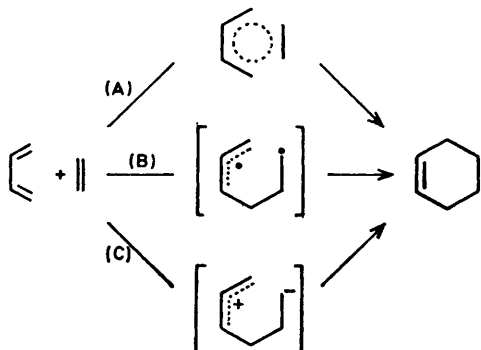


Reaction of *trans,trans*-1,4-Diphenylbutadiene and Maleic Anhydride. Substituent and Solvent Effects

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Diels–Alder adducts from X-substituted diphenylbutadienes (X = *p*-NMe₂, *p*-OMe, *p*-Me, *m*-Me, H, *m*-OMe, *p*-Cl, *m*-Cl, *p*-CN, and *m*-NO₂) and maleic anhydride, and from diphenylbutadiene and some dienophiles (*N*-methylmaleimide, *N*-phenylmaleimide, and 1,4-benzoquinone), have been prepared. Second-order rate constants and activation parameters for these reactions have been measured in *m*-xylene as solvent. The effects of some aprotic solvents (toluene, anisole, chlorobenzene, bromobenzene, benzonitrile, nitrobenzene, and *NN*-dimethylformamide) on the kinetics of diphenylbutadiene and maleic anhydride have been investigated. The stereospecificity of the *endo*-addition and the small substituent and solvent effects on the reaction rate rule out the presence of a zwitterionic intermediate along the reaction co-ordinate. These results, together with the low activation enthalpies and the large negative entropies, can be interpreted in terms of the diradical or concerted mechanism, even though the latter seems to be more acceptable.

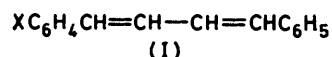
ALTHOUGH the synthetic potential of cycloaddition reactions was outlined by Diels and Alder long ago,^{1,2} the mechanistic interpretation of these reactions is still controversial in some respects.³⁻⁵ The choice between the concerted (A) and the stepwise mechanism by radical (B) or zwitterionic (C) intermediates cannot



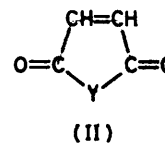
always be made easily. Recently many kinetic studies of substituent and solvent effects have appeared.⁶⁻¹⁰ The small influence of substituents observed for the reaction rates of *p*-substituted 1-phenylbutadienes with maleic anhydride¹¹ as well as the linear correlation found between rate constants and diene HOMO energies¹² were interpreted as suggestive of a concerted reaction mechanism. However, the *p*-methoxy-derivative reacts faster than predicted by the Hammett ρ value but according to its σ^+ value. Such behaviour might suggest the presence of a positively charged intermediate along the reaction co-ordinate. The relative ρ^+ constant would have a small value because the positive charge lies far enough from the substituted aryl ring system. In order to clarify this point it is helpful to extend the kinetic measurements to strongly electron-donating groups and also to determine the activation parameters and solvent effects.

We report here the results of a study of the kinetics of the reaction of *trans,trans*-butadienes (I) with maleic

anhydride in *m*-xylene as solvent in the range 95–135 °C.† We also studied the solvent effects of a variety of aprotic solvents and the effects of some structurally similar dienophiles (II) on the reaction rate of diphenylbutadiene.



