

Reaction of Silicon Difluoride with Ethylene and with Fluorinated Ethylene Derivatives

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SILICON DIFLUORIDE has been shown to react at low temperatures with aromatic systems,¹ and significant differences were found between fluorinated aromatic systems on the one hand and non-fluorinated derivatives on the other. We have studied the reactions of silicon difluoride with ethylene and with fluorinated derivatives of ethylene, to see if the observed differences in aromatic systems extended into the non-aromatic field.

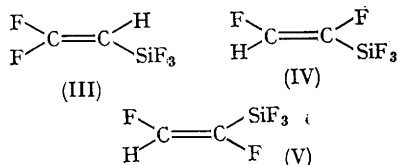
Silicon difluoride gas has been generated at high temperatures² and co-condensed with various reactants as previously described.³

With ethylene, the volatile products, after separation from excess of ethylene and silicon tetrafluoride, have been shown by mass spectrometry to consist of the compounds $C_2H_4Si_2F_4$,

$C_4H_8Si_2F_4$, and small quantities of $C_2H_4SiF_2$. All compounds were handled in a conventional greaseless vacuum system.

The structures of the two more abundant compounds have been identified by n.m.r. spectroscopy. The proton spectrum of $C_2H_4Si_2F_4$ consists of a quintet ($\delta = 1.18$, $J = 4.4$ c./sec.), which is exactly reproduced in the fluorine spectrum ($\Phi = 121.8$, $J = 4.4$ c./sec.). ^{29}SiF satellites were observed in the fluorine spectrum, [$J(^{29}SiF) = 488$ c./sec.] and were found to be broad with a suspicion of triplet structure. These spectra are consistent with a four-membered-ring structure for $C_2H_4Si_2F_4$ (I). The compound is not stable at room temperature, and a white solid is slowly formed from the pure liquid.

The proton n.m.r. spectrum of $C_4H_8Si_2F_4$



shows two broad unresolved peaks ($\delta = 1.13$ and 1.82). The fluorine spectrum similarly shows one peak with unresolved structure ($\Phi = 137.0$), with ^{29}SiF satellites [$J(^{29}\text{SiF}) = 380$] which are also broad and unresolved. It is thought that this compound has a six-membered-ring structure (II).

A study of the mass spectrum of $\text{C}_4\text{H}_8\text{Si}_2\text{F}_4$ using the RPD method* has been completed and a value for the Si-C bond energy of 75 ± 10 kcal. mole $^{-1}$ obtained.⁴

Reaction products from the fluorinated ethylenes are less clearly characterized. Tetrafluoroethylene yields only a polymeric species with no volatile

products at room temperature. This polymer sometimes exploded violently when heated; on other occasions, cautious pyrolysis directly into the mass spectrometer gave fragments indicative of compounds with formulae $\text{C}_2\text{F}_4(\text{SiF}_2)_n$, ($n = 1, 2, 3$).

From trifluoroethylene and silicon difluoride we isolated several products. From the proton n.m.r. spectrum of one sample we have tentatively identified the compound (III) together with smaller amounts of the isomeric species (IV) and (V). The proton n.m.r. spectrum of (III) shows a doublet of five-line multiplets ($\delta = 3.70$, doublet splitting = 38 c./sec., quintet splitting = 3 c./sec.). Both vinyl fluoride and 1,1-difluoroethylene yield complex mixtures of products which are being separated and analyzed.

The results show that the previously observed difference between the reactions of fluorinated and non-fluorinated aromatics with SiF_2 can be extended to the ethylene derivatives. When a compound contains a C-F bond, this is attacked by SiF_2 preferentially over the C=C bond, to form an SiF_3 group.

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* Retarding potential difference method, cf. C. E. Melton, and W. H. Hammill, *J. Chem. Phys.*, 1964, **41**, 546.

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² P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Amer. Chem. Soc.*, 1965, **87**, 2824.

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⁴ J. D. McDonald, J. C. Thompson, and J. L. Margrave, unpublished work, 1966.