# Solvent Effects Resulting from Frontier Molecular-orbital Interactions. Part 2.[1] The Diels–Alder Reaction between 5-substituted 1,4-Naphthoquinones and 2,3-Dimethylbutadiene

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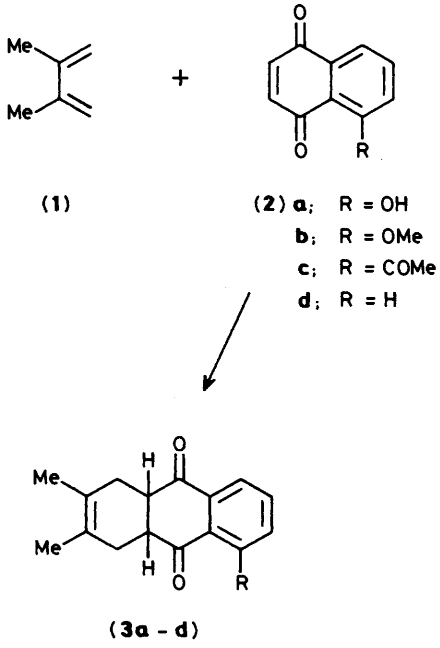
The rates of the Diels–Alder reactions between 2,3-dimethylbutadiene and 5-substituted 1,4-naphthoquinones in different solvents have been measured and found to give hyperbolic correlations with the acceptor numbers of the solvents. This can be interpreted in terms of FMO interactions between the solvent, acting as an electrophile, and naphthoquinones, which influence the LUMO energy of the solvated quinones. Linearization of the hyperbolic functions and comparison of their slopes suggest that the substituent has little influence on the solvent effect.

In the previous paper[1] of this series we investigated the solvent effects of the Diels–Alder (DA) reaction between 1,4-naphthoquinone and 2,3-dimethylbutadiene. A hyperbolic correlation was found between the acceptor number[2] (AN) of the solvent and the logarithm of the rate. This was rationalized in terms of the interaction between the FMOs of solvent and naphthoquinone, which determines the LUMO energy of the solvated quinone.

Considering the solvent as an electrophile which interacts with a specific cycloaddend of the reaction is certainly an oversimplification, and two points have to be taken into account. The kinetic data of the DA reactions do not correlate with the polar parameters of the solvents (Kirkwood function, $E_T$). This generally occurs with cycloadditions[3] (2 + 2 and 1,3-dipolar) that involve either polar cycloaddends or dipolar intermediates. Since ANs correlate with the LUMOs of the solvents,[4] for the first time the solvent is not considered to be a medium acting through its physical properties, but as a reagent (in addition to the diene and dienophile) which acts under the control of the same parameters (FMOs) that control the reactivity of cycloaddends.



(1)

(2) a; R = OH
b; R = OMe
c; R = COMe
d; R = H

(3a - d)

Before turning to other DA-type reactions (with inverse electron demand, intramolecular, acid-catalysed, *etc.*) we wished to check whether the hyperbolic correlation between the rate and AN of the solvent could be found in other Diels–Alder reactions with normal electron demand.[5] We excluded DA reactions involving the formation of detectable charge-transfer complexes[6] since these could be stabilized by the solvent. Thus we investigated the reaction of 2,3-dimethylbutadiene (**1**) with 5-hydroxy-, 5-methoxy-, and 5-acetyl-1,4-naphthoquinones [(**2a**–**c**) respectively] (Scheme), with the further aim of comparing their behaviour with that of the parent 1,4-naphthoquinone (**2d**).[1] Our expectations derived from a recent paper by Houk and co-workers[7] in which MO calculations of 5-substituted-1,4-naphthoquinones had been carried out. The most stable conformations are *syn* for 5-hydroxy in (**2a**), *anti* for 5-methoxy in (**2b**) and perpendicular for 5-acetyl in (**2c**) (this being the most stable conformation of the 5-formyl group[7]). For our purposes the calculated energies of the LUMOs: 3.80 eV (**2a**), 4.28 eV (**2b**), 3.81 eV for 5-formyl derivative taken as a model of (**2c**) and 4.15 eV for the parent (**2d**), were the most important data as the DA reactions we investigated are HOMO (butadiene)–LUMO (naphthoquinone) controlled. Even though calculations probably overestimate the energies,[†],[8] their relative values should predict a reaction rate in the order (**2b**) < (**2d**) < (**2c**) ⩽ (**2a**).[‡]

## Results and Discussion

The kinetic runs were carried out at 80 °C and followed to about 60–70% completion by u.v.–vis spectroscopic analysis of the disappearing naphthoquinones (**2a**–**c**). A 100–1000 molar excess of dimethylbutadiene gave pseudo-first-order rate constants;[§] from which the second-order rate constants were calculated.

