Substituent and Solvent Effects on the Diels–Alder Reactions of Triazolinediones

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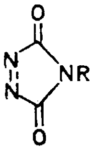
The kinetics and activation parameters for the series of 4-substituted (R) 1,2,4-triazoline-3,5-diones (R = Me, Et, Bu^t, CH_2Ph, Ph, p-$MeOC_6H_4$, p-$NO_2C_6H_4$, or N:CHPh) have been measured for the Diels–Alder reactions with diphenylbutadiene, anthracene, hexachlorocyclopentadiene, and bicyclo[2.2.1]heptadiene. The reactions have been studied in benzene, dioxan, and ethyl acetate. The results are more in accord with the frontier orbital model of reactivity in the Diels–Alder reaction than with a standard linear free-energy approach.

TRIAZOLINEDIONES (1) have been used extensively in cycloadditions and in hydrogen abstractions since the recognition[1] of the high dienophilic reactivity of 4-phenyl-1,2,4-triazoline-3,5-dione (1f) (abbreviated as phenyl-TD). Cycloadditions with carbocyclic[2] and heterocyclic[3] polyenes, cyclopropane ring systems,[4] terpenes,[5] and steroids[6] have all been investigated. Triazolinedione adducts have been used in the synthesis of prismane,[7] semibullvalene and bridged semibullvalene,[8] azo-alkanes,[9] caged compounds, and propellanes.[10] Because of their high reactivity, triazolinediones have been particularly useful in the trapping of unstable intermediates,[11] the characterisation of dienes,[12] and in the simplification of product mixtures containing dienes by adduct formation.[13] Their hydrogen abstraction ability has been studied in the oxidations of alcohols,[14] 1,1-disubstituted hydrazines,[15] and hydrazones and monoacylhydrazones;[16] their participation as enophiles in a variety of ene reactions[17] has also been studied.[18] Sauer and Schröder[19] have demonstrated quantitatively the high reactivity of phenyl-TD. Comparison with tetracyanoethylene (TCNE) has shown that, except in its reaction with anthracene, it is the most reactive dienophile known.



(1)a; R = Bu^t e; R = p-$MeOC_6H_4$
b; R = Et f; R = Ph
c; R = Me g; R = p-$NO_2C_6H_4$
d; R = CH_2Ph h; R = N=CHPh

Because of their utility and extreme reactivity, this study has been undertaken to examine the factors affecting triazolinedione reactivity. The nature of the triazolinedione 4-substituent has been varied [compounds (1a—h)] and kinetic measurements have been made for the Diels–Alder reactions of the triazolinediones with the dienes *trans,trans*-1,4-diphenylbutadiene (DPBD), anthracene, and hexachlorocyclopentadiene, and the homo-Diels–Alder reaction with bicyclo[2.2.1]heptadiene in the solvents benzene, dioxan, and ethyl acetate. The activation parameters have been determined.

RESULTS

The expected adducts (2)—(5) were obtained [reactions (1)—(4)]. The values of the second-order rate constants

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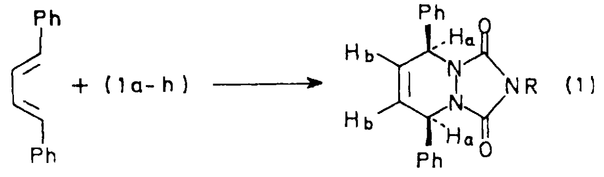
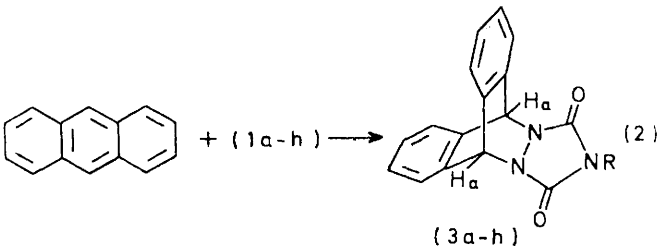
that were obtained are given in Tables 1—4,* and Tables 5—7 give the values of the activation parameters.



(2a-h)



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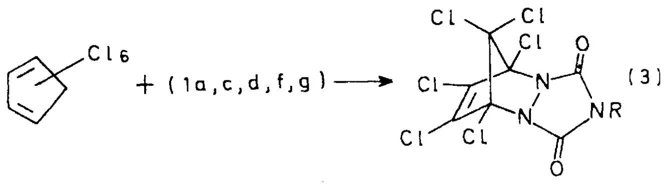
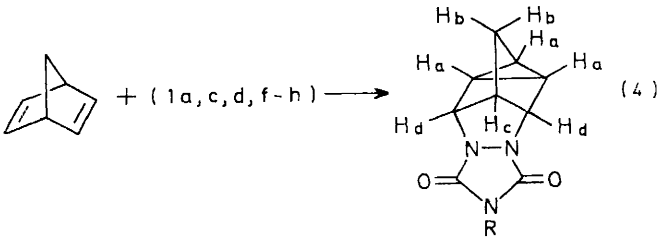


(4a,c,d,f,g)



(5a,c,d,f-h)

Table 3

Reactions with hexachlorocyclopentadiene

Solvent	Dione	10^4k_2/ l mol^{-1} s^{-1} [a, *]	%σ [b]	T/°C	Method [c]
Benzene	(1a)	14.0	0.77	49.84	A
	(1c)	24.3	0.87	49.84	A
	(1d)	32.6	0.70	49.85	A
	(1f)	43.4	0.50	49.85	A
	(1g)	69.0	1.5	49.84	A
Ethyl acetate	(1c)	12.6	0.68	49.78	A
	(1d)	16.5	0.38	49.75	A
	(1g)	15.5	0.92	49.78	A

* See Table 4 for notes.

Table 4

Reactions with bicyclo[2.2.1]heptadiene

Solvent	Dione	10^4k_2/ l mol^{-1} s^{-1} [a]	%σ [b]	T/°C	Method
Benzene	(1a)	8.8	0.90	29.80	A
	(1c)	34.2	0.60	30.59	1
	(1d)	78	0.68	29.85	A
	(1f)	50.3	0.52	20.15	1
	(1f)	92	1.1	30.15	A
	(1f)	253	2.0	46.62	A
	(1g)	358 [d]		29.97	1
	(1g)	355 [d]		29.78	1
	(1g)	344 [e]	0.80	29.85	1
	(1h)	425	0.80	29.60	1
Dioxan	(1a)	2.26	0.82	30.25	1
	(1c)	7.7	0.94	30.12	1
	(1d)	16.8	1.9	29.92	A
	(1f)	8.8	0.50	22.65	1
	(1f)	16.4	0.40	30.15	1
	(1f)	62.1	1.1	46.62	A
	(1g)	71	0.92	30.24	1
	(1h)	55.6	1.0	30.27	1
Ethyl acetate	(1a)	2.1	2.0	30.05	A
	(1c)	5.25	1.5	30.20	A
	(1d)	16.0	1.2	29.92	A
	(1f)	6.01	0.40	23.00	A
	(1f)	16.7	1.2	35.14	A
	(1f)	47.2	1.9	46.57	A
	(1g)	35.1	0.24	30.10	A
	(1g)	33.4	1.1	29.50	A
	(1h)	47.2	2.3	29.65	A

[a] Values of the second-order rate constant from a least squares treatment of the experimental data. [b] Standard deviation expressed as a percentage of k_2. [c] Experimental technique used (see Experimental section): 1 = 1 cm method, A = ampoule technique. [d] Rate constant at 50% reaction; see note *e*. [e] For this reaction only, adduct was insoluble and was deposited after 50% reaction. Value calculated including a correction for scattering.

