Stereochemistry of the Diels–Alder Reaction: Reaction of Dienophiles with Cyclopentadiene and Methylcyclopentadiene

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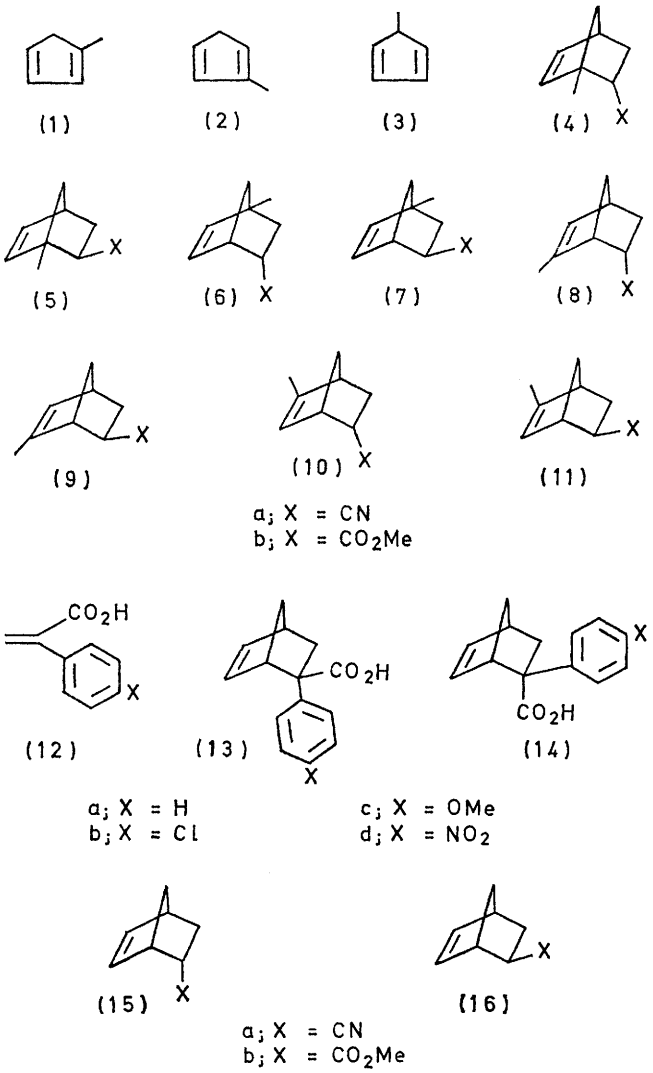
Structures are assigned to adducts of 1-methylcyclopentadiene and 2-methylcyclopentadiene with acrylonitrile and methyl acrylate. Reactions with 1-methylcyclopentadiene are highly regiospecific but 2-methylcyclopentadiene has lower regiospecificity. Methyl acrylate shows similar *endo*-selectivity with cyclopentadiene and methylcyclopentadienes but acrylonitrile shows little selectivity and in one case preferentially gives an *exo*-adduct. Effects of solvent on regiospecificity and *endo*-selectivity are examined. The relative importance of *endo*-selectivity of steric effects, secondary orbital overlap, and electronic effects are discussed. The importance of electronic effects are illustrated in additions of cyclopentadiene to 2-arylacrylic acids.

STUDY of regiospecificity and *endo*-selectivity in the Diels–Alder reaction of 1- and 2-substituted dienes has mainly concerned 1-substituted butadienes [1-5] where both the regiospecificity and *endo*-selectivity of additions may be observed and 2-substituted butadienes [2,6-8] where only the regiospecificity can be observed. If, as suggested, the Diels–Alder reaction proceeds by a non-synchronous bond-forming process then studies of specificity with acyclic dienes may be complicated by the conformational flexibility of the diene, absent with cyclic dienes. Earlier studies [1-8] have assumed the absence of such complications in the transition state and activation volume studies [9] clearly establish that such effects are not large. However, as the factors dictating the regiospecificity and *endo*-selectivity are delicately balanced small conformational factors may affect transition state energies. Such complications are absent in cyclic dienes and we chose to examine the reactions of 1-methyl- (1) and 2-methylcyclopentadiene (2). If the transition state were product-like then 1-methylcyclopentadiene (1) should have enhanced *endo*-selectivity relative to cyclopentadiene, because of the near eclipsing of the 1- and 2-*exo*-substituent bonds. It has been suggested [10] that steric interactions between the 2-substituent of 2-substituted cyclopentadienes and the dienophile might destabilise the *endo*-transition state. Such interactions have not been proved. To examine such effects we describe a study of addition of acrylonitrile and methyl acrylate to methylcyclopentadienes. We conclude by discussing the factors controlling regiospecificity and *endo*-selectivity and present experimental studies with 2-arylacrylic acids to establish the importance of electronic factors.

