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PHOTOCHEMICAL REACTION OF DIBENZOTETRAMETHYLDISILACYCLOHEXADIENE THROUGH CHARGE-TRANSFER COMPLEX$^{1)}$

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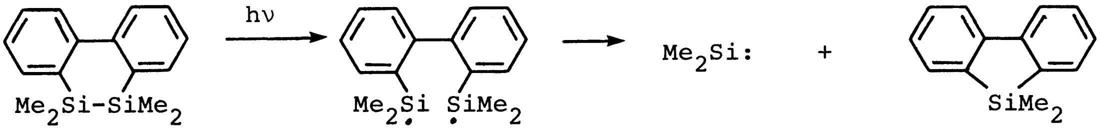
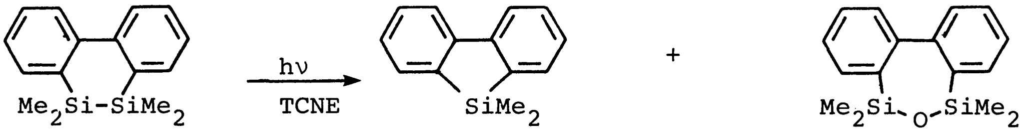
The reaction of dibenzo-1,1,2,2-tetramethyl-1,2-disilacyclohexadiene with tetracyanoethylene under illumination with a sodium lamp gave dibenzo-1,1-dimethyl-1-silacyclopentadiene as a silylene extrusion compound through a charge-transfer complex.

Recently we have described a photochemical reaction of dibenzo-1,1,2,2-tetramethyl-1,2-disilacyclohexadiene (**1**) affording dimethylsilylene and dibenzo-1,1-dimethyl-1-silacyclopentadiene (**2**) after primary silicon-silicon bond homolysis to form **3**, followed by ipso-substitution.$^{2)}$ We now report a novel dimethylsilylene extrusion from a charge-transfer complex of **1** with tetracyanoethylene (TCNE).



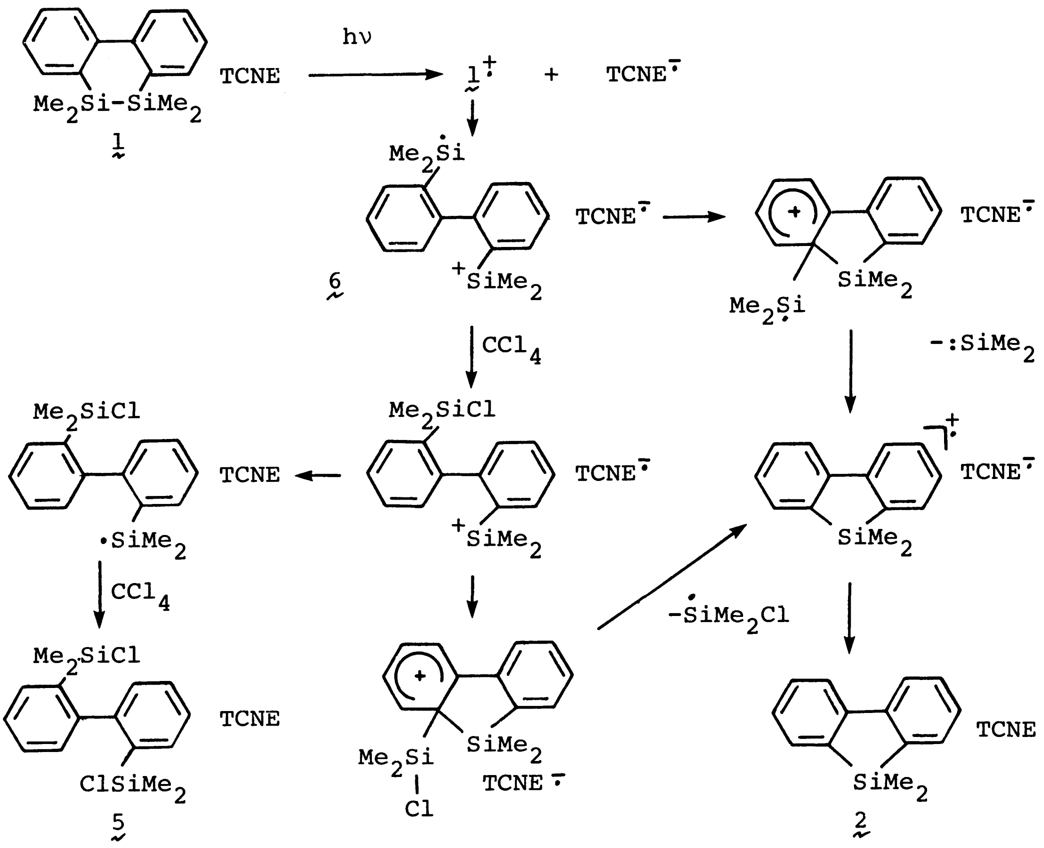
1 **3** **2**

A solution of **1** and TCNE in dichloromethane shows two well defined charge-transfer bands at 17900 and 23800 cm^{-1}. The formation of a charge-transfer complex is also evidenced by the fact that irradiation of the solution, with visible light of wave length longer than 460 nm in a cavity of an ESR spectrometer, gave an ESR spectrum of TCNE anion radicals (a_N = 0.158 mT) at -90 °C.$^{3)}$ Irradiation of **1** and an equimolar amount of TCNE in dichloromethane with a sodium lamp (589 nm) at room temperature afforded only **2** and **4** as volatile products (**2**/**4** = 3/1 by NMR, 5/2 by GLC) along with black precipitates. Since no photochemical reaction of **1** occurs at all by irradiation with a sodium lamp, **2** should be derived from the charge-transfer complex. The origin of oxygen for **4** is unclear at this moment. In spite of every efforts of minimizing moisture and air, **4** was obtained in an appreciable amount.



1 **2** **4**

Irradiation of **1** and TCNE (1:1) in a mixed solvent of dichloromethane and carbon tetrachloride (2:1) under similar conditions gave **2** (11%), **4** (22%), and 2,2'-bis(chlorodimethylsilyl)biphenyl (**5**, 33%). As we have proved kinetically, **2** and **5** are formed competitively from an intermediate diradical (**3**). In the presence of large excess carbon tetrachloride, all the intermediate diradicals are shown to undergo chlorine abstraction to give **5**, no **2** being formed. Therefore, the formation of **2** under the conditions suggests that another intermediate different from **3** should be responsible for the reaction. We propose a radical cation (**6**) to be the intermediate which constitutes the reaction scheme shown below.



A recent ESR evidence demonstrates that the unpaired electron of the cation radical of phenylpentamethyldisilane localizes onto the Si-Si bond.4) The unpaired electron of the cation radical of **1** should also localize onto the Si-Si bond to cause a facile bond breaking to give **6**. Electrophilic ipso-substitution by the silyl cation center results in the formation of **2**. Being not catalytic, the reaction requires an equimolar amount of TCNE. The dimethylsilylene, which can be one of the primary products, could not be trapped by usual trapping reagents such as diethylmethylsilane and 1,1,3,3-tetramethyl-1,3-disila-2-oxacyclopentane. These are unclear facts which still remain to be explained. However, a novel photochemical reaction derived from the charge-transfer complex opens a fascinating new field in organosilicon photochemistry.

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