

Intramolecular Cyclopropanation of an Aromatic Nucleus by an Alkylidenecarbene: a Novel Access to Heptafulvenes

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Thermolysis of the α -silylated α -diazoketone (**1**) at 80 °C generates the electron-rich heptafulvene (**2**); the alkylidenecarbene (**5**) is the key intermediate of the reaction sequence.

Thermal decomposition of aroyldiazomethyl silanes, $\text{ArCO}(\text{N}_2)\text{SiR}_3$, yields siloxyalkynes, $\text{ArC}\equiv\text{COSiR}_3$, in good yields.¹ This transformation has been explained by the intervention of an alkylidenecarbene, $\text{Ar}(\text{R}_3\text{SiO})\text{C}=\text{C}:$, from which the acetylene is produced by aryl migration. In an effort to prove the intermediacy of the alkylidenecarbene by a different trapping experiment, we now turned to *alkyl*-substituted diazoketones, $\text{AlkCO}(\text{N}_2)\text{SiR}_3$, since the migrating tendency of an alkyl group is much less pronounced than of an aryl group^{2,3} and, in fact, has been observed only rarely in alkylidenecarbene chemistry.²

Our interest focused on the α -diazoketone (**1**) which we obtained by electrophilic diazoalkane substitution of $\text{Bu}^t\text{CO}-\text{CHN}_2$ with $\text{Ph}_2\text{Bu}^t\text{Si}-\text{OSO}_2\text{CF}_3$ ⁴ according to our published procedure¹ [67%, m.p. 75 °C (decomp.); i.r. (KBr) 2065 (CN_2) and 1615 ($\text{C}=\text{O}$) cm^{-1}]. Thermolysis of (**1**) in refluxing benzene produced a dark-violet solution from which the heptafulvene (**2**) (Scheme 1) could be isolated as a violet oil by column chromatography (silica gel, CH_2Cl_2) under an argon atmosphere. As for other electron-rich heptafulvenes bearing an electron-donating substituent at C-8,⁵ compound (**2**) is extremely sensitive towards moisture and air oxidation. Its spectral data also accord with expectations⁵ [u.v. (CH_2Cl_2) λ_{max} 274, 303, and 505 nm; ^1H n.m.r. (90 MHz, CDCl_3) δ 1.03 (s, 9 H), 1.20 (s, 9 H), 4.88 (m, 1H), 5.21 (m, 2H), 5.40 (m, 1H), 5.78 (d, 3J 12 Hz, 1 H), and 7.33–7.80 (m, 5 H)].

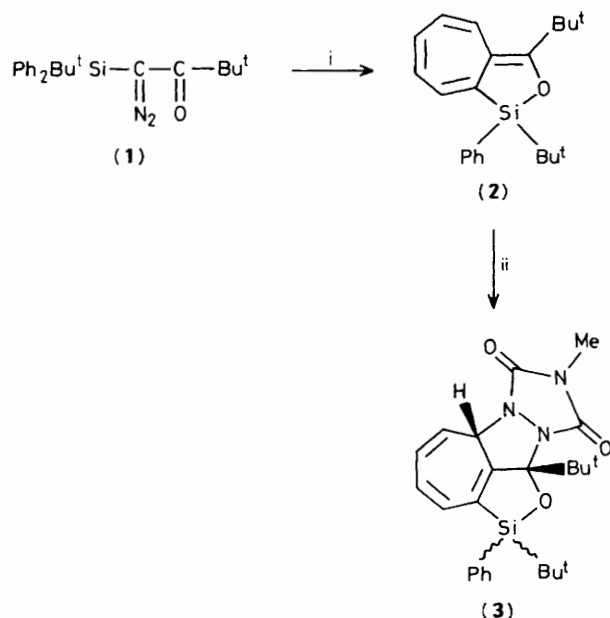
Since the lability of (**2**) prevented complete purification, the

compound was characterized by [8 + 2] cycloaddition⁶ with 4-methyl 1,2,4-triazole-3,5(4*H*)-dione (NMTD) to give the 1:1 adduct (**3**).[†] When the polyenophile was added to the crude reaction mixture of the thermolysis, the colour of the solution was discharged immediately and the cycloadduct was obtained in 62% yield [based on (**1**)] as a single isomer. The *cis* relationship for the substituents (H and Bu^t) at the termini of the 8π component follows from the transition state geometry of the cycloaddition.⁶