Studies with methylcyclopentadiene are complicated by the ready interconversion of the methylcyclopentadienes (1)—(3) at room temperature.[11] Reaction of a monosubstituted dienophile above this temperature may be expected to lead to a complex mixture of 12



adducts, four from each diene. However the equilibrium percentage of 5-methylcyclopentadiene (3) is low [11] and we find that addition of acrylonitrile and of methyl acrylate leads only to adducts of 1-methyl-

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(1) and 2-methyl-cyclopentadiene (2). To determine the structure of the products methyl acrylate or acrylonitrile was treated with the equilibrium mixture of dienes at 80°, and a non-equilibrium mixture enriched in 1-methylcyclopentadiene (1) at −30° and in each case the products were partially separated by preparative g.l.c.

Acrylonitrile at 80° gave a mixture of the eight adducts (4a)—(11a) which could be completely analysed using two separate g.l.c. capillary columns. Preparative g.l.c. gave pure samples of adducts (4a), (5a), (8a), (10a), and (11a) and mixtures of adducts (5a) and (7a) and of (4a) and (9a). By preparative g.l.c. of the reaction of acrylonitrile with impure 1-methylcyclopentadiene (1) at −30° a pure sample of the remaining adduct (6a) was isolated. Structures of the six pure adducts were assigned from their n.m.r. spectra (discussed in the Experimental section). Equilibration of each adduct confirmed the assignment and indicated the structures of adducts (7a) and (9a), which were in accord with the structures tentatively assigned from the n.m.r. spectra of the mixtures (5a) and (7a), and (4a) and (9a). In the equilibration of each pair of epimers equilibrium was approached from both sides and in the products of reaction only equilibration of epimers was observed.[12]

Methyl acrylate at 90° gave a mixture of the eight adducts (4b)—(11b) which could be completely analysed using two separate g.l.c. capillary columns. Preparative g.l.c. gave pure samples of adducts (4b), (5b), (8b), (10b), and (11b) and a mixture of (5b) and (7b). By preparative g.l.c. of the products of methyl acrylate with impure 1-methylcyclopentadiene (1) at −30° (6b) was isolated. With the exception of (7b) and (9b) structures were assigned from the n.m.r. spectra of the adducts (discussed in the Experimental section). Equilibration of (6b) with (7b), and of (8b) and (9b) led to assignment of the remaining structures.

TABLE 1

Product composition for reaction of methylcyclopentadiene with methyl acrylate and acrylonitrile

			% of total products							
Dienophile	Solvent	t/°C	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Acrylonitrile	Decalin	18	15·3	25·3	3·7	2·5	11·2	4·0	20·4	17·6
Acrylonitrile	Benzene	18	15·4	24·1	3·6	2·2	11·6	4·2	21·4	17·5
Acrylonitrile	Benzene	80	14·3	19·5	3·3	2·4	12·8	6·6	22·4	18·7
Acrylonitrile	1,2-Dimethoxyethane	18	16·2	20·8	3·5	2·1	11·8	4·9	23·4	17·3
Acrylonitrile	Methanol	18	18·0	15·8	3·6	1·8	11·4	5·8	25·0	16·6
Acrylonitrile	Gas phase	18	16·4	19·1	4·0	2·3	12·0	4·7	22·6	18·9
Methyl acrylate	Decalin	18	27·2	12·1	6·1	1·8	11·8	2·8	30·0	8·2
Methyl acrylate	Benzene	18	27·2	9·4	3·5	1·4	12·5	2·5	35·3	8·2
Methyl acrylate	Benzene	80	21·9	7·9	3·5	1·2	14·8	4·0	34·6	12·1
Methyl acrylate	1,2-Dimethoxyethane	18	27·4	8·5	3·1	1·2	13·6	2·1	36·8	7·3
Methyl acrylate	Methanol	18	34·1	5·7	3·2	0·8	11·3	1·7	37·5	5·7

TABLE 2

Regioselectivity and *endo*-selectivity in reactions of acrylonitrile and methyl acrylate with 1- and 2-methylcyclopentadiene

