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SOLVENT EFFECT AS THE RESULT OF FRONTIER MOLECULAR ORBITAL INTERACTION. VI. THE DIELS-ALDER REACTIONS OF AN N-ACYL-o-QUINONE MONOIMIDE BEHAVING AS DIENE OR DIENOPHILE

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Abstract - The solvent effect of the Diels-Alder (D A) reactions of N-(2',4'-dichloro-6'-oxo-2',4'-cyclohexadien- 1'-ylidene)-4-nitrobenzamide (**1**) was kinetically investigated **1**, with 2,3-dimethylbutadiene (DMB), behaves mainly as heterodienophile whereas, with ethyl vinyl ether (EVE), reacts as heterodiene

The mechanism of solvation is the same in both D A. reactions and involves **1** since log k_{DMB} is linearly related to log k_{EVE}

The monoparametric inverse relationship between rate and basicity D_π parameters shows that solvent behaves as a nucleophile This relationship is largely improved by a bi-parametric equation with solvent basicity and polarity contributions

The negative polarity contribution of the solvent to the rate is discussed in terms of change of polarity for these D A reactions going from reactants to transition states

Previous papers of this series[(1-5)] investigated the solvent effect of Diels-Alder (D A) and Hetero-D A (H D A) reactions with either heterodienes or heterodienophiles

Both the results obtained from the above studies and those of the solvent effect[(6)] of D A reactions reported in the literature fit into three different classes with the kinetic data correlating·

A) with the electrophilic parameters of the solvent and the rate increases with the increase of the electrophilic character of the solvent,

B) with the nucleophilic parameters and the rate decreases with the increase of the nucleophilic character of the solvent,

C) with the cohesive pressure parameters of the solvent and the rate sligthly increases (as expected for a bimolecular reaction) with the increase of the cohesive pressure

The same result is obtained if the Kamlet-Taft(7) multiparametric equation is applied to the same set of reactions The main contribution remains that outlined with the monoparametric approach, and the secondary contribution in general derives from the polarity effect of the solvent

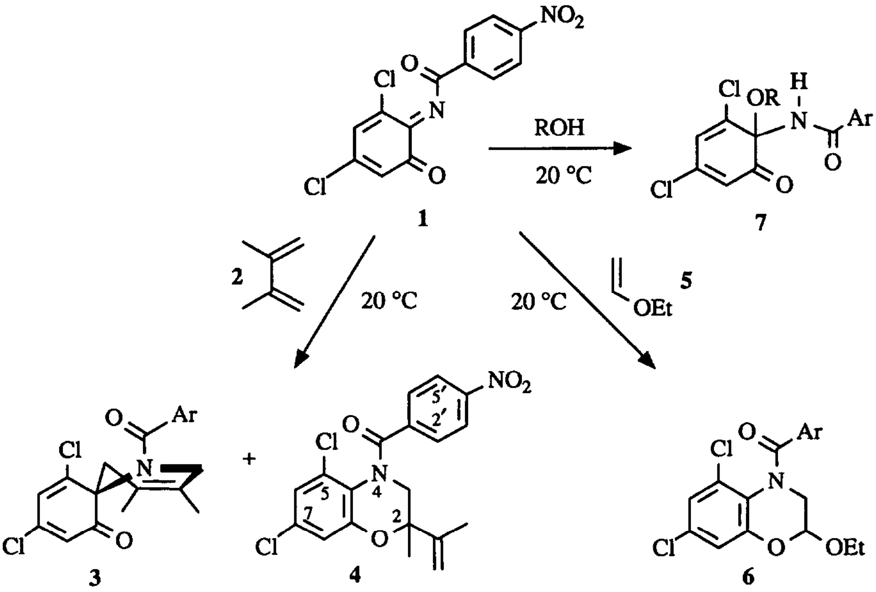
This model assumes, in classes **A** and **B**, a specific solvation of the reagent involved in the solvent effect. Hence the solvent effect should be the same for different D A reactions involving the same solvatable reagent, independent of playing the role of diene or dienophile

