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Preliminary communication

REVERSIBLE DI-π-METHANE REARRANGEMENTS OF BICYCLIC ORGANOSILICON COMPOUNDS

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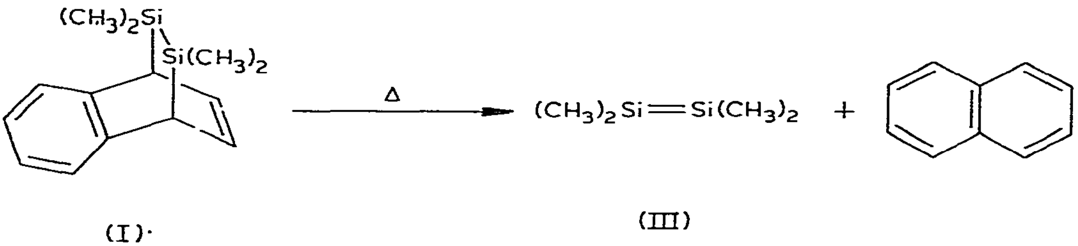
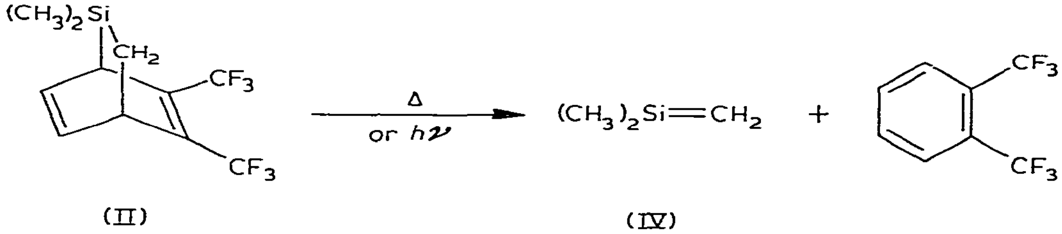
Summary

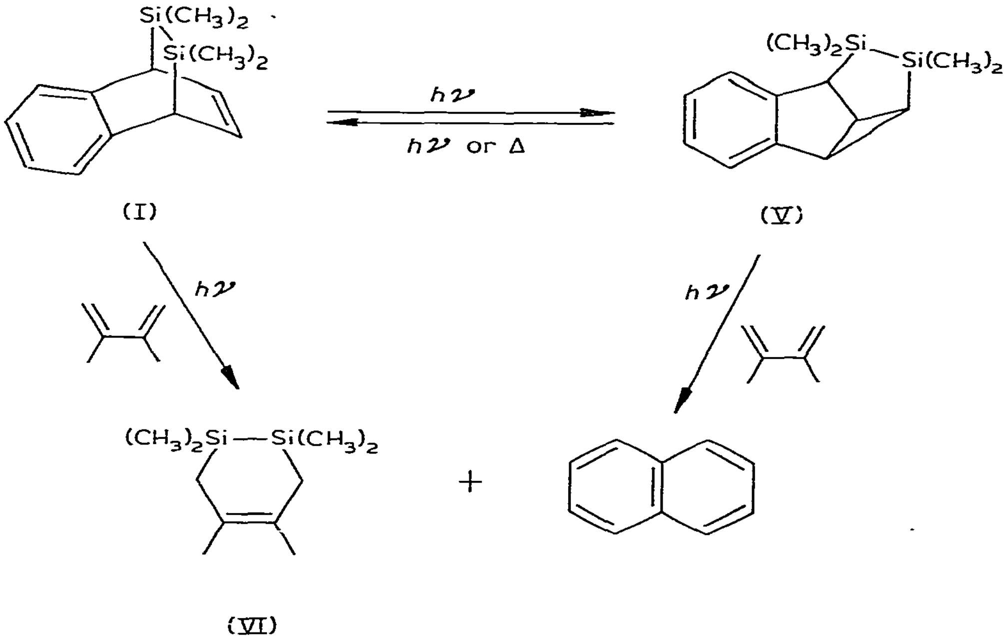
The photochemistry of 5,6-benzo-2,2,3,3-tetramethyl(2,3-disilabicyclo-[2.2.2]octa-5,7-diene) (I) has been investigated. Unlike thermolysis of I, which produces tetramethyldisilene as intermediate, irradiation at 10 K in an argon matrix or 77 K in a 3-methylpentane glass led to a di-π-methane photorearrangement to give 3,4-benzo-6,7-disila-6,6,7,7-tetramethylbicyclo[3.3.0.0^{2,8}]-octane. Photolysis of I at room temperature in cyclohexane did, however, give tetramethyldisilene.

It has been previously shown that thermolysis of I [1] and thermolysis or photolysis of II [2] lead to tetramethyldisilene (III) and dimethylsilene (IV) as reactive intermediates. We report herein our preliminary results concerning the photochemistry of I. Photolysis of I at low temperatures did not lead to the expected intermediate III. Instead, irradiation of I (254 nm) at 10 K in an argon matrix or 77 K in a 3-methylpentane (3-MP) glass gave a 9 : 1 mixture of 3,4-benzo-6,7-disila-6,6,7,7-tetramethyltricyclo[3.3.0.0^{2,8}]octane (V) and starting material I. The structure of V was confirmed by 270 MHz NMR and mass spectra [3]. This isomerization of I to V can be described as a di-π-methane photorearrangement [4].

