

Relative Reactivities of Conjugated Dienes Towards Silicon Difluoride

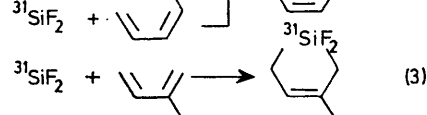
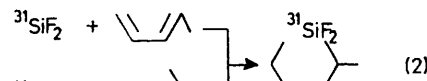
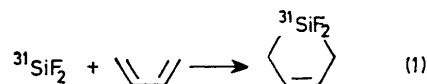
By RICHARD A. FERRIERI, E. EDWIN SIEFERT, MICHAEL J. GRIFFIN, OTTO F. ZECK, and YI-NOO TANG*
(Department of Chemistry, Texas A & M University, College Station, Texas 77843)

Summary The relative reactivities of buta-1,3-diene, *trans*-penta-1,3-diene, *cis*-penta-1,3-diene, and 2-methylbuta-1,3-diene towards monomeric $^{31}\text{SiF}_2$ have been measured; since a large steric effect has been observed between *cis*- and *trans*-pentadienes for their reactivities towards triplet $^{31}\text{SiF}_2$ -donor, a direct 1,4-addition process is indicated for such $^{31}\text{SiF}_2$ -donating complexes.

THE relative addition rates of carbenes and carbenoids with various olefins have been a topic of major interest to chemists during the past two decades.¹ Such information is definitely lacking in the literature for the silylenes.² Recently, we have formed singlet and triplet monomeric $^{31}\text{SiF}_2$ in the ratio of 1.0:3.3 by the nuclear recoil method, and have demonstrated that their addition to buta-1,3-diene yields difluoro[^{31}Si]silacyclopent-3-ene (DFSCP*)³ [equation (1)]. In the present work, by using the competitive technique, we have evaluated the relative addition efficiencies of both singlet and triplet $^{31}\text{SiF}_2$ towards various conjugated dienes.

Monomeric $^{31}\text{SiF}_2$ was formed through the formation of energetic ^{31}Si atoms by the nuclear transmutation, $^{31}\text{P}(n,p)^{31}\text{Si}$, followed by their abstraction of F atoms from PF_3 .^{3,4} The reactions of $^{31}\text{SiF}_2$ with *trans*- and *cis*-penta-1,3-diene gave 2-methyl-1,1-difluoro[^{31}Si]silacyclopent-3-

ene (2MDFSCP*) as a product, while with 2-methylbuta-1,3-diene the 3-methyl isomer (3MDFSCP*) of 2MDFSCP* was obtained [equations (2) and (3)]. Both 2MDFSCP* and 3MDFSCP* were identified by co-injection of authentic samples during radio-gas chromatographic analysis. These samples were synthesized by the co-pyrolysis technique and identified by their i.r. spectra.⁵



Three types of experiments have been performed. First, butadiene standards and pentadiene samples, with or without the addition of nitric oxide were irradiated simultaneously in separate ampoules using a rotisserie system to

normalize the neutron flux. The samples without NO indicated that an equivalent amount of singlet $^3\text{SiF}_2$ was captured by butadiene and each of the pentadienes, while the NO addition samples gave the same results for triplet $^3\text{SiF}_2$. Moreover, since a four-fold increase in the product yields is always observed with the addition of NO, it was confirmed that for $^3\text{SiF}_2$ produced by the nuclear recoil method, the singlet to triplet ratio is *ca.* 1:3, regardless of the type of diene present in the system. This further strengthens earlier deduction that singlet $^3\text{SiF}_2$ reacted with dienes to give the DFSCP*'s directly, but triplet $^3\text{SiF}_2$ only gave these products in the presence of paramagnetic molecules such as NO.³

In the second type of experiments, varying amounts of NO or O₂ were added to both the *trans*- and *cis*-penta-1,3-diene samples. In the NO case, a sharp rise in the 2MDFSCP* specific yield was observed in the range 0.01–0.1% NO concentration, and was followed by a constant plateau which was *ca.* 4 times higher than the yield from samples without NO. In the O₂ case, a sharp rise in the 2MDFSCP* specific yield was observed in the low O₂ concentration range which was followed by an eventual decline to the level of non-additive samples. This phenomenon is again consistent with the supposition that triplet $^3\text{SiF}_2$ reacts with paramagnetic molecules to give $^3\text{SiF}_2$ -donating complexes, while in the oxygen systems, the $^3\text{SiF}_2$ -O₂ complex is further removed by a higher concentration of oxygen.³