To test this, the solvent effects of two different D.A reactions of *o*-quinone imine **1** were studied This is reported(8) to behave as heterodienophile with 2,3-dimethylbutadiene (DMB-**2**) to give the azaspiro derivative **3** In our hands, the reaction gave, in addition to **3**, a minor adduct (8-12% yield depending on the solvent) identified as 5,7-dichloro-2,3-dihydro-2-isopropenyl-2- methyl-4-(4′-nitrobenzoyl)-1,4-benzoxazine (**4**) With ethyl vinyl ether (EVE-**5**), **1** behaves as heterodiene to give(8) the benzoxazine **6** (Scheme 1)

To compare these two reactions, a common set of solvents was tested This does not include acetic acid, reacting with EVE, and alcohols that nicely add to **1** to give **7** Finally **1** is not stable in DMSO, DMF, and HMPT

The kinetic runs with **2** and **5** were studied at 20 °C by u v -vis spectroscopic analysis of the disappearing **1** at the suitable wavelength, following the reactions to about 70% completion The product mixture was monitored during the reaction by h p l c for a significant number of solvents to exclude the conversion of **3** to **4** under the experimental conditions Finally, blank experiments at 20 °C excluded a subsequent second D A reaction of **3** with **2** already observed with tetrahalo-*o*-quinones and **2** (1)

Scheme 1



In the presence of 50-200 fold excess of **2** or **5**, pseudo first order rate constants were determined and the second order rate constants were then calculated. The kinetic data reported in Table 1 represent the average of at least 6 kinetic runs, each with varying reagent ratios.

The rate of the reaction with EVE is about 10 times faster than that with DMB, but, more significantly, the solvent effect is nearly the same. 30 and 35 respectively, in the range cyclohexane-acetone. The implications of this become more evident when log k_{DMB} is plotted *vs* log k_{EVE} (Fig. 1) since a nice linear correlation is obtained with a slope nearly equal to 1. The solvent effect being the same for both H.D.A. reactions, we conclude that the interaction of **1** with the solvent must be independent of its behaviour as a diene or a dienophile.

About the mechanism of solvation of **1**, the fast reaction in cyclohexane immediately suggests that the electrophilic properties of the solvent are not involved in. From simple considerations on the effect of substituents, **1** is expected to be characterized by a low-lying LUMO. If the rate of **1** and DMB is about 3 times faster than that of DMB and tetrachloro-*o*-quinone at 20 °C (*e.g.* 110 x 10^{-3} *vs* 33 x 10^{-3} in cyclohexane resp.),(1) the LUMO of **1** should be at least equal, if not lower, than -2.60 eV.(9) Therefore the solvent should behave as a nucleophile in the solvation of **1** and the rate of both H.D.A. reactions of **1** with DMB and EVE should decrease with the increase of the nucleophilic character of the solvent (B-type D.A.).

Table 1 Rate constants for the reaction of 1 and DMB (2) or EVE (5) at 20 °C in various solvents with D_π parameters of the solvent

No	Solvent	D_π	10^3 x k (L mol^{-1}s^{-1})	
			2	**5**
1	Carbon tetrachloride	---	69.1 ± 0.5	620 ± 10
2	Chloroform	- 1.56	35 ± 1	225 ± 10
3	1,2-Dichloroethane	- 1.22	16.3 ± 0.1	114 ± 3
4	Cyclohexane	---	110 ± 5	770 ± 10
5	Chlorobenzene	- 0.903	17.4 ± 0.1	143 ± 1
6	Nitromethane	- 0.724	8.88 ± 0.08	41.8 ± 0.8
7	Nitrobenzene	- 0.583	12.0 ± 0.4	83.5 ± 1.0
8	Acetonitrile	- 0.440	5.25 ± 0.05	27.8 ± 0.7
9	PDC	---	6.25 ± 0.05	40.8 ± 0.3
10	Methyl benzoate	- 0.225	6.65 ± 0.15	59 ± 1
11	Benzene	0	13.1 ± 0.2	119 ± 2
12	Butanone	0.177	4.18 ± 0.05	34.7 ± 0.3
13	Acetone	0.261	3.10 ± 0.07	25.5 ± 1
14	Ethyl acetate	0.289	6.22 ± 0.06	55.7 ± 0.6
15	Dimethoxymethane	0.383	9.9 ± 0.1	79.7 ± 0.7
16	Toluene	0.394	9.7 ± 0.5	98 ± 2
17	1,4-Dioxane	0.590	4.50 ± 0.08	43 ± 1
18	THF	0.639	3.28 ± 0.05	29.5 ± 0.3