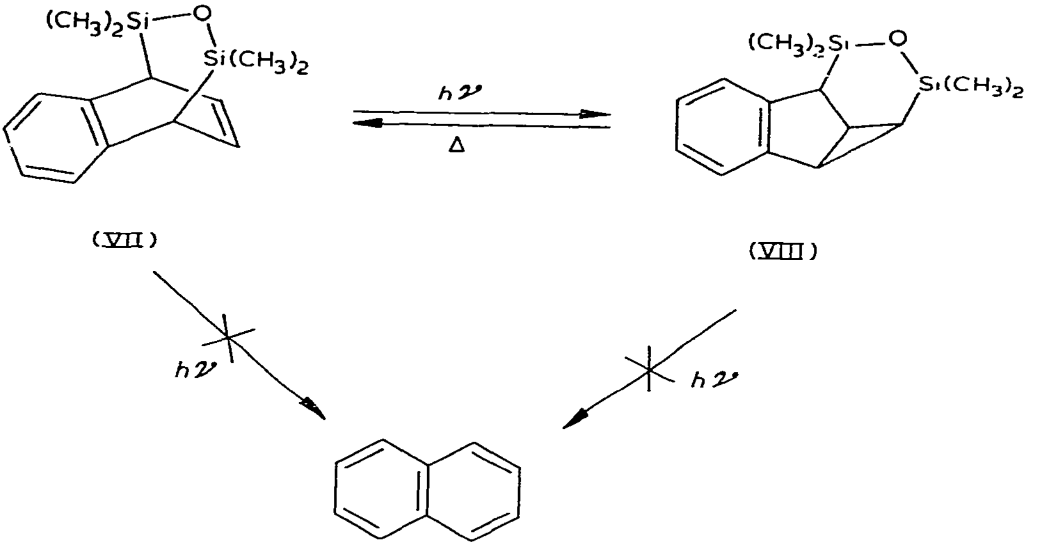
However, photolysis of I in cyclohexane solution at room temperature does appear to give low yields of III. 1,3-Dienes are known trapping reagents for tetramethyldisilene [1,5], and in the presence of 2,3-dimethyl-1,3-butadiene, photolysis of I for 4.5 hours at 254 nm yields 13% of the Diels-Alder adduct VI along with 16% of V. Photolysis of V in solution at room temperature with 2,3-dimethyl-1,3-butadiene produces I in 5% yield and VI. Prolonged photolysis of either I or V in solution without a trapping agent leads ultimately to naphthalene and polysilane polymer.







In a similar reaction photolysis of 6,7-benzo-2,2,4,4-tetramethyl-2,4-disila-3-oxobicyclo[3.2.2]nona-6,8-diene [1,6] (VII) (254 nm) in a cyclohexane solution at room temperature gave only the benzotricyclic isomer VIII [7]. No decomposition of either VII or VIII to yield naphthalene was observed under either thermal or photochemical conditions. Thermolysis at 200°C of both V and VIII in sealed tubes yielded quantitative isomerizations to starting materials I and VII, respectively.



From these experiments it is apparent that I and V photo-interconvert at all temperatures studied. Our tentative explanation of the results is that in solution, loss of III and isomerization to V are competing reaction pathways for disappearance of I. In the argon matrix or 3-MP glass, loss of III from I is prevented and only photoisomerization is observed.

These isomerizations provide unusual examples of reversible di-π-methane rearrangements. Another example of this type of thermally reversible di-π-methane reaction was recently reported by Schaffner and coworkers [8] who suggested that a diradical intermediate may be involved in the reversion step.

Acknowledgement

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References and notes

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3 NMR (C_6D_6); δ 6.8—7.5 (m, 4H), 2.78 (d, 1H, J = 6.25 Hz), 2.73 (d of d, 1H, J = 9.19, 6.25 Hz), 2.42 (d of d of d, 1H, J = J = 6.25, 8.09 Hz), 0.26 (d of d, 1H, J = 8.09, 9.19 Hz), 0.24 (s, 3H), 0.18 (s, 3H), 0.16 (s, 3H), −0.52 ppm (s, 3H). Mass spec. $C_{14}H_{20}Si_2$ calcd. 244.1098. Obs. 244.1092.
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7 NMR (270 MHz, C_6D_6): δ 7.15—7.04 (m, 4H), 2.55 (d of d, 1H, J = 8.73, 5.97 Hz), 2.45 (d, 1H, J = 6.80 Hz), 2.22 (d of d of d, 1H, J = 8.73, 6.80, 5.97 Hz), 0.30 (s, 3H), 0.26 (s, 3H), 0.19 (s, 3H), —0.15 (t, 1H, J = 8.73 Hz), —0.51 ppm (s, 3H). Compounds V, VII and VIII are all colorless crystalline solids.
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