Stereochemistry of the Diels–Alder Reaction: Steric Effects of the Dienophile on *endo*-Selectivity

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Structures are assigned to adducts of cyclopentadiene with αβ-unsaturated nitriles, ketones, and esters. Product ratios are determined for series of dienophiles which differ in their position of alkyl substitution relative to the double bond. In each series increased size of the alkyl group enhances the *endo*-selectivity of that group. This effect is attributed to non-bonding repulsive interactions in the transition state.

THE synchronous or non-synchronous nature of the Diels–Alder reaction has been discussed extensively.[1-4] The extreme views of a synchronous reaction requiring the two new bonds to be formed to an equal extent in the transition state,[5] and of a non-synchronous reaction involving a diradical intermediate [6] have given way to the suggestion of a one step mechanism in which in the transition state the two new bonds are formed to an unequal extent.[7-9] More recently discussion has centred on explanations of the regiospecificity [10,11] and *endo*-selectivity of the reaction.[12,13]

The first explanation of high *endo*-selectivity was given by the Alder rule of maximum accumulation of unsaturation.[14] Subsequently high *endo*-selectivity has been explained by secondary orbital interactions [15,16] stabilising the *endo*-transition state, more favourable geometry for primary overlap of orbitals in the *endo*-transition state,[17] and attractive van der Waals dispersion forces favouring an *endo*-product [13] or repulsive forces favouring an *endo*-product.[12] The relative importance of different factors in controlling *endo*-selectivity has been examined using both substituted dienes and substituted dienophiles but rarely have conditions been chosen to isolate the different factors.

In a series of *para*-substituted cinnamic acids electron-withdrawing substituents augment [18] the aryl *endo*-selectivity. In addition to a series of substituted cyclobutenes [19,20] remote substituents, which could not alter the steric requirements of an attacking diene, markedly influence reactivity. Such effects must be entirely due to non-steric factors. The addition of

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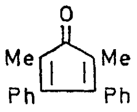
methyl methacrylate to cyclopentadiene has been recognised for sometime as an example of the failure of the *endo*-rule [21,22] and this has been attributed to steric factors. More recently two explanations for the *endo*-selectivity in this and related additions have been given. Comparison of the *endo*-selectivity in additions to 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (1) and related polysubstituted cyclopentadienes has led to the view that a repulsive non-bonding interaction between a substituent entering on the *exo*-face and a hydrogen of the methylene of a cyclopentadiene leads to a preference for *endo*-attack.[12] An alternative explanation of attractive non-bonding forces, which are important only in the *endo* transition state, has been given.[13] To clarify the importance of factors influencing *endo*-selectivity a study with cyclic dienes avoids conformational uncertainties inherent in the use of acyclic dienes. In this and the accompanying papers [23,24] we analyse the effect of alkyl substitution of both diene and dienophile upon *endo*-selectivity and regioselectivity. Here we describe the effect of varying the structure of the dienophile upon the *endo*-selectivity with cyclopentadiene. In the accompanying papers [23,24] we describe the importance of diene structure upon *endo*-selectivity and regioselectivity.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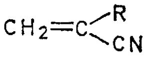
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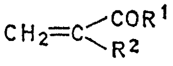
e; $R = Bu^t$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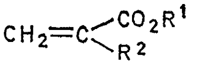
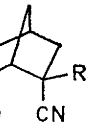
(3)

a; $R^1 = R^2 = H$
b; $R^1 = H, R^2 = Me$
c; $R^1 = Me, R^2 = H$
d; $R^1 = R^2 = Me$
e; $R^1 = Et, R^2 = H$
f; $R^1 = Et, R^2 = Me$
g; $R^1 = Pr^i, R^2 = Me$
h; $R^1 = Bu^t, R^2 = Me$


