Tetrahedron Letters No.20, pp. 2479-2482, 1968. Pergamon Press. Printed in Great Britain.

PHENYLFLUOROCARBENE

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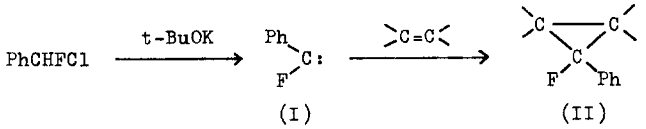
(Received in Japan 9 February 1968; accepted for publication 19 February 1968)

Phenylfluorocarbene (I), in spite of its potential utility in the synthesis of *gem*-phenylfluorocyclopropanes, seems to have received much less attention than its chloro(1) or bromo analogue.(2) The present communication describes its generation as well as its reaction with some olefins.

The carbene (I) was successfully generated by treatment of α-chloro-α-fluorotoluene(3) with potassium t-butoxide at 60-80°C. In the presence of an olefin,(4) the addition to the double bond occurred, yielding the corresponding 1-fluoro-1-phenylcyclopropane (II).

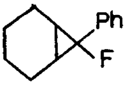
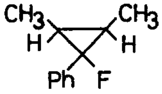
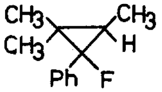
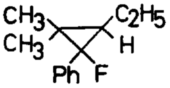
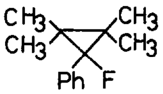


The experimental results are summarized in TABLE I. The products were identified by elemental analysis, and by ir and nmr spectroscopy. The isomer distributions were determined by vpc before distillation. The assignments of *anti* and *syn* configurations(5) were made based on the generalizations that in fluorocyclopropanes J_{HF}^{cis} is larger than J_{HF}^{trans} and that cyclopropyl fluorines are shielded by *cis*-, and deshielded by *trans*-, alkyl groups.(6-8) The nmr spectral data are presented in TABLE II.

The structure of the product from *cis*-2-butene indicates the stereospecific nature of the addition, suggesting the singlet state of the carbene thus prepared. The isomer distributions in the products show that in the addition to *cis*-2-butene or to cyclohexene the phenyl-*anti* addition predominates over the phenyl-*syn* addition, whereas the latter predominates in the addition to 2-methyl-2-butene or to

TABLE I

Synthesis of 1-Fluoro-1-phenylcyclopropanes and Their Properties

Olefin	Product	Yield (%)	B.p. (°C/mm Hg)	Ir* (cm^{-1})	Isomer Ratio (_anti_-/_syn_-)
Cyclohexene	 (III)	23	94-97/2	1011	2.1
cis-2-Butene	 (IV)	17	48-50/3**	1016	2.0
2-Methyl-2-butene	 (V)	54	50-51/3	1020	0.77
2-Methyl-2-pentene	 (VI)	62	61-67/3	1011	0.85
2,3-Dimethyl-2-butene	 (VII)	76	54-56/3	1010	—

* Only absorption due to cyclopropane ring is given.

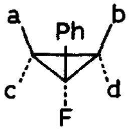
** For the _anti_-phenyl isomer.

2-methyl-2-pentene. This behavior of phenylfluorocarbene is in sharp contrast to that of phenylchloro- or phenylbromocarbene, either of which is known to add to both di- and trialkyl-substituted ethylenes with preferential formation of phenyl-_anti_ adducts.(1,2)

The stereoselectivity of halogen-containing carbenes has been rationalized as being determined by a delicate balance of steric and electronic forces operating between carbene substituents and olefinic alkyl groups.(2,6) Based on this postulation, the predominance of phenyl-_syn_ addition observed with trialkyl-substituted ethylenes must be ascribed to the electronic attraction between phenyl and alkyl groups (or the electronic repulsion between fluorine and alkyl groups) outweighing

TABLE II

Chemical Shifts of Methyl Protons and Fluorine in 1-Fluoro-1-phenylcyclopropanes, and Vicinal H-F Coupling Constants