			Regioselectivity (ratios)		*endo*-Selectivity (ratios)			
Dienophile	Solvent	t/°C	(4) + (5) : (6) + (7)	(8) + (9) : (10) + (11)	(4) : (5)	(6) : (7)	(8) : (9)	(10) : (11)
Acrylonitrile	Decalin	18	86·6 : 13·4	28·6 : 71·4	37·7 : 62·3	59·7 : 40·3	73·7 : 26·3	53·7 : 46·3
Acrylonitrile	Benzene	18	87·2 : 12·8	28·9 : 71·1	39·0 : 61·0	62·1 : 37·9	73·4 : 26·6	56·0 : 44·0
Acrylonitrile	Benzene	80	85·5 : 14·5	32·1 : 67·9	42·3 : 57·7	57·9 : 42·1	66·0 : 34·0	54·5 : 45·5
Acrylonitrile	1,2-Dimethoxyethane	18	86·8 : 13·2	29·1 : 70·9	43·8 : 56·2	62·5 : 37·5	70·7 : 29·3	57·5 : 42·5
Acrylonitrile	Methanol	18	86·2 : 13·8	31·6 : 68·4	53·3 : 46·7	66·7 : 33·3	65·9 : 34·1	60·3 : 39·7
Acrylonitrile	Gas phase	18	84·9 : 15·1	28·7 : 71·3	46·2 : 53·8	63·5 : 36·5	71·8 : 28·2	54·4 : 45·6
Methyl acrylate	Decalin	18	83·3 : 16·7	27·7 : 72·3	69·7 : 30·3	77·0 : 23·0	82·1 : 17·9	78·5 : 21·5
Methyl acrylate	Benzene	18	88·2 : 11·8	25·7 : 74·3	74·3 : 25·7	71·4 : 28·6	83·3 : 16·7	81·4 : 18·6
Methyl acrylate	Benzene	80	86·4 : 13·6	28·7 : 71·3	73·4 : 26·6	74·5 : 25·5	78·7 : 21·3	74·1 : 25·9
Methyl acrylate	1,2-Dimethoxyethane	18	89·3 : 10·7	26·3 : 73·7	76·4 : 23·6	72·1 : 27·9	86·6 : 13·4	83·4 : 16·6
Methyl acrylate	Methanol	18	90·9 : 9·1	23·1 : 76·9	85·7 : 14·3	80·0 : 20·0	86·9 : 13·1	86·8 : 13·2

Product distributions for reactions of methylcyclopentadiene are given in Table 1, the regioselectivity and *endo*-selectivity in Table 2, and equilibration results in Table 3. Reaction of methylcyclopentadiene with acrylonitrile and with methyl acrylate was examined in a number of solvents and reaction with acrylonitrile in the gas phase. Products were determined by g.l.c. (capillary columns). By analysis on two different columns all products except (9a) gave peaks with base line separation. Determinations of the ratio (8a) : (9a) and of (6) : (7), because of the low yield of adducts (6) and (7), were less accurate than other ratios but in all cases results were reproducible within 0·2%.

We analyse the results considering (a) the relative

[12] J. M. Mellor and C. F. Webb, *Tetrahedron Letters*, 1971, 4025.

percentage of products from 1-methyl- (1) and 2-methylcyclopentadiene (2), (b) the regiospecificity of the additions, and (c) the *endo*-selectivity of the additions.

TABLE 3

Product composition of adducts after equilibration

Reactant	Product composition *endo*-Adduct (%)	*exo*-Adduct (%)	Reactant	Product composition *endo*-Adduct (%)	*exo*-Adduct (%)
(4a)	63·6	36·4	(5a)	63·6	36·4
(6a)	49·2	50·8	(7a)	49·2	50·8
(8a)	49·2	50·8			
(10a)	51·6	48·4			
(15a) [a]	51	49	(16a) [a]	52	48
(4b)	60·3	39·7	(5b)	60·3	39·7
(6b)	50·2	49·8	(7b)	50·2	49·8
(8b)	49·9	50·1			
(10b)	49·9	50·1			
(15b) [b]	47·7	52·3	(16b) [b]	47·7	52·3

[a] P. Wilder and D. B. Knight, *J. Org. Chem.*, 1965, **30**, 3078. [b] R. J. Oullette and G. E. Booth, *J. Org. Chem.*, 1965, **30**, 423.