$\mathrm{CH_2{=}C}\genfrac{}{}{0pt}{}{\mathrm{CO_2R^1}}{\mathrm{R^2}}$

(4)

a; $R^1 = Me, R^2 = CN$
b; $R^1 = Et, R^2 = CN$
c; $R^1 = Pr^i, R^2 = CN$
d; $R^1 = Bu^t, R^2 = CN$
e; $R^1 = Me, R^2 = H$
f; $R^1 = Et, R^2 = H$
g; $R^1 = Pr^i, R^2 = H$
h; $R^1 = Bu^t, R^2 = H$
i; $R^1 = R^2 = Me$
j; $R^1 = Et, R^2 = Me$
k; $R^1 = Pr^i, R^2 = Me$
l; $R^1 = Bu^t, R^2 = Me$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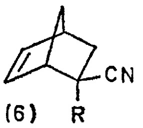
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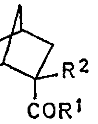
a; $R = H$
b; $R = Me$
c; $R = Et$
d; $R = Pr^i$
e; $R = Bu^t$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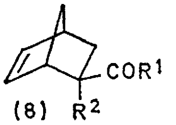
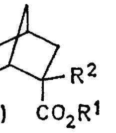

(8)

a; $R^1 = R^2 = H$
b; $R^1 = H, R^2 = Me$
c; $R^1 = Me, R^2 = H$
d; $R^1 = R^2 = Me$
e; $R^1 = Et, R^2 = H$
f; $R^1 = Et, R^2 = Me$
g; $R^1 = Pr^i, R^2 = Me$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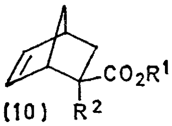
(10)

a; $R^1 = Me, R^2 = CN$
b; $R^1 = Et, R^2 = CN$
c; $R^1 = Pr^i, R^2 = CN$
d; $R^1 = Bu^t, R^2 = CN$
e; $R^1 = Me, R^2 = H$
f; $R^1 = Et, R^2 = H$
g; $R^1 = Pr^i, R^2 = H$
h; $R^1 = Bu^t, R^2 = H$
i; $R^1 = R^2 = Me$
j; $R^1 = Et, R^2 = Me$
k; $R^1 = Pr^i, R^2 = Me$
l; $R^1 = Bu^t, R^2 = Me$

Dienophiles (2a—e) with α-substitution to the double bond, dienophiles (3a—d) with β-substitution, and dienophiles (4a—l) with γ-substitution were prepared by standard methods or by suitable modifications described in the Experimental section. Adducts with cyclopentadiene were prepared at a variety of temperatures (see Experimental section) and pairs of adducts were separated by chromatography over silica gel where necessary. Structures were assigned to adducts by consideration of earlier studies, their n.m.r, spectra (discussed fully in the Experimental section), and in one case from g.l.c. analysis.

Adducts of cyclopentadiene with acrylonitrile and 2-methylacrylonitrile have been previously prepared and structures assigned.[25,26] Similarly we assign structures to the adducts of 2-ethylacrylonitrile (2c) and 2-isopropylacrylonitrile (2d) from their n.m.r. spectra. Adducts of 2-t-butylacrylonitrile were not isolated, but mass spectroscopy–g.l.c. established their formation in low yield. Respective structures were assigned by consideration of g.l.c. retention times of these and the other adducts (5a—d) and (6a—d).

Structures of adducts of cyclopentadiene with acrolein,[27] methacrolein,[28] and methyl vinyl ketone [27,29] are well established. Structures were assigned to adducts (7d—g) and (8d—g) by considering the chemical shifts of the signals associated with the protons of the substituents.

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Structures of adducts of esters of acrylic acid and methacrylic acid and their stability under the conditions of their formation were assumed on the basis of earlier studies.[21,25,30] Structures were assigned to adducts of esters of 2-cyanoacrylic acid by considering chemical shifts of the signals associated with the protons of the alkoxy-groups. In the *endo*-ester protons were shielded relative to the *exo*-ester.

