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PHENYLFLUOROCARBENE

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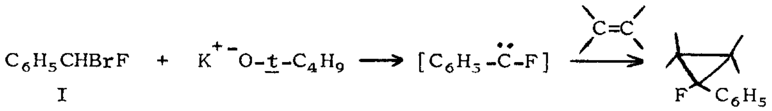
The addition of fluorocarbenes to olefins has been among the least studied of the halocarbene cyclopropanation reactions (1). However, much progress has recently been made in the study of difluorocarbene (2) and chlorofluorocarbene (3). Examples of fluorocarbene (4) and bromofluorocarbene (5) addition reactions have also been reported. One spur to the recent interest in fluorocarbenes is the potential biological activity of certain fluorocyclopropanes derived from them (6).

Our previous studies of phenylchlorocarbene (7) and phenylbromocarbene (8), as well as an inspection of the data for carbene production from mixed haloforms (9), convinced us that α-bromo-α-fluorotoluene, I, would be an ideal precursor for the unknown phenylfluorocarbene. We wish to report the synthesis of I; the probable generation from it of the novel phenylfluorocarbene; and the latter's addition to several olefins, in good yield and under mild conditions.

α-Bromo-α-fluorotoluene, I, was obtained in 60% yield by the photo-initiated action of N-bromosuccinimide on benzyl fluoride in refluxing carbon tetrachloride (10). Dihalide I was a clear lachrymatory liquid, b.p. 48-52°/3.25 Torr. Its proton NMR spectrum featured a one proton doublet centered at 7.20δ (CCl_4, with internal Me_4Si) J_{HF} = 50 cps, and a five proton multiplet centered at *ca.* 7.25δ. The ^{19}F NMR spectrum showed a doublet centered 130.8 ppm (upfield from internal Cl_3FC), J_{HF} = 49 cps. [Calcd. for C_7H_6BrF; % Br = 42.3. Found 42.6%]

Treatment of I with a slight excess of potassium-*t*-butoxide in tetramethylethylene, *iso*-butene, and *trans*-butene (sealed tube, 3 days, 25°) led to 1-fluoro-1-phenylcyclopropanes, eq. [1].

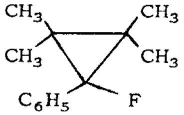
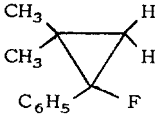
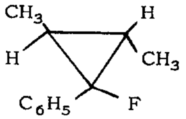


[1]

Products were isolated by dilution with water, ethereal extraction, drying and stripping of solvent, followed by vacuum distillation and/or preparative gas chromatography (11). Data for the new cyclopropanes is collected in Table I.

TABLE I

1-Fluoro-1-phenylcyclopropanes[a]

No.	Olefin	Product	B.Range[b]	Yield[c]
II	Tetramethylethylene		73-74°/3 Torr.	81%
III	*iso*-Butene		49-52°/3 Torr.	74%
IV	*trans*-Butene		51-58°/3.25 Torr.	56%

[a] All cyclopropanes gave satisfactory elemental analyses for carbon and hydrogen. [b] Observed during distillation of crude product. [c] From weight and gas chromatographic analysis of crude product.

Structures II-IV were assigned on the basis of satisfactory elemental analysis, IR, and NMR spectra. The NMR data are of particular interest and are summarized in Table II.

The products II-IV showed no vinyl proton absorption, correct alkyl/aryl integral ratios, and fluorine chemical shifts consistent with the assigned structures (12). The spectra indicate the anticipated methyl signals, the chemical shifts of which are consistent with expectations based on data for the analogous bromophenyl- (8) and chlorophenyl cyclopropanes (13). Of further interest is the observation that 4-bond, H-F coupling is seen in all methyl groups, whether they are *cis* or *trans* to the fluorine. In both cases,

TABLE II

NMR Data for 1-Fluoro-1-phenylcyclopropanes

Cyclopropane	Resonance Position (Area) Character^{a,b}		
	Aryl	Methyl	Fluorine
II	441 (5.0) M^c	77 (5.9) D; 59 (6.0) D	170.2 E^d
III	438 (5.0) M^c	83 (3.0) D; 47 D^e	174.5 M
IV	439 M^c	78 M^e; 50 M^e	179.7 M

^{a}Proton NMR were determined as dilute solutions in CCl_4 with internal TMS, using a Varian A-60 instrument. Resonance positions in cps downfield from TMS. D = doublet, E = envelope, M = multiplet. ^{b} ^{19}F spectra were determined as dilute solutions in CCl_4 on a Varian HA-100 instrument; reported in ppm upfield from internal Cl_3FC. ^{c}These were very narrow multiplets. ^{d}Width at base was 24 cps. ^{e}Overlap with absorptions of the cyclopropyl protons precluded exact integration of this signal.

J_{H-F} = ca. 2 cps. The spectra of II are definitive. Those of III are more complex, the ring protons forming the AB portion of the ABX system which can be analyzed to yield reasonable parameters, in particular J_{AB} = 6.5 cps; the corresponding value for the bromine analog of III was 6.0 cps (8, 14).

The present results, taken together with recent studies of phenylbromocarbene generation (15), and the known stabilizing effect of fluorine atoms on carbene centers [Ref. (3), Moss and Gerstl], suggest that we have produced phenylfluorocarbene. Studies of the steric and kinetic selectivity of the new carbene are in progress; its addition to more complex substrates is anticipated.

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References

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3. R. A. Moss and R. Gerstl, *ibid.*, **32**, 2268 (1967); R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967); T. Ando, *et*. *al*., *J. Am. Chem. Soc*., **89**, 5719 (1967); *Tetrahedron Letters*, 1183, 2587 (1967); M. Schlosser and G. Heinz, *Angew. Chem*., *Int. Ed*., **6**, 629 (1967); L. Ghosez, *et*. *al*., *Tetrahedron Letters*, 2773 (1967); J. Buddrus, F. Nerdel, and P. Hentschel, *ibid*., 5379 (1966).

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6. *Chem. and Eng. News*, **45**, No. 41, 57 (Sept. 25, 1967). For other examples of difluorocarbene additions to steroids, see: C. Beard, N. H. Dyson, and J. H. Fried, *Tetrahedron Letters*, 3281 (1966); C. Beard, *et*. *al*., *ibid*., 3287 (1966); L. H. Knox, *et*. *al*., *J. Am. Chem. Soc*., **85**, 1851 (1963).

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8. R. A. Moss and R. Gerstl, *Tetrahedron Letters*, 3445 (1965); *Tetrahedron*, **22**, 2637 (1966).

9. See J. Hine, *Divalent Carbon*, pp. 36 ff., Ronald Press Co., New York (1964).

10. Benzyl fluoride was obtained from Columbia Organic Chemicals Co., Columbia, S. C. Light and heat were provided by a G. E. PH/RFL2 "Photoflood" lamp.

11. A 20% SE-30 on 60/80 Gas-Chrom R, 0.25 inch, 5 ft. column was used. Temperatures were: Column, 118-150°; injector, 200-225°. Product II displayed some instability under these conditions and was more conveniently isolated by distillation.

12. Compare with data for chlorofluorocyclopropanes: R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967).

13. G. L. Closs and J. J. Coyle, *J. Org. Chem*., **31**, 2759 (1966).

14. A detailed discussion of this and related spectra will be forthcoming.

15. R. A. Moss, *Tetrahedron Letters*, 4905 (1967).