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THE TRANSFORMATION OF DIFLUOROCARBENE INTO 3,3-DIFLUOROCYCLOPROPENE

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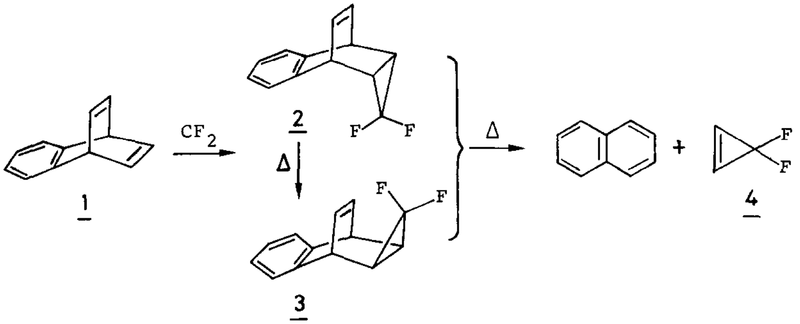
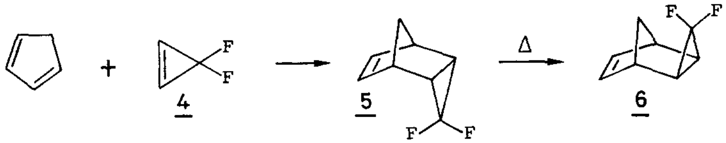
The addition of difluorocarbene to benzobarrelene gives the *syn* and *anti* 1,2 mono-adducts. Heating of either of them at 200°C in hexadeuteriobenzene generates naphthalene and 3,3-difluorocyclopropene.

Fluorinated molecules command attention on account of the special chemical and physical properties conferred by the fluorine substituent.[1] Two of the smallest members of this large class, difluorocarbene and 3,3-difluorocyclopropene, are potentially useful intermediates because of their reactivity in cyclo-additions. In principle, the 1,2 addition of difluorocarbene to acetylene would be a plausible way of preparing the relatively unknown 3,3-difluorocyclopropene.[2] Unfortunately, for practical reasons, this direct approach is hard to realize.[3] We now describe a simple means of circumventing this difficulty which exploits the mechanistic device of a molecular relay.

Difluorocarbene, generated by the thermal decomposition of phenyltrifluoromethylmercury,[4] was allowed to react with an equimolar quantity of benzobarrelene (1).[5] Two mono-adducts were obtained in 10 and 40% yields. They were separated by preparative gas chromatography[6] and identified respectively as the *syn* and *anti* isomers,[7] 2 and 3 (Tables).

Heating a solution of 2 in hexadeuteriobenzene at 200°C in the autoclave for 24 h resulted in the retro-Diels-Alder reaction giving naphthalene and 3,3-difluorocyclopropene (4). There was also some conversion[8] of 2 to its more stable isomer 3. Further heating of 3, in a separate experiment, similarly caused extrusion of 4. The latter was easily recognized by its NMR spectra (Tables). However, more tangible proof for its existence was provided by its reaction with cyclopentadiene. An excess of the latter subsequently added to the thermolyzed solution of 2 or 3 led principally to the *endo* [4+2] adduct 5, notwithstanding the expected slowness of the reaction. Even after 48 h at 30°C, some 4 still remained, however longer times simply enriched the proportion of *exo* adduct 6 by virtue of the stereomutation of the cyclopropane moiety.[10] Both adducts were unambiguously characterized by their NMR spectral data and their identity with the 1,2 adducts obtained from the addition of difluorocarbene to norbornadiene.[10]





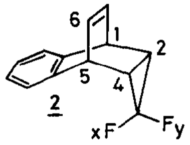
$^1H^a$ and $^{19}F^b$ Chemical Shifts |δ (ppm)| of Compounds 2, 3 and 4

Compound	C2-H	C1-H	C6-H	Ar-H	Fx	Fy
2	2.04	4.28	6.84	7.00-7.30	149.0	101.6
3	1.94	4.28	6.38	7.00-7.30	143.1	102.1
4	6.65[c]				104.0[c]	

[a] Relative to internal Me_4Si in $CDCl_3$ at 100.1 MHz
[b] In $CDCl_3$ at 94.1 MHz. All values are upfield from $CFCl_3$
[c] In C_6D_6 as solvent

