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ON THE NATURE OF THE HOMO-1,4 ADDITION OF DICHLOROCARBENE TO NORBORNADIENES

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Summary. Nucleophilic behaviour postulated for difluorocarbene in its homo-1,4 additions to norbornadienes is not found for dichlorocarbene in its homo-1,4 additions.

Recently, Jefford and Huy have studied the influence of various substituents at C-2 of norbornadiene upon the ratio of *exo*-1,2 and homo-1,4 addition products from difluorocarbene[1]. The decrease of this ratio observed with electron attracting substituents was taken to indicate increased nucleophilic character of difluorocarbene in homo-1,4 addition[2]. However, from their work it is not clear, whether the decrease of the product ratio is due to a genuine increase of the rate constant of homo-1,4 addition or to a disproportionate decrease of the rate constant of *exo*-1,2 addition without any unusual change of the rate constant of homo-1,4 addition[3,4]. For the homo-1,4 addition of dichlorocarbene[3] we have avoided this ambiguity by measuring partial relative rate constants and by gauging the effects of substituents at C-7 on homo-1,4 addition against their effects on the concomitant *endo*-1,2 additions.

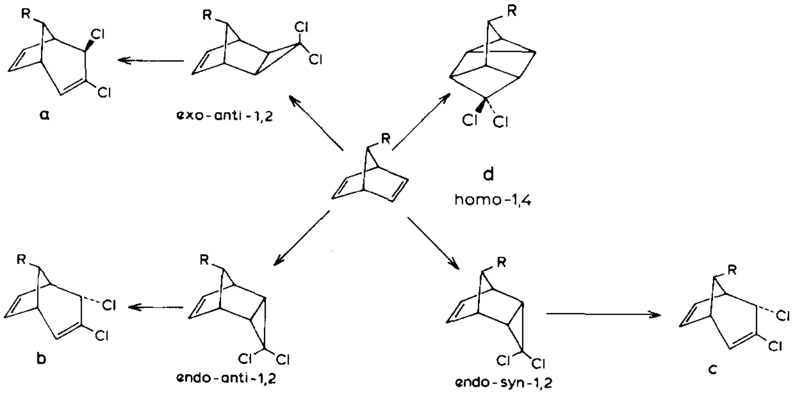
In the Table relative rate constants (k^R_{rel})[5] and product ratios (%)[6] of the reactions of (PTC-generated) dichlorocarbene with a series of 7-R-norbornadienes are given together with the calculated[7] partial relative rate constants (k^R_{rel-m}) of the four modes of addition.

It is seen that substituent induced changes are much more pronounced for the *exo*-1,2 addition manifested by %-a than for the *endo* additions manifested by %-b, %-c and %-d. We therefore place *exo* addition and *endo* additions (1,2 and homo-1,4) of dichlorocarbene into two different categories. Only the *endo*-1,2 additions are considered appropriate models with which the homo-1,4 addition can be compared. These comparisons are carried out in Figs. 1a and 1b.

Lines are drawn in Figs. 1a and 1b to depict the general trends. The lines have about unit slopes, suggesting that homo-1,4 addition and *endo*-1,2 additions respond similarly to changes of the polar character of a substituent at C-7. For the homo-1,4 addition of dichlorocarbene a linear homocheletropic transition state with an anomalous degree of charge transfer from the carbene to the diene[2] therefore seems untenable and alternative interpretations taking into account the similarity with the *endo*-1,2 additions have to be sought.

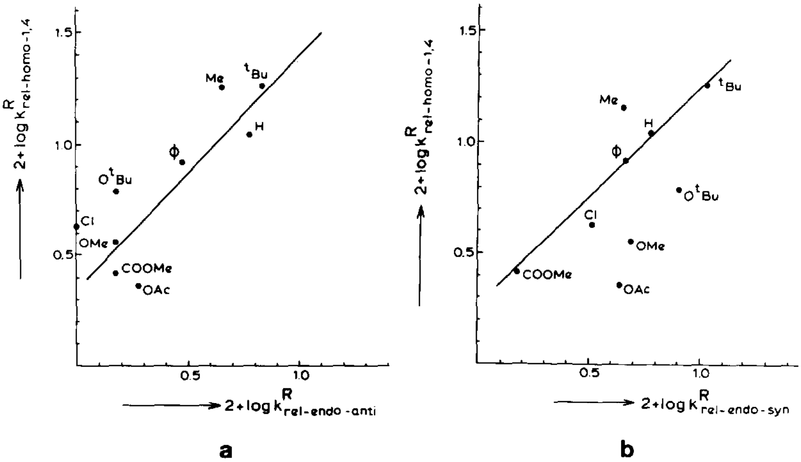
Table. Addition of dichlorocarbene to 7-substituted norbornadienes.

Relative rate constants ($k^{R}_{rel} = k^{R}_{total} : k^{H}_{total}$)[5], proportions of products[6] and partial relative rate contants (k^{R}_{rel-m}; m = *exo-anti*, *endo-anti*, *endo-syn*, homo-1,4)[7]; T = 22.5 ± 1.0 °C.



