Tetrahedron Letters No. 51, pp 4959 - 4962.
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0040-4039/79/1215-4959$02.00/0

ANTI/SYN-SELECTIVITIES IN THE ADDITION OF ELECTROPHILES TO 8-METHYLENE-endo-TRICYCLO[3.2.1.$0^{2,4}$]OCTANE

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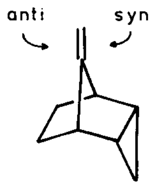
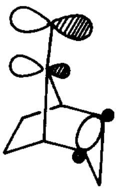
Summary: The addition of a variety of electrophiles to the semicyclic double bond of 1 and 4 has been studied. The anti/syn-product ratios show that the interaction between the Walsh- and π-orbitals causes only small selectivities.

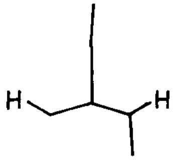
Photoelectron spectra revealed a sizeable (H_{ij} = -0.33β) through space interaction between the e_S Walsh orbital of the cyclopropane ring in 1 with the semicyclic double bond[1]. The molecule can relieve this destabilizing interaction by both polarisation of the semicyclic double bond[2] and by rehybridization at C-8[3] resulting in "orbital distortion"[4] of the semicyclic double bond, cf. 1a.



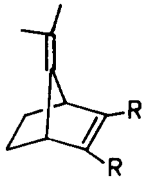
1



1a



1b



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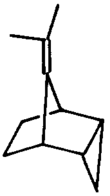

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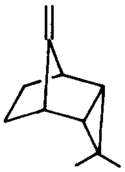
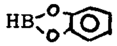


4

Consequently the two faces of the semicyclic double bond should have unequal electron densities in the HOMO and this should become manifest in the relative rates of attack by electrophiles on the anti and syn face of the double bond. Similar considerations have been made for the consequences of the orbital inter action between the endocyclic and semicyclic double bond in 2[3,5]. There, however, the anti/syn ratio of attack by electrophiles is not only governed by electronic factors but also by the different steric situations of the anti and syn face of the semicyclic double bond. Since in 1 the steric situation of the two faces is well balanced (cf. the projection 1b) we studied the anti/syn-ratios of the reactions of a variety of electrophiles with 1. The recent report[6] on the reaction of 3 with singlet oxygen prompts us to communicate our results now.

The details for the structural assignments of the anti- and syn-products is given in[7]. The results show (cf. the table) that the anti/syn-selectivities in the addition to 1 are not marked. Especially the reactive carbenes show practically the same small stereoselectivity, which is perhaps the expression of the small steric difference between the two faces of the double bond. The reagents d - g, however, gave rise to varying stereoselectivities.

Table: Anti/syn-product ratios on addition to 1 and 4 *).

	Reagent	1	4
a	$|CF_2$	56.7 : 43.3	
b	$|CCl_2$	56.1 : 43.9 (0,14)	66 : 34 (0,39)
c	$|CBr_2$	55 : 44	
d	HN=NH	42.5 : 57.5 (-0,18)	58 : 42 (0,19)
e	H_2/Pt	59.7 : 40.3 (0,23)	75 : 25 (0,65)
f		77.6 : 22.4 (0,92)	84 : 16 (1,23)
g	9BBN	88.8 : 11.2 (1,22)	95 : 5 (1,73)

*) The values in brackets are $\Delta G^{\ddagger}_{anti} - \Delta G^{\ddagger}_{syn}$ in kcal/mol;

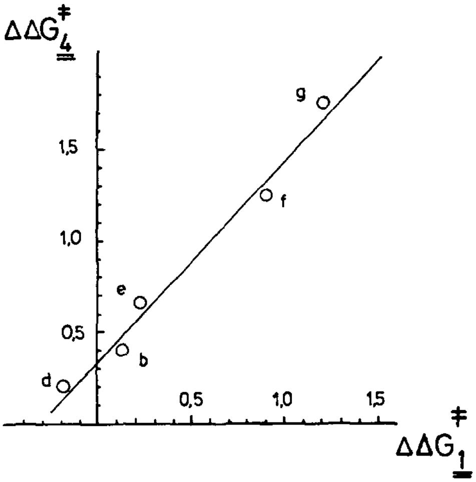
a) $C_6H_5HgCF_3$, NaI, C_6H_6, 20h, 80° C; b) 50% aq. $NaOH/C_6H_5CH_2\overset{\oplus}{N}Et_3Cl^{\ominus}$, $CHCl_3$, 4h, 40° C; c) as b) with $CHBr_3$; d) $H_2N\text{-}NH_2$, aq. CH_3OH, $Cu(OAc)_2$, O_2, 15h, 25° C; e) 5% Pt on carbon, 1 at H_2, CH_3OH, 45 min. 25° C; f) Catecholborane, neat 4h, 100° C; g) 9BBN, THF, 1.5h, 25° C.

If these stereoselectivities are a consequence of the through space orbital interaction they should be different in the addition of electrophiles to 4. The interaction integral H_{ij} for the orbital interaction in 4 has not been determined yet, but the ^{13}C-NMR-spectra suggest a somewhat larger interaction in 4 compared to that in 2[2]. Indeed, upon addition of the reagents b, d - g to 4, an increased selectivity is observed (cf. the table). This could be due to differences in either or both of orbital distortion or steric effects. It is therefore noteworthy that the

$\Delta\Delta G^{\ddagger}$-values of the two series obey a linear free energy relationship (cf. fig.):

$$\Delta\Delta G^{\ddagger}_{\underline{\underline{4}}} = 1.1 \cdot \Delta\Delta G^{\ddagger}_{\underline{\underline{1}}} + 0.32\ \text{kcal/mol.}$$

The intercept has been shown[7)] to correspond to $\Delta G^{\ddagger}_{\text{syn}\ \underline{\underline{1}}} - \Delta G^{\ddagger}_{\text{syn}\ \underline{\underline{4}}}$ and it is unclear why this term should be constant or nearly so. The intercept probably reflects steric differences on the syn-side between **1** and **4**. The slope >1 signals that **4** is indeed (slightly) more selective than **1**.



Another observation deserves comment: diimide reduction of **1** favored syn attack, whereas **4** behaved normally giving preference for anti reduction. The fact that the values for the diimide reduction fall on the correlation line of the linear free energy relationship suggest that the inverted selectivity of **1** towards diimide is no artifact. Perhaps diimide is not a pronounced electrophilic reagent, but rather one, in which on reaction with olefins both HOMO/LUMO interaction pairs are of similar importance[8)]. Further discussion of these and other phenomena is deferred to the detailed publication of our results.

Acknowledgement: This investigation was initiated in 1975 by the provocative question of A. Eschenmoser, whether the top and bottom face of a double bond should always have the same electron density. We thank the Fonds der Chemischen Industrie for support and the Deutschen Shell Chemie GmbH for chemicals.

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(Received in Germany 10 October 1979)