(a) A variable temperature n.m.r. study of the methylcyclopentadienes showed that the ratio (1) : (2) was insensitive to temperature. At 27° the ratio was 48·7 : 51·3 and at 56° 49·5 : 50·5. In benzene at 18° with acrylonitrile products (4a)—(7a) (45%) came from 1-methylcyclopentadiene (1) and products (8a)—(11a) (55%) from 2-methylcyclopentadiene (2). With methyl acrylate the ratio of products from (1) and (2) under similar conditions was 41·5 : 58·5. Hence addition to 2-methylcyclopentadiene (2) is slightly faster than addition to 1-methylcyclopentadiene (1). The relative reactivity of dienes (1) and (2) is little affected by solvent.

This result compares with the greater reactivity of penta-1,3-diene relative to 2-methylbutadiene,[13] and the conclusion [14] derived from an MO treatment that electron-releasing substituents at the 1-position should lead to a greater rate enhancement than 2-substituents in the normal Diels–Alder reaction.

(b) In benzene at 18° the additions of both acrylonitrile and methyl acrylate to 1-methylcyclopentadiene (1) have high regioselectivity. Additions to 2-methylcyclopentadiene (2) are less specific, but in additions to both dienes (1) and (2) acrylonitrile has similar regioselectivity to that of methyl acrylate. A change of solvent only slightly influences the regioselectivity, but the results, which are significant and not attributable to experimental errors, show that the regioselectivity of methyl acrylate additions increases with increased solvent polarity. Comparison with the reported regiospecificities of additions to penta-1,3-diene and 2-methylbutadiene is difficult because in earlier studies [1-3] less accurate methods of product analysis were available, and the extent to which the observed temperature dependences might be attributed to formation of non-kinetic products is not clear. Our results with methylcyclopentadienes are similar to the reported regiospecificities of the acyclic dienes.[15] The results substantiate the direction of addition predicted [16] on the basis of primary orbital overlap, and more recently on the Pearson ' hard and soft ' concept [17] applied to a non-synchronous addition.[18] Further they substantiate the prediction [16] that regioselectivity will be greater with 1-methyl- (1) than with 2-methyl-cyclopentadiene (2) but are in disagreement with the prediction [16] that methyl acrylate would be much more selective than acrylonitrile.

(c) With cyclopentadiene *endo*-selectivity is greater with methyl acrylate (ratio 80 : 20 [19] in 1,2-dimethoxyethane at 3°) than with acrylonitrile (ratio 57·5 : 42·5 [20] in an excess of cyclopentadiene at 25°). In all the possible modes of addition to dienes (1) and (2) methyl acrylate has greater *endo*-selectivity than acrylonitrile. Further, in addition of acrylonitrile to give adducts (4a) and (5a) with diene (1) in benzene, decalin, and 1,2-dimethoxyethane the preferred product is the *exo*-adduct (5a). In all other cases acrylonitrile gives the *endo*-adduct preferentially. Careful analysis shows that in addition to give adducts (6) and (7) and to give adducts (10) and (11) *endo*-selectivity is close to that observed with cyclopentadiene. In addition to give (4) and (5) more *exo*-product is formed than in comparable reactions with cyclopentadiene and in addition to give (8) and (9) more *endo*-product is formed. The observed solvent effects in which increased solvent polarity enhances the *endo*-selectivity are similar to those reported in the detailed study of addition of methyl acrylate to cyclopentadiene.[19] However, increased solvent polarity has little effect on the ratio of (8b) to (9b) and with adducts (8a) and (9a) increased solvent polarity decreases *endo*-selectivity.

Reactions of methyl acrylate and acrylonitrile at 80° have reduced regiospecificity and *endo*-selectivity [*exo*-selectivity with (4a) and (5a)] compared with reactions at 18°. In the gas phase acrylonitrile gave products (4a)—(11a) of similar composition to those obtained in hydrocarbon solvents.

Discussion of the factors determining regiospecificity and *endo*-selectivity must concern a number of possible effects. Before discussing the relative importance of these effects the reaction of cyclopentadiene with a series of 2-arylacrylic acids is described.