TABLE 1

Product composition for Diels–Alder reactions of cyclopentadiene with substituted acrylonitriles

Dienophile	Substituent	Solvent (t/°C)	Adducts (%)		Yield (%)	Column used for g.l.c. separation t/°C
(2a)	H	Benzene (80)	(5a) 54·9	(6a) 45·1		D(120)
(2a)	H	*p*-Xylene (138)	(5a) 53·8	(6a) 46·2		
(2b)	Me	Benzene (80)	(5b) 15·9	(6b) 84·1		F(110)
(2b)	Me	*p*-Xylene (138)	(5b) 17·1	(6b) 82·9	86	
(2b)	Me	Diethyl ether (18)	(5b) 12·3	(6b) 87·7		
(2b)	Me	Diethyl ether (0)	(5b) 11·8	(6b) 88·2		
(2c)	Et	Benzene (80)	(5c) 12·3	(6c) 87·7		F(120)
(2c)	Et	*p*-Xylene (138)	(5c) 13·5	(6c) 86·5	52	
(2d)	$\mathrm{Pr^i}$	Benzene (80)	(5d) 8	(6d) 92		F(125)
(2d)	$\mathrm{Pr^i}$	*p*-Xylene (138)	(5d) 9	(6d) 91	30	
(2e)	$\mathrm{Bu^t}$	Benzene (80)	No reaction observed			
(2e)	$\mathrm{Bu^t}$	*p*-Xylene (138)	(5e) 2·4	(6e) 97·6	5	F(130)

TABLE 2

Product composition for Diels–Alder reactions of cyclopentadiene with unsaturated ketones and unsaturated aldehydes

	Substituents						
Dienophile	Alkyl	Acyl	Solvent (t/°C)	Adducts (%)		Yield (%)	Column used for g.l.c. separation (t/°C)
(3a)	H	CHO	Benzene (20)	(7a) 76·4	(8a) 23·6		D(75)
(3b)	Me	CHO	Benzene (20)	(7b) 15·4	(8b) 81·6		D(75)
(3b)	Me	CHO	Benzene (80)	(7b) 20·4	(8b) 79·6	90	
(3c)	H	COMe	Benzene (20)	(7c) 84·4	(8c) 15·6		D(80)
(3c)	H	COMe	Benzene (80)	(7c) 83	(8c) 17	80	
(3d)	Me	COMe	Benzene (20)	(7d) 35·9	(8d) 64·1		D(80)
(3d)	Me	COMe	Benzene (80)	(7d) 41·8	(8d) 58·2	73	
(3e)	H	COEt	Benzene (20)	(7e) 86	(8e) 14		D(80)
(3e)	H	COEt	Benzene (80)	(7e) 84·4	(8e) 15·6	77	
(3f)	Me	COEt	Benzene (20)	(7f) 37·3	(8f) 62·7		D(88)
(3f)	Me	COEt	Benzene (80)	(7f) 43·1	(8f) 56·9	62	
(3g)	Me	$\mathrm{COPr^i}$	Benzene (20)	(7g) 40·6	(8g) 59·4		D(88)
(3g)	Me	$\mathrm{COPr^i}$	Benzene (80)	(7g) 46·2	(8g) 53·8	50	

TABLE 3

Product composition for Diels–Alder reactions of cyclopentadiene with 2-substituted acrylate esters