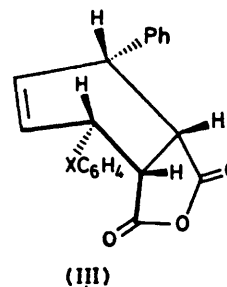
X = *p*-NMe₂, *p*-OMe, *p*-Me, *m*-Me, H,
m-OMe, *p*-Cl, *m*-Cl, *p*-CN, *m*-NO₂



Y = O, NMe, NPh, CH=CH

RESULTS AND DISCUSSION

The addition of maleic anhydride to a *trans,trans*-1,4-diphenylbutadiene solution yields the cyclohexene derivative (III; X = H) quantitatively, in which both phenyl groups are *cis* to the anhydride moiety,¹³ because *endo*-addition is energetically more favourable as shown by MO treatment.¹⁴ The *endo*-structure of the adducts



† °C = K – 273.15.

derived from *p*-X-diphenylbutadienes was always checked by ^1H n.m.r. spectroscopy (see Experimental section).

The observed stereospecificity of this reaction can be interpreted by a synchronous one-step mechanism. However, in principle, two-step mechanisms cannot be ruled out, the stereospecificity being a necessary but not a sufficient condition for a concerted mechanism.^{3,5}

The kinetics were performed by g.l.c. determination of both residual diene and adduct formed. Where g.l.c. analysis was not possible owing to the bulk of the adduct the kinetics were followed by spectrophotometric determination of the diene at an appropriate wavelength.

The reaction follows a second-order rate law, first order with respect to each reactant. The second-order rate constants and the activation parameters are reported in Table 1.

alone do not provide a clear diagnostic tool to elucidate the reaction mechanism.

The relatively small enthalpies of activation (ΔH^\ddagger 13–17 kcal mol⁻¹)* and the large negative entropies of activation (ΔS^\ddagger -31 to -42 cal mol⁻¹ K⁻¹) are typical of Diels–Alder reactions.^{3,19}

Theoretical calculations predict a small activation energy for the concerted mechanism with respect to the stepwise diradical mechanism,²⁰ but such calculations have been recently criticized.⁵ It turns out that low activation parameters as well as small substituent effects do not constitute definitive evidence in favour of the concerned mechanism.

Rate constants for cycloaddition of various dienophiles (II) with diphenylbutadiene in *m*-xylene are reported in Table 2, together with the activation parameters.

The observed reactivity sequence, O > NPh >

TABLE 1

Second order rate constants and activation parameters for the reactions of *trans,trans*-butadienes (I) with maleic anhydride in *meta*-xylene

X	$10^4 k_2 / \text{l mol}^{-1} \text{s}^{-1}$				ΔH^\ddagger a/ kcal mol ⁻¹	$-\Delta S^\ddagger$ a/ cal mol ⁻¹ K ⁻¹
	95 °C	110 °C	125 °C	135 °C		
<i>p</i> -NMe ₂	2.96	4.68	12.1	18.6	13.5	38.8
<i>p</i> -OMe	1.16	2.76	7.08	12.1	16.9	31.1
<i>p</i> -Me	0.807	1.72	3.27	4.45	14.3	38.9
<i>m</i> -Me	0.666	1.54	2.72	5.13	14.0	40.2
H	0.603	1.26	2.40	4.23	13.5	41.6
<i>m</i> -OMe	0.588	1.35	2.49	4.62	14.2	39.8
<i>p</i> -Cl	0.552	1.16	2.38	3.45	13.0	43.0
<i>m</i> -Cl	0.405	0.873	1.85	3.42	15.0	38.5
<i>p</i> -CN	0.243	0.519	1.10	1.79	14.1	41.7
<i>m</i> -NO ₂	0.165	0.438	1.05	1.58	16.3	36.5
ρ	-0.75	-0.66	-0.69	-0.70		

* Calculated at 125 °C. The standard errors in ΔH^\ddagger and ΔS^\ddagger are 0.6 kcal mol⁻¹ and 2 cal mol⁻¹ K⁻¹, respectively.

The electron-donating substituents in the diene accelerate the rate of cycloaddition. The substituent effects are well correlated by the Hammett equation with low ρ values (-0.70 ± 0.04). The change of temperature does not influence the ρ values appreciably. The observed substituent effects indicate charge donation from the diene to maleic anhydride by the HOMO(diene)–LUMO(dienophile) interaction,¹² as normally occurs in a Diels–Alder reaction.¹⁵ The *p*-methoxy-derivative behaves irregularly in this reaction, showing a reaction rate higher than predicted by the Hammett plot. However, the reactivity of the strongly electron-donating *p*-dimethylamino-derivative, which lies on the Hammett line, seems to rule out the hypothesis of a polar intermediate along the reaction pathway.