Coupling Constants (Hz) of Compounds 2, 3 and 4

Compound	$^2J_{FF}$	$^3J_{HF}$	$^5J_{HF}$
2	159	C2H, Fx = 1.7 C2H, Fy = 15.0	
3	158	C2H, Fx = 1.8 C2H, Fy = 15.2	C6H, Fx = 1.8
4		C2H, F = 1.8	



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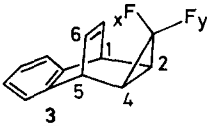

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There are several mechanistic points worth mentioning. Firstly, the choice of relay molecule is crucial. Trials with dibenzobarrelene showed it to be unsuitable in that the easily obtained difluorocarbene adduct proved resistant to thermolysis, presumably owing to the lack of driving force accruing from the formation of anthracene.[11] Another *sine qua non* is the non-occurrence of the thermal intramolecular [2+2] addition in 2 and 3.[10] Lastly, although the present type of reaction is not without precedent (*cf.* the preparation of difluorobenzocyclopropene),[12] it nonetheless provides a modest basis for preparing other cyclopropenes from suitable carbenes.

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REFERENCES AND NOTES

1) R.D. Chambers, Fluorine in Organic Chemistry, Wiley-Interscience, New York, 1973.

2) Although the chemistry of polyhalogenated derivatives of difluorocyclopropene is well documented (*cf.* B.E. Smart, J. Am. Chem. Soc. 96, 927 (1974); D.C.F. Law, S.W. Tobey & R. West, J. Org. Chem. 38, 768 (1973); P.B. Sargeant, J. Am. Chem. Soc. 91, 3061 (1969); P.B. Sargeant & C.G. Krespan, ibid. 91, 415 (1969); W. Stuckey & J. Heicklen, ibid. 90, 3952 (1968); and S.W. Tobey & R. West, ibid. 88, 2481 (1966)), a sample of 3,3-difluorocyclopropene has only been prepared for physical measurements (N.C. Craig, R.A. MacPhail & D.A. Spiegel, J. Phys. Chem. 82, 1056 (1978); K.R. Ramaprasad, V.W. Laurie & N.C. Craig J. Chem. Phys. 64, 4832 (1976).

3) Hexafluorobut-2-yne adds difluorocarbene giving the cyclopropene (W. Mahler, J. Am. Chem. Soc. 84, 4600 (1962)).

4) D. Seyferth & S.P. Hopper, J. Org. Chem. 37, 4070 (1972).

5) R.P. Johnson, A. Exarchou, C.W. Jefford & R.C. Hahn, J. Org. Chem. 42, 3758 (1977).

6) A column, 2 m x 8 mm, at 150°C, packed with 5% silicon OV 225 on Chromosorb W with nitrogen as carrier was used.

7) The *anti* isomer is characterized by its $^5J_{HF}$ coupling.[8]

8) For a similar case of double epimerization see C.W. Jefford, A. Delay, T.W. Wallace & U. Burger, Helv. Chim. Acta 59, 2355 (1976).

9) Cyclopropenes undergo [4+2] cyclo-addition (review: M.L. Deem, Synthesis. 675 (1972)) according to the rules. The *exo* adduct often encountered with halocyclopropenes is usually a thermodynamic artefact (C.W. Jefford, J.C.E. Gehret, J. Mareda, nT. Kabengele, W.D. Graham & U. Burger, Tetrahedron Letters, 823 (1975)). The effect of fluorine substituents is to retard addition (ref. 2).

10) C.W. Jefford, J. Mareda, J.C.E. Gehret, nT. Kabengele, W.D. Graham and U. Burger, J. Am. Chem. Soc. 98, 2585 (1976).

11) Thermolysis of 9,10-ethano-9,10-dihydroanthracene derivatives usually requires high temperatures (∿750°C)(J.L. Ripoll & A. Thuillier, Tetrahedron 33, 1333 (1977)). Moreover, the adduct of 1,2-dibromo-3,3-difluorocyclopropene and anthracene undergoes rearrangement instead of cycloreversion (M.A. Battiste & R.G. Posey, J. Org. Chem. 41, 3333 (1976))

12) E. Vogel, S. Korte, W. Grimme & H. Günther, Angew. Chem. 80, 279 (1968).

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