Formation of a Benzosilacyclopentene. Formation of a Silacyclopropane by Intramolecular Insertion of a Silylcarbene.

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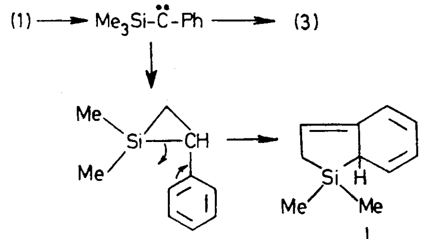
Summary Pyrolysis of phenyltrimethylsilyldiazomethane gave 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene and the dimerization product of the silylcarbene, whilst photolysis in benzene, gave only the dimerization product.

Alkyl(alkoxycarbonyl)carbenes react predominantly by insertion into β- and γ-C–H bonds to give olefins and cyclopropanes.[1] The intramolecular reactions of alkylcarbenoids, derived from organometallic precursors, are often similar. In contrast the silicon analogues do not undergo intramolecular reactions, but insert into the C–H bonds of hydrocarbon solvents,[2] an example of the inertness of the α-C–H in the silicon analogue toward attack by carbenes.[3] One case has been reported where phenyl- and alkoxycarbonylcarbenes insert into the C–H bond α to silicon efficiently,[4] in the reaction between chloromethyltrimethylsilane and alkali metals.[5] In this case, the silacyclopropane undergoes nucleophilic ring opening to produce high molecular weight products.

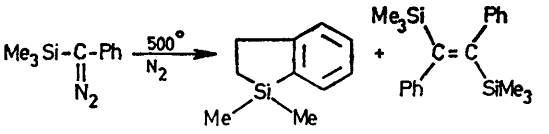
We now report the formation of a silacyclopropane by intramolecular 1,3-insertion of a silylcarbene generated in the thermolysis of phenyltrimethylsilyldiazomethane.

Complete pyrolysis of phenyltrimethylsilyldiazomethane[6] took place in a nitrogen flow system (30 cm^3/min, 500°) and the pyrolysate was collected at $-78°$. Analysis by gas chromatography showed two products and no phenyltrimethylsilyldiazomethane. Separation of the products by preparative gas chromatography afforded pure (**2**) (15%); [τ(CCl_4) 2·5—3·1 (4H, m, Ar-H), 6·95(2H, t, Ar-CH_2, *J* 7·0 Hz), 9·05 (2H, t, Si-CH_2, *J* 7·0 Hz) and 9·73 (6H, s, Si-Me_2); ν_{max} 1441, 1251, 1122 and 843 cm^{-1}], and (**3**) (14%) [τ (CCl_4) 2·5—3·2 (10H, m, Ph_2) and 10·38 (18H, s, $2SiMe_3$); ν_{max} 1247 cm^{-1}, and *m/e*: 324·1762 ($C_{20}H_{28}Si_2$)]. The structure and purity of (**2**) were confirmed by comparison of i.r. and n.m.r. spectra with those of a known sample.[7] The formation of 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene (**2**) suggests the intermediate silacyclopropane (**4**), a compound formed by 1,3-insertion of phenyltrimethylsilylcarbene. The trapping of (**4**) has proved difficult. The addition of alcohols or olefins to the reaction process did not inhibit the formation of the benzosilacyclopentene under these reaction conditions.

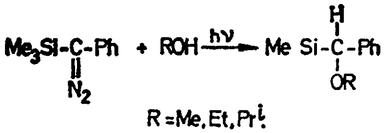


(4) (2)

The pyrolysis of phenyldimethylphenylsilyldiazomethane did not give benzosilacyclopentene derivatives. When phenyltrimethylsilyldiazomethane is photolysed in alcohols using a high pressure mercury lamp, the O–H insertion product of the silylphenylcarbene is obtained in high yield, and products (**2**) and (**3**) are not obtained, in benzene solution (**3**) is the principal product.



(1) (2) (3)



$$\underset{N_2}{\underset{\|}{Me_3Si\text{-}C\text{-}Ph}} + ROH \xrightarrow{h\nu} Me\ Si\text{-}\overset{H}{\underset{OR}{C}}\text{-}Ph$$

R =Me.Et.Prⁱ

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