2-Arylacrylic acids (12a—d), with cyclopentadiene gave adducts (13a—d) and (14a—d). Adducts (13a) and (14a) have been assigned structures earlier [21] and were conveniently analysed as a mixture by integration of 1-H at τ 5·83 for adduct (13a) and at τ 6·06 for adduct (14a). Adducts (13b) and (14b) gave signals

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[20] Y. Kobuke, T. Fueno, and J. Furukawa, *J. Amer. Chem. Soc.*, 1970, **92**, 6548.
[21] K. Alder, W. Gunfz, and K. Wolf, *Chem. Ber.*, 1960, **93**, 809.

for 1-H at τ 5·85 and 6·10 respectively, adducts (13c) and (14c) at 5·84 and 6·07, and adducts (13d) and (14d) at 5·84 and 6·07. At 80° in benzene the following ratios were obtained: (13a) : (14a) 47·9 : 52·1 (13b) : (14b) 52·4 : 47·6, (13c) : (14c) 45·5 : 54·5, and (13d) : (14d) 58·2 : 41·8. In all reactions yields were high (>90%) and products did not equilibrate under the conditions of their formation. Reaction of 2-arylacrylic acid (12a) with methylcyclopentadiene gave after treatment of the reaction mixture with diazomethane a mixture of esters which could not be analysed by g.l.c. The results establish that an electron-withdrawing substituent enhances *endo*-selectivity and the magnitude of the effect is proportional to the Hammett σ value in this series of arylacrylic acids. Our results show that with 1,1-disubstituted dienophiles electron withdrawal by a group augments the *endo*-selectivity of that group. Similar results have been observed with 1,2-disubstituted dienophiles.[22-24] Earlier [25,26] we have shown that steric effects are important. Neither regiospecificity nor *endo*-selectivity of addition of acrylonitrile to methylcyclopentadiene is markedly influenced by steric factors. The addition to give adducts (4a) and (5a) has high regiospecificity but in the opposite sense from that predicted on steric grounds. Comparison of the ratio (4a) : (5a) with the ratio (6a) : (7a) shows that the transition state occurs too early to be affected by the destabilising, near-eclipsing interaction of the 1- and 2-*exo*-substituent bonds. Equilibration studies indicate that the transition states are not influenced by the relative thermodynamic stability of the adducts. We consider the high regiospecificity of addition of acrylonitrile to be due to the polarisation of the diene and the low *endo*-selectivity to the lack of importance of steric factors and secondary orbital overlap. The changes of *endo*-selectivity in the different modes of addition are attributed to minor effects. A repulsive steric interaction between methyl group and nitrile group in the *endo*-transition state leading to adduct (4a) accounts for preferred addition to give adduct (5a). The greater *endo*-selectivity to give adduct (8a) is attributed to the particularly favoured dipolar interaction in the transition state.

Regiospecificity in methyl acrylate additions is attributed to polarisation of the diene, in accord with the similarity of products from acrylonitrile and methyl acrylate. The same trends in *endo*-selectivity are observed, only modified by the greater preference in all cases of methyl acrylate for *endo*-addition. The respective roles of secondary orbital overlap and so-called electronic effects remain to be evaluated. The electronic effects may either directly influence the primary orbital overlap to alter the *endo*-selectivity or alter the magnitude of dipolar interactions in the transition states. It is noted that our solvent studies show that *endo*-selectivity is changed more than regiospecificity by enhanced solvent polarity. This suggests that a factor influencing *endo*-selectivity and which is solvent dependent is of little importance in determining regiospecificity. As the solvent dependence is observed with acrylonitrile, where secondary orbital overlap is unimportant, our results suggest that in both additions of methyl acrylate and acrylonitrile dipolar interactions are important in determining *endo*-selectivity. This result accords with earlier conclusions concerning additions to cyclopentadiene,[19] and indicates that results of addition to halogenodienes and dienones, where dipolar interactions will be large, should not be used to substantiate the factors governing addition to cyclopentadiene and other simple dienes.

In conclusion we attribute the high regiospecificities to primary orbital overlap, the low *endo*-selectivity with acrylonitrile to the absence of significant steric factors or secondary orbital overlap, and the moderate *endo*-selectivity of methyl acrylate to a greater importance of secondary orbital overlap.

Our results confirm the contribution of a number of factors to the control of stereochemistry in the Diels–Alder reaction. Regiospecificity is controlled by primary orbital overlap. *endo*-Selectivity is controlled by a combination of secondary orbital overlap, repulsive non-bonding interactions, particularly important in for example spiro[2,4]hepta-1,3-diene,[26] and dipolar interactions. This study with methylcyclopentadienes shows that minor changes in diene structure can influence *endo*-selectivity and cautions against comparisons made with dienes such as tetracyclone where large substituent effects will operate.

