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THE ROLE OF ENTROPIC AND ELECTRONIC FACTORS IN CONTROLLING HOMO-1,4 ADDITION OF DIHALOCARBENES TO NORBORNADIENE-TYPE MOLECULES

Charles W. Jefford, Viktor de los Heros, Jean-Claude E. Gehret and Georges Wipff[1]

Département de Chimie Organique, Université de Genève, 1211 Genève 4, Switzerland

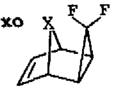
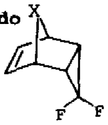
Summary. The proportion of 1,2 and homo-1,4 adducts obtained from the reaction of difluorocarbene with norbornadiene and its 7-oxa, 7-methyl, and 7,7-difluoro derivatives is reflected by the calculated energies of the frontier molecular orbitals of the dienes. It appears that the product composition is dictated by competing 1,2 electrophilic and homo-1,4 nucleophilic cheletropic reactions.

Norbornadiene (1) possesses the singular property of permitting the homo-1,4 addition of dihalocarbenes to compete with the usual 1,2 addition.[2] Moreover, on passing from dibromo, through dichloro, fluorochloro, to difluorocarbene the ratio of 1,2 to homo-1,4 adducts decreases (respectively ∞, 6.70, 6.14 and 1.94).[3] *Ab initio* calculations have indicated,[4] in keeping with these findings, that both the LUMO and HOMO energies are raised along the series. Perturbation analysis has also indicated that for a given carbene the homo-1,4 addition should be favoured when the diene partner becomes more electrophilic.[4] In order to clarify these ideas we now report experiments and calculations with some norbornadienes in which the energies of the frontier orbitals are varied systematically.

Difluorocarbene was allowed to react with norbornadiene (1), 7-oxanorbornadiene (2), 7-methyl (3) and 7,7-difluoronorbornadiene (4) [5,6] The proportion of homo-1,4 adduct increases along the series (Table 1). This trend is paralleled by the calculated energies of the frontier orbitals (Tab.2).[7,12] Comparing norbornadiene (1) with its 7,7-difluoro derivative (4), it is seen that the LUMO/HOMO energy gap is essentially the same, but in 4 both levels are depressed.[8] Diene 4 should thus have more electrophilic and less nucleophilic character than 1. The experimental result is that 4 undergoes both more homo-1,4 and less 1,2 addition [9] Similarly, 7-oxanorbornadiene (2) and 1 have commensurate HOMO energies, but the presence of the oxygen atom stabilizes

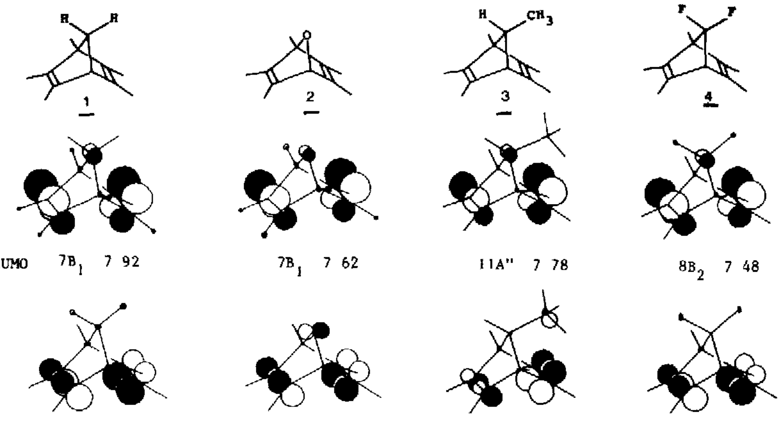
Table 1.

Products obtained on addition of CF_2 to Norbornadienes[a]

Substrate	1,2 Adduct		Homo-1,4 Adduct	Ratio
	exo 	endo 		1,2 / Homo-1,4
1 X = CH_2	55	11	34	1.94
2 X = O	59	--	41	1.44
3 X = $CHCH_3$	33	6	61	0 64
4 X = CF_2	22	2	76	0 32

[a] Yields normalized to 100%

Table 2 Calculated energies (eV) for the frontier orbitals of norbornadienes 1-4



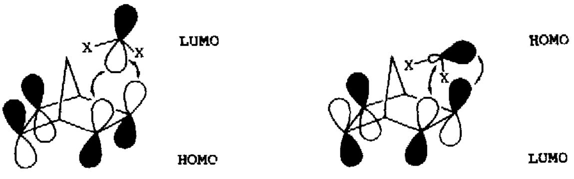
	1	2	3	4
LUMO	$7B_1$ 7 92	$7B_1$ 7 62	11A" 7 78	$8B_2$ 7 48
HOMO	$6B_2$ -6 94	$6B_2$ -7 07	19A' -6 58	-7 40

Fig 1

Non-linear (1,2) and linear (homo-1,4) cheletropic reactions of a σ^2 carbene with norbornadiene

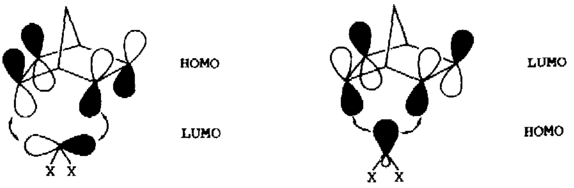
a) 1,2 Electrophilic

b) 1,2 Nucleophilic



c) homo-1,4 Electrophilic

d) homo-1,4 Nucleophilic



the LUMO. Experimentally, the product composition contains more of the homo-1,4 adduct. The methyl group at C7 in 3 scarcely disturbs the LUMO, but raises the HOMO appreciably Normally, 1,2 adducts would predominate, but the methyl group completely blocks off one of the *exo*-cycloprotonation modes so that more homo-1,4 adduct is formed than with norbornadiene [10]

