Pyrolysis of Silylphenyldiazomethanes.[1] Rearrangement of Silylcarbenes to Compounds Containing an Si=C Double Bond

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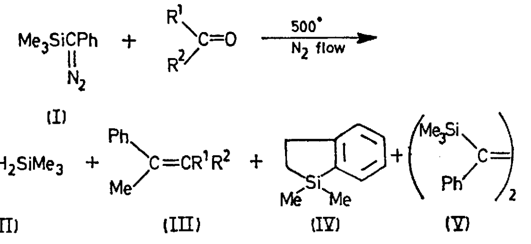
Summary Pyrolysis of phenyltrimethylsilyldiazomethane with carbonyl compounds gave styrene derivatives, whilst pyrolysis with 2,3-dimethylbuta-1,3-diene gave silacyclohexene derivatives together with benzosilacyclopentene and the dimerization product of silylcarbene; the reactions probably involve methyl migration from silicon to carbenic carbon in the silylphenylcarbene followed by 2 + 2 and 2 + 4 reactions with the carbonyl compounds and butadiene.

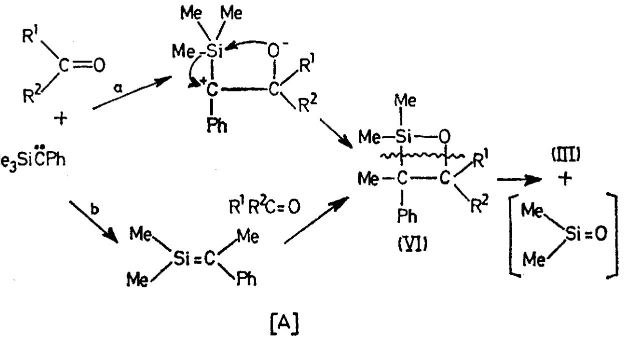
Diazo-compounds decompose thermally into carbenes which give olefins by hydrogen, phenyl, or alkyl migration, and cyclic derivatives by intramolecular insertion.[2] While the rearrangement of such carbenes has been extensively studied, there are few reports on the rearrangement of silylcarbenes. We reported previously that the photochemical decomposition of trimethylsilyl diazoacetate in EtOH led to the possible formation of a silicon–carbon double bond by methyl migration from silicon to carbenic carbon.[3] We report here some reactions of silylphenyldiazomethane with carbonyl compounds and butadienes on pyrolysis.

$Me_3SiC(Ph)=N_2$ in excess of Me_2CO was pyrolysed in a nitrogen flow system (30 ml/min; 500 °C) and the pyrolysate was collected at −78°. G.l.c. analysis showed that it contained compounds (II) (2% yield), (IIIa) (23%), (IV) (37%), and (V) (13%), the structural assignments being confirmed by i.r. and n.m.r. comparison with known samples.[1]



a; $R^1 = R^2 = Me$
b; $R^1,R^2 = -[CH_2]_5-$
c; $R^1,R^2 = -[CH_2]_4-$
d; $R^1 = H$, $R^2 = Ph$
e; $R^1 = H$, $R^2 = Et$

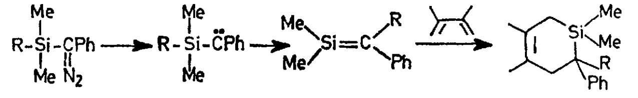
Similar thermal decomposition of (I) in cyclohexanone and cyclopentanone yielded the cyclohexylidene (IIIb) (11%) and cyclopentylidene (IIIc) (5%) compounds, together with compounds (II), (IV), and (V). Benzaldehyde and propionaldehyde afforded the analogous styrene derivatives (IIId) and (IIIe) in 28 and 7% yields, respectively.



SCHEME

The somewhat puzzling product (III) could be formed by processes a or b (Scheme). Silylphenylcarbene is thought to attack initially the carbonyl carbon (process a). The resulting 'oxyanion' may attack silicon followed by methyl migration to give compound (VI) which is known to decompose with the formation of (III). However, an oxyanion intermediate is unlikely since silylphenylcarbene generated by photolysis did not give styrene derivatives. We feel that process b is more likely, in which compound (III) arises from a methyl migration from silicon to carbenic carbon to give an intermediate similar to (A). An analogous Wittig-type pathway has been observed in the pyrolysis of 1,1-dimethyl-1-silacyclobutane with carbonyl compounds.[4] This intramolecular migration of methyl and phenyl groups from silicon to carbenic carbon is supported by results of the pyrolysis of (I) and the diazomethane (VII) in the presence of excess of conjugated olefins (nitrogen flow; 500 °C).

The reaction of (VII) with 2,3-dimethylbuta-1,3-diene afforded compound (VIII) as principal product (33%) and a trace of the adduct of the carbene with the olefin. The product (VIII) was probably formed from a phenyl migration from silicon to carbenic carbon in the silylphenylcarbene followed by a Diels–Alder reaction[5] with 2,3-dimethylbuta-1,3-diene; [τ (CCl_4) 2·6—3·1 (10H, m, CPh_2), 7·1—7·4 (2H, m, $CH_2C{=}C$), 8·28br (3H, s, C=CMe), 8·48br (3H, s, MeC=C), 8·7—8·9 (2H, m, $SiCH_2$), and 9·89 (6H, s, $SiMe_2$); no Si–Ph i.r. bands at 1429 and 1117 cm^{-1}; *m/e* 306·1811 (calc. 306·1804)]. The reaction with 2,3-dimethylbuta-1,3-diene at 250° gave the cyclopropane derivatives as the major products and the adduct (VIII) became a minor product. At higher temperature, phenyl migration in dimethylphenylsilylphenylcarbene competes effectively with the addition of silylcarbene to the double bond.



(I) R = Me
(VII) R = Ph
(VIII) R = Ph
(IX) R = Me

Similarly, in copyrolysis of (I) with excess of 2,3-dimethylbuta-1,3-diene at 500°, the Diels–Alder adduct (IX) was obtained in 8% yield together with cyclopropane derivatives (two isomers in 2% yield), a cyclopentene derivative (formed in the isomerization of cyclopropane derivatives;[6] 25%), and compounds (IV) (22%) and (V) (8%), respectively. The structures of these products were determined by n.m.r. and i.r. spectroscopy and elemental analysis.

We feel that our results provide examples of 1,2-methyl and -phenyl migrations in silylphenylcarbenes in which the unstable silicon-carbon double bonded intermediates have been trapped with carbonyl compounds and butadienes.

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