DISCUSSION

Effect of Solvent.—The effect of solvent on the activation parameters of the Diels–Alder reaction has been studied in only a few cases. A significant variation in activation enthalpy has been found for the reactions between cyclopentadiene and benzoquinone (seven solvents),[20] between TCNE and anthracene (16 solvents),[21] and between TCNE and bicyclo[2.2.1]heptadiene (six solvents); [21] no significant variation was found for the reaction between maleic anhydride and isoprene (10 solvents).[22] For some of these Diels–Alder reactions, for which there is a significant change in activation enthalpy between two selected solvents, Haberfield [23] has made calorimetric measurements of the heat of solution of the reactants and so obtained the enthalpies of solvent transfer of reactants and transition state. The enthalpy of transfer of the reactants, and particularly of the dienophile, was found to be significant and at variance with that expected from the change in solvent polarity as measured by dielectric constant or dipole moment. Thus, the polar dienophile TCNE was found to be solvated better in the less polar solvent. It was therefore concluded that the electron-donating capacity of the solvent was the important factor involved, dienophile solvation being increased by such electron donation. Differential solvation of the tran-

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* Tables 1 (reactions with diphenylbutadiene) and 2 (reactions with anthracene) are given in Supplementary Publication No. SUP 21408 (9 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

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TABLE 5

Activation parameters for reactions with diphenylbutadiene

Solvent	Dione	$10^4k_2(30°)$ [a]/ l mol^{-1} s^{-1}	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}	$\Delta G^‡$/ kcal mol^{-1}	r [b]
Benzene	(1a)	6 090	8.4	−31.9	18.1	0.998
	(1b)	21 900				
	(1c)	14 000	8.3	−30.7	17.6	0.995
	(1d)	75 000	5.8	−35.3	16.5	1.000
	(1e)	49 800				
	(1f)	61 900	8.3	−27.7	16.7	0.996
	(1g)	340 000				
	(1h)	225 000				
Dioxan	(1a)	2 220	8.1	−34.9	18.7	1.000
	(1b)	9 800				
	(1c)	6 660	9.3	−29.7	18.0	0.995
	(1d)	22 000	8.7	−28.2	17.3	0.999
	(1e)	13 600				
	(1f)	16 600	7.8	−31.8	17.5	0.997
	(1g)	95 000	8.6	−25.9	16.4	0.998
	(1h)	59 300	6.0	−35.3	16.7	0.987
Ethyl acetate	(1a)	1 630	9.6	−30.5	18.8	1.000
	(1b)	5 820				
	(1c)	4 500	8.5	−32.0	18.2	0.994
	(1d)	20 600	8.2	−30.2	17.3	0.996
	(1e)	10 300				
	(1f)	12 700	8.6	−29.6	17.6	0.995
	(1g)	57 900	9.0	−25.5	16.7	0.998
	(1h)	58 800	7.0	−31.9	16.7	0.996

[a] Second-order rate constants at 30° from least squares line of Arrhenius plot. Other rate constants at 30° are included for comparison purposes. [b] Correlation coefficient for points on Arrhenius plot.

TABLE 6

Activation parameters for reactions with anthracene

Solvent	Dione	$10^4k_2(30°)$ [a]/ l mol^{-1} s^{-1}	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}	$\Delta G^‡$/ kcal mol^{-1}	r
Benzene	(1a)	285	10.0	−32.7	19.9	0.997
	(1b)	1 650				
	(1c)	2 310	10.0	−28.7	18.6	1.000
	(1d)	2 260	9.4	−30.4	18.7	1.000
	(1e)	5 220				
	(1f)	6 700	9.3	−28.7	18.0	0.997
	(1g)	59 300	8.5	−26.9	16.7	0.998
	(1h)	22 200	8.7	−28.2	17.3	0.997
Dioxan	(1a)	87	10.5	−33.4	20.6	1.000
	(1b)	538				
	(1c)	710	11.1	−27.3	19.3	0.999
	(1d)	478	12.2	−24.4	19.6	1.000
	(1e)	1 180				
	(1f)	1 310	10.5	−28.0	19.0	0.997
	(1g)	10 600	10.8	−22.9	17.7	0.998
	(1h)	4 540	9.2	−29.9	18.2	0.995
Ethyl acetate	(1a)	55.7	11.5	−30.9	20.9	1.000
	(1b)	333				
	(1c)	477	12.1	−24.7	19.6	0.995
	(1d)	522	11.3	−27.2	19.5	0.997
	(1e)	680				
	(1f)	830	11.6	−25.4	19.3	0.999
	(1g)	5 180	11.4	−22.1	18.2	0.999
	(1h)	4 300	11.1	−23.6	18.3	0.988

[a, b] See notes to Table 5.

TABLE 7

Activation parameters for reactions with bicycloheptadiene

Solvent	Dione	$10^4k_2(30°)$ [a]/ l mol^{-1} s^{-1}	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}	$\Delta G^‡$/ kcal mol^{-1}	r [b]
Benzene	(1f)	94	10.8	−32.3	20.6	1.000
Dioxan	(1f)	16.4	14.8	−22.5	21.6	1.000
Ethyl acetate	(1f)	11.2	15.8	−19.9	21.9	0.999

sition state was regarded as indicating that the transition state was stabilised by electron-accepting solvents and was therefore electron rich.

In the absence of heats of solution, the relative enthalpies of reactants and transition states cannot be ascertained for the reactions of the triazolinediones. However, assuming dienophile solvation to be most important, it seems that solvent induced changes in triazolinedione reactivity have a different origin. The effect of solvent on the reaction rate is most clearly seen in the results for the reaction of phenyl-TD with bicyclo[2.2.1]heptadiene (Table 7). The same effect is observed for any other diene–dienophile combination, and this is that the rate of reaction is greatest in benzene and least in ethyl acetate. The increase in rate brought about by changing the solvent from dioxan to benzene is always considerably greater than that in changing from ethyl acetate to dioxan. The greater free energy of activation in ethyl acetate than in benzene is the result of the opposing effects of a larger activation enthalpy and a less negative activation entropy. For the reaction of phenyl-TD with bicyclo[2.2.1]heptadiene these changes are most marked with $\delta\Delta H^{\ddagger}$ 5 kcal mol^{-1} and $\delta\Delta S^{\ddagger}$ 12.4 cal mol^{-1} K^{-1} and, whilst the same trend is observable for the other dienes, the changes tend to be obscured by the uncertainties in $\Delta H^{\ddagger}$ (0.7 kcal mol^{-1}) and in $\Delta S^{\ddagger}$ (2 cal mol^{-1} K^{-1}).

