

PHOTOLYSIS OF Silyldiazomethane.

THE MIGRATING TENDENCIES OF THE GROUPS ON SILICON ATOM

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Photolysis of silyldiazomethane in alcohols gave alkoxysilanes. The reaction probably involves isomerization of silylcarbene to Si=C double bond intermediates. The migrating ability of the groups on silicon atom decreases in the order; methyl > phenyl  $\approx$  benzyl group.

There has been considerable interest in the silicon-carbon double bond intermediates.<sup>1),2)</sup> We reported previously the formation of Si=C double bond intermediates in the liquid phase photolysis of silyldiazoacetate<sup>2-a)</sup> and the gas phase pyrolysis of silylphenyldiazomethane.<sup>2-b)</sup> However, recently we reported the absence of Si=C double bond in the gas phase decomposition of silyldiazoacetate.<sup>2-c)</sup> We consider that the formation of Si=C double bond may strongly be influenced by the reaction conditions. Extended studies involving trimethylsilyl, dimethylphenylsilyl, and benzyldimethylsilyl carbenes have been carried out and revealed the unique migrating tendency of the groups on silicon atom. The reason of this interesting tendency is not clear at present. However, a recent report of Kreeger and Shechter,<sup>3)</sup> which describes the behaviour of trimethylsilylcarbene, urges us to communicate our results so far.

When trimethylsilyldiazomethane (I) was photolyzed with a high pressure mercury lamp in alcohols at room temperature, two products, alkoxytrimethylsilane (II) and alkoxyethyldimethylsilane (III), were obtained. The yields of the reaction products are shown in Table 1.

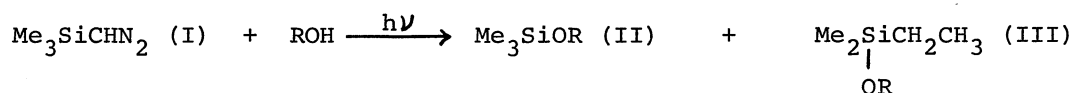


Table 1. Photolysis of trimethylsilyldiazomethane in alcohols

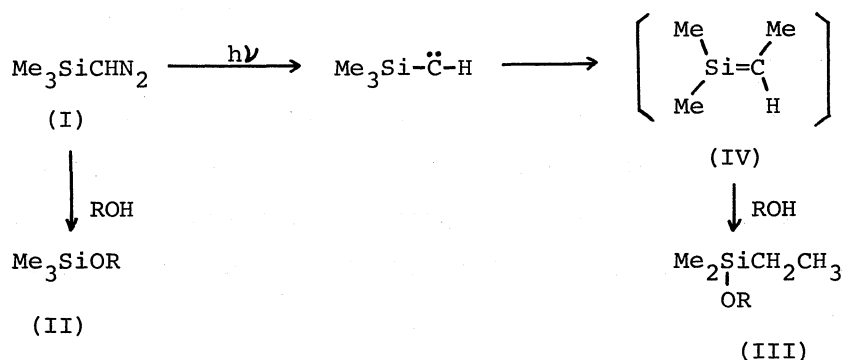
Alcohol	Yield of product (%)	
	(II)	(III)
MeOH	80	16
EtOH	45	51
i-PrOH	23	43
t-BuOH	0	45

Yields of (II) decreased with increase of pKa of the alcohols. Thermal decomposition of (I) in refluxing alcohols in the dark afforded (II) quantitatively, but did not (III). Furthermore, the decomposition of (I) in the presence of Lewis acids ( $\text{BF}_3 \cdot \text{Et}_2\text{O}$  or  $\text{CuCl}$ ) also produced only (II) quantitatively.

On the basis of these results we feel that the products (II) are formed by the substitution reaction via ionic process, not involving a carbene intermediate. On the other hand, yields of (III) in the photoreaction did not vary significantly with the change of the alcohols, except for the case of methanol.

The photodecomposition of (I) in ethanol- $\text{O-d}$  showed that the deuterium from ethanol- $\text{O-d}$  was introduced only to the  $\alpha$ -carbon of ethyl group in (III) and not to the migrated methyl group.

These results are completely consistent with those shown by Kreeger and Shechter<sup>3)</sup> and suggest that (III) can be formed by the methyl migration from the silicon to a carbenic carbon to produce an intermediate (IV).



Phenyl and benzyl substituted silyldiazomethane, (V) and (VI),<sup>4)</sup> were also photolyzed in alcohols under similar conditions. The results are summarized in Tables

2 and 3.

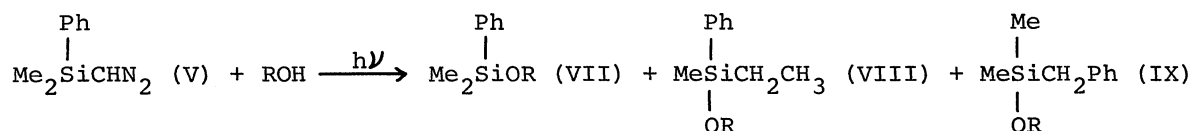


Table 2. Photolysis of dimethylphenylsilyldiazomethane in alcohols

Alcohol	Relative yield of product (%)		
	(VII)	(VIII)	(IX)
MeOH	52	39	9
EtOH	34	47	19

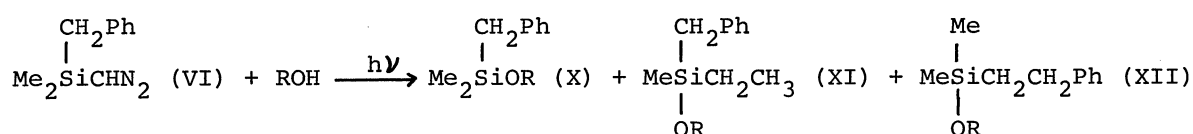


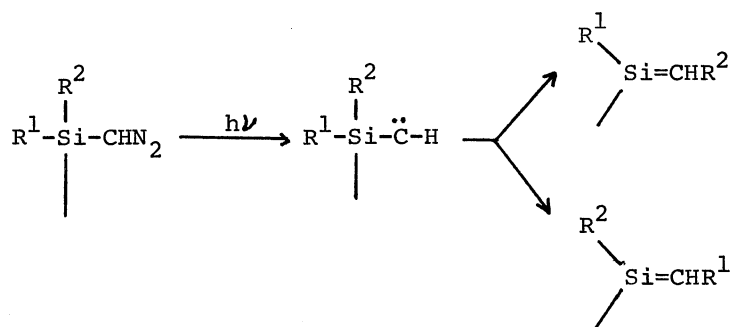
Table 3. Photolysis of benzyldimethylsilyldiazomethane in alcohols

Alcohol	Relative yield of product (%)		
	(X)	(XI)	(XII)
MeOH	49	43	8
EtOH	31	57	12

Products (IX) and (XII) are phenyl and benzyl migration products, respectively. Both (VIII) and (XI) are methyl migration products, while (VII) and (X) are the substitution products. Products (VIII), (IX), (XI), and (XII) may be produced through Si=C double bonds, while products (VII) and (X) may be formed through ionic process.

Relative yields of the migration products indicate that the migrating ability of methyl group is larger than that of phenyl or benzyl group, even though statistical factors are considered. This tendency is quite different from that observed in rearrangement of the carbon analogous carbene.<sup>5)</sup> But, the reason of this tendency is not clear at present.

Thus, photolysis of the substituted silyldiazomethane in alcohols can produce some Si=C double bond intermediates by the competitive migration of the groups on silicon atom to a carbenic carbon.



## References

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