Substituent R	k^{R}_{rel}	*exo-anti*		*endo-anti*		*endo-syn*		homo-1,4	
		%-a	k^{R}_{rel-m}	%-b	k^{R}_{rel-m}	%-c	k^{R}_{rel-m}	%-d	k^{R}_{rel-m}
H	1.00[a]	77	0.770	6	0.060	6	0.060	11	0.110
COOMe	0.15	63	0.095	10	0.015	10	0.015	17	0.026
Phenyl	0.38	58	0.220	8	0.030	12	0.046	22	0.084
Me	0.50	46	0.230	9	0.045	9	0.045	36	0.180
t-Bu	0.61	42	0.256	11	0.067	17	0.104	30	0.183
O-t-Bu	0.21	25	0.055	7	0.015	38	0.080	30	0.062
OAc	0.11	22	0.024	17	0.019	40	0.044	21	0.023
OMe	0.12	16	0.019	13	0.015	41	0.049	30	0.036
Cl	0.10[b]	14	0.014	10	0.010	33	0.033	43	0.043
Br	c	7		13		33		47	
OMe Me[d]	c	0		13		39		48	

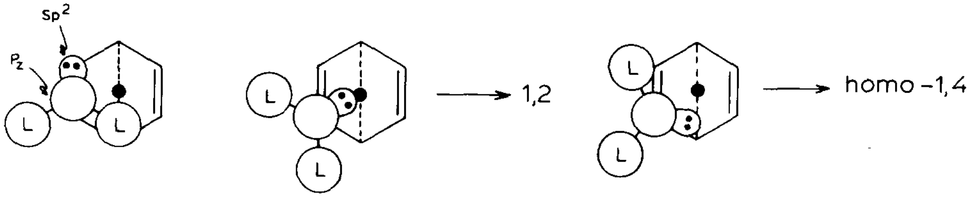
[a] By definition; [b] tentative value; [c] not determined; [d] 7-methoxy-7-methyl-norbornadiene.



a b

Figure 1. Plots of $\log k^R_{\text{rel-homo-1,4}}$ vs. $\log k^R_{\text{rel-}\mathit{endo\text{-}anti}}$ (a) and $\log k^R_{\text{rel-}\mathit{endo\text{-}syn}}$ (b) for the reaction of dichlorocarbene with 7-R-norbornadienes. In plot b the *endo-syn* 1,2-additions of the three norbornadienes carrying oxygen substituents at C-7 are considered to be accelerated by special factors whose nature is still unknown[8].

Considering the unique role of norbornadienes in displaying homo-1,4 addition, we speculate that in *endo* additions of certain carbenes to norbornadienes unfavorable steric interactions between the "inner" carbene ligand L and the C-5, C-6 bridge destabilize the transition state I of the ideal[9] reaction path of carbene 1,2 addition. Other, normally less favorable, modes of attack may then become competitive, e.g. II and III in which both ligands L are "outside". Of these II leads to the 1,2 product and III to the homo-1,4 product if it is assumed that in a least motion proces interaction between the carbene HOMO and the norbornadiene LUMO (at C-3 and C-6, respectively) increases continuously throughout the addition proces. In the transition states related to II and III charge transfer from norbornadiene to carbene could be rather similar, in line with the substituent effects observed for the three modes of *endo* addition[10].



I II III

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1) C.W. Jefford and P.T. Huy, Tetrahedron Lett., 755 (1980).

2) C.W. Jefford, V. de los Heros, J.-C.E. Gehret and G. Wipff, ibid., 1929 (1980).

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4) Various theoretical studies (cf. P.H. Mazzocchi, B. Stahly, J. Dodd, N.G. Rondan, L.N. Domelsmith, M.D. Rozeboom, P. Caramella, and K.N. Houk, J.Amer.Chem.Soc., 102, 6482 (1980); G. Wipff and K. Morokuma, Tetrahedron Lett., 4445 (1980)) indicate stronger interaction of an electrophile with the *exo* face of a norbornene π orbital. Consequently, variations of substituent effects will be "felt" more strongly in *exo* than in *endo* electrophilic additions.

5) Determined from the rates of disappearance of two different 7-R-norbornadienes in competition experiments.

6) Determined by GLC (8% Carbowax 1540 and 15% Carbowax 1540 both on Chromosorb W 60-80; 1.5 m x 4-5 mm; all glass) between 100 and 180°C.

7) $k^{R}_{rel-m} = k^{R}_{rel} \cdot \frac{(\%-m)_R}{100}$; (m = *exo-anti* (a); *endo-anti* (b); *endo-syn* (c); homo-1,4 (d).

8) A (slight) preference for *endo-syn* over *endo-anti* attack in the case of (mainly) 7-oxygenated norbornadienes was first noted by us (G.W. Klumpp, A.H. Veefkind, W.L. de Graaf, and F. Bickelhaupt, Ann., 706, 47 (1967)) and has since been observed in other cases. For pertinent literature and a discussion of these findings see: P.H. Mazzocchi et al. in ref. 4.

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10) The suggestion that homo-1,4 additions of dihalocarbenes to norbornadienes may involve electrophilic attack on the latter has been advanced before: R.A. Moss and M. Jones, Jr., in "Reactive Intermediates", M. Jones, Jr. and R.A. Moss, Edts., J. Wiley and Sons, Vol. 1, 1978, p. 92 ff..

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