Table 8 gives some macroscopic and empirical measures of solvent polarity, namely dielectric constant, dipole moment, and Dimroth's E_T values [24a] and also the ionisation potentials for the solvents. The ionisation potential is taken as a measure of the electron-donating capacity of the solvent. The solvents used were not included in Berson's Ω scale [25] for solvent polarity.

TABLE 8

Measures of solvent polarity

Solvent	Dielectric constant [24b] ε(25°)	Dipole moment [a] μ/D	E_T [24a] (25°)	Ionisation potential [b] (eV)
Benzene	2.27	0	34.5	9.25
Dioxan	2.21	0 *	36.0	9.52
Ethyl	6.03	1.78	38.0	10.10

* *Cf.* dimethyl ether 1.30, diethyl ether 1.15, tetrahydrofuran 1.63 D. The zero dipole moment is misleading and arises because of the symmetry of the molecule.

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It seems likely that the principal cause of the increased activation enthalpy in ethyl acetate is increased solvation of the dienophile. This view is consistent with the larger extinction coefficients for the $n\rightarrow\pi^*$ absorption observed when benzene, rather than ethyl acetate, is the solvent. For phenyl-TD, for example, the appropriate extinction coefficients are 247.8, 186.2, and 172.2 in the solvents benzene, dioxan, and ethyl acetate respectively; this change in extinction coefficient is not the result of an alteration in the shape of the absorption peak, for integration of the band leads to the same relative figures.

In contrast to the reactions studied by Haberfield, the highest activation enthalpy occurs in the solvent of highest polarity and lowest electron-donating capacity: it is therefore reasonable to attribute the superior solvation of the electron-poor dienophile to the higher solvent polarity. As a consequence the transition state must be regarded as being little different in polarity from the reactants indicating that partial charge formation does not occur, a view which is consistent with the relatively low observed sensitivity of the reaction to changes in dienophile substituent (see below).

The solvent effect is different for only one dienophile, benzylideneamino-TD (1h). In benzene and dioxan this dienophile has are activity intermediate between those of phenyl- and *p*-nitrophenyl-TD and the magnitude of the change in reactivity brought about by changing the solvent from dioxan to benzene is similar to that for the other dienophiles; but it differs from them in that its reactivity is almost unaltered when the solvent is changed from dioxan to ethyl acetate with the result that it is of equivalent reactivity to *p*-nitrophenyl-TD in ethyl acetate.

Certain changes in the relative reactivities of the dienophiles, towards a given diene, are brought about by changing the solvent and arise because the alkyl- and aryl-triazolinediones show a different sensitivity to solvent variation. The reactivity of the aryltriazolinediones as a group is reduced proportionately much more than that of the alkyltriazolinediones when the solvent is changed from benzene to ethyl acetate. For example, *p*-nitrophenyl-TD is 36 times more reactive than ethyl-TD in its reaction with anthracene in benzene and is only 16 times more reactive in ethyl acetate because the reactivity of the *p*-nitrophenyl-TD has been reduced by a factor of 11.5 by the solvent change, whereas the reactivity of ethyl-TD has been reduced by a factor of only 5 (Table 6). For the reactions of benzyl- and phenyl-TD with bicyclo[2.2.1]heptadiene and with hexachlorocyclopentadiene the order of dienophile reactivity actually changes with solvent; phenyl-TD is the more reactive dienophile in benzene and benzyl-TD is the more reactive dienophile in ethyl acetate (Tables 3 and 4).

Diene Reactivity.—The frontier orbital method has been used by Sustmann,[26] and Anh [26,27] in an attempt to obtain a quantitative model for the electronic effect of substituents in cycloadditions. For the normal Diels–Alder reaction the log of the rate constant is predicted

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[27] O. Eisenstein and N. T. Anh, *Bull. Soc. chim. France*, 1973, 2723.

to be inversely proportional to the energy separation of the highest occupied molecular orbital (HOMO) of the diene and the lowest unoccupied molecular orbital (LUMO) of the dienophile, from which it follows that (*a*) for the reactions of a given dienophile with several dienes, the diene with the highest HOMO energy should be the most reactive, and that (*b*) the electronic effect of a substituent will be greatest when the HOMO–LUMO energy separation is least. The data used to test this model indicated the importance of effects other than the electronic effect of the substituents in determining reactivity so that, for example, dienes having fixed *cisoid* conformations showed enhanced reactivity. The importance of more than one effect in determining reactivity has been demonstrated by variations in diene–dienophile reactivity series, for example, in the reactions of phenyl-substituted butadienes with maleic anhydride and with TCNA.[28]

TABLE 9

10^4k_2 Values (l mol^{-1} s^{-1}) for reactions of dienes with dienophiles in dioxan

Diene	Ionisation potential (eV)	Maleic anhydride [c] (30°)	TCNE [d] (20°)	Phenyl-TD (20°)
Anthracene	7.43	0.092	2 760	700
PhCH:CH·CH:CH·Ph	7.54	0.0296	84	10 300
Bicycloheptadiene	8.67 [a]			6.9
Chloroprene	8.83 [b]	0.069	0.102	2 400 [d]
Hexachlorocyclopentadiene	8.93	0.000114	No reaction	2.76 [d]

[a] S. Meyerson, *J. Amer. Chem. Soc.*, 1961, **83**, 1401. [b] W. C. Price, *Chem. Rev.*, 1947, **41**, 257. [c] J. Sauer, D. Lang, and A. Mielert, *Angew. Chem. Internat. Edn.*, 1962, **1**, 268. [d] Ref. 19.

Table 9 summarises some ionisation potential and rate data for the dienes studied, together with chloroprene, in reactions with TCNE, maleic anhydride, and phenyl-TD. Anthracene would be predicted to be the most reactive diene of the series by virtue of its having the lowest ionisation potential. This is the case with maleic anhydride and TCNE as dienophiles, but not with phenyl-TD. The kinetic measurements made for the other triazolinediones show that for any particular dienophile and solvent combination the order of reactivity is the same: DPBD (most reactive) > anthracene > bicyclo[2.2.1]heptadiene > hexachlorocyclopentadiene. Table 9 also shows that the reactivity of chloroprene towards phenyl-TD is greater than might be expected from considerations of diene ionisation potential alone and that the same is also true for the reaction of chloroprene with maleic anhydride (over twice as reactive as DPBD). For the reactions of the triazolinediones the best approach would seem to be to consider the cyclic and acyclic dienes separately. The steric bulk present in a diene such as anthracene, and not in the acyclic dienes, must be expected to have some effect on triazolinedione reactivity. That benzyl- and t-butyl-TDs show reduced reactivity in their reactions with anthracene supports this view (see below).

The reactivity of the electron-poor diene hexachlorocyclopentadiene towards the triazolinediones (Table 4) is indicative of the high reactivity of the triazolinediones. The reactions of substituted styrenes with hexachlorocyclopentadiene have been shown to be Diels–Alder reactions with inverse electron demand by the order of dienophile reactivity (negative Hammett ρ).[29] In contrast, the Diels–Alder reactions of substituted triazolinediones with hexachlorocyclopentadiene are of normal electron demand because although the effect of dienophile substituent on reactivity is small, the direction of the effect is the same as that for normal Diels–Alder reactions (positive ρ).