EXPERIMENTAL

For general details see ref. 25.

Reaction of Methylcyclopentadienes with Acrylonitrile.—Methylcyclopentadiene (7·55 g) and acrylonitrile (5·0 g) were heated under reflux in benzene (150 ml) for 16 h. Removal of the solvent under reduced pressure and then distillation gave a mixture of methylbicyclo[2.2.1]hept-5-ene-2-carbonitriles, b.p. 112—116° at 60 mmHg, $\nu_{max.}$ 3060, 2970, 2870, 2255, 1628, 1451, 1422, 1388, 1342, 1282, 1261, 1137, 1084, 932, 831, 728, and 717 cm^{-1}, in 98% yield. G.l.c. analysis of the crude reaction mixture on a 50 ft TCEP coated capillary column at 106° showed 19·5% (5a), 2·4% (7a), 20·9% (4a) + (9a), 18·7% (11a), 12·8% (8a), 3·3% (6a), and 22·4% (10a) with R_t 26·0, 27·8, 39·4, 41·8, 45·4, 46·8, and 58·7 min respectively. Analysis on a 50 ft EGA coated capillary column at 110° showed 19·5% (5a), 2·4% (7a), 14·3% (4a), 41·4% (6a) + (8a) + (9a) + (11a), and 22·4% (10a) with R_t 13·6, 14·4, 18·0, 21·4, and 26·0 min respectively. Preparative g.l.c. on a 15 ft 10% TCEP on Chromosorb W column at 115° gave pure (4a), (5a), (8a), (10a), and (11a) and mixtures of (5a) and (7a) and of (4a) and (9a). Mass spectroscopy–g.l.c. showed each adduct had *m/e* 133 (M^+), 118 (M − 15) 105 (M − C_2H_4N), and 80 (M − C_3H_3N).

1-Methylcyclopentadiene was reacted with acrylonitrile

[22] F. Kaplan and H. Conroy, *J. Org. Chem.*, 1963, **28**, 1593.
[23] C. D. Ver Nooy and C. S. Rondestvedt, *J. Amer. Chem. Soc.*, 55, **77**, 3583, 4878.
[24] P. C. Jain, Y. N. Kukerjee, and N. Anand, *Chem. Comm.*, 1971, 303.
[25] J. M. Mellor and C. F. Webb, *J.C.S. Perkin II*, 1974, 17.
[26] B. C. C. Cantello, J. M. Mellor, and C. F. Webb, preceding paper.

at −30° to give after column chromatography on silica gel a mixture of adducts (4a)—(7a). Preparative g.l.c. afforded (6a) and (7a).

The products of addition of acrylonitrile to methylcyclopentadienes in a variety of solvents and also in the gas phase were examined: the results are presented in Tables 1 and 2. Typically a solution of methylcyclopentadiene (0·00313M) and acrylonitrile (0·00313M) in methanol was analysed by g.l.c. after 16 h at 18°.

Equilibration of Methylbicyclo[2.2.1]*hept-5-ene-2-carbonitriles.*—Adduct (4a) (33 mg) was heated under reflux in t-butyl alcohol (5 ml) containing potassium t-butoxide (4 mg) for 26 h. The cold solution was poured into an equal volume of water and extracted with light petroleum (b.p. <40°) (3 × 10 ml). The combined organic extracts were washed with water and dried ($MgSO_4$). Removal of the solvent afforded (4a) (36·4%) and (5a) (63·6%). Reaction under similar reaction conditions for 48 h gave (4a) (36·4%) and (5a) (63·6%). Adduct (5a) when similarly treated gave (4a) (36·4%) and (5a) (63·6%). Other adducts were equilibrated in a similar manner: results are presented in Table 3.