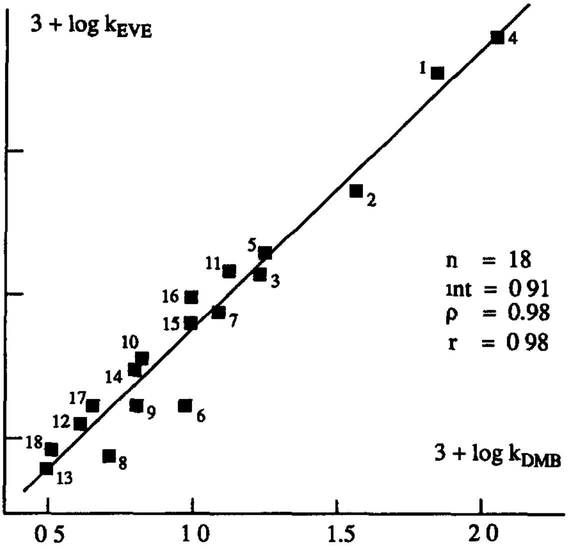


Figure 1 Plot of the rate constants of the reaction between 1 and 2 vs those of 1 and 5 (Table 1)

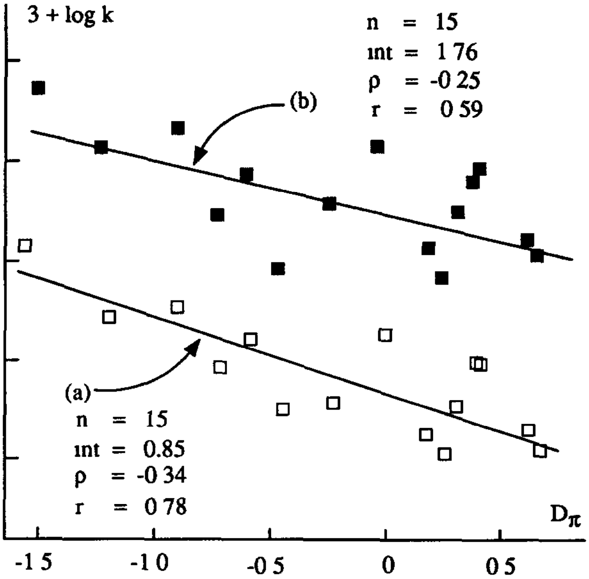


Figure 2 Rate constants of H D A reactions between 1 and 2 (a-□) or 5 (b-■) at 20 °C in differing solvents plotted vs the D_π parameters of the solvent

When the kinetic data in Table 1 are plotted *vs* empirical parameter D_π[(10)] of solvent nucleophilicity (Fig 2) two linear correlations of rather poor quality are obtained, both with a negative slope.

The reason of the heavy deviations from linearity is easily explained if the Kamlet-Taft[(7)] (K T) multiparametric equation (1) is tested In this equation different contributions of the solvent are considered π^* is the index of solvent polarity-polarizability (corrected by a discontinuous polarizability term δ), α and β are the acidity and basicity contributions (the latter integrated by the co-ordinate covalency parameter ξ) and $\delta_H{}^2$ is the cohesive pressure of the solvent

$$A = A^\circ + s(\pi^* + d\,\delta) + a\,\alpha + b\,\beta + h\,\delta_H^2/100 + e\,\xi \qquad (1)$$

When the K.T. equation is applied to the kinetic data in Table 1, the contributions of acidity and cohesive pressure are negligible, but the polarity-polarizability term π^* (corrected by δ) contributes significantly to solvation and two good linear relationships are obtained (Fig 3)

A polarity contribution to the solvent effect of D A reaction is not an unusual phenomenon (more than 50% of the D.A reactions analyzed in ref. 1 with the K T equation have a positive contribution of the polarity-polarizability term in the range 20-40%) What is new is that both reactions of **1** with DMB and EVE show a *negative* contribution of the polarity term