Overall Variation in Dienophile Reactivity.—Before the actual order of reactivity of the dienophiles is considered, the relation between the overall variation of dienophile reactivity and the HOMO–LUMO energy separation will be examined. Table 10 gives the variation of the relative rates of the *p*-nitrophenyl- and phenyl-TDs and this may be used as a measure of the variation of the electronic effect of substituent with diene. The change in rate from *p*-nitrophenyl to phenyl is greatest with anthracene, and least with hexachlorocyclopentadiene, and parallels the order of ionisation potential of the diene. Therefore, whilst deviations from the frontier orbital model exist in the order of reactivity of the dienes, the effect of a substituent on reactivity is greatest when the HOMO–LUMO separation is least and is in accord with the model. A similar variation of increased sensitivity to substituent change paralleling increased reactivity has recently been reported.[30]

TABLE 10

Relative reactivity of triazolinediones $k(p\text{-}NO_2C_6H_4)/k(Ph)$

	Diene			
Solvent	DPBD 30°	Anthracene 30°	Bicyclo-hepta-diene 30°	Hexa-chloro-cyclo-penta-diene 50°
Benzene	5.5	8.9	3.8	1.6
Dioxan	5.7	8.1	4.4	
Ethyl acetate	4.6	6.3	3.2	

Effect of Dienophile Substituent.—For the Diels–Alder reaction, the effect of variation of the substituent has been studied for a number of aryl-substituted dienes and dienophiles.[31] The low ρ values (under 0.7) that have usually been obtained from Hammett $\rho\sigma$ plots indicate the low sensitivity of the Diels–Alder reaction to the electronic effect of substituents and presumably the uncharged nature of the transition state. In most cases

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[28] R. Huisgen, R. Grashey, and J. Sauer, 'The Chemistry of the Alkenes,' ed. S. Patai, Interscience, London, 1964, p. 921.

[29] J. Sauer and H. Wiest, *Angew. Chem. Internat. Edn.*, 1962, **1**, 269.

[30] N. A. Porter, I. J. Westerman, T. G. Wallis, and C. K. Bradsher, *J. Amer. Chem. Soc.*, 1974, **96**, 5104.

[31] H. D. Barnstorff and J. S. Meek, 125th American Chemical Society Meeting, 1954, Abstract 29N; E. J. DeWitt, C. T. Lester, and G. A. Ropp, *J. Amer. Chem. Soc.*, 1956, **78**, 2101; Y. Okamato and H. C. Brown, *J. Org. Chem.*, 1957, **22**, 485; I. Benghiat and E. I. Becker, *ibid.*, 1958, **23**, 885; M. G. Romanelli and E. I. Becker, *ibid.*, 1962, **27**, 662; D. N. Matthews and E. I. Becker, *ibid.*, 1966, **31**, 1135; J. Hamer, M. Ahmed, and R. E. Holliday, *ibid.*, 1963, **28**, 3034.

an improved correlation has been observed with the substituent constants σ^+ for substituted dienes and σ^- for substituted dienophiles although such a correlation, using adjusted substituent constants which allow for the importance of a resonance interaction, is inconsistent with the low ρ values.[32]

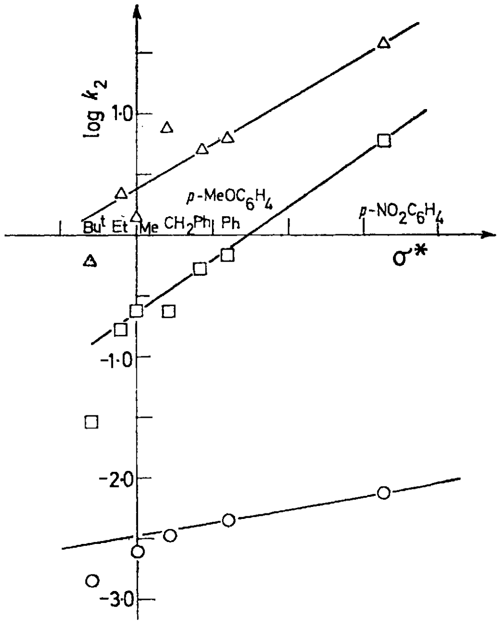
Hammett plots against σ for the reactions of *p*-methoxyphenyl-, phenyl-, and *p*-nitrophenyl-TD with anthracene and DPBD in the three solvents show marked curvature; which is substantially removed when σ^- is used. The reaction constants are given in Table 11.

TABLE 11

ρ Values for reactions of the triazolinediones (at 30°)

	Diene	
Solvent	DPBD	Anthracene
Benzene	0.58	0.74
Dioxan	0.58	0.65
Ethyl acetate	0.52	0.64

Thus Hammett $\rho\sigma$ plots for the aryltriazolinediones are typical of those obtained for Diels–Alder reactions.



Rates of reaction for 4-substituted triazolinediones with dienophiles in benzene *versus* σ^*: △ with DPBD at 30°; □ with anthracene at 30°; ○ with hexachlorocyclopentadiene at 50°

In an attempt to obtain comparable substituent constants for alkyl and aryl substituents, the equation[33] $\sigma^*_{XC_6H_4} = 0.9\sigma_X + \sigma^*_{C_6H_5}$ was used to obtain σ^* values from σ^- values for the aryl substituents. These values and Taft σ^* values have been used to obtain the plots shown in the Figure for the reactions of the triazolinediones with DPBD, with anthracene, and with hexachlorocyclopentadiene in benzene. (The lines have been drawn by considering the aryl substituents only.) The failure to give a reasonable correlation shows clearly that factors other than purely electronic ones are involved.

The order of dienophile reactivity predicted on the grounds of electronic effect of substituent alone, *p*-nitrophenyl (most reactive) > phenyl > *p*-methoxyphenyl > benzyl > methyl > ethyl > t-butyl, is not followed and changes in the order occur both with solvent (see earlier) and with diene. Thus with DPBD and anthracene in benzene (Figure), the orders differ both from that predicted and from each other. With anthracene as diene the benzyl- and methyl-TDs are of equivalent reactivity whereas the greater electron-withdrawing ability of the benzyl group (σ^* +0.215, σ^* for methyl 0.0) would have been expected to make benzyl-TD more reactive. The most reasonable explanation is that with benzyl-TD there is a substantial steric interaction in the transition state for reaction with anthracene reducing its reactivity. Similarly, the reactivity of t-butyl-TD is reduced (Figure). This view is consistent with that proposed in the discussion of diene reactivity, namely that the general reactivity of anthracene towards triazolinediones is reduced by the importance of steric effects.

For reactions with DPBD (Table 5 and Figure), benzyl-TD is more reactive than phenyl-TD and ethyl-TD is more reactive than methyl-TD. Whilst this order of dienophile reactivity is unexpected the enhanced reactivity of benzyl-TD may be explicable either in terms of solvation differences for the alkyl- and aryl-triazolinediones or as the result of the smaller steric size of the benzyl group as compared with the phenyl group. The greater reactivity of ethyl-TD compared to methyl-TD is difficult to rationalise.

