

ORBITAL SYMMETRY CONSERVATION IN THE CYCLOADDITION

REACTIONS OF TETRAFLUORODISILYLENE

C S. Liu

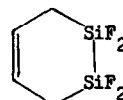
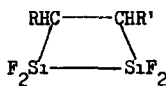
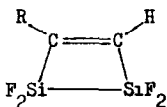
Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan.

J. C. Thompson

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

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The recent interest in the addition reactions between silicon difluoride and unsaturated organic compounds<sup>1-5</sup> has led to a successful synthesis of a series of new organosilicon compounds. The most reactive species in these reactions has been the dimeric tetrafluorodisilylene diradical  $\cdot\text{SiF}_2\text{SiF}_2\cdot$ . Almost in all these reactions there is a cyclic product which has been postulated as the result of a cycloaddition of the  $\cdot\text{SiF}_2\text{SiF}_2\cdot$  diradical to the organic molecules. The general molecular structures of these compounds can be represented as I for the alkyne reactions, II for the alkene reactions and III for the product from the reaction of butadiene:



The reaction with cyclopropane was of interest because the result could be compared with that of the reaction with ethylene. However, no detectable volatile products were observed.<sup>7</sup>

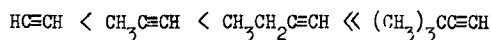
The present work deals with the analysis of these reactions by Woodward and Hoffmann's symmetry conservation rule<sup>8</sup> and reports the rationalization of some experimental data with the results

The analysis of orbital symmetry is based on the assumption that there is no, or only insignificant amount of, d-orbital involvement in the bondings of the  $\cdot\text{SiF}_2\text{SiF}_2\cdot$  species. The

microwave spectroscopic data<sup>9</sup> and the X-ray diffraction data<sup>10</sup> showed no evidence for d-orbital character in the Si-F bonds

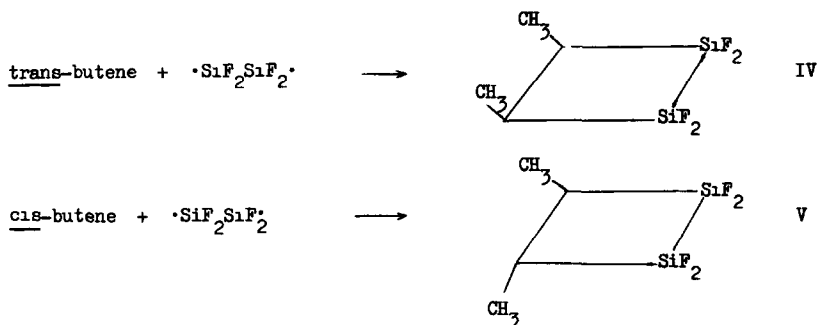
With d-orbital playing no part in the bondings, we can assume that the silicon atoms use either  $sp^2$  or  $sp^3$  hybridization to form the  $\text{SiF}_2\text{SiF}_2$  species. It is probably more convenient to use  $sp^2$  hybridization in this case, silicon atom uses its third p-orbital to accommodate the unpaired electron. (The use of  $sp^3$  hybridization gives the same result in this analysis.)

The analysis for the reaction with acetylene is based on a symmetry plane bisecting the C-C and Si-Si axes for the suprafacial addition path, and a  $C_2$  symmetry axis at the centers of and perpendicular to the C-C and Si-Si axes for the antarafacial addition path. Thus the situation is similar to that of the dimerization of ethylene: only the antarafacial addition is thermally allowed and the suprafacial addition is thermally forbidden. This means, as far as the symmetry is concerned, the only reaction path which is thermally allowed is the one in which the  $\text{SiF}_2\text{SiF}_2$  unit approaches the acetylene molecule perpendicularly. In the reactions between silicon difluoride and a series of alkyl-substituted alkynes, the relative yields of the four-membered ring products were found to be the sequence:



It is clear that as the substituent alkyl group becomes bulkier the relative yield increases. This is in agreement with the analysis described above. As the substituent alkyl group becomes larger, the parallel approach of the two reactants is, to a greater extent, sterically hindered, and the perpendicular approach becomes relatively more favored. Therefore, the "frequency" of the thermally allowed approach becomes higher.

The same symmetry argument is also applicable to the reactions with alkenes. A good test for this analysis would be the study of the reactions with trans and cis-butene. According to the thermally allowed antarafacial reaction path, one would expect that the reaction products should be IV and V respectively.



Both reactions with trans and cis-butene do show the four-membered ring products with the same molecular formula  $\text{C}_4\text{H}_8\text{Si}_2\text{F}_4$ . The  $^{19}\text{F}$  nmr spectra show that the compounds from the two reactions are different.<sup>6</sup> The facts that there are only two possible isomers (IV and V) in this case and that the  $^{19}\text{F}$  nmr spectra show completely different patterns lead to the belief that the products from trans and cis-butene reactions each contain one compound instead of a mixture of isomers. The spectra are very complicated and so far it has not been possible to tell which one is IV and which one is V. Nevertheless, the reactions appear to be completely stereospecific.

For the reaction of cyclopropane, the symmetry element taken into consideration is the plane bisecting the triangular plane and the Si-Si axis. Again, the orbital correlation is dependent on how the combining reactant molecules approach to each other. On approaching the cyclopropane molecule, the  $\cdot\text{SiF}_2\text{SiF}_2\cdot$  diradical seeks the electron-rich part of the molecule<sup>11</sup> and most likely it would approach the triangular face of the cyclopropane ring where the electron cloud is concentrated, and then react with two carbon atoms on one edge of the ring. From this point of view, it does not seem likely that the  $\cdot\text{SiF}_2\text{SiF}_2\cdot$  species would approach one edge of the cyclopropane ring perpendicularly, which is the only path that the reaction becomes thermally allowed.

The situation for the reaction of butadiene is very similar to the cycloaddition between ethylene and butadiene.<sup>8</sup> A simple analysis with respect to the symmetry plane bisecting the middle C-C bond of butadiene and Si-Si bond of  $\text{Si}_2\text{F}_4$  shows that it is a thermally allowed

reaction. That is what was found experimentally:<sup>4</sup> the cycloaddition product III was obtained

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#### References

- (1) C. S. Liu, J. L. Margrave, J. C. Thompson and P. L. Timms, *Can. J. Chem.*, 50, 459 (1972).
- (2) C. S. Liu, J. L. Margrave and J. C. Thompson, *Can. J. Chem.*, 50, 465 (1972).
- (3) C. S. Liu and J. C. Thompson, *J. Organometall. Chem.*, 38, 249 (1972).
- (4) J. C. Thompson and J. L. Margrave, *Inorg. Chem.*, 11, 913 (1972).
- (5) J. C. Thompson, P. L. Timms and J. L. Margrave, *Chem. Commun.*, 566 (1966).
- (6) C. S. Liu and J. C. Thompson, unpublished results.
- (7) C. S. Liu and J. C. Thompson, unpublished results.
- (8) R. B. Woodward and R. Hoffmann, *Accounts Chem. Res.*, 1, 17 (1968).
- (9) V. M. Rao, R. F. Curl, P. L. Timms and J. L. Margrave, *J. Chem. Phys.*, 43, 2557 (1965).
- (10) C. S. Liu, S. C. Nyburg, J. T. Szymanski and J. C. Thompson, *J. Chem. Soc., (Dalton)* 1129 (1972).
- (11) C. S. Liu and J. C. Thompson, *Inorg. Chem.*, 10, 1100 (1971).