A positive contribution of the solvent polarity to the rate of a cycloaddition was rationalized by Huisgen[(11)] as the result of the increasing charge separation during the activation process Sometimes the monoparametric relationship between rate and the Dimroth-Reichardt parameters E_T[(6)] allows to represent this effect.[(11)] The large solvent effect on the rate of [2+2] cycloaddition of donor and acceptors olefins were well reproduced by the multi-parametric Koppel-Palm equation,[(12)] only the two parameters of eq (2), *i e* Kirkwood's function of the dielectric constant and the nucleophilic solvating power B, were essential [(11)] Instead of B, the mentioned parameter D_π (eq 3) was likewise suitable [(13)]

$$\log k = \log k^\circ + a\,(\epsilon-1)/(2\epsilon+1) + b\,B \qquad (2)$$

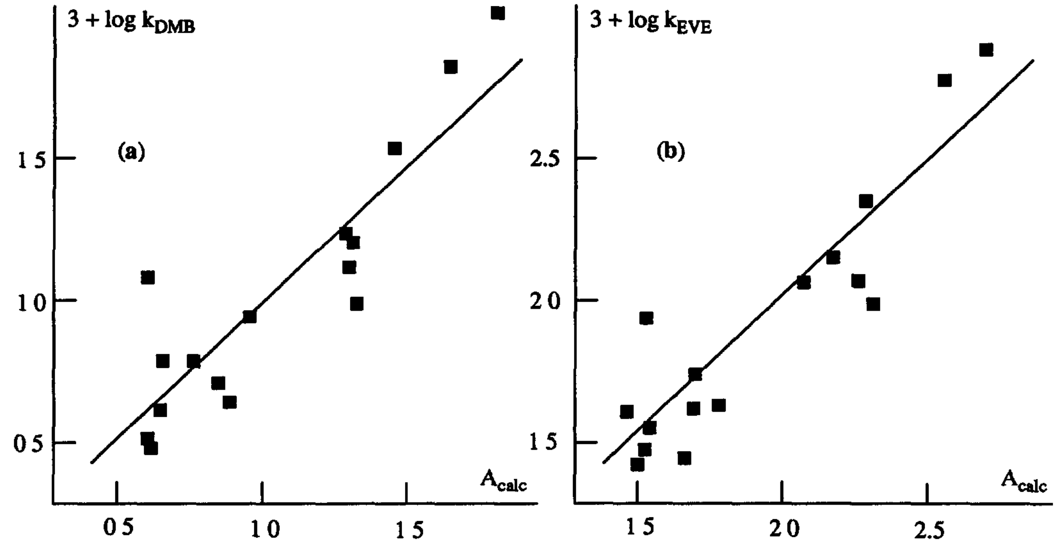
$$\log k = \log k^\circ + a\,(\epsilon-1)/(2\epsilon+1) + b\,D_\pi \qquad (3)$$

The statistical treatment of the kinetic data of Table 1 with eq 2 or 3 is reported in Table 2 Again the coefficients of the polarization term are always negative and the rate *decreases* with the increase of the dielectric constant ϵ of the solvent

This solvent effect, which is similar to that of the 1,3-dipolar cycloaddition between N-methyl-C-phenylnitrone and ethyl acrylate,[(14)] suggests that polarity in these H.D A reactions is slightly reduced in going from diene and dienophile to the transition states A probe of this is offered by the dipole moments of reactants and cycloadducts

Scheme 2 reports the measured dipole moments (benzene, 25 °C) of **1**, **3**, and **6** plus those of DMB[(15)] and EVE[(16)] taken from the literature (due to the low yield, **4** can be ignored)

If log k_2 is a linear function of $(\epsilon-1)/(2\epsilon+1)$ for a reaction of two neutral dipolar molecules, Kirkwood's function allows an approximate determination of the dipole moment of the t s .[(17)] However, this is meaningful only for large solvent effect dictated essentially by the polarity term and cannot be applied to a situation where the rate is a function of two parameters



$A = 1\ 80 - 0\ 63\ \pi^* + 0.04\ \delta - 1\ 57\ \beta$
$(n = 16, r = 0\ 90)$

$A = 2\ 73 - 0\ 97\ \pi^* + 0.23\ \delta - 1.16\ \beta$
$(n = 16, r = 0.92)$

Figure 3 The K T relationships for the reactions of 1 + DMB (a) (relative weights of coefficients are π, 31%, δ, 4%, β, 65%) and 1 + EVE (b) (relative weigths of coefficients are π*, 40%, δ, 18%, β, 42%)*

Table 2 Treatment of the kinetic data in Table 1 with the biparametric equations 2 and 3