Similar substituent effects have been observed for a variety of aryl-substituted dienes and dienophiles.¹⁶ The low ρ values have been ascribed to an uncharged transition state.

It is recognized that low ρ values and irregular behaviour by some substituents are typical of pericyclic reactions,¹⁷ as well as processes involving radical intermediates.¹⁸ Typically U-shaped Hammett plots are obtained when biradical intermediates are formed,⁵ while the observed linearity might be indicative of a concerted mechanism. However, the substituent effects

NMe > CH=CH, accords with the expected trend that electron-withdrawing groups accelerate the rate of cycloaddition in a normal electron demand Diels–Alder reaction.

The dependence of cycloaddition rate constants on solvent polarity is a significant mechanistic criterion.^{9,21} The effects of various aprotic solvents on the reaction of diphenylbutadiene with maleic anhydride are shown in Table 3. The observed solvent effects are quite small. On going from non-polar solvents such as *m*-xylene or toluene to more polar ones (nitrobenzene, *NN*-dimethylformamide) the rate constant increases only by a factor of *ca.* 3–4.

It is well known that a significant influence by the solvent polarity indicates a zwitterionic intermediate, whereas a small change in the rate is indicative of only a slight development of charge during the activation process. The trend here observed is similar to that in other Diels–Alder reactions^{3,9} which are little affected by solvent polarity, in agreement with an uncharged character for the transition state. Detailed analysis of the solvent effects on the rate of cycloaddition, in terms of the more usual multiparameter approaches,^{22,23} is of little use because of the minute changes of reactivity.

In conclusion, the overall mechanistic criteria clearly

* 1 cal = 4.184 J.

TABLE 2

Second-order rate constants and activation parameters for the reactions of *trans,trans*-1,4-diphenylbutadiene with some dienophiles in *meta*-xylene

Dienophile	$10^4 k_2 / \text{l mol}^{-1} \text{s}^{-1}$		135 °C	ΔH^\ddagger ^a / kcal mol ⁻¹	$-\Delta S^\ddagger$ ^a / cal mol ⁻¹ K ⁻¹
	110 °C	125 °C			
<i>N</i> -Phenylmaleimide	1.11	1.99	3.83	14.3	40.0
<i>N</i> -Methylmaleimide	0.420	1.07	1.94	18.2	31.5
1,4-Benzoquinone ^b	0.088	0.189	0.294	14.2	45.0

^a Calculated at 125 °C. The standard errors in ΔH^\ddagger and ΔS^\ddagger are *ca.* 1 kcal mol⁻¹ and 3 cal mol⁻¹ K⁻¹ respectively. ^b For a correct comparison the reactivity of the 1,4-benzoquinone must be halved because of the double possibility of addition with respect to the other dienophiles.

rule out the presence of a polar intermediate. However, at the moment, a definitive choice between diradical and concerted mechanisms is not possible, even though the latter seems to be more acceptable.

TABLE 3

Second order rate constants for the reactions of *trans,trans*-1,4-diphenylbutadiene with maleic anhydride in various solvents

Solvent	Dielectric constant	E_T ^a	$10^4 k_2 / \text{l mol}^{-1} \text{s}^{-1}$	
			110 °C	125 °C
Toluene	2.38	33.9	2.13	4.68
Anisole	4.33	37.2	2.80	6.73
Chlorobenzene	5.62	37.5	4.08	8.32
Bromobenzene	5.40	37.5	4.93	12.5
Benzonitrile	25.2	42.0	6.43	13.2
Nitrobenzene	34.8	42.0	5.88	14.4
<i>NN</i> -Dimethylformamide	36.7	43.8	4.70	10.4

^a Empirical parameter of the solvent electrophilicity.²²

EXPERIMENTAL

Materials.—*trans,trans*-1,4-Diphenylbuta-1,3-diene and the dienophiles (II) were commercial products purified by crystallisation. *m*-Xylene (AnalaR grade) was used without further purification.

