomers of alkylidenesilacyclopropanes 7Z, 7E and 8, in 31, 22 and 8% yields respectively, on NMR studies,[5] together with 7% of unexpected tert-butylacetylene 9. Whereas 7Z was purified by recrystallization from hexane, the other 7E and 8 were not able to isolate as stable form. The explanation for the formation of 9 is not apparent at the present stage.

Much of the attractiveness of alkylidenesilacyclopropane lies in the reactivities for nucleophiles. Alkylidenesilacyclopropane 7Z reacted smoothly with methanol in benzene to give methoxysilane 10 in quantitatively, and with benzaldehyde in $CDCl_3$ to give two oxasilacyclopentanes 11a and 12a in 40 and 30% yields respectively. The stereochemistry of 11a and 12a was confirmed by X-ray analysis[6] and 400 MHz ^{1}H-NMR spectroscopic studies[7] respectively. The reaction with p-anisaldehyde yielded two adducts 11b and 12b in quantitatively, in contrast to the reaction with p-chlorobenzaldehyde with 15% of the adduct 11c. In view of these results, nucleophilic attack of methanol oxygen and carbonyl oxygen on silicon is probably the first step followed by Si-C bond cleavages.[8] The Si-vinyl bond cleavage for the formation of 10 and 12 is quite surprising since the systems of a simple alkylidenecyclopropane and its hetero analogue, have found to proceed with the cleavage of C-C or C-hetero bond not bonding to double bond. This reactivities can be explained by the higher polarity of Si-vinyl bond which is additionally caused by alkylidene



7Z and 7E 8 9



10 7Z 11a; X= H b; X= OMe c; X= Cl 12a; X= H b; X= OMe

substitution.[9] Whereas, the facile Si-C bond cleavage and simultaneous π-bond migration reaction seems to be suitable for the formation of 11.

Further studies are continued for the photochemistry of alkylidenesilacyclopropanes.

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References and Notes

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(3) ^{1}H-NMR of 2 ($CDCl_3$) δ 1.08(s,9H),2.06(s,3H),2.19(s,3H),2.38(s,6H),2.70 (s,12H),7.01(s,4H). A ring proton was obscured in methyl or mesityl region. ^{13}C-NMR of 2 ($CDCl_3$) δ 21.14(q),24.01(q),24.19(q),24.89(q),26.83 (q),32.00(q),34.70(s),41.20(d),128.34(d),128.58(d),129.40(s),134.39(s), 138.79(s),139.03(s),141.90(s),144.55(s),145.13(s). Mass m/e 390(M^+).

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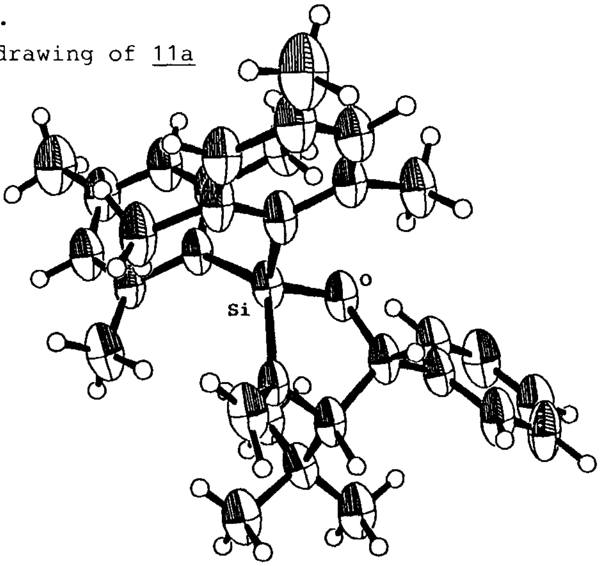
(5) Two fractions of a mixture of 7Z and 8, and a mixture of 7E and 9, were separated by HPLC. 7Z; m.p. 116-118°C, 400 MHz ^{1}H-NMR($CDCl_3$)δ 1.03(s,9H), 1.52(d,2H,J=2.6Hz),2.24(s,6H),2.46(s,12H),6,46(t,1H,J=2.6Hz),6.78(s,4H). Stereochemistry of 7Z was determined by the NOE spectrum. Irradiation at ring proton(1.52ppm) caused a nuclear Overhauser effect(NOE) of vinyl proton(6.46ppm). However, irradiation at tert-butyl proton(1.03ppm) was not effective to ring proton. ^{13}C-NMR ($CDCl_3$)δ 16.43(t),21.15(q), 23.75(q),29.65(q),35.29(s),128.41(d),129.22(s),139.30(s),144.56(s), 148.43(d). Mass m/e 362(M^+). 7E; ^{1}H-NMR (CCl_4)δ 1.15(s,9H),1.69(d,2H, J=3Hz),2.25(s,6H),2.53(s,12H),6.52(t,1H, J=3Hz),6.85(s,4H). 8; ^{1}H-NMR (CCl_4)δ 0.95(s,9H),1.81(br.t,1H),J=3.6Hz),2.24(s,12H),2.58(s,6H), 6.24(br.d,2H,J=3.6Hz),6.69(s,4H).

(6) The crystal has triclinic space group $P\bar{1}$ with a=8.578Å, b=13.604Å, c=14.442Å and α=70.30°,β=96.66°,γ=106.86°. The structure was refined to an R value of 0.0895.

Figure. ORTEP drawing of 11a



(7) 400MHz ^{1}H-NMR of 12a ($CDCl_3$) δ 1.07(s,9H),2.07(d,1H,J=15Hz),2.21(s,3H), 2.23(s,6H),2.24(s,3H),2.43(s,6H),5.45(br.s,1H),6.23(br.s,1H),6.76(s,2H), 6.78(s,2H),7.19-7.26(m,3H),7.38(br.d,2H). Irradiation at tert-butyl proton(1.07ppm) caused a NOE of a benzyl proton(5.45ppm),a vinyl proton (6.23ppm) and ortho protons of phenyl group(7.38ppm). The authers wish to thank Mr. Yasushi Nagai for a help of 400MHz ^{1}H-NMR the spectroscopic measurement.

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(9) In methylenecyclopropane, sp^2 ring carbon atom has the most anionic character in calculation. See; N.C.Braid, M.J.S.Dewar, J.Am.Chem.Soc., 89,3966(1967).

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