Reaction		eq 2	eq 3
	n^a	15	15
	a^b	-1 09 (24%)	-1 80 (37%)
1 + DMB	b^c	-0 010 (76%)	-0 43 (63%)
	log k°	2 15	1 51
	r^d	0 91	0 94
	n^a	15	15
	a^b	-1 72 (36%)	-2 24 (46%)
1 + EVE	b^c	-0 008 (64%)	-0 37 (54%)
	log k°	2 18	1 58
	r^d	0 92	0 90

$^{a)}$Number of solvents, $^{b)}$coefficient of the Kirkwood's function, in parentheses its relative weight, $^{c)}$coefficient of the basicity parameters, in parentheses its relative weight, $^{d)}$correlation coefficient

Scheme 2

$$\begin{array}{ccccccccc} & & 3 & \xleftarrow{\text{DMB}} & 1 & \xrightarrow{\text{EVE}} & 6 & \\ \mu & = & 5\ 6 & 0\ 52 & 5\ 1 & 1\ 27 & 4\ 8 & \text{D} \end{array}$$

When considering a hypothetical D A reaction where the rate is insensitive to the change of the solvent polarity, the dipole moment of the transition state ($\mu^{\neq}$) can be derived by eq 4

$$\left(\frac{\mu^2}{r^3}\right)^{\neq} = \left(\frac{\mu^2}{r^3}\right)_{\text{diene}} + \left(\frac{\mu^2}{r^3}\right)_{\text{dienophile}} \tag{4}$$

If the cubes of the radii of the molecules were approximated by their molecular masses,$^{(11)}$ eq (4) furnishes 5 9 D and 6 4 D for the $\mu^{\neq}$ values of the reactions with DMB and EVE respectively These are somewhat higher than the dipole moments of the cycloadducts **3** (5 6 D) and **6** (4 8 D). Taking into account that the rates of both the above H D A reactions have a negative contribution from the polarity of the solvent, the dipole moments of their t s s will be lower than the calculated $\mu^{\neq}$ values

Since the H D A reaction **1** + **2** $\leftrightarrows$ [t s]$^{\neq}$ $\rightarrow$ **3** seems to occur with nearly no variation of the dipole moment along the reaction coordinate, these data alone do not explain the weight of the polar term evidenced in Table 2 On the contrary, for the H D A reaction **1** + **5** $\leftrightarrows$ [t s]$^{\neq}$ $\rightarrow$ **6**, the data suggest a significant loss of polarity from reactants to the transition state Both reactions are probably concerted, but not synchronous

CONCLUSION.

In conclusion, the main result obtained from the kinetic investigation of the solvent effect of the H D A reactions of **1** is that solvent behaves mainly as a nucleophile, with the same mechanism of solvation if **1** behaves as heterodiene or heterodienophile Furthermore a polar contribution of the solvent in a D A reaction can be either positive or negative and cannot be ignored

EXPERIMENTAL SECTION.

Melting points were determined by the capillary method on a Tottoli apparatus (Buchi) Elemental analyses were made on Carlo Erba CHN analyzer mod 1106 ^{1}H-n m r spectra were recorded on Bruker WP80SI spectrometer, i r spectra (nujol mulls) on a Perkin Elmer 983 spectrophotometer, and massa spectra on a Finnigan MAT 8222 mass spectrometer

Materials - 2,3-dimethylbutadiene (**2**) and ethyl vinyl ether (**5**) were commercial freshly distilled products The solvents for the kinetic runs were freshly distilled reagent grade (u v spectroscopic grade when available)

N-(2′,4′-dichloro-6′-oxo-2′,4′-cyclohexadien-1′-ylidene)-4-nitrobenzamide (**1**) - The product was prepared as described in the literature$^{(8)}$ and was recrystallized from benzene as small orange crystals, m p 163-165°C (lit $^{(8)}$ 170-173 °C).