A mechanistic picture of the transformation (**1**) \rightarrow (**2**) is given in Scheme 2. The sequence begins with a thermal 1,3 C \rightarrow O silyl migration which yields a diazoethene (**4**). There is general agreement that diazoethenes split off N_2 extremely rapidly,³ and all efforts to isolate such compounds have failed so far; the first successful trapping experiments have been published recently.⁷ Extrusion of N_2 from (**4**) leads to the alkylidenecarbene (**5**) which undergoes [2 + 1] cycloaddition to one of the Si-phenyl rings. A norcaradiene \rightarrow cycloheptatriene valence tautomerisation, (**6**) \rightarrow (**2**), constitutes the last step of the transformation (**1**) \rightarrow (**2**).

Whereas intermolecular cyclopropanation of an aromatic

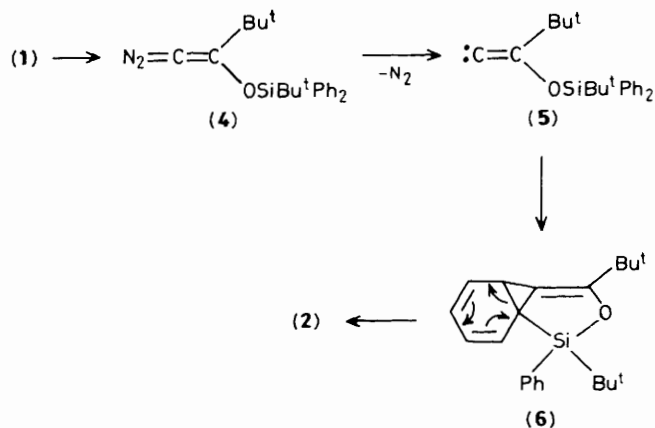
[†] Physical data for (**3**): m.p. 132 °C (from Et_2O); i.r. (KBr) 1750 and 1695 cm^{-1} ; ^1H n.m.r. (200 MHz, CDCl_3): δ 1.15 (s, 9 H), 1.16 (s, 9 H), 2.94 (s, 3 H), 5.84 (m, 3 H), 6.10 (m, 1 H), 6.31 (dd, J 11.0 and 0.8 Hz, 1 H), 7.3 (m, 3 H), and 7.52 (m, 2 H).



Scheme 1. Reagents and conditions: i, benzene, 80°C, 2 h, hydroquinone (5 mol %), argon atmosphere; ii, NMTD, room temp.

system by an alkylidene carbene seems to have not been realised so far,² an intramolecular version similar to (5) \rightarrow (6) has been proposed to explain the pyrolytic rearrangement of *o*-ethynylbiphenyl to 1,2-benzazulene.⁸ As far as the alkylidene carbene (5) is concerned, the intramolecular mode of cyclopropanation dominates at the complete expense of an intermolecular version. No products which would be expected from addition of (5) to the π systems of benzene or cyclohexene could be detected after chromatographic work-up of the corresponding reaction solutions.

Preliminary experiments have shown that thermal decomposition of $\text{Ph}_2\text{Bu}^t\text{Si}-\text{C}(\text{N}_2)\text{COMe}$ results in a transformation analogous to (1) \rightarrow (2). These two syntheses represent a novel access to electron-rich heptafulvenes; the few known representatives of this highly reactive class of compounds have been obtained from appropriately functionalised cycloheptatrienes.⁵



Scheme 2

Support of this work by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie is acknowledged.

Received, 1st July 1986; Com. 910

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