Cyclopropane	Configuration	δ_{CH_3} (ppm)*				δ_F (ppm)**	J^{vic}_{HF} (Hz)
		a	b	c	d		
III	anti-Ph					126.5 s	17***
	syn-Ph					60.8 t	23
IV	anti-Ph			8.85	8.85	136.3 s	10***
	syn-Ph					70.1 t	21.5
V	anti-Ph	9.22		8.80	8.83	107.5 s	7***
	syn-Ph	9.10	9.00	8.62		78.5 d	12
VI	anti-Ph	9.22		8.97		109.5 s	8***
	syn-Ph	9.08		8.62		89.7 d	15.5
VII		9.04	9.04	8.75	8.75	92.5 s	

* Downfield from internal TMS (60 MHz, CCl_4, 30-35%).

** Upfield from external trifluoroacetic acid (56.4 MHz, CCl_4, 40-50%); s, d, and t denote singlet, doublet, and triplet, respectively.

*** Half-height width.

**** Could not be determined because of the failure to obtain a pure sample due to decomposition during the distillation. The chemical shift of fluorine was measured by submitting the reaction mixture to nmr measurement without further treatment.

the steric repulsion between phenyl and alkyl groups. Probably the fluorine of phenylfluorocarbene, contrary to chlorine or bromine, plays as a sufficiently strong electron-releasing substituent in transition state formation to make the phenyl-syn addition preferred.(9) The repulsive forces between phenyl and alkyl groups become more important, however, in the addition to cis-dialkyl-substituted ethylenes, as is evidenced by the anti-/syn- ratios greater than unity. The difference in behavior between tri- and dialkyl-substituted ethylenes may be accounted for by the difference in the "tightness" of the transition states,(6b) although the scarcity of data does not allow to draw any decisive conclusions at present.

References and Notes

(1) (a) J.E. Hodgkins, J.D. Woodward, and D.L. Stephenson, *J. Amer. Chem. Soc.*, **86**, 4080 (1964); see also F.R. Jensen and D.B. Patterson, *Tetrahedron Letters*, **1966**, 3837. (b) G.L. Closs and J.J. Coyle, *J. Org. Chem.*, **31**, 2759 (1966).

(2) R.A. Moss and R. Gerstl, *Tetrahedron*, **22**, 2637 (1966).

(3) α-Chloro-α-fluorotoluene was prepared in a 84% yield by reducing α,α-dichloro-α-fluorotoluene with an equimolar amount of tri-*n*-butyltin hydride. B.p. 60-70°C at 20 mm Hg, n_D^{32} 1.5013, δ_F 56.3 ppm (upfield from external trifluoroacetic acid, doublet, J=52 Hz).

(4) The reactions with *cis*-2-butene and with 2-methyl-2-butene were effected in an autoclave.

(5) Throughout the present paper, the prefix *anti* is used to indicate the configuration in which phenyl is *trans* to the larger number of alkyl groups.

(6) (a) R.A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967). (b) R.A. Moss and R. Gerstl, *J. Org. Chem.*, **32**, 2268 (1967).

(7) K.L. Williamson, Y. Li, F.H. Hall, and S. Swager, *J. Amer. Chem. Soc.*, **88**, 5678 (1966).

(8) (a) T. Ando, H. Yamanaka, S. Terabe, A. Horike, and W. Funasaka, *Tetrahedron Letters*, **1967**, 1123. (b) T. Ando, H. Yamanaka, and W. Funasaka, *ibid.*, **1967**, 2587.

(9) Enhancement of the ground state stability of fluorine-containing carbenes by the electron-releasing mesomeric effect of fluorine $(\mathrm{R{-}C{-}F} \longleftrightarrow \mathrm{R{-}\overset{-}{C}{=}\overset{+}{F}})$ is well known: see J. Hine, "Divalent Carbon," Ronald Press Co., New York, N.Y. (1964).