*Reaction of **1** and **2*** - Compound **1** (0 65 g - 2 mmol) dissolved in few cm^3 of acetone was allowed to react at room temperature for a night with an excess of **2** The solvent and the excess diene were evaporated and the residue was crystallized from ethanol to give 0 60 g (74 % yield) of **3** as yellow crystals, m p 185-186 °C (lit $^{(8)}$ 188-189 °C) The mother liquors were evaporated and the residue was column cromatographed [Merck silica gel 230-400 mesh, eluant cyclohexane-ethyl acetate (9·1)] The first fraction gave **4** (0 08 g -

10% yield) which crystallized from diisopropil ether as white crystals, m p =139-140°C (Found C, 56 1, H, 3 9, N, 7.0 Calc. for $C_{19}H_{16}Cl_2N_2O_4$ C, 56 0, H, 4 0, N, 6 9%) Mass spectrum 406 $(M)^+$ m/z ^{1}H-NMR (DMSO-d_6), temperature 115 °C.$^{(17)}$ 1 43 (s, 3H, methyl in 2 position), 1.89 (broad s, 3H, allylic methyl), 2 49 (m, 2H, H-3), 4 98 (broad s, 2H, vinylic H), 7 03 and 7 11 (two doublets, J=2 Hz, 2H, H-6 and H-8), 7 79 (d, J=9 Hz, 2H, H-2′ and H-6′), 8 24 (d, 2H, H-3′ and H-5′) I r 1684 cm^{-1} (ν_{CO}) The second fraction gave a further corp of **3** (0 08 g - 84% total yield)

*Reaction of **1** and **5*** - Compound **1** (0 65 g - 2 mmol) dissolved in few cm^3 of acetone was allowed to react at room temperature with an excess of ethyl vinyl ether **5** After few hours the discoloured reaction mixture was evaporated and the residue crystallized from ethanol to give **7**, in nearly quantitative yield, as white crystals, m.p. 174-176 °C (lit ,$^{(8)}$ 176-177 °C)

*Reaction of **1** and ethanol* - Compound **1** (0 65 g - 2 mmol) was boiled for 15 minutes with 10 cm^3 ethanol The solution rapidly discoloured and the solvent was evaporated to give quantitatively N-(1′-ethoxy-2′,4′-dichloro-6′-oxo-2′,4′-cyclohexadienyl)-4-nitrobenzamide (**7**, R=Et) as white crystals, m p (diisopropil ether): 178-179 °C (Found C, 48 3, H, 3 2; N, 7 5. Calc for $C_{15}H_{12}Cl_2N_2O_5$. C, 48 5, H, 3 3, N, 7 5%). ^{1}H-NMR (benzene-d_6) 0 97 (t, 3H, methyl), 3.08 (m, 2H, diastereotopic -OCH_2-), 6.23 and 6 34 (two doublets, J=2 Hz, 2H, H-3′ and H-5′), 6 69 (broad s, 1H, NH), 6 98 (d, J=8 5 Hz, 2H, H-2 and H-6), 7.52 (d, 2H, H-3 and H-5) I r 3150 cm^{-1} (ν_{NH}), 1685 and 1641 cm^{-1} (ν_{CO}) Similar products were obtained with different alcohols

Determination of the [3]:[4] ratios - These were performed by h p l c on a Waters Associated ALC/CPC 244 liquid chromatograph with a Beckman mod 25 spectrophotometer operating at 255 nm as detector The chromatographic separations were performed on a stainless column (25 cm length x 4 mm internal diameter) pre-packed with Lichrosorb Si 60 (10 μm) Merck, eluant cyclohexane-ethyl acetate 85 15, flow. 0.7 cm^3 min^{-1}, retention times. **3** 8 5 min, **4** 5 6 min

Five solutions of known compositions of **3** and **4** were prepared with the ratio [**3**]/[**4**] in the range 80/20 - 97/3, each composition being tested on two indipendent samples at least four times each A calibration curve (which is in practice a straight line) was obtained by fitting the composition *vs* $h_1/(h_1+h_2)$, $h_1$and h_2 being the peak heights of **3** and **4** respectively The unknown compositions were determined by fitting the ratio of the peak heights on the calibration curve

Solutions of **1** (0 01 M) and **2** (1 5 M) in a selected number of solvents were thermostatted at 20 °C until the colour of the solution disappeared The solvent was evaporated under vacuum at room temperature and the residue was dissolved in a small volume of eluant Each solvent was tested on three independent samples at least four times each and the data obtained are reported in table 3 The reaction mixtures were tested at different degrees of completion and the ratio [**3**] [**4**] was found to be constant within the limits of the experimental error (±0.5%)

Table 3. Products distribution of the H D A adducts **3** and **4** in differing solvents at 20 °C

Solvent	3%^{a}	4%
Chloroform	91 9	8 1
Nitromethane	90 7	9 3
Benzene	90 5	9 5
Acetone	90 7	9 3
Ethyl acetate	90 6	9 4
1,4-Dioxane	88 1	11 9