The above discussion illustrates the difficulties encountered in obtaining a quantitative reactivity model based on a consideration of the electronic effect of substituents above. Nevertheless, for the *para*-substituted aryltriazolinediones a satisfactory Hammett $\rho\sigma$ plot is obtained when the substituent constant σ^- is used. An alternative possible explanation for the curvature of the plot with σ is that it is to be expected from the frontier orbital model and that the correlation obtained with σ^- in these reactions, and with either σ^- or σ^+ for other Diels–Alder reactions, is fortuitous and does not signify the importance of a resonance interaction. Thus, if the Diels–Alder reactions of a series of dienes with a given dienophile are considered, the frontier orbital treatment relates reactivity with the reciprocal of the HOMO–LUMO separation and hence with the reciprocal of the energies of the diene HOMOs. These are given by the ionisation potentials of the dienes which reflect changes in the inductive and mesomeric effects of the substituents. A linear relationship between Hammett's σ and ionisation potential is evident from ionisation potential data for substituted benzenes[34] and has been demonstrated for alkyl groups

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[32] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

[33] Ref. 32, p. 333.

[34] A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc.* (*B*), 1968, 22.

and Taft's σ^*.[35,36] For the reactions of a series of dienes with a given dienophile, it follows that the HOMO–LUMO energy separations will be linearly related to the appropriate substituent constants. The use of the frontier orbital treatment and the expectation of a linear free energy relationship are therefore two incompatible approaches since they lead to two different relationships between log k and substituent constant. If this analysis is correct, *meta*-substituted aryl reactants, for which a resonance interaction is not possible, would also therefore be expected to have non-linear Hammett plots, but no kinetic measurements have been made for such compounds.

Activation Parameters.—The large negative values for activation entropy are typical for the Diels–Alder reaction. The greater reactivity of DPBD, compared with that of anthracene, is almost entirely due to its reactions having lower activation enthalpies ($\delta\Delta H^{\ddagger}$ *ca.* 3 kcal mol^{-1}). If the variation of the activation parameters with dienophile substituent is considered then it is seen that the variation in activation enthalpy is small and usually within the limits of experimental error, and that the variation in activation entropy is significant. The series for reaction with anthracene in ethyl acetate (Table 6) illustrates this best. For a 100-fold change in rate the variation in activation enthalpy is 1 kcal mol^{-1} and in activation entropy 8.8 cal mol^{-1} K^{-1}.

As has previously been proposed for the dichlorocarbene–olefin reaction,[37] we suggest that this is a reflection of a greater degree of separation of the reactants at the transition state for the more reactive triazolinediones and a tighter transition state for the less reactive ones, and hence a more negative $\Delta S^{\ddagger}$. This explanation is in good accord with the theoretical calculations of Eisenstein and Anh,[27] who have carried out Hückel calculations on a number of Diels–Alder reactions in an attempt to predict the reactivity order. They find that the most satisfactory treatment is one that uses only frontier orbitals, and allows the separation of the reactants at the transition state to vary with the magnitude of the orbital coefficients of the frontier molecular orbitals involved. This resulted in the more reactive dienes (or dienophiles) reaching the transition state at greater separations than the less reactive ones.

EXPERIMENTAL

I.r. spectra were recorded on either a Unicam SP 200 or a Perkin-Elmer 157G spectrometer as either Nujol mulls or thin films, u.v. and visible spectra on a Perkin-Elmer 402 spectrometer, ^{1}H n.m.r. spectra on a Perkin-Elmer R12 spectrometer at 60 MHz, and mass spectra on an A.E.I. MS 12 spectrometer. The vertical ionisation potentials were obtained from photoelectron spectra recorded on a Perkin-Elmer PS 18 spectrometer.

Preparation of the Triazolinediones.—The preparation of 4-t-butyl- (1a), -methyl- (1c), -phenyl- (1f), -*p*-nitrophenyl- (1g), and -benzylideneamino- (1h) triazolinediones has been described in ref. 38. The remaining triazolinediones were prepared similarly. There is an upper limit to the reactivity of the triazolinediones that may be synthesised by this method since cyclisation of an ethoxycarbonylsemicarbazide to give a urazole (tetrahydro-1,2,4-triazole-3,5-dione) does not occur when there is an extremely electron-withdrawing substituent present, hydrolysis and decomposition occurring instead. Thus, 4-(2,4-dinitrophenyl)-1,2,4-triazoline-3,5-dione could not be prepared since the corresponding urazole was not obtained from base treatment of 4-(2,4-dinitrophenyl)-1-ethoxycarbonylsemicarbazide. The triazolinediones were purified by vacuum sublimation.

4-*t-Butyl*-1,2,4-*triazoline*-3,5-*dione* (1a). This had m.p. 119° (sublimed at 50° and 0.1 mmHg), $\nu_{max.}$ 1 720, 730, and 690 cm^{-1}, $\lambda_{max.}$ (benzene) 540 (ε 247.5) and 564 nm (194), $\lambda_{max.}$ (dioxan) 529 nm (ε 181.4), $\lambda_{max.}$ (ethyl acetate) 528 nm (ε 173.3), τ (CDCl$_3$) 8.36 (s), ionisation potentials 9.82 (adiabatic 9.35), 10.71, and 11.63 eV.

4-*Ethyl*-1,2,4-*triazoline*-3,5-*dione* (1b). Ethyl isocyanate (15 g) was condensed with ethyl hydrazinecarboxylate (22 g) in benzene (45 ml) to give 4-ethyl-1-ethoxycarbonylsemicarbazide (37 g, 100%), m.p. 133° (from ethyl acetate), $\nu_{max.}$ 3 340 and 3 250br, 1 755, 1 735, and 1 215 cm^{-1}, τ ([^{2}H$_6$]Me$_2$SO) 1.35br (1 H, s), 2.34br (1 H, s), 3.70br (1 H, s), 5.94 (2 H, q, J 7.0 Hz), 7.00 (2 H, q, J 7.0 Hz), 8.80 (3 H, t, J 7.0 Hz), and 8.99 (3 H, t, J 7.0 Hz). The semicarbazide (34 g) was cyclised with aqueous 4M-potassium hydroxide (100 ml) by heating on a water-bath for 1.5 h to give, after acidification, 4-*ethylurazole* (24 g, 96%), m.p. 200° (from ethanol) (Found: M, 129. $C_4H_7N_3O_2$ requires M, 129), $\nu_{max.}$ 3 400br, 3 150, 1 755, 1 675, and 800 cm^{-1}. 4-Ethylurazole (1.29 g) was oxidised with t-butyl hypochlorite (1.1 ml) in ethyl acetate (15 ml) at room temperature and under nitrogen to give 4-ethyl-1,2,4-triazoline-3,5-dione (1b) (0.83 g, 65%), m.p. 53° (sublimed at 40° and 0.1 mmHg), $\nu_{max.}$ 1 775, 1 730, 790, 730, and 680 cm^{-1}, $\lambda_{max.}$ (benzene) 539 (ε 254.7) and 566 nm (210), $\lambda_{max.}$ (dioxan) 529 nm (ε 190.5), $\lambda_{max.}$ (ethyl acetate) 529 nm (ε 184.5), τ (CDCl$_3$) 6.24 (2 H, q, J 7.3 Hz) and 8.65 (3 H, t, J 7.3 Hz), ionisation potentials 10.15 (adiabatic 9.6), 11.17, and 12.10 eV.