Reaction of Methylcyclopentadienes with Methyl Acrylate.—Methylcyclopentadienes (2·8 g) and methyl acrylate (3·0 g) were heated under reflux in benzene (60 ml) for 16 h. Removal of the solvent under reduced pressure and then distillation gave a mixture of methyl bicyclo[2.2.1]hept-5-ene-2-carboxylates, b.p. 90—91° at 18 mmHg, $\nu_{max.}$ 3050, 2960, 2860, 1732, 1629, 1440, 1392, 1353, 1331, 1273, 1254, 1193, 1175, 1108, 1057, 1028, 954, 906, 878, 850, 821, 785, 762, 712, and 683 cm^{-1}, in 88% yield. G.l.c. analysis of the crude reaction mixture on a 50 ft TCEP coated capillary column at 91° showed 7·9% (5b), 21·9% (4b), 1·2% (7b), 3·5% (6b), 4·0% (9b), 14·8% (8b), and 46·7% (10b) + (11b) with R_t 17·2, 18·8, 23·6, 26·1, 27·7, 30·2, and 33·0 min, respectively. Analysis on a 50 ft EGA coated capillary column at 96° showed 12·1% (11b) and 34·6% (10b) with R_t 16·2 and 14·6 min respectively. Mass spectroscopy–g.l.c. showed each adduct had *m/e* 166 (M^+), 135 ($M - CH_3O$), 107 ($M - C_2H_3O_2$), 91 ($M - C_5H_5$), and 80 ($M - C_3H_6O_2$). Preparative g.l.c. on a 30 ft 10% Ucon on Chromosorb W column at 117° gave pure (4b), (5b), 10b), and (11b) and on a 30 ft 20% TCEP on Chromosorb W column at 126° gave pure (8b) and a mixture of (4b) and (6b).

1-Methylcyclopentadiene was reacted with methyl acrylate at −30° to give after chromatography on silica gel a mixture of adducts (4b)—(7b). Preparative g.l.c. afforded pure (6b).

The products of addition of methyl acrylate to methylcyclopentadiene in a variety of solvents were examined: the results are presented in Table 3.

Equilibration of Methyl Bicyclo[2.2.1]*hept-5-ene-2-carboxylates.*—Adduct (4b) (30 mg) was heated in a sealed tube with sodium methoxide in dry methanol (3 ml; 0·15M in sodium methoxide) for 296 h at 100°. The cold solution was poured into an equal volume of water and extracted as described above for the nitriles. G.l.c. analysis showed (5b) 39·7% and (4b) 60·3%. Adduct (4b) when similarly treated gave (5b) 39·7% and (4b) 60·3%. Other adducts were equilibrated in a similar manner: results are presented in Table 3.

2-*Arylacrylic acids.*—2-Phenylacrylic acid (12a), m.p. 106—107° (lit.,[27] m.p. 106—107°) was prepared as described [27] from 2-hydroxy-2-phenylpropionic acid. Similarly 2-*p*-chlorophenylacrylic acid (12b), m.p. 107—108° (lit.,[28] m.p. 107—109°) and 2-*p*-methoxyphenylacrylic acid (12c), m.p. 117—119° (lit.,[29] m.p. 118—119°) were prepared. 2-*p*-Nitrophenylacrylic acid (12d), m.p. 177—178° (lit.,[30] m.p. 176—177°) was prepared in 15% yield by the method of Gupta and Seshadri.[29]

Reaction of 2-*Arylacrylic Acids with Cyclopentadiene.*—2-Phenylacrylic acid and cyclopentadiene were heated under reflux in benzene for 90 min. Acid products were extracted into saturated sodium hydrogen carbonate solution. Acidification and extraction with ether gave an extract which was washed with water, dried (Na_2SO_4), and the ether removed to give adducts (13a) and (14a) in 91% yield. The adducts were separated by the iodolactone route to give (13a), m.p. 135—136·5° (lit.,[21] m.p. 137°), $\nu_{max.}$ 2630, 1703, and 1605 cm^{-1}, *m/e* 214 (M^+) and (14a) m.p. 130—131·5° (lit.,[21] m.p. 132°), $\nu_{max.}$ 2620, 1704, and 1602 cm^{-1}, *m/e* 214 (M^+). Similarly 2-*p*-methoxyphenylacrylic acid (12c) gave adducts (13c) and (14c) in 96% yield, 2-*p*-chlorophenylacrylic acid (12b) gave adducts (13b) and (14b) in 91% yield, and 2-*p*-nitrophenylacrylic acid (12d) gave adducts (13d) and (14d) in 94% yield. Adducts (13a) and (14a) were separately heated under reflux in benzene for 48 h and were recovered unchanged. The stability of the other adducts was assumed. The composition of the crude reaction mixtures was estimated by n.m.r. spectroscopy (see Discussion section).