Dienophile	2-Substituent	Alkyl group of ester	Solvent (t/°C)	Adducts (%)		Yield (%)	Column used for g.l.c. separation (t/°C)
(4a)	CN	Me	Benzene (40)	(9a) 74·5	(10a) 25·5	52	A(83)
(4b)	CN	Et	Benzene (40)	(9b) 75·2	(10b) 24·8	50	A(80)
(4c)	CN	$\mathrm{Pr^i}$	Benzene (40)	(9c) 78·5	(10c) 21·5	50	A(80)
(4d)	CN	$\mathrm{Bu^t}$	Benzene (40)	(9d) 83·6	(10d) 16·4	40	A(90)
(4e)	H	Me	Benzene (20)	(9e) 74·7	(10e) 25·3		
(4f)	H	Et	Benzene (20)	(9f) 75·2	(10f) 24·8		
(4g)	H	$\mathrm{Pr^i}$	Benzene (20)	(9g) 76·6	(10g) 23·4		
(4h)	H	$\mathrm{Bu^t}$	Benzene (20)	(9h) 78·2	(10h) 21·8		
(4i)	Me	Me	Benzene (20)	(9i) 31·2	(10i) 68·8		
(4j)	Me	Et	Benzene (20)	(9j) 31·8	(10j) 68·2		
(4k)	Me	$\mathrm{Pr^i}$	Benzene (20)	(9k) 32·8	(10k) 67·2		
(4l)	Me	$\mathrm{Bu^t}$	Benzene (20)	(9l) 34·0	(10l) 66·0		

Results of product studies are given in Tables 1—3. In most cases the kinetic nature of products was established; in other cases [using dienophile (2e) and acrylate esters] it is assumed. Addition to dienophiles (2a—e) and (3a—g) was examined at two temperatures and to dienophiles (4a—l) at a single temperature. Results were obtained by reaction in dilute solution in benzene, *p*-xylene, and ether; g.l.c. analyses were of crude reaction mixtures. In all cases the observed *exo* : *endo* ratios were independent of reaction time.

Increase of size of the alkyl group in the series of 2-alkylacrylonitriles enhances the *endo*-selectivity of that group. As previously noted[13] there is little selectivity with acrylonitrile (2a) but considerable selectivity with methacrylonitrile (2b). Now we note further enhancement of this selectivity with 2-ethylacrylonitrile (2c) and 2-isopropylacrylonitrile (2d) and a

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[30] R. Frazer, *Canad. J. Chem.*, 1962, **40**, 78.

marked increase with 2-t-butylacrylonitrile (2e). Yields and rates decrease with increased size of dienophile.

Increase of size of an alkyl group in the series of alkyl vinyl ketones and alkyl isopropenyl ketones enhances the *endo*-selectivity of that group; the effect is less marked than with the 2-alkylacrylonitriles but yields are again reduced with increased size of dienophile. In the three series of esters examined increased size of the alkoxycarbonyl group leads to slight enhanced *endo*-selectivity. This enhancement is more pronounced with esters of 2-cyanoacrylic acid than with esters of acrylic or methacrylic acid.

The Alder rule [14] or the Woodward–Hoffmann [15] view of secondary orbital overlap fail to account for our results. This failure could be explained by the dominance of other factors or by the conformational requirements of secondary orbital overlap which are absent in the above examples. With acrylonitrile and other αβ-unsaturated nitriles the centrosymmetric nature of the nitrile group leads to unfavourable geometry for secondary orbital overlap and therefore other factors must account for the observed products. This may partly, but we believe, not entirely, account for the low *endo*-selectivity of the nitrile group. Analysis of the role of secondary orbital overlap with the αβ-unsaturated ketones, aldehydes, or esters is complicated by conformational uncertainties. Although methyl isopropenyl ketone (3d) exists mainly in the *s-trans*-conformation [31] reaction from the *s-cis*-conformation of this and related compounds is possible as the barrier to rotation is low. Without either a knowledge of the relative reactivities, or *endo*-selectivities of the *s-cis*- or *s-trans*-conformers the role of secondary orbital overlap is in these cases less clear. However we note that in the three series of esters examined similar trends are observed. If conformational differences were responsible for these trends it would be surprising if all three series with different conformational requirements gave the same results. We conclude that the differing product ratios obtained within each series of dienophiles are explained neither by secondary orbital overlap nor by differences in the conformational equilibria of the dienophile.