The dienes (I) were synthesized by the Wittig reaction using equimolar amounts (0.1 mol) of the X-substituted-benzyltriphenylphosphonium halide (Cl or Br) and cinnamaldehyde with sodium ethoxide in ethanol. The dimethyl-amino-derivative was prepared by condensation of cinnamyltriphenylphosphonium chloride with *p*-dimethylaminobenzaldehyde.²⁴ The reaction mixtures were filtered and the solid dienes were crystallised from benzene-cyclohexane.

For ethanol-soluble compounds (X = *m*-Me, *m*-OMe and *m*-Cl) the following purification procedure was used. After evaporation of ethanol from the reaction solution, cyclohexane was added to the residue. After cooling the diene precipitated together with triphenylphosphine oxide. The precipitate was washed by ethanol-water-37% HCl (1:1:1) with stirring at 70–80 °C in order to eliminate triphenylphosphine oxide. The residue was crystallised from cyclohexane. The purity of dienes (*trans,trans*-isomers), checked by g.l.c., is >99%. Table 4 gives the m.p.s and u.v. and i.r. spectral details. Elemental analysis of new compounds were as follows: (I; X = *m*-Me) (Found: C, 92.5; H, 7.2. C₁₇H₁₆ requires C, 92.7; H, 7.3%) (I; X = *m*-OMe) (Found: C, 86.5; H, 6.6. C₁₇H₁₆O requires C, 86.4; H, 6.8%); (I; X = *p*-CN) (Found: C, 88.1; H, 5.6. C₁₇H₁₃N requires C, 88.3; H, 5.7%).

Cycloaddition Reactions.—During work-up we observed that upon addition of maleic anhydride to a solution of diphenylbutadiene a yellow or orange colour was produced. At this point no formation of adduct was observed. The more electron-donating the substituent in the diene the more intense is the colour. At the end of the reaction the solution was not coloured. In addition we observed that maleic anhydride, which is sparingly soluble in cold xylene, becomes very soluble in a xylene solution of diphenylbutadiene. These facts might indicate the formation of a charge transfer complex, but we were not able to obtain direct or indirect evidence.

Many workers have suggested that the reactants in the Diels-Alder reaction form charge transfer complexes.^{10,25,26} Such a complex, which may have a sandwich structure, is probably the precursor of the concerted transition state.

Kinetic Procedure.—The kinetics were performed by mixing thermostatted solutions of diene and dienophile in

TABLE 4

M.p.s and u.v. and i.r. characteristics of *trans,trans*-butadienes (I)

X	M.p. (°C)	U.v. spectra ^a		I.r. spectra ^b (ν/cm^{-1})	
		$\lambda_{\text{max}}/\text{nm}$	$\log \epsilon$	C=C stretch	CH (<i>trans</i>) bend
H	153	232; 315; 329; 346 ^{c,d}	4.10; 4.65; 4.74; 4.56		990
<i>p</i> -NMe ₂	178 ^{d,e}	279; 368 ^d	3.93; 4.69	1 600	985
<i>p</i> -OMe	160 ^e	228; 327; 338; 352	4.09; 4.65; 4.73; 4.60	1 595	990
<i>p</i> -Me	157–158 ^e	235; 320; 332; 348	4.07; 4.53; 4.57; 4.36	1 600	990
<i>m</i> -Me	93–94 ^f	235; 318; 331; 348	3.76; 4.33; 4.41; 4.21	1 595	990
<i>m</i> -OMe	78–79 ^f	230; 321; 332; 347	4.18; 4.65; 4.72; 4.54	1 595	990
<i>p</i> -Cl	161–162 ^g	342; 320; 333; 350	4.07; 4.64; 4.69; 4.51	1 585	985
<i>m</i> -Cl	186–187 ^g	235; 317; 332; 348	4.07; 4.62; 4.70; 4.55	1 585	990
<i>p</i> -CN	161–162 ^f	238; 333; 346	4.04; 4.60; 4.67	1 600	990
<i>m</i> -NO ₂	144–146 ^h	233; 329	4.09; 4.65	1 615	990

