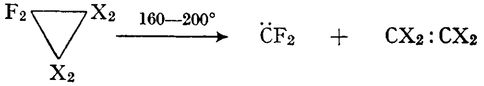
Cyclopropanes as Sources of Difluorocarbene

By J. M. Birchall, R. N. Haszeldine, and D. W. Roberts

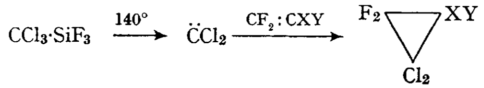
(*Chemistry Department, University of Manchester Institute of Science and Technology, Manchester* 1)

The thermal decomposition of chlorofluorocyclopropanes has been found to provide a useful source of difluorocarbene:



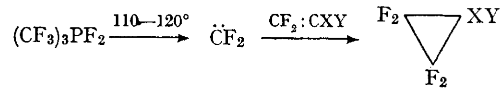
where X = Cl or F. The decompositions involve exclusively, or predominantly (> 70%) ejection of difluoro- rather than chlorofluoro- or dichlorocarbene, and thus provide clear examples of the degree of stabilisation of a carbene by fluorine.

The required chlorofluorocyclopropanes are readily obtained by the gas-phase reaction of dichlorocarbene, generated from trichloromethyltrifluorosilane,[1] with an olefin



X=Y=F, 59% yield; X=F, Y=Cl, 87% yield; X=Y=Cl, 66% yield.

or by reaction of difluorocarbene, generated from difluorotristrifluoromethylphosphorane,[2] with an olefin



X=Y=F, 86% yield; X=F, Y=Cl, 91% yield.

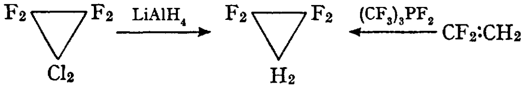
These readily-available chlorofluorocyclopropanes are particularly useful sources of difluorocarbene since, unlike the phosphorane, they are not Lewis acids and do not form decomposition products which lead to undesirable side-reactions. They can be readily manipulated in glass apparatus, and their volatility enables gas-phase reactions of $\ddot{C}F_2$ to be studied under neutral, mild conditions; previous routes to difluorocarbene have involved solutions in polar solvents, the presence of strong bases, or the thermal decomposition of solids such as sodium chlorodifluoroacetate, *etc.*

The decomposition of gaseous hexafluorocyclopropane, chloropentafluorocyclopropane, or 1,1-dichlorotetrafluorocyclopropane at 160—170° is slow but quantitative. At these temperatures the liberated difluorocarbene reacts with a hydrocarbon olefin, such as cyclohexene or but-2-ene, to give the corresponding *gem*-difluorocyclopropane, often in 85—99% yield. Reaction of the difluorocarbene with *cis*- or with *trans*-but-2-ene is stereospecific, indicating that the carbene is liberated in the singlet state.

Thermal decomposition of 1,1,2-trichlorotrifluorocyclopropane or 1,1,2,2-tetrachlorodifluorocyclopropane requires temperatures near 200°. Under these conditions the former cyclopropane reacts with cyclohexene to give 7,7-difluoronorcarane (67%) and trichlorofluoroethylene (92%). The formation of small amounts of 1,1-dichlorodifluoroethylene suggests that the cyclopropane decomposes to a small extent by the alternative route.

1,1,2,2-Tetrachlorodifluorocyclopropane reacts with *cis*-but-2-ene to give 3,3-difluoro-*cis*-1,2-dimethylcyclopropane (86%) and the *trans*-dimethylcyclopropane (2%); the yield of tetrachloroethylene is 88%, and the olefin $CF_2Cl{\cdot}CCl{:}CCl_2$ (12%) is also formed. A control experiment showed that the loss of stereospecificity in this last reaction can be attributed to the slow isomerisation of the *cis*-cyclopropane to its *trans*-isomer under these conditions.

A hydrogen-containing cyclopropane, obtained by the reactions:



is thermally the most stable of the series so far studied, since 74% of the cyclopropane is recovered after being heated with cyclohexene at 200° for 200 hr.; however, 7,7-difluoronorcarane is produced, and the formation of difluorocarbene is thus not restricted to the decomposition of perchlorofluorocyclopropanes.

Parallel work to our own, reported recently, suggests that carbenoid decomposition occurs with arylcyclopropanes,[3] perfluoroallylcyclopropane,[4] and hexafluorocyclopropane,[5] and doubtless other examples will be established.

(*Recevied, January 26th,* 1967; *Com.* 080.)

---

[1] W. I. Bevan, J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, "Organic Reaction Mechanisms", *Chem. Soc. Special Publ.*, 1964, No. 19, p. 174.

[2] W. Mahler, *Inorg. Chem.*, 1963, **2**, 230.

[3] D. B. Richardson, L. R. Durrett, J. M. Martin, W. E. Putnam, S. C. Slaymaker, and I. Dvoretzky, *J. Amer. Chem. Soc.*, 1965, **87**, 2763; P. A. Leermakers and M. E. Ross, *J. Org. Chem.*, 1966, **31**, 301.

[4] R. A. Mitsch and E. W. Neuvar, *J. Phys. Chem.*, 1966, **70**, 546.

[5] B. Atkinson and D. McKeagan, *Chem. Comm.*, 1966, 189.