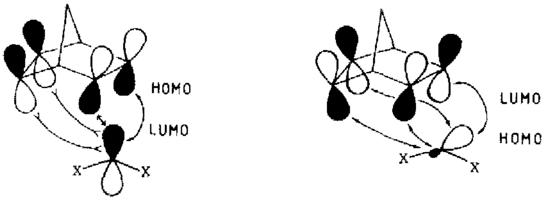
These results confirm the elementary notion that the balance of electrophilic to nucleophilic character in the diene partner controls the amount of homo-1,4 adduct formed They further provide valuable insights into the nature of the competition between the 1,2 and homo-1,4 addition modes. The two modes can be represented as non-linear[11] and linear cheletropic reactions respectively, each of which has an electrophilic and nucleophilic component (Fig. 1). The perturbation energy depends to a first approximation on the energy difference between the frontier orbitals of the reactants and on the square of their overlap. It can be readily appreciated from the calculated energies of the dienes (Table 2) and difluorocarbene (HOMO -9.30 eV, LUMO 6.50 eV)[4] that the smallest gap is that between the HOMO of the diene and the LUMO of the carbene Nevertheless, the size of this gap cannot alone be responsible for the selectivity observed on varying the diene partner If overlap factors are neglected, both 1,2 and homo-1,4 electrophilic additions would be equally disfavoured, whereas both 1,2 and homo-1,4 nucleophilic additions would be equally favoured on replacing 1 by 4. Consequently, the selectivity must spring from differences in the value of the overlap integral of the interacting orbitals. Indeed, the 1,2 nucleophilic and homo-1,4 electrophilic interactions, on account of poor overlap, lead to small perturbation energies and are thus inconsequential components (Fig. 1b,c) On the other hand, overlap is highly effective for the orbital topologies arising from the 1,2 electrophilic and homo-1,4 nucleophilic interactions (Fig. 1a,d) As a result these two components are in formal competition and are thus sensitive to substituent effects.

Another point deserves mention. The 1,2-*exo* adduct is not only the more stable, but it is the kinetic product too. Two electronic factors could be contending. A repulsive interaction could develop between the LUMO of the carbene and the HOMO of the diene on *endo* approach, while attraction would arise between the HOMO of the carbene and the LUMO of the diene (Fig. 2). However, the 1,2 nucleophilic interaction would be poor on account of the disparate size of the lobes of the orbitals. The latter factor would only operate if the transition state were late, since the carbene evolves from electrophilic to nucleophilic in nature.

Fig 2

Non-linear 1,2 cheletropic reaction on endo approach of a σ^2 carbene to norbornadiene

a) electrophilic b) nucleophilic



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

3) C.W. Jefford, V de los Heros & U Burger, Tetrahedron Letters 703 (1976), P.M Kwantes & G W Klumpp, Tetrahedron Letters 707 (1976).

4) Y Jean, Tetrahedron Letters 2689 (1977) and footnotes 5 and 6 therein

5) The method of D.J. Burton and D G Naae (J Am. Chem Soc 95, 8467 (1973)) was used for dienes 1, 3 and 4 Diene 2 was submitted to the method of D. Seyferth and S. Hopper (J. Org Chem 37, 4070 (1972)).

6) Diene 2 was prepared from 7-oxanorborn-5-en-2,3-diol obtained from the addition of ethylene carbonate to furane Hydrolysis was followed by conversion to the thiocarbonate using N,N'-thiocarbonyldiimidazole Treatment with triethyl phosphite at 110° gave 2 (H. Prinzbach & H. Babsch, Angew Chem. Int Ed. Engl 40, 753 (1975)).

7) *Ab initio* calculations were performed using the STO 3G minimum basis set of the Gaussian 70 program (QCPE No 236) The MO's in Table 2 were plotted using the program of E. Haselbach and A Schmelzer, Helv Chim Acta 54, 1299 (1971).

8) 4 has also a higher ionization potential (9 3 eV) than 1 (8 7 eV) C. Batich & J C.E. Gehret unpublished work

9) A little hindrance, possibly negligible, could also operate in the same sense, since the F atom has a slightly larger Van der Waals radius than the H atom (respectively 1.4 and 1.2 Å) and the C-F bond is longer than the C-H bond (respectively 1 4 and 1 0 Å).

10) Methyl substituents at C7 even induce dichlorocarbene to give sizable (∼45%) amounts of homo-1,4 adducts (C W Jefford, W D Graham & U Burger, Tetrahedron Letters 4717 (1975))

11) R Hoffmann, J Am Chem. Soc 90, 1475 (1968), N Bodor, M J S Dewar & J W Wasson, *ibid* 94, 9095 (1972), R Hoffmann, D M Hayes & P S Skell, J. Phys Chem. 76, 664 (1972), T Fueno, S Nagase, K. Tatsumi & K Yamaguchi, Theor Chim. Acta 26, 43 (1972), B. Zurawski & W Kutzelnigg, J Am. Chem Soc 100, 2654 (1978), N G Rondan, K.N Houk & R.A. Moss, submitted for publication.

12) Another factor facilitating the 1,4 addition could be the decrease of the repulsion between the HOMO of the carbene and the subjacent orbital of the diene (W W Schoeller & E Yurtsever, J Am Chem Soc 100, 7548 (1978), H Fujimoto & R Hoffmann, J. Phys. Chem 78, 1167 (1974)). However, we find no correlation between this energy gap (1 25, 1 28, 1.72, 0 76 eV for 1-4 respectively) and the observed 1,2/homo-1,4 ratio.

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