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Regiospecific BF_3 Catalysed Fluorine Addition to Fluoro-substituted Benzene Derivatives using Xenon Difluoride

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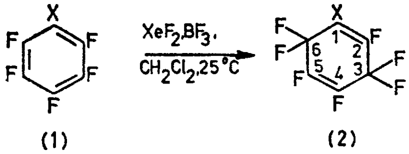
Summary BF_3 catalysed room temperature fluorine addition using XeF_2 to 1-substituted (H, Cl, Br, or C_6F_5) pentafluorobenzene occurred regiospecifically, thus forming 1-substituted heptafluorocyclohexa-1,4-dienes in yields of > 80%.

IT has been demonstrated that xenon difluoride is an easily handled, mild reagent for fluorination of alkenes,[1] acetylenes,[2] aromatic[3] and heteroaromatic molecules,[4] and some organic molecules containing heteroatoms.[5] These reactions are usually catalysed by HF or CF_3CO_2H, and the present experimental evidence suggests that the use of XeF_2 is limited to fluorination of substrates of sufficiently high reactivity. However, it has recently been demonstrated that XeF_2 reacted with 1,2-dibromoethene in the presence of boron trifluoride–diethyl ether, resulting in four products.[6]

We now report that a methylene chloride solution of hexafluorobenzene (10 mmol) reacted immediately with XeF_2 (10 mmol) at room temperature after BF_3 had been introduced into the reaction mixture. The reaction was complete in 30 min. The crude mixture was separated by preparative g.l.c., and 80% of perfluorocyclohexa-1,4-diene was isolated. Further, we have studied the regioselectivity of fluorine addition to pentafluorobenzene, its chloro- and bromo-derivatives, and perfluorobiphenyl (Scheme). In all cases the addition occurred regiospecifically, forming 1-substituted heptafluorocyclohexa-1,4-dienes (2) in yields of > 80%. Their structures were established from spectroscopic data. N.m.r. data are presented in the Table and full interpretation was aided by spin decoupling experiments.



(1) (2)

X = F, H, Cl, Br, or C_6F_5

SCHEME

TABLE. N.m.r. data for (**2**).[a]

X	2-F	3-F	4-F	5-F	6-F
H	129 ttdd	116 dddtd	156 ttdd	161 ttd	102 dddtd
Cl	131 ttd	115 dddt	156 ttdd	161 ttd	108 dddt

X	$^3J_{2,3}$	$^3J_{3,4}$	$^3J_{5,6}$	$^3J_{3,5}$	$^4J_{3,4}$	$^4J_{4,6}$	$^4J_{2,4}$	$^4J_{2,6}$	$^5J_{3,6}$
H	21	21	21	6	10·5	10·5	1	10·5	5·25
Cl	24	21·5	21·5	6	10·5	10·5	3	10·5	5·25

[a] Spectra were recorded on a Jeol JNM-PS-100 spectrometer for CCl_4 solutions, with CCl_3F as internal standard, chemical shifts are given in p.p.m. and coupling constants in Hz.

The conformations of cyclohexa-1,4-dienes have been studied extensively and a planar structure was suggested.[7] The equivalence of the two fluorine atoms on C-3 or C-6 was shown by ^{19}F n.m.r. spectroscopy and this equivalence remained even when 1-chloroheptafluorocyclohexa-1,4-diene was cooled to −135 °C, thus indicating that under these conditions the planar conformation is probably preferred.

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