Houk and Luskus [12] have compared the reactions of cyclopentadiene and 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (1) with methyl acrylate, methyl methacrylate, and methyl crotonate. Adduct ratios (*endo*-CO_2Me : *exo*-CO_2Me) with dienone (1) were methyl acrylate 17·9, methyl methacrylate 15·7, and methyl crotonate 12·2; with cyclopentadiene ratios were methyl acrylate 2·73, methyl methacrylate 0·43, and methyl crotonate 1·05. It was concluded that with dienone (1) secondary orbital overlap stabilised the *endo*-transition state but with cyclopentadiene the steric interference between methyl substituents and the methylene hydrogens [absent in (1)] led to greater amounts of *exo*-adducts. Such an explanation assumes that in dienone (1) the effect of the substituent methyl and phenyl groups and the effect of dipolar interactions between dienone and dienophile, are small. Later studies [24] with 1-methylcyclopentadiene and 2-methylcyclopentadiene show the first assumption to be questionable. *exo* : *endo*-Ratios with these dienes are different from those of cyclopentadiene. With polysubstitution, and with phenyl groups which will adopt out-of-plane conformations larger interactions would be expected. Although the importance of dipolar interactions are recognised [12] in the case of addends with highly polar groups, solvent studies suggest that such interactions cannot be neglected even in the absence of polar groups.[24] Therefore, although a sharp distinction can be made between dienone (1) and cyclopentadiene it is not clear whether this distinction arises from interaction between methyl substituent of dienophile and methylene hydrogens of cyclopentadiene, as suggested,[12] or from interactions between methyl substituents of dienophile and substituents (mainly the phenyl groups) of dienone (1). Both possibilities might account for the results and the role of dipolar interactions between the carbonyl groups is uncertain.

In considering our own studies it is clear that increased steric bulk of substituents on the dienophile destabilises *both* the *endo*- and *exo*-transition states. Alkyl substituents, both at the α- and β-positions, retard both *exo*- and *endo*-attack. However the transition state with the bulky substituent entering into the *exo*-position is the more affected. Although the effect of substitution at a γ-position upon rate is not established, results in Table 3 show that the *exo*-transition state is destabilised with respect to the *endo*-transition state. The retardation of both *exo*- and *endo*-modes of addition implies repulsive non-bonding interactions between alkyl substituent and the diene in both transition states. The observation of the decreasing importance of such interactions as the site of substitution is further removed from the double bond is consistent with this view. At the α-position replacement of hydrogen by methyl markedly influences the *endo*-selectivity [21,22,25,26,32] but replacement through the series ethyl, isopropyl, and t-butyl further influences the *endo*-selectivity (Table 1). In particular substitution by a t-butyl group leads to almost entirely *endo*-t-butyl product but both additions are very slow.

The view that *endo*-selectivity is modified by non-bonding repulsive interactions,[12] which are greater in the *exo*-transition state, accords with our observations. The alternative view of non-bonding attractive interactions [13] requires, in order to account for reduction in reactivity by alkyl substitution, and of changes in *endo* selectivity by substitution at α-, β- and γ-positions, the operation of both attractive and repulsive interactions. We prefer the former view and consider that alkyl substitution in dienophiles introduces repulsive interactions in the transition states of both

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[31] F. H. Cottee, B. J. Straughan, C. J. Timmons, W. F. Forbes, and R. Shilton, *J. Chem. Soc.* (*B*), 1967, 1146.

