

Reaction of Dimethylsilylene with Allyl Ethers

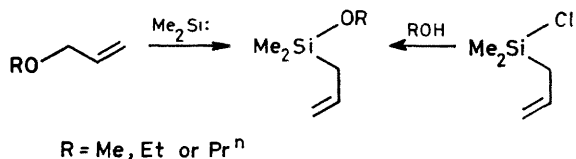
By VICTOR J. TORTORELLI and MAITLAND JONES, JR.*

(*Department of Chemistry, Princeton University, Princeton, New Jersey 08544*)

Summary Dimethylsilylene, generated by photolysis of dodecamethylcyclohexasilane, reacts with alkyl allyl ethers to give alkoxyallyldimethylsilanes.

THE strength of the silicon-oxygen bond¹ makes reactions of silylenes with oxygen-containing compounds of particular interest. We report here the first reaction of divalent

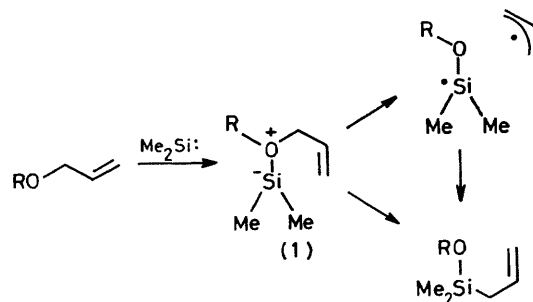
silicon with acyclic ethers.² When dodecamethylcyclohexasilane³ is irradiated in an alkyl allyl ether with a medium-pressure mercury arc, alkoxyallyldimethylsilanes



are isolated in 40–50% yield. The products are identified by comparison with authentic samples produced by the reaction of the appropriate alcohol with allylchlorodimethylsilane in the presence of a small amount of pyridine, and by elemental analysis.

Although on the surface the reaction appears to be a carbon–oxygen insertion, we think stepwise processes are far more likely and as a first step we propose formation of an ylide (1) which can react further, either by direct allyl rearrangement or by cleavage into a pair of radicals which

recombine. Radical pairs are apparently involved in a related carbene reaction,⁴ and Tzeng and Weber² have postulated a similar mechanism (although they drew ionic rather than radical intermediates) in their description of the reaction of dimethylsilylene with vinyl epoxides.



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¹ 'Organometallic Compounds of the Group IV Elements,' ed. A. G. MacDiarmid, Marcel Dekker, New York, Vol. I, 1968.

² D. Tzeng and W. P. Weber, *J. Am. Chem. Soc.*, 1980, **102**, 1451.

³ M. Ishikawa and M. Kumada, *J. Organomet. Chem.*, 1972, **42**, 325.

⁴ H. Iwamura, Y. Imahashi, and K. Kushida, *Tetrahedron Lett.*, 1975, 1401.