

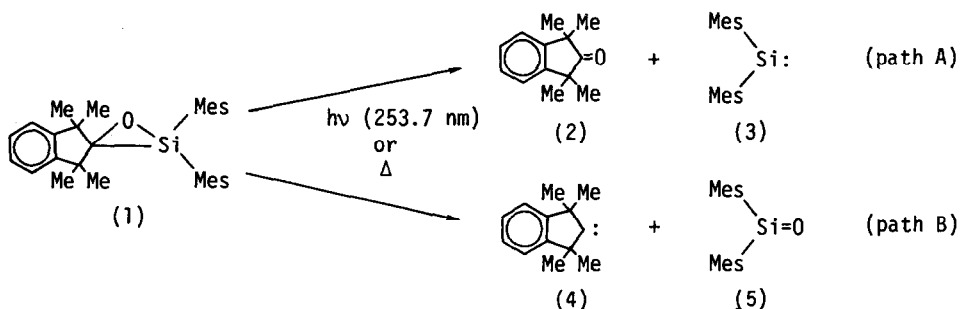
PHOTOSENSITIZED DECOMPOSITIONS OF OXASILACYCLOPROPANE ;  
 UNUSUAL CARBENE FORMATION

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Summary: TCNE photo-sensitized decompositions of oxasila-  
 cyclopropane (1) generated carbene and silanone, while the  
 DCA sensitized or direct photolysis of (1) gave silylene and  
 indanone.

The direct photolyses and photo-sensitized decompositions of epoxides are  
 well studied by Arnold et. al.<sup>1)</sup>, Schaap et. al.<sup>2)</sup> and Whiting et. al.<sup>3)</sup>  
 Recently, we have reported the formation of indanone (2) and silylene (3)  
 in the photolysis and thermolysis of oxasilacyclopropane (1) (Scheme I,  
 path A)<sup>4)</sup>.

Scheme I

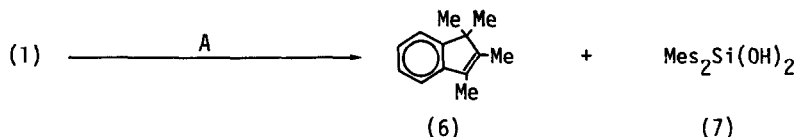


We have now carried out photolysis of oxasilacyclopropane (1) in the presence of tetracyanoethylene (TCNE) which provides the new fragmentation pattern leading to carbene (4) and silanone (5) (path B). Oxasilacyclopropane (1) exhibited an ultraviolet absorption at 237 nm, but showed a new absorption band at 450 nm attributable to a charge-transfer band in the presence of TCNE.

A dichloromethane solution of 0.1 mmol of (1) was irradiated with halogen lamp for 24 hr.<sup>5)</sup> in the presence of TCNE (0.03 mmol). The tetramethylindene (6) (81%) and the dimesitylsilanediol (7) (99%) were obtained as major products, and the products from indanone and silylene were not observed. In the absence of TCNE, oxasilacyclopropane (1) was stable under the conditions.

The irradiation of (1) in acetonitrile in the presence of pyrylium salt<sup>6)</sup> which is known as electron-transfer reagent, produced the indene (6) (77%) and the silanediol (7) (100%) (Scheme II).

