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COMPETING CHELETROPIC REACTIONS OF DIFLUOROCARBENE WITH VARIOUS 2-SUBSTITUTED NORBORNADIENES

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Summary. Norbornadienes substituted at C2 with electron donating, conjugating, and withdrawing groups react with difluorocarbene to give a ratio of 1,2 to homo-1,4 adducts, which reflects a diminishing response of electrophilic character in the carbene.

We have shown that norbornadiene (1) possesses the special property of undergoing homo-1,4 cycloaddition with dihalocarbenes.[1] This unprecedented cheletropic reaction is best exemplified by difluorocarbene. In addition to the usual *exo* (2) and *endo* (3) cyclopropane adducts, the novel tetracyclic structure 4 is also formed.[2] In contrast, dibromocarbene gave only the rearranged products of the initially formed 1,2 adducts.[3] We originally attributed this difference in behaviour to the diminished electrophilic character of difluorocarbene, which permitted its nucleophilicity to be expressed on approach to the *endo* face of the homo-conjugated diene.[1] Subsequent calculations of the energies and coefficients of the doubly occupied and vacant orbitals for the dihalocarbenes corroborated the reciprocity of electrophilic and nucleophilic character.[4,5] However, no tangible experimental proof has been produced so far to confirm the correctness of our supposition.[5]

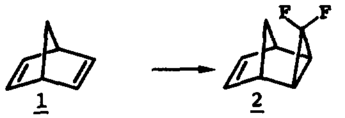
We now report on the addition of difluorocarbene to three classes of norbornadienes bearing electron-donating (X), attracting (Z), and conjugating (C) substituents in the C2 position. Our goal was to see to what extent modification of the frontier orbitals would affect the ease of addition and the composition of the adducts.[6]

The various norbornadienes[7] were allowed to react with a 1.5 and 5 fold molar excess of triphenyldifluorobromomethylphosphonium bromide and potassium fluoride respectively in dimethoxyethane as solvent at room temperature for 48 h.[8] For X and C-substituted olefins (5, 10, 15 and 18), conversion to products was essentially complete, except for the oxygen-substituted derivatives 5 and 10 which inevitably underwent some ketonization.[9] Reaction was more sluggish for the remaining olefins and conversions of 40, 8, 24 and 28% were typical for the parent (1) and Z-substituted olefins (22, 27 and 31). Products were separated by gas-liquid chromatography[10] and characterized by their NMR spectra. Although the homo-1,4 adducts were thermally stable, the more substituted *exo*-cyclopropane adducts were not. Both 7 and 11 underwent ring enlargement to 3-fluorobicyclo[3.2.1]oct-2-en-4-one (9) with loss of methyl fluoride and trimethylfluorosilane[11] respectively. The other *exo* adducts, for example 19 and 32, were thermally prone to undergo intramolecular [2+2] cycloaddition to the tetracyclic products 35 and 36. Under similar conditions the *exo* isomers 12, 20, 24, 29 and 33 were stable.

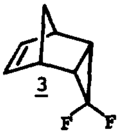
In all cases *exo*-cyclopropanation occurred on both sides of the homo-conjugated diene (Table).[12] The nature of the substituent had little effect on the regioselectivity, since the carbene consistently attacked the more substituted bond. *endo*-Cyclopropane adducts were not detected and it can be assumed that if they were formed they isomerized to the thermodynamically more stable *exo-cis*-fused adduct.[1] *endo*-Homo-1,4 adducts, on the other hand, were found for all three classes, but this time, of the two possibilities, the least encumbered product predominated regardless of the nature of the substituent.

Inspection of the Table reveals no meaningful trend within each of the 1,2 and homo-1,4 addition modes. There is, however, a marked variation between the incidence of the two modes which mirrors the nature of the C2 substituent. Norbornadienes bearing X substituents (5 and 10) gave a high ratio of 1,2 to homo-1,4 adducts (8.1 and 4.2). Clearly, here the electrophilic behaviour of difluorocarbene is paramount. At the other end of the scale, Z substituents (22, 27 and 31) resulted in a smaller ratio (1.1-1.4) which points to the attenuation of electrophilic reactivity to the advantage of the linear cheletropic reaction. Substituents of the C type (15 and 18) led to intermediate values (1.9 and 3.0) as both electrophilic and nucleophilic behaviour would be reinforced.

In principle, singlet carbenes could display four reaction modes, *viz.* 1,2 electrophilic, 1,2 nucleophilic, homo-1,4 electrophilic and homo-1,4 nucleophilic addition.[5] Our results show that for difluorocarbene, which borders on ambiphilic behaviour[13] competition exists essentially between 1,2 electrophilic and homo-1,4 nucleophilic additions.[14] Why this is so remains to be explored further and will be discussed elsewhere.