^a In 95% ethanol. ^b In KBr disks. ^c Y. Hirshberg, E. Bergmann, and F. Bergmann, *J. Am. Chem. Soc.*, 1950, **72**, 5120. ^d F. B. Kipping and J. J. Wren, *J. Chem. Soc.*, 1959, 2465. ^e R. N. McDonald and T. W. Campbell, *J. Org. Chem.*, 1959, **24**, 1969. ^f This work. Satisfactory combustion analytical data for C and H ($\pm 0.2\%$) were obtained. ^g F. Bergmann, J. Weizman, and D. Schapiro, *J. Org. Chem.*, 1944, **9**, 408. ^h A. J. G. van Rossum, A. H. M. De Bruin, and R. J. F. Nivard, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1036.

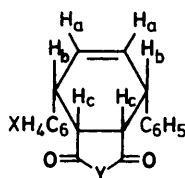
m-xylene (0.03–0.06M). Maleic anhydride and the other dienophiles were used in slight excess (*ca.* 20%) with respect to the butadiene concentration. At intervals, portions were taken up by a microsyringe and analysed by g.l.c. The percentages of the residual diphenylbutadiene and the adduct formed were calculated by the corrected peak areas.

The adduct of *N*-phenylmaleimide was very hard to analyse by g.l.c. owing to its size. Therefore the concentration of diphenylbutadiene was determined by monitoring the disappearance of its u.v. peak at 329 nm or by g.l.c. by the internal standard method.

stituted phenyl-5-*phenyl*-8-oxabicyclo[4.3.0]non-3-ene-7,9-diones were as follows: (III; X = *p*-NMe₂) (Found: C, 83.6; H, 6.7. C₂₂H₂₁O₃N requires C, 83.8; H, 6.7%); (III; X = *p*-OMe) (Found: C, 75.3; H, 5.5. C₂₁H₁₈O₄ requires C, 75.4; H, 5.4%); (III; X = *m*-Me) (Found: C, 79.0; H, 5.5. C₂₁H₁₈O₃ requires C, 79.2; H, 5.7%); (III; X = *m*-OMe) (Found: C, 75.4; H, 5.3. C₂₁H₁₈O₄ requires C, 75.4; H, 5.4%); (III; X = *p*-CN) (Found: C, 76.4; H, 4.5. C₂₁H₁₅O₃N requires C, 76.6; H, 4.6%); (III; X = *m*-NO₂) (Found: C, 68.7; H, 4.1. C₂₀H₁₅O₅N requires C, 68.8; H, 4.3%). *cis*-8-Methyl-2,5-diphenyl-8-azabicyclo-

TABLE 5

M.p.s and ¹H n.m.r. chemical shifts of the adducts between butadienes (I) and maleic anhydride and other dienophiles (II)



