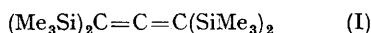


Tetrakis(trimethylsilyl)allene from some Pentafluorobenzene and Tetrafluorobenzene Derivatives

By F. W. G. FEARON and HENRY GILMAN

(Department of Chemistry, Iowa State University, Ames, Iowa, 50010)

Work in these laboratories has shown¹ that reaction of hexachlorobenzene, trimethylsilylpentachlorobenzene, or 1,4-bis(trimethylsilyl)tetrachlorobenzene, with a liberal excess of chlorotrimethylsilane and lithium in tetrahydrofuran gives the unexpected tetrakis(trimethylsilyl)allene^{1,2} (I) in 30–50% yields.



However under similar conditions hexafluorobenzene, in marked contrast, did not react.

In an extension of the above work we have found that bromopentafluorobenzene, chloropentafluorobenzene, trimethylsilylpentafluorobenzene, and 1,4-bis(trimethylsilyl)tetrafluorobenzene all give (I) in 6–10% yields when treated under the above conditions. In addition, hexamethyldisilane and fluorotrimethylsilane have been identified as products of these reactions, all compounds being identified by spectroscopic comparison with authentic materials.

Work is currently in progress to establish the mode of formation of (I) from the perchloro- and

perfluoro-compounds. Possible reactive intermediates being considered include perhalogeno-substituted benzyne and anion-radicals.³ In preliminary attempts to demonstrate the presence of highly reactive⁴ benzyne intermediates the reactions of hexachlorobenzene and chloropentafluorobenzene were carried out in 50% tetrahydrofuran. The reactions proceeded extremely slowly compared with reactions in the absence of furan, and no (I) could be detected. The only products so far identified were small amounts of the respective trimethylsilylpentahalogenobenzenes, $\text{Me}_3\text{SiC}_6\text{X}_5$.

At present it would appear that the fluorotrimethylsilane isolated from the perfluorobenzene reactions may have been largely formed by reaction of chlorotrimethylsilane with lithium fluoride liberated during the course of the reaction. However, as it has been shown that a trimethylsilyl radical can abstract halogen atoms from a halogenobenzene,⁵ the possibility that a trimethylsilyl radical abstracted fluorine from the perfluorinated compound cannot be excluded at this stage.

This research was supported by the United States Air Force.

(Received, December 6th, 1966; Com. 963.)

¹ K. Shiina and H. Gilman, *J. Amer. Chem. Soc.*, 1966, **88**, 5367.

² R. West, P. A. Carney, and J. C. Mineo, *J. Amer. Chem. Soc.*, 1965, **87**, 3788.

³ D. R. Weyenberg and L. H. Toporcer, *J. Amer. Chem. Soc.*, 1962, **84**, 2843. See also D. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *J. Org. Chem.*, 1965, **30**, 4096.

⁴ D. D. Callander, P. L. Coe, and J. C. Tatlow, *Chem. Comm.*, 1966, 143.

⁵ A. G. Beaumont, C. Eaborn, R. A. Jackson, and R. W. Walshingham, *J. Organometallic Chem.*, 1966, **5**, 297.