N.m.r. Spectra of Adducts of Methylcyclopentadiene (*Table* 4).—Adducts of 1-methylcyclopentadiene could be distinguished from adducts of 2-methylcyclopentadiene by the number of olefinic resonances, and confirmed by the number of resonances attributable to bridgehead protons, and by the position of the methyl resonance at τ 8·45—8·75 in adducts of 1-methylcyclopentadiene and at τ 8·10—8·35 in adducts of 2-methylcyclopentadiene. Adducts of 5-methylcyclopentadiene would be expected to give a signal near τ 9·0 with *J* 7·0 Hz, but in no case was this observed. *endo*-Adducts were distinguished from *exo*-adducts by the position of 2-H, which in *endo*-adducts occurs at lower field by *ca.* 50 Hz. This assignment was confirmed in the case of adducts of methyl acrylate by a corresponding shift in the position of the signal associated with the ester group to higher field in the *endo*-adducts. Further confirmation is given by observation of $J_{2ex,3ex}$ 8·5—9·5 Hz in all *endo*-adducts. Distinction between pairs of *endo*-isomers of adducts of 1-methylcyclopentadiene was made by observation of $J_{1,2ex}$ and $J_{3ex,4}$. Adduct (4a) had $J_{3ex,4}$ 4 Hz but no similar coupling to 2_{ex}-H was observed. Hence the *endo*-isomers could be assigned unambiguously. Equilibration of each *endo*-adduct to give the corresponding *exo*-adduct enabled structures to be assigned to the *exo*-adducts.

Distinction between pairs of *endo*-isomers of adducts of 2-methylcyclopentadiene is not possible by consideration of coupling constants. However, decoupling experiments established that in adduct (10a) the bridgehead proton at τ 6·90 was coupled with the olefinic proton at τ 4·30 but the bridgehead proton at τ 7·30 was coupled with

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TABLE 4
N.m.r. data for adducts of methylcyclopentadiene

	τ Values										
Compound	1-H	4-H	2_{ex}-H	2_{en}-H	3_{ex}-H	3_{en}-H	5-H	6-H	7_a- and 7_s-H	Me	CO_2Me
(4a)		7·07	7·41		7·86	8·59	3·71	4·04	8·6—8·8	8·53	
(5a)		7·07		7·80	7·92	8·27	3·85	4·23	8·7—8·85	8·48	
(4b)		7·22	7·36		7·94	8·52	3·85	4·26	8·6—8·75	8·56	6·42
(5b)		7·17		7·82	7·98	8·21	3·89	4·18	8·6—8·75	8·75	6·35
(6a)	6·86		7·06		8·10	8·61	3·92	3·82	8·7—8·9	8·66	
(7a)	6·88			*a*	*a*	*a*	*a*	*a*	*a*	8·61	
(6b)	6·88		6·96		8·42	8·66	4·06	4·06	8·7—8·9	8·69	6·40
(7b)	7·04			*a*	*a*	*a*	4·18	3·90	*a*	8·65	6·35
(8a)	7·08	7·08	7·71		7·87	8·51	4·20		8·5—8·75	8·10	
(9a)	6·89	7·25		*a*	*a*	*a*	4·46		8·75—8·85	8·27	
(8b)	7·02	7·22	7·07		8·15	8·49	4·27		8·5—8·75	8·36	6·39
(9b)	*a*	*a*		*a*	*a*	*a*	4·45		*a*	8·35	6·33
(10a)	6·90	7·30	7·17		7·89	8·73		4·30	8·65—8·8	8·20	
(11a)	6·92	7·25		7·80	7·91	8·05		4·46	8·5—8·8	8·28	
(10b)	6·93	7·36	7·06		8·10	*a*		4·56	8·5—8·8	8·26	6·39
(11b)	7·06	7·37		7·72	*a*	*a*		4·41	8·6—8·8	8·28	6·33

[a] Signal not identified.

3_{ex}-H at τ 7·89. Therefore the structure of adduct (10a) is established. Similarly in adduct (10b) the bridgehead proton at τ 6·93 was coupled with the proton at τ 4·56 and the bridgehead proton at τ 7·36 with 3_{ex}-H at τ 8·10. Equilibration studies then led to assignment of the remaining adducts.

Comparison of our results with the only other reported spectra of a series of adducts of 1- and 2-methylcyclopentadiene shows similar trends. Masar and Krieger [31] have described spectra of methylbicyclo[2.2.1]hept-5-en-2-ols. In 5-methylbicyclo[2.2.1]hept-5-en-2-ols the signal of the olefinic proton is at higher field than that of the olefinic proton in 6-methylbicyclo[2.2.1]hept-5-en-2-ols. Bridgehead protons are coincident in the 6-methyl series but separated by 30 Hz in the 5-methyl series.

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