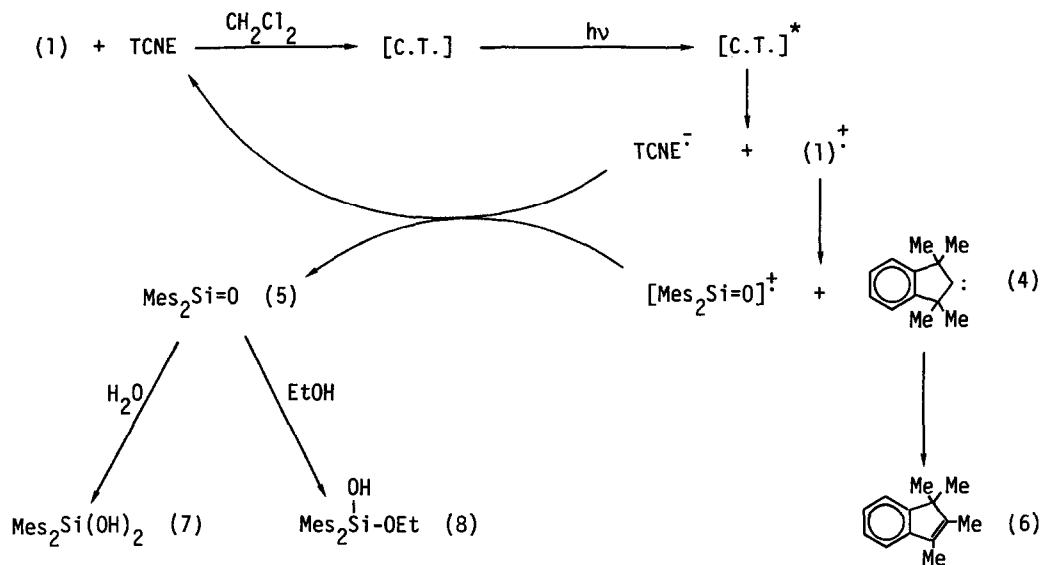
Scheme II



A ; TCNE / hv, pyrylium salt / hv.

Now a plausible mechanism for the photo-reactions of (1) consistent with products is shown in Scheme III. Irradiation of the C. T. complex forms the "Exciplex" which may cleave very efficiently to TCNE<sup>-</sup> and (1)<sup>+</sup>. The indene (6) may be the product from 1,2-methyl-migration of the carbene (4) and the silanone (5) was obtained from the radical cation of silanone through the back electron transfer from TCNE<sup>-</sup>. Convincing evidences of the silanone (5) formation have been presented by detection of silanediol (7) in the presence of trace of water in solvent, and by trapping reaction with ethanol to give ethoxysilanol (8).

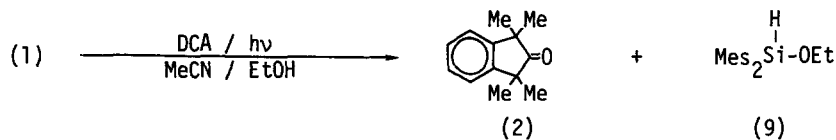
Scheme III



Electrolysis<sup>7)</sup> of (1) also produced the indene (6) in 100% yield together with mesitylene (166%) which is produced from the radical cation of silanone.

In contrast to the above results, 9,10-dicyanoanthracene (DCA) sensitized photo-decomposition of (1) led to completely different fragmentation pattern. The indanone (2) (100%) and the ethoxysilane (9) (78%) were formed as major products<sup>8)</sup> (Scheme IV). These products are the same as those formed by direct photolysis of (1). It seems likely that the rapid back-electron transfer may cause between the initially formed  $(1)^+$  and  $\text{DCA}^-$ . Indeed, (1) did not decompose in the absence of DCA.

Scheme IV



## References and notes

- 1) A. Albini and D. R. Arnold, *Can J. Chem.*, 1979, 56, 2985.
- 2) a) A. P. Schaap, L. Lopez and S. D. Gagnon, *J. Am. Chem. Soc.*, 1983, 105, 663.  
b) A. P. Schaap, S. Siddqui, S. D. Gagnon and L. Lopez, *J. Am. Chem. Soc.*, 1983, 105, 5149.
- 3) P. Clawson, P. M. Lunn and D. A. Whiting, *J. Chem. Soc., Chem. Commun.*, 1984, 134.
- 4) W. Ando, Y. Hamada and A. Sekiguchi, *J. Chem. Soc., Chem. Commun.*, 1983, 952.
- 5) All irradiations were conducted in pyrex tube under nitrogen atmosphere at running water temperature using halogen lamp (500 W x 2).
- 6) Pyrylium salt : 4-(p-butoxyphenyl)-2,6-diphenylpyrylium perchlorate.  $\lambda_{\max} = 416 \text{ nm (MeCN)}$ .
- 7)  $E_{ox}(1) = 1.37 \text{ V}$ . The electrolysis of (1) was carried out in dichloromethane at 1.5 V, tetrabutylammonium perchlorate as electrolyte, under nitrogen bubbling conditions.
- 8) Conversion yields.

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