syn–anti-Stereoselection in the Diels–Alder Reactions of 1,2,3,4,5-Pentamethylcyclopentadiene

D. Jean Burnell[a,b] and Zdenek Valenta[a]*

[a] *Department of Chemistry, University of New Brunswick, Bag Service No. 45222, Fredericton, New Brunswick, Canada E3B 6E2*

[b] *Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR6*

Very similar *syn–anti*-adduct ratios were observed when 1,2,3,4,5-pentamethylcyclopentadiene reacted with a variety of (*Z*)-ethylenic dienophiles, suggesting that in the *exo* region the transition-state geometries are very similar.

Previous work with the plane-nonsymmetrical diene (**1**) had shown us that dienophile reactivity had little bearing on facial (*syn–anti*) stereoselectivity.[1] This made the seemingly contradictory reports concerning *syn–anti*-stereoselection in the cycloadditions of 5-methylcyclopentadiene (**2**) particularly puzzling. On the one hand, Mironov *et al.*[2] claimed that with maleic anhydride the two possible *endo* adducts are formed in a ratio of 12:1 in favour of the *anti* (to the C-5 methyl) product. In contrast, McLean and Haynes[3] reported that with *N*-phenylmaleimide the two *endo* adducts are produced in a ratio of roughly 1:1, *i.e.* that there is no facial selectivity. We now report the results of cycloadditions involving 1,2,3,4,5-pentamethylcyclopentadiene (**3**),† which presents the same stereochemical alternatives as (**2**) but avoids the problem of sigmatropic rearrangement inherent in (**2**).[3,5] One Diels–Alder cycloaddition involving (**3**) has been reported.[6]

Various (*Z*)-ethylenic dienophiles reacted with (**3**) in dichloromethane in yields of >90% at room temperature. The four possible modes of dienophile attack on (**3**) are shown in Figure 1. In practice, the more reactive dienophiles (maleic anhydride, *N*-phenylmaleimide, *p*-benzoquinone, and 1,4-naphthoquinone) gave only the two *endo* adducts. However, cycloadditions involving the less reactive dienophiles (dimethyl maleate, methyl acrylate, and butenone), which would have weaker *endo*-directing secondary interactions, yielded three products. The *syn–exo* adducts, which must be highly disfavoured for obvious steric reasons, were not observed. Facial stereoselectivity was evident in all cases; the results of these cycloadditions are summarized in Table 1.

It is important to note that there was an insignificant difference in the ratios of the adducts obtained from the cycloadditions with maleic anhydride and with *N*-phenylmaleimide. In fact, the *anti–endo* to *syn–endo* product ratios were fairly similar in all the reactions.‡

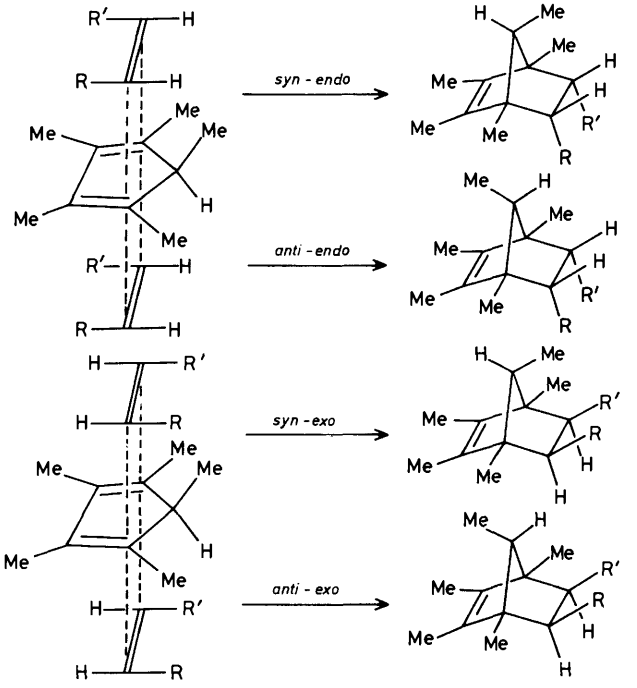
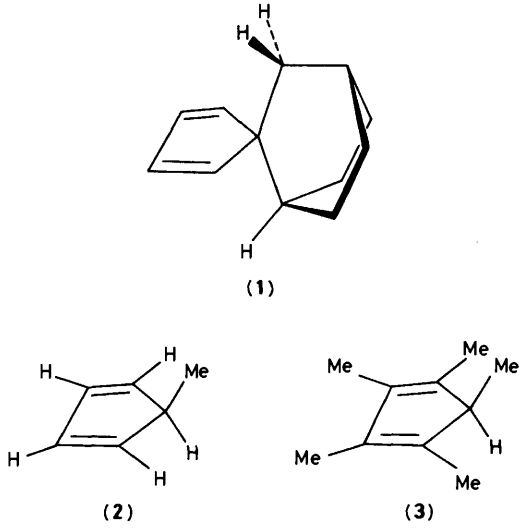


Figure 1. Four possible modes of dienophile attack on (**3**).