4-*Methyl*-1,2,4-*triazoline*-3,5-*dione* (1c). This had m.p. 104° (sublimed at 50° and 0.1 mmHg), $\nu_{max.}$ 1 760, 1 705, 1 270, 955, 740, and 675 cm^{-1}, $\lambda_{max.}$ (benzene) 536 (ε 247.7) and 564 nm (214), $\lambda_{max.}$ (dioxan) 527 nm (ε 193.2), $\lambda_{max.}$ (ethyl acetate) 527 nm (ε 188.0), τ (CDCl$_3$) 6.80 (s), ionisation potentials 10.31 (adiabatic 9.7) (vibrational fine structure 880 cm^{-1}), 11.35 (910 cm^{-1}), 12.30 (1 320 cm^{-1}), and 12.87 eV (*ca.* 1 800 cm^{-1}).

4-*Benzyl*-1,2,4-*triazoline*-3,5-*dione* (1d). Benzyl isocyanate (10.3 g) and ethyl hydrazinecarboxylate (8 g) were condensed in benzene (30 ml) to give 4-benzyl-1-ethoxycarbonylsemicarbazide (17.7 g, 97%), m.p. 144—145°, $\nu_{max.}$ 3 400, 3 330, 3 200, 1 690, 1 660, 1 220, 780, 750, 730, and 690 cm^{-1}. The semicarbazide (10 g) was treated as above to give 4-benzylurazole (7.3 g, 91%), m.p. 186—188° (from water) (lit.,[39] 187°), $\nu_{max.}$ 3 500, 3 400, 1 740, and 1 675 cm^{-1} (Found: M, 191. Calc. for $C_9H_9N_3O_2$: M,

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[35] B. J. Cocksey, J. H. D. Eland, and C. J. Danby, *J. Chem. Soc.* (*B*), 1971, 790; A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Analyt. Chem.*, 1971, **43**, 375.

[36] The first (vertical) ionisation potentials of the alkyl-TDs (1a—c) are also linearly related to the Taft σ^* value: M. Burrage, Ph.D. Thesis, Southampton, 1973.

[37] P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.*, 1969, **91**, 7131.

[38] R. C. Cookson, S. S. Gupte, I.D. R. Stevens, and C. T. Watts, *Org. Synth.*, 1971, **51**, 121

[39] E. Nachbauer and W. Gottardi, *Monatsh.*, 1963, **94**, 584.

191). 4-Benzylurazole (0.75 g) was oxidised as above to give 4-benzyl-1,2,4-triazoline-3,5-dione (0.65 g, 85%), m.p. 57° (decomp.; sublimed at 55° and 0.1 mmHg), $\nu_{max.}$ 1 765, 1 720, 740, 710, and 680 cm^{-1}, $\lambda_{max.}$ (benzene) 538 (ε 269.0) and 563 nm (215), $\lambda_{max.}$ (dioxan) 526 nm (ε 195.0), $\lambda_{max.}$ (ethyl acetate) 526 nm (ε 195.0), τ ($CDCl_3$) 2.63 (5 H, s) and 5.25 (2 H, s).

4-p-*Methoxyphenyl*-1,2,4-*triazoline*-3,5-*dione* (1e). 4-*p*-Methoxyphenyl-1-ethoxycarbonylsemicarbazide was prepared as above, m.p. 172—172.5° (lit.,[40] 171.5°), $\nu_{max.}$ 3 270, 1 735, 1 680, 1 245, 835, 775, 760, and 665 cm^{-1}. The semicarbazide was cyclised as above to give 4-*p*-methoxyphenylurazole (95%), m.p. 221—222° (from water) (lit.,[40] 220.5°), $\nu_{max.}$ 3 230, 1 765, 1 685, 1 242, 850, 838, 805, 790, and 765 cm^{-1} (Found: *M*, 207. Calc. for $C_9H_9N_3O_3$: *M*, 207). 4-*p*-Methoxyphenylurazole was oxidised as above to give 4-*p*-methoxyphenyl-1,2,4-triazoline-3,5-dione (79%), m.p. 124—126° (sublimed at 100° and 0.2 mmHg), $\nu_{max.}$ 1 770, 1 750, 1 260, 830, 745, and 680

TABLE 12

R	Yield (%)	M.p. (°C)	Recrystallisation solvent	ν_{max} (cm^{-1})	Found (%) C	Found (%) H	Found (%) N		Required (%) C	Required (%) H	Required (%) N
				1,4-Diphenylbuta-1,3-diene adducts (2)							
Bu^t	96	175	Benzene–petrol (b.p. 60—80°)	1 755, 1 690	73.55	6.65	11.2	$C_{22}H_{23}N_3O_2$	73.15	6.35	11.65
Et	95	159	Petrol (b.p. 60—80°)	1 770, 1 695	*M* 333			$C_{20}H_{19}N_3O_2$	*M* 333		
Me	95	175	Benzene–petrol (b.p. 60—80°)	1 765, 1 700	71.75	5.75	13.5	$C_{19}H_{17}N_3O_2$	71.45	5.35	13.15
CH_2Ph	90	163	Benzene–petrol (b.p. 60—80°)	1 755, 1 705	*M* 395			$C_{25}H_{21}N_3O_2$	*M* 395		
p-$MeOC_6H_4$	90	161	Ethyl acetate	1 773, 1 760, 1 700	*M* 411			$C_{25}H_{21}N_3O_3$	*M* 411		
Ph	85	163	Benzene–petrol (b.p. 60—80°)	1 765, 1 705	75.3	4.9	10.8	$C_{24}H_{19}N_3O_2$	75.6	5.0	11.05
p-$NO_2C_6H_4$	75	230	Benzene	1 760, 1 700	67.55	4.15	13.4	$C_{24}H_{18}N_4O_4$	67.6	4.25	13.15
N=CHPh	90	202	Acetone	1 780, 1 715	73.85	5.25	13.6	$C_{25}H_{20}N_4O_2$	73.5	4.9	13.75
				Anthracene adducts (3)							
Bu^t	95	206	Acetone	1 750, 1 700	71.9	5.6	12.6	$C_{20}H_{19}N_3O_2$	72.05	5.7	12.6
Et	90	198	Petrol (b.p. 60—80°)	1 770, 1 710	*M* 305			$C_{18}H_{15}N_2O_3$	*M* 305		
Me	90	234	Chloroform–ethanol	1 765, 1 700	69.95	4.4	14.15	$C_{17}H_{13}N_3O_2$	70.1	4.45	14.45
CH_2Ph	90	232	Benzene	1 765, 1 710	*M* 367			$C_{23}H_{17}N_3O_2$	*M* 367		
p-$MeOC_6H_4$	90	222	Ethyl acetate	1 775, 1 720	*M* 383			$C_{23}H_{17}N_3O_3$	*M* 383		
Ph	Characterised in ref. 1										
p-$NO_2C_6H_4$	70	276	Benzene	1 765, 1 695							
N=CHPh	89	234	Ethyl acetate	1 760, 1 705	72.45	4.35	14.45	$C_{23}H_{16}N_4O_2$	72.65	4.2	14.75
				Hexachlorocyclopentadiene adducts (4)							
					M Found *				*M* Required		
Bu^t	40	124		1 810, 1 745, 1 580	427			$C_{11}H_9Cl_6N_3O_2$	427		
Me	85	167	Ethanol	1 815, 1 735, 1 580	385			$C_8H_3Cl_6N_3O_2$	385		
CH_2Ph	85	91	Ethanol–water	1 810, 1 745, 1 580	461			$C_{14}H_7Cl_6N_3O_2$	461		
Ph	80	137	Ethanol–water †	1 810, 1 755, 1 595, 1 575	447			$C_{13}H_5Cl_6N_3O_2$	447		
p-$NO_2C_6H_4$	75	212	Ethanol	1 800, 1 750, 1 595, 1 575	492			$C_{13}H_4Cl_6N_4O_4$	492		
				Bicyclo[2.2.1]heptadiene adducts (5)							
					Found (%) C	Found (%) H	Found (%) N		Required (%) C	Required (%) H	Required (%) N
Bu^t	95	91	Benzene–petrol (b.p. 60—80°)	1 745, 1 705	63.15	6.65	17.1	$C_{13}H_{17}N_3O_2$	63.1	6.9	17.0
Me	90	109	Ethyl acetate–petrol (b.p. 60—80°)	1 750, 1 705	58.25	5.4	20.1	$C_{10}H_{11}N_3O_2$	58.55	5.35	20.5
CH_2Ph	90	98	Benzene–petrol (b.p. 60—80°)	1 775, 1 705	*M* 281			$C_{16}H_{15}N_3O_2$	*M* 281		
Ph	Characterised in ref. 1										
p-$NO_2C_6H_4$	65	188	Acetone	1 760, 1 700	57.7	3.85	17.6	$C_{15}H_{12}N_4O_4$	57.7	3.85	17.95
N=CHPh	85	159	Benzene–petrol (b.p. 60—80°)	1 760, 1 700	65.0	4.5	19.5	$C_{16}H_{14}N_4O_2$	65.3	4.75	19.05

