Reaction of Fluoro-olefins with Phenyl(trihalogenomethyl)mercurials

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Summary Resonance forms of α-fluoro-olefinic linkages are involved in reactions with carbenoids or carbenes; these reactions also exhibit stereoelectronic influences during the formation of polyhalogeno-cyclopropanes.

ISOLATION of new polyhalogeno-cyclopropanes from the reactions of a variety of α-fluoro-olefins with phenyl(tribromomethyl)mercury[1] has been achieved. Each carbene, or carbenoid, reaction[2] has served to test the influence of α-fluorine atoms on the reactivities of olefins. Previous evidence for participation of fluoro-olefins in carbenoid or carbene reactions[3] is meagre; hence, unsaturated fluorocarbons have been used as solvents for carbene or carbenoid reactions. In the only previous reports of the mercurial reaction with fluorinated olefins, perfluorocyclohexene did not react with bromodichloromethylphenylmercury,[4] and

TABLE

Yields and mass spectra[a] *of new polyhalogenocyclopropanes*

Reactants	Products	Yield (%)	Significant *m/e* values with assignments
Fluoroethylene/A[b]	1,1-Dibromo-2-fluorocyclopropane	33	137,139 (C_3H_3BrF); 216, 218, 220 ($C_3H_3Br_2F$)
1,1-Difluoroethylene/A	1,1-Dibromo-2,2-difluorocyclopropane	44	155, 157 ($C_3H_2BrF_2$)
1-Chloro-1-fluoroethylene/A	1,1-Dibromo-2-chloro-2-fluorocyclopropane	25	93, 95 (C_3H_3ClF); 137, 139 (C_3H_3BrF)
2-Fluoropropene/A	1,1-Dibromo-2-fluoro-2-methylcyclopropane	11	151, 153 (C_4H_5BrF); 230, 232, 234 ($C_4H_5Br_2F$)
Fluoroethylene/B[c]	1-Bromo-1-chloro-2-fluorocyclopropane	10·5	93, 95 (C_3H_3ClF); 137,139 (C_3H_3BrF)
1,1-Difluoroethylene/B	1-Bromo-1-chloro-2,2-difluorocyclopropane	33[d]	—
Trifluoroethylene/B	1-Bromo-1-chloro-2,2,3-trifluorocyclopropane	8	129, 131 (C_3HClF_3); 158, 160 ($C_2HBrClF$)
Tetrafluoroethylene/B	1-Bromo-1-chloro-2,2,3,3-tetrafluorocyclopropane	11	145, 147, 149 (CBrClF); 147, 149 (C_3ClF_4)
Chloroethylene/B	1-Bromo-1,2-dichlorocyclopropane	22	109, 111, 113 ($C_3H_3Cl_2$); 188, 190 ($C_3H_3BrCl_2$)

[a] Mass spectra were obtained using CEC 21-130 and EAI 250 instruments operated at 70 ev without use of source heaters. An analysis of *all* fragments with relative intensities > 10 will be published elsewhere. [b] A = phenyl(tribromomethyl)mercury. [c] B = dibromochloromethyl(phenyl)mercury. [d] See ref. 5.

1,1-difluoroethylene and dibromochloromethyl(phenyl)mercury led to a moderate yield of 1-bromo-1-chloro-2,2-difluorocyclopropane.[5] It is possible to rationalize these reports from information given herein.

A vacuum-distillate, which contained the desired cyclopropane, was obtained by the method of Boudakian and Hofmann[5] from reaction of a mercurial with an excess of an olefin. [Since all distillates were shown by g.l.c. to be contaminated by dichlorobenzenes and minor species, detailed analyses of distillates were made in the phenyl(tribromomethyl)mercury reaction series. The relative order of mercurial–olefin reaction yields was independent of any brominated, unbrominated, or lower-boiling contaminants in the distillates.] Maximum yields for cyclopropanes are in the Table. In all reactions the yields of phenylmercuric bromide exceeded those of the tabulated cyclopropanes. Previously, bromodihalogenomethyl(phenyl)mercurials mixed with relatively unreactive olefins have been observed[4] to form oligomers of the dihalogenomethylene unit.

Common assignments from i.r. spectra of the distillates include unsubstituted methylene groups of cyclopropyl rings at 3012—3005, cyclopropyl rings at 1058—1046 and 888—812, and brominated methylene species at 679—666 cm.$^{-1}$. From each distillate appropriately pure product was isolated by g.l.c.; structurally significant peaks from the mass spectra are given in the Table.

Steric effects may be more important in reactions of phenyl(tribromomethyl)mercury than of dibromochloromethyl(phenyl)mercury. With both fluoroethylene and 1,1-difluoroethylene, phenyl(tribromomethyl)mercury was more reactive than dibromochloromethyl(phenyl)mercury. However, with olefins which bore bulkier vinyl substituents dibromochloromethyl(phenyl)mercury led to higher yields of substituted cyclopropanes than phenyl(tribromomethyl)mercury; the product yield from tetrachloroethylene and dibromochloromethyl(phenyl)mercury was higher[6] than that from this olefin and phenyl(tribromomethyl)mercury. The sensitivity of reactions of phenyl(tribromomethyl)mercury to bulky vinyl substituents is illustrated by decreases in cyclopropyl product yields in going from the reactant fluoroethylene to 1-chloro-1-fluoroethylene to 2-fluoropropene.

The greater reactivity of dibromochloromethyl(phenyl)mercury with chloroethylene than with fluoroethylene is attributable to an electronic effect, and not to steric or resonance effects. Electronic effects have been used[2] to rationalize outcomes of reactions between olefins and mercurials.

Neither steric not inductive effects serve as rationalizations for the greater reactivity of both phenyl(tribromomethyl)mercury and dibromochloromethyl(phenyl)mercury with 1,1-difluoroethylene than with fluoroethylene. This may be a manifestation of the greater contributions to αα-difluoro-olefins than to α-fluoro-olefins by resonance forms of which an extreme example is $>\bar{C}-\underset{|}{C}=F^{+}$. Resonance may counteract the electronegativity of fluorine.[7]

We thank Mr. J. Improta for autoclave operation; Mr. L. Barnes, jun., for bromine analyses; Mrs. M. S. Pawlak for i.r. spectra; and Dr. J. Roboz for mass spectra.

(*Received, July 21st,* 1969; *Com.* 1085.)

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