[32] A. I. Konovalov, G. I. Kamasheva, and M. P. Loskutov, *Doklady Akad. Nauk. S.S.S.R.*, 1972, **204**, 103.

exo- and *endo*-addition but this interaction is greater in the *exo*-transition state.*

EXPERIMENTAL

I.r. spectra were measured for chloroform solutions with a Unicam SP 200 spectrophotometer. N.m.r. spectra were measured for deuteriochloroform solutions with a Varian HA 100 spectrometer. U.v. spectra were measured for solutions in ethanol with a Unicam SP 800 spectrophotometer. Mass spectra were measured with an A.E.I. MS12 spectrometer. Analytical g.l.c. was carried out with a Perkin-Elmer F-11 chromatograph using the following columns: A, 2 m 20% TCEP on Chromosorb W; B, 2 m 15% Ucon on Chromosorb W; C, 2 m 25% γ-nitro-γ-methylpimelonitrile on Chromosorb W; D, 2 m 17% TCEP on Chromosorb W; E, 2 m 15% PPG on Chromosorb W; F, 2 m 20% Ucon on Chromosorb W; and G, 2 m 20% XE60 on Chromosorb G. Preparative g.l.c. was carried out with a Pye–Unicam 105 chromatograph using columns of 3/8 in internal diameter. cyclopentadiene was obtained by cracking dicyclopentadiene at 170° and was stored in a dry ice-bath. The following dienophiles were commercially obtained and distilled before use: acrylonitrile, methacrylonitrile, acrolein, methacrolein, methyl vinyl ketone, ethyl vinyl ketone, methyl isopropenyl ketone, methyl acrylate, and methyl methacrylate. Full details of the n.m.r. spectra of the adducts are presented later. Unless otherwise stated all adducts were shown to be stable under the reaction conditions of their formation: in no case was epimerisation observed.

Synthesis of Dienophiles.—2-Ethylacrylonitrile (2c), b.p. 112—113°, was prepared in 60% yield by heating 2-cyanobutyric acid [33] (7·25 g), dimethylammonium hydrochloride (5·25 g), and 37% aqueous formaldehyde solution (6·1 ml) under reflux for 3 h and isolating the product by ether extraction. Similarly 2-isopropylacrylonitrile (2d), b.p. 125—127° was prepared in 41% yield from 2-cyano-3-methylbutyric acid.[33] 2-t-Butylacrylonitrile (2e), b.p. 73—75° at 80 mmHg was prepared in 38% yield by dehydration of 2-cyano-3,3-dimethylbutan-2-ol with phosphorus oxychloride in pyridine. Ethyl isopropenyl ketone (3f), b.p. 120—121°, was prepared in 44% yield by heating diethyl ketone (38·7 g), dimethylammonium hydrochloride (40·5 g), and 37% aqueous formaldehyde solution (40 ml) at 80° for 18 h and isolating the product by steam distillation and ether extraction of the distillate. Similarly isopropyl isopropenyl ketone (3 g), b.p. 126—127°, was prepared in 44% yield from ethyl isopropyl ketone by reaction at 85° for 72 h. The attempted preparation of the ketone (3h) by this route failed. Ethyl 2-cyanoacrylate (4b) was prepared according to the method of Ardus [34] and was used directly. Similarly esters (4a), (4c), and (4d) were prepared. Esters (4f—h) and (4j—l) were prepared by reaction of the appropriate acid chloride and alcohol in pyridine, were isolated by extraction with ether, and were distilled before use.