Table 1. Diels–Alder adducts obtained in cycloadditions with (**3**).

Dienophile	Relative amounts of adducts[a]			
	anti–endo	*syn–endo*	*anti–exo*	*syn–exo*
Maleic anhydride	79	21	0	0
N-Phenylmaleimide	83	17	0	0
p-Benzoquinone	83	17	0	0
1,4-Naphthoquinone	85	15	0	0
Dimethyl maleate	89	11	26	0
Methyl acrylate	82	18	19	0
Butenone	89	11	7	0

[a] Unambiguous structural assignments were made on the basis of 200 and 500 MHz ^{1}H and 20 MHz ^{13}C n.m.r. spectra; relative amounts were estimated by integration of the ^{1}H n.m.r. spectra of adduct mixtures.



† Diene (**3**), which was synthesized in a few steps,[4] is now available commercially.

‡ Some of the less reactive dienophiles had perhaps marginally better selectivity, but the significance of this is questionable. Reaction of (**3**) with *N*-phenylmaleimide in solutions in different solvents, all at room temperature, produced adducts with ratios (*anti–endo*:*syn–endo*) ranging from 78:22 to 86:14, with no correlation with the solvent polarity.

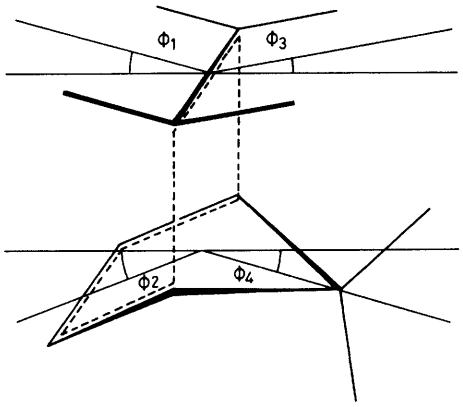


Figure 2. Diagramatic representation of the transition state of the Diels–Alder reaction.

Calculations have shown that perturbation of the diene HOMO by the C-5 methyl is negligible.[7] Therefore, facial stereoselecivity in (**3**) must be governed by the steric interactions encountered by an incoming dienophile on either side of (**3**), and this must be a function of the distances between the sterically interacting groups at the transition state. Our results suggest that, at least in the *exo* region, the transition-state geometry is remarkably constant. This is in contrast to the hypothesis involving 'tighter' transition states for more reactive systems which has been proposed to explain stereoselectivity in the *endo* region.[8,9] Thus, the reactions of (**3**) lend strength to the idea that the transition-state geometry must reflect reactivity mainly by the relative orientation of the *endo* regions of the addends.[1] This would mean that in Figure 2 the angles ϕ_1 and ϕ_2 are smaller in more reactive systems (the addends are more reactant-like, *i.e.* less pyramidalized), but the angles ϕ_3 and ϕ_4 are roughly constant.

The support of this work by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Received, 29th April 1985; Com. 557

References

1 D. J. Burnell, H. B. Goodbrand, S. M. Kaiser, and Z. Valenta, *Can. J. Chem.*, 1984, **62**, 2398.
2 V. A. Mironov, T. M. Fadeeva, and A. A. Akhrem, *Dokl. Akad. Nauk SSSR*, 1967, **174**, 852.
3 S. McLean and P. Haynes, *Tetrahedron*, 1965, **21**, 2313.
4 R. S. Threlkel and J. E. Bercaw, *J. Organomet. Chem.*, 1977, **136**, 1.
5 V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, 1963, **19**, 1939.
6 V. A. Mironov, T. M. Fadeeva, V. S. Pashegorova, A. U. Stepanyants, and A. A. Akhrem, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 423; V. A. Mironov, V. S. Pashegorova, T. M. Fadeeva, Y. M. Kimel'fel'd, and A. A. Akhrem, *ibid.*, 1968, 609.
7 S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, 1976, **98**, 4054.
8 K. N. Houk and R. W. Stozier, *J. Am. Chem. Soc.*, 1973, **95**, 4094.
9 K. Seguchi, A. Sera, Y. Otsuki, and K. Maruyama, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3641.