Tetrahedron Letters No. 22 + 23, pp 1819 - 1822, 1975. Pergamon Press. Printed in Great Britain.

MONOFLUOROCARBENE: THE SYNTHESIS OF FLUOROCYCLOPROPANES

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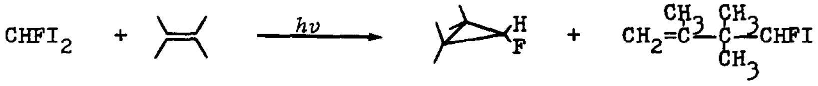
(Received in U.S.A. 26 February 1975; received in UK for publication 16 April 1975)

We have found that irradiation of fluorodiiodomethane at 3500Å in the presence of an olefin trapping agent provides a synthetically useful one-step procedure for the preparation of a variety of monofluorocyclopropanes. Data for the results obtained *via* this procedure are given in Table I.



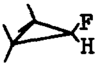
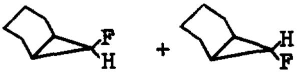
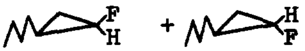
(I), 45% (II), 10%

In recent years considerable attention has been focused on the chemistry of halogenated carbenes, especially fluorinated carbenes.[1,2] Despite this attention, however, the preparation of monofluorocarbene, and subsequently monofluorocyclopropanes, remains one of the more difficult synthetic transformations to accomplish.[2] Low yields of monofluorocyclopropanes were obtained by Schlosser and Heinz from the reaction of dibromofluoromethane and organolithium compounds.[3] Similarly, Marolewski and Yang obtained only 9% of the monofluoronorcarane adduct from the photolysis of dibromofluoromethane in the presence of cyclohexene.[4] Excellent yields of monofluorocyclopropanes were reported by Tang and Rowland from the nuclear recoil reaction of energetic tritium with methylene fluoride.[5] However, this mode of generation is generally unavailable to most chemists and is useful only on a small scale. The reaction of diethyl zinc and fluorodiiodomethane with cyclohexene to give 91% 7-fluoronorcarane has been reported by Nishimura and Furukawa.[6] Unfortunately, no other olefins were reported and the generality of this procedure remains in question.[7] In addition, the use of the pyrophoric[8] zinc reagent also makes this reaction somewhat less attractive on a large scale.

As a result of the lack of a reasonably useful procedure for monofluorocarbene generation, most monofluorocyclopropanes have been prepared by a two-step procedure. First, the preparation of fluorochloro- or fluorobromocyclopropanes is accomplished by standard carbene reactions; secondly, the resultant carbene adducts are reduced to monofluorocyclopropanes.[9]

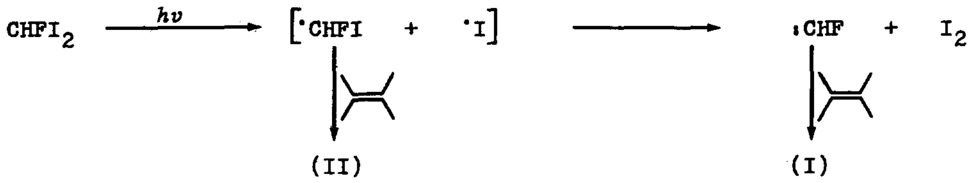
The method reported herein provides modest yields of cyclopropanes for di-, tri-, and tetrasubstituted olefins.[10] The production of (II) presumably occurs from free-radical addition of $CHFI_2$ to the olefin followed by loss of HI. A control experiment has shown that (I) is not ring-opened by iodine under these conditions to give (II). Consequently, the photolysis reaction of fluorodiiodomethane most likely proceeds *via* initial dissociation to form free-radicals. Subsequent loss of an iodine atom from the fluoroiodomethyl radical yields the

Table I

OLEFIN	PRODUCTS[11]	YIELD[12]	SYN/ANTI RATIO
2,3-dimethyl-2-butene		45%	
2-methyl-2-butene		37%	1.1
trans-4-methyl-2-pentene		37%	
cis-4-methyl-2-pentene		36%	0.8
cyclohexene		40%	1.0
2-methyl-1-pentene		14%	
1-hexene		14%	1.2

monofluorocarbene (Scheme I).

Scheme I



The monofluorocyclopropanes are formed stereospecifically as shown by the reactions with cis- and trans-4-methyl-2-pentene. This is in agreement with the formation of the fluorocarbene followed by addition of the carbene to the olefin rather than addition of the fluoroiodomethyl radical followed by ring-closure with loss of iodine atom.

In agreement with the results of Tang and Rowland,[5] the syn/anti ratios (Table I) of approximately unity suggests a "free carbene" generation. In contrast, the high syn/anti ratio of 5.7 with cyclohexene observed by Nishimura and Furukawa[6] suggests a metal-carbenoid intermediate.

A representative experimental procedure used in carrying out these reactions is exemplified by the following description: A 250ml round-bottom Pyrex flask equipped with reflux condenser and magnetic stirrer is charged with 36 mmoles of olefin, 9.43 g (33 mmoles) of fluorodiiodomethane,[13] 175 ml of CH_2Cl_2,[15] and 50 ml of 5M NaOH solution. Irradiation is carried out with 3500Å lamps in a commercial Rayonet® photochemical chamber for 24 hours. After separation of the organic layer and drying over anhydrous $MgSO_4$, the solvent is removed by distillation amd the monofluorocyclopropanes separated and purified by glpc on either Carbowax 20M or SE-30 columns.

NOTES AND REFERENCES

1. W. Kirmse, "Carbene Chemistry", 2nd Ed., Academic Press, N.Y., 1971 for a good review of halogenated carbenes.
2. W.A. Sheppard and C.M. Sharts, "Organic Fluorine Chemistry", W.A. Benjamin, N.Y., 1969 for a general review of fluorinated carbenes and carbenoids.
3. M. Schlosser and G. Heinz, *Chem. Ber.*, **104**, 1934 (1971).
4. T. Marolewski and N.C. Yang, *Chem. Communications*, 1225 (1967).
5. Yi-Noo Tang and F.S. Rowland, *J. Amer. Chem. Soc.*, **89**, 6420 (1967).
6. J. Nishimura and J. Furukawa, *Chem. Communications*, 1375 (1971).
7. Reaction of fluorodiiodomethane and Zn(Cu) with cyclohexene in our hands gave only traces of norcarane product.
8. L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, N.Y., 1967, p. 1293.
9. T. Ando, H. Hosaka, W. Funasaka, and H. Yamanaka, *Bull. Soc. Chem. Japan*, **46**, 3513 (1973), T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970), and references therein.
10. Reactions carried out at 2537Å and 3000Å (in a quartz vessel) gave reduced yields (relative to 3500Å) of fluorocyclopropanes.
11. All fluorocyclopropanes reported in Table I were unambiguously identified by NMR and mass spectral analysis.
12. Yields of fluorocyclopropanes were determined by ^{19}F NMR using benzotrifluoride as an internal standard.
13. Prepared by the method of Hine, *et. al.*[14] To facilitate distillation from the reaction flask, stirring was accomplished with an Ace Trubore stirrer fitted with an Ace bearing (no. 8051), an aluminum packing box (no. 8111), and a high vacuum lubricant trap adapter (no. 8113).
14. J. Hine, R. Butterworth, and P.B. Langford, *J. Amer. Chem. Soc.*, **80**, 819 (1958).
15. Methylene chloride is used as solvent when high boiling cyclopropanes are produced. 1,1,2,2-tetrachloroethane is used as solvent for low boiling cyclopropanes with comparable results.