* Mass ion given is that for $^{35}Cl_5{}^{37}Cl$ adduct. Isotopic distribution patterns were consistent with the number of chlorines present in the mass ion and ion fragments. † Lit.,[19] 136°.

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[40] J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, 1966, **31**, 3444.

cm^{-1}, $\lambda_{max.}$ (benzene) 543 nm (ε 241.6), $\lambda_{max.}$ (dioxan) 530 nm (ε 191.0), $\lambda_{max.}$ (ethyl acetate) 532 nm (ε 169.0), τ (CDCl$_3$) 2.63 (2 H, d, *J* 9.0 Hz) and 2.97 (2 H, d, *J* 9.0 Hz) both with secondary splitting (t, A_2B_2), and 6.13 (3 H, s).

4-*Phenyl*-1,2,4-*triazoline*-3,5-*dione* (1f). This had m.p. 180° (decomp.; sublimed at 100° and 0.1 mmHg), $\nu_{max.}$ 1 760, 1 740, 725, and 680 cm^{-1}, $\lambda_{max.}$ (benzene) 540 nm (ε 247.8), $\lambda_{max.}$ (dioxan) 527 nm (ε 186.2), $\lambda_{max.}$ (ethyl acetate) 528 nm (ε 172.2), τ (CDCl$_3$) 2.52 (s).

4-p-*Nitrophenyl*-1,2,4-*triazoline*-3,5-*dione* (1g). This had m.p. 130° (sublimed at 110° and 0.1 mmHg; *p*-nitrophenyl- and benzylideneamino-TD are especially liable to decompose completely during sublimation if overheated), $\nu_{max.}$ 1 765, 860, 730, and 670 cm^{-1}, $\lambda_{max.}$ (benzene) 538 nm (ε 246.3), $\lambda_{max.}$ (dioxan) 524 nm (ε 175.1), $\lambda_{max.}$ (ethyl acetate) 523 nm (ε 168.2), τ ([$^2H_6$]Me$_2$SO) 1.53 (2 H, d, *J* 9.0 Hz) and 2.22 (2 H, d, *J* 9.0 Hz) both with secondary splitting (t, A_2B_2).

4-*Benzylideneamino*-1,2,4-*triazoline*-3,5-*dione* (1h). This had m.p. 130° (sublimed at 110° and 0.1 mmHg), $\nu_{max.}$ 1 830, 1 765, 1 720, 770, 730, 690, and 660 cm^{-1}, $\lambda_{max.}$ (benzene) 558 nm (ε 217.2), $\lambda_{max.}$ (dioxan) 541 nm (ε 172.6), $\lambda_{max.}$ (ethyl acetate) 542 nm (ε 163.0), τ (CDCl$_3$) 0.77 (1 H, s), 2.16 (2 H, m), and 2.42 (3 H, m).

Dienes and Solvents.—*trans,trans*-1,4-Diphenylbutadiene (DPBD) was prepared by the method of ref. 41 and obtained as fine crystals by recrystallisation from benzene, m.p. 153°, $\lambda_{max.}$ (ethanol) 329 nm (ε 63 800) [lit.,[42] 329 nm (ε 55 300)].

Anthracene, bicyclo[2.2.1]*heptadiene, and hexachlorocyclopentadiene*. The procedure used by Brown [21] was followed. Purity was checked by comparison with literature data.[43,44]

Dioxan was purified using Hess and Frahm's method,[45] and ethyl acetate by Fieser's method.[46]

Diels–Alder Adducts.—All adducts were prepared by the reaction of equimolar amounts of diene and dienophile and were obtained pure by recrystallisation. Physical constants are recorded in Table 12 and ^{1}H n.m.r. spectra in Table 13.

Kinetic Measurements.—The progress of each Diels–Alder reaction was followed quantitatively by observing the rate of disappearance of the *n*→π* absorption maximum of the dienophile in the visible region, at *ca*. 530 nm, and the corresponding diene concentration was calculated from the degree of adduct formation.

A Perkin-Elmer 402 u.v.–visible spectrometer with an interval timer and thermostatted cell block was used for all absorption measurements, using matched spectrosil cells of 1 and 4 cm path-length. For reactions carried out in the spectrometer cell, the cell block was thermostatted at the required temperature with a Churchill thermo-circulator; the temperature was measured with a chromel P–alumel thermocouple.

Because the reactions studied varied in rate by a factor of *ca*. 2 × 10^5 three different experimental techniques were required. For reactions with second-order rate constants under *ca*. 0.05 l mol^{-1} s^{-1} sealed ampoules containing the reaction mixture were placed in a thermostatted bath and were withdrawn at intervals for analysis. For more rapid reactions, with k_2 under *ca*. 1.0 l mol^{-1} s^{-1}, the reaction mixture was introduced into a thermostatted 1 cm cell in the spectrometer and the disappearance of the dienophile absorption maximum observed directly. Thermostatted 4 cm cells were used for faster reactions, the rate of disappearance of dienophile being reduced by the lower concentrations of reactants possible compared with the 1 cm cell technique. Second-order rate constants up to 20 l mol^{-1} s^{-1} were measurable by this method.