In the third type of experiments, approximately equal amounts of buta-1,3-diene and one of the pentadienes were mixed so that the competition for the available $^3\text{SiF}_2$ in the system could be observed. The relative reactivities of the dienes towards $^3\text{SiF}_2$ can be evaluated through the observed specific yields of DFSCP*, 2MDFSCP*, and 3MDFSCP*, and the relative amounts of the two dienes employed. From the results measured in both the presence and absence of NO, it is deduced that the relative reactivities of buta-1,3-diene, *trans*-penta-1,3-diene, *cis*-penta-1,3-diene, and 2-methylbuta-1,3-diene towards singlet and

triplet $^3\text{SiF}_2$ are 1.0:0.89:0.91:1.06 and 1.0:0.80:0.52:0.89, respectively. The latter set of values were derived from the differences in the normalized yields with and without NO. These results indicate the following points. (i) The reactivities of the dienes towards both singlet and triplet $^3\text{SiF}_2$ -donors are, in most cases, decreased slightly by the presence of methyl substituents. Since SiF_2 is likely to behave like an electrophile and therefore the opposite trend is expected to be true, the present reversal indicates that certain steric requirements must be important in the transition state.⁶ It is also noted here that methyl substituents at the terminal carbon atoms hinder the yield slightly more than when they are attached to the middle carbon atoms. (ii) For singlet $^3\text{SiF}_2$, the efficiencies of addition to *trans*- and *cis*-pentadienes yielding 2MDFSCP* are about the same. Earlier studies have shown that singlet carbenes and silylenes undergo 1,2-addition to dienes, where such 1,2-addition is not expected to be very sensitive to steric factors.⁷ Therefore, a similar addition efficiency of singlet $^3\text{SiF}_2$ to *trans*- and *cis*-pentadienes is consistent with the expectation that an 1,2-addition process is occurring for such singlet species. (iii) For the addition of $^3\text{SiF}_2$ -donor derived from triplet $^3\text{SiF}_2$, *trans*-pentadiene is *ca.* 50% more reactive than its *cis*-counterpart. Such a difference has been noted before in methylene reactions with certain cyclic molecules of very special steric arrangements.⁸ In the present case, this observation implies the operation of a 1,4-addition process of the $^3\text{SiF}_2$ -donor to the conjugated double bonds. If such a 1,4-addition process requires the two double bonds to be oriented on the same side of the molecule, it is obvious that the methyl group in the *cis*-compound will introduce some hindrance to the approach of the reactants, while in the *trans*-compound such additional hindrance is absent.

The authors acknowledge the financial support provided by E.R.D.A., and the irradiation time provided by the Texas A&M Nuclear Science Center and Cyclotron Institute.

(Received, 22nd September 1976; Com. 1080.)

¹ For a review and references, see W. Kirmse, in 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971, Ch. 8 and 9.

² See for example, P. P. Gaspar and B. J. Herold, Ch. 13, ref. 1; for a summary of SiF_2 reactions, see J. C. Thompson and J. L. Margrave, *Science*, 1967, **155**, 669; J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, 1971, **4**, 145.

³ G. P. Gennaro, Y. Y. Su, and Y.-N. Tang, *J. Amer. Chem. Soc.*, 1972, **94**, 4355; O. F. Zeck, Y. Y. Su, G. P. Gennaro, and Y.-N. Tang, *ibid.*, 1976, **98**, 3474; O. F. Zeck, Y. Y. Su, and Y.-N. Tang, *J.C.S. Chem. Comm.*, 1975, 156.

⁴ P. P. Gaspar, S. A. Bock, and W. C. Eckelman, *J. Amer. Chem. Soc.*, 1968, **90**, 6914.

⁵ For information concerning the co-pyrolysis of disilanes, see E. M. Tebben and M. A. Ring, *Inorg. Chem.*, 1969, **8**, 1787; P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *ibid.*, 1970, **9**, 1068; E. A. Chernyshev, N. G. Kamalnikov, and S. A. Bashkerova, *Zhur. Obshchei Khim.*, 1971, **41**, 1175; for i.r. spectral data, see T. H. Chao, S. L. Moore, and J. Laane, *J. Organometallic Chem.*, 1971, **33**, 157.

⁶ E. P. Blanchard and H. E. Simmons, *J. Amer. Chem. Soc.*, 1964, **86**, 1337; M. Jones, Jr., W. J. Baron, and Y. H. Shen, *ibid.*, 1970, **92**, 4745; U. Burger and R. Huisgen, *Tetrahedron Letters*, 1970, **34**, 3057.

⁷ P. M. Crane and T. L. Rose, *J. Phys. Chem.*, 1975, **79**, 403; P. P. Gaspar and R.-J. Hwang, *J. Amer. Chem. Soc.*, 1974, **96**, 6198.

⁸ J. Graefe, M. Mühlstadt, and P. Kuhl, *Z. Chem.*, 1970, **10**, 192; 1969, **9**, 23; *Tetrahedron Letters*, 1969, 3431; H. Nozaki, M. Kawanisi, and R. Noyori, *J. Org. Chem.*, 1965, **30**, 2216.