$^{a)}$The error was in the limit ± 0 5%

Kinetics - The overall reaction rates were measured by following the disappearance of **1** on a Perkin Elmer Lambda 5 spectrophotometer provided with a thermostatted-cell transport assembly and an automatic multicell programmer The solutions were measured in 1 00 cm OS Hellma cuvettes of 3 cm^3 capacity Measuraments were taken at the wavelength of 440 nm for nitrobenzene and 420 nm for other solvents

A sample of **1** (2-5 mg) was weighed accurately and dissolved in the required solvent in a 25 cm^3 volumetric flask Dimethylbutadiene or ethyl vinyl ether (*ca* 0 5-1 cm^3) were poured into an accurately weighed 10 cm^3 volumetric flask containing *ca* 5 cm^3 of the required solvent The flask was again weighed to determine accurately the amount of **2** or **5** and then filled with solvent Six samples of the solution of **1** (2 00 cm^3 measured using a pipette) were placed in six cuvettes thermostatted at 20 °C and variable amounts (from 0 25 to 0 75 cm^3, accurately measured with a microsyringe) of the DMB or EVE solutions were added After vigorous mixing, the kinetic determinations were initiated

The activation parameters in benzene and 1,4-dioxane (Table 4) were determined by measuring the reaction rates at 25, 30, and 35 °C, following the same method described above

Table 4. Rates and activation parameters of the reaction between **1** with **2** and **5** in benzene and 1,4-dioxane

Reaction	T/°C	10^3 x k (l $mol^{-1}s^{-1}$)	
		Benzene	1,4-Dioxane
1 + 2	20	13 1±0 2	4 50±0 08
	25	16 9±0.1	5 7 ±0 2
	30	22 6±0 2	8 0 ±0 1
	35	29.4±0 1	10 7 ±0 1
	$\Delta H^{\neq a}$	9 1 ±0 5	9 9 ±0 5
	$-\Delta S^{\neq b}$	36 ±1	35 5 ±1 5
1 + 5	20	119 ±2	43 ±1
	25	164 ±2	56 ±1
	30	189 ±1	71 ±1
	35	224 ±3	86 5±1 5
	$\Delta H^{\neq a}$	6 7±0 5	7 8 ±0 5
	$-\Delta S^{\neq b}$	39 ±1	38 ±1

[a] kcal mol^{-1}, [b] cal $K^{-1}mol^{-1}$

Dipole moments - The dipole moments of products **1**, **3**, and **6** were measured by using the instrument and the methodology described by Huisgen (19) In table 5 are reported γ_2, molecular fractions of the solutions, ϵ_{12} and d_{12}, dielectric constant and density of the solutions, $\Delta\epsilon/\gamma_2$, slope of the plot ϵ_{12} *vs* γ_2, $\Delta d/\gamma_2$, slope of the plot d_{12} *vs* γ_2; $P_{2\infty}$, molar polarization at infinitive dilution, R_D, molecular refraction at D-line

Table 5. Dielectric constant and density measures in benzene solutions at 25 °C

Compound	Dielectric constant		Density	
	10^4 x γ_2	ϵ_{12}	10^4 x γ_2	d_{12}
1	2 158	2 2808	3 908	0 87328
	3 324	2848	7 111	379
$P_{2\infty}$=598 8	4 451	2889	8 971	403
R_D=74 7	5 923	2938	13 12	466
	7 116	2982		
	$\Delta\epsilon/\gamma_2$ = 35 7		$\Delta d/\gamma_2$ = 1 49	
3	1 028	2 2780	3 903	0 87346
	2 230	2830	5 821	385
$P_{2\infty}$=574 7	3 809	2910	8.875	441
R_D=97 3	4 919	2953	12 44	511
	6 101	3010		
	$\Delta\epsilon/\gamma_2$ = 46 2		$\Delta d/\gamma_2$ = 1 92	
6	1 349	2 2770	4 571	0 87351
	3 193	2825	6 830	400
$P_{2\infty}$=750 3	5 205	2897	9 019	429
R_D=101 3	6 346	2941	13 87	523
	7 351	2971		
	$\Delta\epsilon/\gamma_2$ = 33 6		$\Delta d/\gamma_2$ = 1.88	

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