TABLE 13

R	τ (CDCl$_3$)
	1,4-Diphenylbuta-1,3-diene adducts (2)
Bu^t	2.60 (10 H, s), 4.10 (2 H, d, *J* 1.5 Hz, H$_b$), 4.62 (2 H, d, *J* 1.4 Hz, H$_a$), 8.48 (9H, s)
Et	2.55 (10 H, s), 4.02 (2H, d, *J* 1.5 Hz, H$_b$), 4.53 (2 H, d, *J* 1.5 Hz, H$_a$), 6.49 (2 H, q, *J* 7.2 Hz), 8.83 (3 H, t, *J* 7.2 Hz)
Me	2.59 (10 H, m), 4.07 (2H, d, *J* 1.6 Hz, H$_b$), 4.58 (2 H, d, *J* 1.5 Hz, H$_a$), 7.08 (3 H, s)
CH$_2$Ph	2.56 (10 H, m), 2.73 (5 H, s), 4.06 (2 H, d, *J* 1.5 Hz, H$_b$), 4.55 (2 H, d, *J* 1.5 Hz, H$_a$), 5.42 (2 H, s)
p-MeOC$_6$H$_4$	2.62 (12 H, m), 3.15 [2 H, d, *J* 8.7 Hz and secondary splitting (t)], 4.03 (2 H, d, *J* 1.4 Hz, H$_b$), 4.48 (2 H, d, *J* 1.4 Hz, H$_a$), 6.29 (3 H, s)
Ph	2.58 (15 H, m), 4.00 (2 H, d, *J* 1.4 Hz, H$_b$), 4.46 (2 H, d, *J* 1.4 Hz, H$_a$)
p-NO$_2$C$_6$H$_4$	1.78 (2 H, d, *J* 9.2 Hz), 2.18 (2 H, d, *J* 9.2 Hz) both with secondary splitting (t, A_2B_2), 2.55 (10 H, m), 3.92 (2 H, d, *J* 1.5 Hz, H$_b$), 4.43 (2 H, d, *J* 1.5 Hz, H$_a$)
N=CHPh	0.65 (1 H, s), 2.52 (14 H, m), 4.00 (2 H, d, *J* 1.4 Hz, H$_b$), 4.47 (2 H, d, *J* 1.4 Hz, H$_a$)
	Anthracene adducts (3)
Bu^t	2.67 (8 H, m), 3.84 (2 H, s, H$_a$), 8.68 (9 H, s)
Et	2.70 (8 H, m), 3.81 (2 H, s, H$_a$), 6.72 (2 H, q, *J* 7.2 Hz), 9.11 (3 H, t, *J* 7.2 Hz)
Me	2.67 (8 H, m), 3.78 (2 H, s, H$_a$), 7.21 (3H, s)
CH$_2$Ph	2.73 (13 H, m), 3.78 (2 H, s, H$_a$), 5.53 (2 H, s)
p-MeOC$_6$H$_4$	2.60 (8 H, m), 3.04 (4 H, m, A_2B_2 system), 3.67 (2 H, s, H$_a$), 6.23 (3 H, s)
p-NO$_2$C$_6$H$_4$	1.80 (2 H, m), 2.60 (10 H, m), 3.32 (2 H, s, H$_a$) *
N=CHPh	0.73 (1 H, s), 2.60 (13 H, m), 3.68 (2 H, s, H$_a$)
	Hexachlorocyclopentadiene adducts (4)
Bu^t	8.83 (s)
Me	6.95 (s)
CH$_2$Ph	2.68 (5 H, m), 5.43 (2 H, s)
Ph	2.61 (m)
p-NO$_2$C$_6$H$_4$	1.66 (2 H) and 2.37 (2 H) (both m, A_2B_2, $J_{AB} = J_{A'B'} = 9.0$, $J_{AA'} = J_{BB'} = 2.7$ Hz)
	Bicyclo[2.2.1]heptadiene adducts (5)
Bu^t	5.63 (2 H, d, *J* 2.5 Hz, H$_d$), 7.62 (1 H, m, H$_c$) 8.20 (2 H, s, H$_b$), 8.42 (12 H, s, Bu^t and H$_a$)
Me	5.58br (2 H, s, H$_d$), 6.97 (3 H, s, Me), 7.55 (1 H, m, H$_c$), 8.17 (2 H, s, H$_b$), 8.42 (3 H, s, H$_a$)
CH$_2$Ph	2.59 (5 H, s), 5.37 (2 H, s), 5.61br (2 H, s, H$_d$), 7.65br (1, s, H$_c$), 8.25 (2 H, s, H$_b$), 8.49 (3 H, s, H$_a$)
p-NO$_2$C$_6$H$_4$	1.67 (2 H, d, *J* 9.0 Hz) and 2.08 (2 H, d, *J* 8.5 Hz) both with secondary splitting (t, A_2B_2), 5.40 (2 H, d, *J* 2.1 Hz, H$_d$), 7.39 (1 H, m, H$_c$), 8.09 (2 H, s, H$_b$), 8.28 (3 H, s, H$_a$)
N=CHPh	0.57 (1 H, s), 2.13 (2 H, m), 2.55 (3 H, m), 5.40 (2 H, d, *J* 2.5 Hz, H$_d$), 7.48 (1 H, m, H$_c$), 8.16 (2 H, s, H$_b$), 8.37 (3H, s, H$_a$)

* In [$^2H_6$]dimethyl sulphoxide.

In all cases the progress of the reaction was followed to *ca*. 90% completion and the results obtained fitted the expected second-order treatment. In most cases an excess of diene was used. Reproducibility was established by

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repeated measurements. In some cases, where the rate constant had a conveniently intermediate value, two different techniques were used to measure the rate of the same reaction.

Solutions of diene and dienophile were made up by weighing and were thermostatted for 0.5 h before mixing and transfer to the spectrometer cell.

Second order rate constants were calculated by standard techniques,[47] and a least squares treatment was used to obtain the line of best fit for plots of $\ln(B/A)$ against time.

Except in one case, the absorption of the reaction product at *ca.* 530 nm was zero. For the reaction between *p*-nitrophenyl-TD and bicyclo[2.2.1]heptadiene in benzene the adduct produced was insoluble and was deposited in the spectrometer cell during the reaction. The absorption measurements made during the last 40% of the reaction were therefore affected by scattering and a correction was made. The rate constant of 0.0344 l mol^{-1} s^{-1} was in agreement with the values of 0.0358 and 0.0355 l mol^{-1} s^{-1} at 50% reaction found from two other determinations in which a correction was not applied.

Activation parameters were obtained from the line of best fit for a plot of $\ln(k_2)$ against $1/T$. For most of the rate constants the probable error is ±4—7%; but for the reactions of *p*-nitrophenyl- and benzylideneamino-TD with DPBD in benzene the error is *ca.* ±10% because of the short reaction time involved. The consequent error in activation energy, enhanced by the low temperature dependence is *ca.* ±0.7 kcal mol^{-1}, and in activation entropy ±2 cal mol^{-1} K^{-1}.

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