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ETHYLIDENE INSERTION IN PHENYLSILANE

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As a continuation of our work on the reaction of diazoalkanes with silanes[1], we examined the reaction of diazoethane with phenylsilane in ethereal solution at 20°C. No reaction occurred during twelve hours in the dark, but when the mixture was photolysed with ultraviolet light from a "Hanau" mercury arc lamp in a silica dipping tube, there was a rapid reaction. Phenylethylsilane was formed in 5% yield, as was shown by infrared and mass spectrometry, and by the identity of its residence time on a gas-liquid chromatogram in comparison with a reference sample prepared by the method of Mack Harvey et al[2], using silicone and dibutyl phthalate stationary phases. There was no evidence for the formation of phenyldiethylsilane, and polyethylidene was formed only in traces.

The photolysis of diazoalkanes is known to involve the initial formation of carbenes, and the reaction of phenylsilane with diazomethane gave methylenation not only of the silane but also the ether solvent[3]. Using diazoethane we found no evidence for reaction with ether. This is in agreement with Frey's finding that ethylidene (UV-radiation) does not

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2. Mack Harvey, C., Nebergall, W.H. and Peake, J.S., J. Amer. Chem. Soc. 76, 4555 (1954).
3. Meerwein, H., Rathjen, H. and Werner, H., Ber. Dtsch. Chem. Ges. 75, 1610 (1942).

insert into carbon hydrogen bonds[4]. However, silane groups have been shown to react very readily with free radicals so that they might be expected to react more readily with carbenes. Thus the yield of phenylmethylsilane we obtained[1] from diazomethane in ether showed that the relative rate of Si-H attack to C-H attack must be at least 10:1, and probably 30:1. The reaction mechanism is therefore probably:

$$CH_3CHN_2 \xrightarrow{h\nu} CH_3CH + N_2$$

$$C_6H_5SiH_3 + CH_3CH \longrightarrow C_6H_5Si(CH_2CH_3)H_2$$

An alternative mechanism for the formation of phenylethylsilane would involve reaction of the phenylsilane with ethylene formed from the diazoethane through rearrangement of ethylidene[4].

To identify the mechanism unambiguously, the reaction was repeated in a closed system, using less diazoethane (approximately one tenth of that in the previous experiments) while circulating a mixture of ethylene (in excess to the diazoethane used in previous experiments) and nitrogen. The yield of phenylethylsilane was then reduced to below 1%. When C^{14}-labelled ethylene was used, the total activity of the product corresponded to less than an 0.1% yield of active phenylethylsilane. Analysis of this active material on a Vapour Phase Chromatogram fitted with dual Katharometer and C^{14} detectors, showed that the activity was not associated with the phenylethylsilane.

Therefore, the formation of phenylethylsilane must involve insertion of ethylidene into a silicon-hydrogen bond.

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4. Frey, H.M., Chem. and Ind., 218, (1962).