1 2



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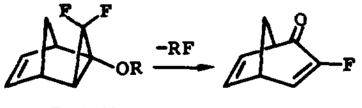
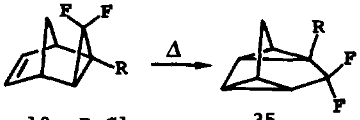
4



7 R=Me

11 R=$SiMe_3$

9



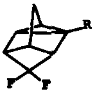
19 R=Cl

32 R=CO_2Et

35

36

Adducts Obtained from the Addition of Difluorocarbene to some 2-Substituted Norbornadienes[a]

Reactant	1,2 Adducts		homo-1,4 Adducts		1,2/homo-1,4 Additions
					
5 R= -OMe	7 89.0	-	8 11.0	-	8.1
10 $-OSiMe_3$	11 75.0	12 6.0	13 6.0	14[b]	4.2
15 $-\phi$	16 75.0	-	17 25.0	-	3.0
18 -Cl	19 62.0	20 4.0	21 34.0	-	1.9
1 -H	2 66.0		4 34.0		1.9
22 -CN	23 35.0	24 23.0	25 30.0	26 12.0	1.4
27 $-CO_2Me$	28 38.0	29 15.0	30 47.0	-	1.1
31 $-CO_2Et$	32 44.0	33 12.0	34 44.0	-	1.3

[a] Yields are normalized to 100%

[b] Three other products are formed (13%) which have eluded characterization so far, which may contain traces of 14.

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REFERENCES AND NOTES

1) C.W. Jefford, J. Mareda, J.C.E. Gehret, nT. Kabengele, W.D. Graham & U. Burger, J. Am. Chem. Soc. 98, 2585 (1976).
2) Appropriate modification of the homo-1,4 adduct 4 provides a convenient entry to the versatile family of C_8H_9 cations (C.W. Jefford, J. Mareda, J.C. Perlberger & U. Burger, J. Am. Chem. Soc. 101, 1370 (1979); C.W. Jefford, S. Genevay-Höck, A. Delay, J. Mareda & U. Burger, Tetrahedron Letters 1979, 2549; C.W. Jefford & V. de los Heros, ibid., in press).
3) C.W. Jefford, V. de los Heros & U. Burger, Tetrahedron Letters 1976, 703.
4) Y. Jean, Tetrahedron Letters 1977, 2689.
5) Various olefins of the norbornadiene type have been submitted to reaction with difluorocarbene. Good correlation exists between the calculated energies of the frontier orbitals and the observed 1,2/homo-1,4 ratios (C.W. Jefford, V. de los Heros & G. Wipff, unpublished results.
6) For a description of how X, Z and C substituents affect the regioselectivity of pericyclic reactions, see: I. Fleming, Frontier Orbitals in Organic Chemical Reactions, John Wiley & Sons, London, 1976; K.N. Houk, in Pericyclic Reactions, ed. A.P. Marchand et R.E. Lehr, Academic Press, New York, 1977, vol. II, pp. 181-271.
7) Known dienes were prepared according to standard procedures: 18 (D.I. Davies,J. Chem. Soc. 1960, 3669; 22 (C. Moureu & J.C. Bongrand, Ann. Chim. 14, 47 (1920); C. Dietrich-Buchecker, D. Martina & M. Franck-Neumann, J. Chem. Res. (M), 1978, 1014; 27 and 31 (K. Alder & H. Wirz, Liebigs Ann. Chem. 601, 138 (1956). Experimental details for the preparation of the other dienes 5, 10 and 15 will be reported elsewhere. Briefly, however, 15 was prepared by the Diels-Alder reaction of β-bromostyrene and cyclopentadiene followed by base treatment. Treatment of norborn-5-en-2-one with an equivalent of lithium diisopropylamide in THF at -78° followed by quenching with trimethylchlorosilane gave 10. 5 was obtained from the preceding ketone by ketalization and elimination (F. Barbot & P. Miginiac, Helv. 62, 1451 (1979).
8) D.J. Burton & D.G. Naae, J. Am. Chem. Soc. 95, 8467 (1973).
9) Nucleophile, most probably fluoride anion, partially converted 5 and 11 to norborn-2-en-5-one.
10) Separations were effected on columns of 15% Apiezon L and 15% FFAP, both pre-treated with triethanolamine on Chromosorb DMCS (2.5 m x 6 mm) operating at 160 and 150° respectively. Products obtained from 27, 31 & 5 were separated on the first column and products from 10 and 18 on the second. The composition of the products obtained from 15 and 22 were estimated by inspection of the NMR spectra of crude mixtures.
11) We could not detect methyl fluoride, but trimethylfluorosilane was isolated and identified by its NMR spectrum (*cf.* R. Schmutzler, J. Chem. Soc. 1964, 4551).
12) In order to facilitate comparison, rearranged products were normalized and are represented as their 1,2 adduct precursors.
13) Difluorocarbene lies next to methoxychlorocarbene on the continuum of carbenic behaviour (R.A. Moss, M. Fedorynski & W.-C. Shieh, J. Am. Chem. Soc. 101, 4736 (1979).
14) Our results roughly parallel those calculated for the addition of singlet methylene to substituted butadienes (H. Fujimoto & R. Hoffmann, J. Phys. Chem. 78, 1167 (1974)).

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