TABLE 4

N.m.r. data for adducts of cyclopentadiene

Compound	τ Values 1-H	4-H	3_{ex}-H	3_{en}-H	5- and 6-H	7_a- and 7_s-H	2_{ex}-Substituent	2_{en}-Substituent
(5a) [a]	6·83	7·03	7·90	8·80	3·70, 3·85	8·60, 8·80	6·15	
(5b) [b]	7·20	7·04	~8·35	~8·35	3·73	~8·35	8·48	
(5c)	7·08	7·08	~8·40	~8·40	3·74	~8·40	~8·20, 8·91	
(5d)	6·98	7·08	~8·45	~8·45	3·74	~8·45	7·36, 8·87, 8·91	
(6a) [a]	6·82	6·98	8·08	8·50	3·80, 3·97	8·45, 8·57		7·82
(6b) [b]	6·98	7·06	7·73	8·95	3·78, 4·02	8·22, 8·35		8·80
(6c)	6·93	7·08	7·80	~8·40	3·79, 4·05	8·32, 8·38		~8·40, 8·98
(6d)	6·86	7·07	7·82	~8·45	3·78, 4·04	8·73, 8·82		8·30, 8·97, 8·99
(7b)	7·32	7·20	8·15	8·65	3·83	8·41, 8·52	8·75	0·66
(7c)	6·78	7·12	8·22	8·42	3·90, 4·19	8·59, 8·66	7·04	7·90
(7e)	6·80	7·13	8·21	8·41	3·80, 4·22	8·59, 8·66	7·02	7·59, 8·99
(7d)	7·22	7·22	8·03	8·67	3·93, 4·04	8·42, 8·51	8·66	7·93
(7f)	7·22	7·22	7·99	8·68	3·92, 4·06	8·42, 8·51	8·67	7·57, 9·01
(7g)	7·23	7·24	8·10	8·66	3·99	8·46, 8·56	8·67	7·16, 9·01, 9·05
(8b)	7·20	7·20	7·77	9·29	3·76, 3·94	8·54, 8·66	0·37	9·03
(8c)	7·03	7·13	8·13	8·80	3·90	8·67, 8·67	7·81	7·64
(8e)	7·09	7·09	8·15	~8·40	4·09	8·67, 8·76	7·51, 8·95	~7·63
(8d)	7·05	7·25	7·62	9·27	3·79, 3·94	8·68, 8·78	7·82	8·95
(8f)	7·02	7·23	7·62	9·27	3·79, 3·95	8·65, 8·78	7·45, 8·94	8·96
(8g)	6·97	7·24	7·57	9·28	3·77, 3·95	8·67, 8·82	6·95, 8·94	8·95

[a] Ref. 25. [b] Ref. 26.

Reaction of Dienophiles with Cyclopentadiene.—Adducts were prepared as shown in Tables 1—3. For example methacrylonitrile (2b) (3·58 g) and cyclopentadiene (3·58 g) were heated [35] under reflux in *p*-xylene (70 ml) for 16 h. Pairs of adducts were separated by chromatography on

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* A Referee has commented that ' inductive effects must play a considerable part ' since in the light of recent results (E. T. McBee, M. J. Keogh, R. P. Levek, and E. P. Wesseler, *J. Org. Chem.*, 1973, **38**, 632) they might be expected to reproduce the observed trends. Although the experimentally determined differences in free energy $\delta\Delta G^{\ddagger}$ between the transition states leading to epimeric adducts are always small (<1 kcal mol^{-1}) we observe that *endo*-selectivity is influenced by the nature of the alkyl substituent at branching points α, β, and γ to the double bond of the dienophile. It is probable that inductive effects of the type suggested by McBee *et al.* will contribute to the observed selectivity of dienophiles branched at the α-position. There is no evidence to suggest that such effects ' play a considerable part ' in those dienophiles branched at the β- or γ-position. Our results establish that increasingly bulky dienophiles suffer a major reduction in rate of both *endo*- and *exo*-modes of addition, an effect which we attribute to steric repulsion and which is greater in the *exo*-transition state.

[33] J. Kovas and C. S. Marvel, *J. Polymer Sci.*, 1967, 563.

[34] A. E. Ardus, U.S.P. 2,467,926 (*Chem. Abs.*, 1949, **43**, 6222).

[35] W. Kraus and P. Schutte, *Tetrahedron*, 1968, **24**, 1537.

silica gel and individual adducts were characterised (i.r., n.m.r., and mass spectra.

N.m.r. Spectra of Adducts.—Structures were assigned to adducts of dienophiles (2a—e), (3a—g), and (4a and b) by a consideration of their spectra (see Table 4). Noteworthy features which facilitated assignments were the relative chemical shifts of 3_{ex}-H and 3_{en}-H and the relative chemical shifts of protons of an *endo*- and of an *exo*-substituent. The data accord with related studies.[25,26]

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