X	Y	M.p. (°C)	Chemical shifts ^a δ						
			C ₆ H ₅	C ₆ H ₄ X	H _a	H _b	H _c	X	Y
H	O	208–209 ^b	7.5s		6.7s	4.03s			
<i>p</i> -NM ₂	O	218–219 ^c	7.5s	(6.5–7.4)m	6.55s	3.95s	2.90 (6 H)s		
<i>p</i> -OMe	O	185–187 ^c	7.5s	(7.0–7.5)m	6.65s	4.0s	3.85 (3 H)s		
<i>p</i> -Me	O	216 ^d	7.6s	7.4s	6.7s	4.05s	2.40 (3 H)s		
<i>m</i> -Me	O	188–190 ^c	7.5s	7.35s	6.7s	4.03s	2.40 (3 H)s		
<i>m</i> -OMe	O	188–189 ^c	7.6s	(7.1–7.7)m	6.7s	4.05s	3.90 (3 H)s		
<i>p</i> -Cl	O	217 ^e	7.6s	7.5s	6.65s	4.03s			
<i>m</i> -Cl	O	188–189 ^e		(7.3–7.8)m	6.75s	4.15s			
<i>p</i> -CN	O	225–257 ^c		(7.7–8.1)m	6.7s	(3.95–4.15)m			
<i>m</i> -NO ₂	O	215 ^c	7.45s	(7.7–8.5)m	6.7s	(3.95–4.25)m			
H	NPh	177 ^f		(6.8–7.5)m	6.4s	(3.57–4.05)m			
H	NMe	232–234 ^c		7.4s	6.5s	(3.50–4.00)m			^h
H	CH=CH	140–141 ^g		7.25s	6.8s				2.7 (3 H)s 7.45 (2 H)s

^a In CDCl₃ from internal Me₃Si. ^b Ref. 13. ^c This work: satisfactory combustion analytical data for C and H ($\pm 0.25\%$) were obtained. ^d A. V. Dombrovskii and N. I. Gamushchak, *Zhur. Obshch. Khim.*, 1961, **31**, 1896 (*Chem. Abstr.*, 1961, **55**, 24 675). ^e F. Bergmann, J. Weizman, and D. Schapiro, *J. Org. Chem.*, 1944, **9**, 408. ^f H. A. El-Mangari, M. A. Ibrahim, and F. M. Ghourab, *Arab. Sci. Congr. 5th Bagdad, II*, 1966, 287 (*Chem. Abstr.*, 1969, **70**, 283). ^g According to Y. Lepage (*Bull. Soc. Chim. Fr.*, 1963 2019), we have isolated the 5,8-diphenyl-1,4-naphthoquinone from the reaction mixture because the dienophile dehydrogenates the adduct. ^h The five protons of the *N*-phenyl group are included among the signals of the other aromatic protons.

These analytical procedures were also applied to standard reactions, in order to check the reproducibility of the rate constants by different analytical methods.

Reaction Products.—Solutions containing equimolar amounts (0.015 mol) of the diene and dienophile in *m*-xylene (50 ml) were allowed to react for 1–10 h* at 130 °C, depending on the reactivities. After cooling, the adducts were filtered off and crystallised from cyclohexane–benzene, benzene, or chlorobenzene. Yields were >80% before crystallisation. The m.p.s of the adducts are reported in Table 5, together with the ¹H n.m.r. chemical shifts.

The accidental isochronism (*ca.* 4 p.p.m.) of the four *cis*-hydrogen atoms, apart from the *p*-CN, *m*-NO₂, NMe, and NPh derivatives, represents a peculiar characteristic of the *endo*-structure in these compounds.

The reaction product from 1,4-benzoquinone was isolated by column chromatography on silica gel with CCl₄ and CHCl₃ as eluents and it was crystallised from *n*-hexane. This compound is the dehydrogenation product of the expected Diels–Alder adduct, as indicated by the n.m.r. spectrum (Table 5). Elemental analyses for *cis*-2-(*sub*-

* 1 h = 60 min = 3 600 s.

[4.3.0]non-3-ene-7,9-dione gave C, 79.4; H, 5.9% (C₂₁H₁₈O₃N requires C, 79.5; H, 6.0%).

Instrumental Analysis.—G.l.c. determinations were carried out by a Carlo Erba instrument with a 80 cm column packed with 25% SE 30 on Chromosorb P at 240–250 °C, using helium as carrier. Microanalyses were performed by a Carlo Erba CHN Analyzer. N.m.r. spectra were recorded on a Varian A 60 spectrometer. I.r. and u.v. spectra were measured on Perkin-Elmer 237 and Hitachi–Perkin-Elmer EPS 3T spectrometers, respectively.

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