Of the seventeen solvents investigated in the reaction between the parent naphthoquinone and (**1**),[1] ten were selected to test

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[†] The electron affinities of 1,4-naphthoquinone and 5-hydroxy-1,4-naphthoquinone, which are the average of those determined from charge-transfer spectra and the half-wave reduction potentials, are 1.75 and 1.97 eV, respectively.[8]

[‡] If the LUMO coefficients reported in ref. 7 are also considered, the first-order perturbation equation predicts a reaction rate in the order (**2b**) < (**2c**) ≃ (**2d**) < (**2a**).

[§] Second-order kinetics are followed if a 15–34 molar excess of 2,3-dimethylbutadiene is used [experiments performed on (**2a**) in acetic acid at 80 °C].

**Table 1.** Rate constants for the reactions of 2,3-dimethylbutadiene with 5-hydroxy-, 5-methoxy-, and 5-acetyl-1,4-naphthoquinones, (**2a**–**c**) respectively, at 80 °C in different solvents and varying solvent AN.

| | | | $k/10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | | |
|---|---|---|---|---|---|
| N | Solvent | AN | (**2a**) | (**2b**) | (**2c**) |
| 1 | Cyclohexane | 0 | 5.2 ± 0.3 | 2.36 ± 0.08 | 1.53 ± 0.02 |
| 2 | Benzene | 8.2 | 6.4 ± 0.2 | 2.58 ± 0.08 | 2.78 ± 0.08 |
| 3 | Ethyl acetate | 9.3 | 7.6 ± 0.5 | 3.31 ± 0.06 | 3.69 ± 0.04 |
| 4 | Acetone | 12.5 | 13.4 ± 0.5 | 6.05 ± 0.1 | 7.34 ± 0.08 |
| 5 | Dimethyl sulphoxide | 19.3 | 28.0 ± 0.5 | 14.8 ± 0.3 | 19.5 ± 0.1 |
| 6 | t-Butyl alcohol | 27.1 | 30.4 ± 0.4 | 11.2 ± 0.8 | 19.3 ± 0.6 |
| 7 | Isopropyl alcohol | 33.8 | 35.3 ± 0.3 | 14.8 ± 0.3 | 25.3 ± 0.1 |
| 8 | Ethanol | 37.9 | 33.2 ± 0.8 | 18.5 ± 0.3 | 21.5 ± 0.1 |
| 9 | Methanol | 41.3 | 35.8 ± 0.4 | 29.2 ± 0.8 | 32.3 ± 0.5 |
| 10 | Acetic acid | 52.9 | 56.1 ± 0.8 | 36.9 ± 0.8 | 40.2 ± 0.9 |

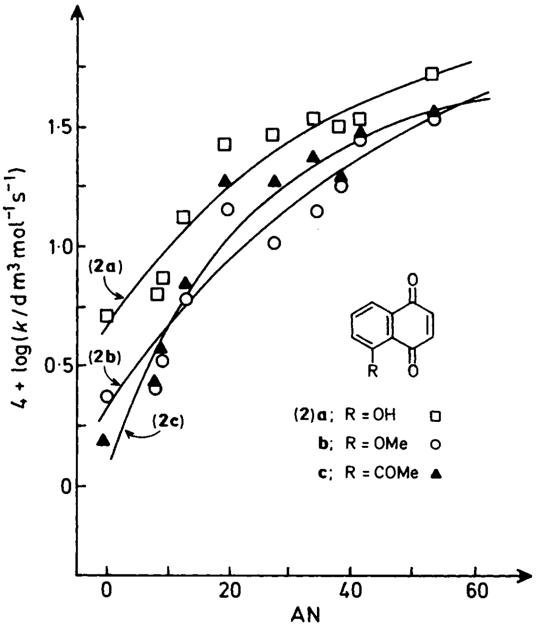

**Figure 1.** Rate constants of the Diels–Alder reactions between 2,3-dimethylbutadiene (**1**) and 5-substituted 1,4-naphthoquinones (**2a**–**c**) at 80 °C in different solvents, plotted *vs.* the AN of the solvent.

the solvent effect in the reactions of (**2a**–**c**). The extremes of the reactivity (cyclohexane, benzene, and acetic acid), four alcohols (t-butyl alcohol, isopropyl alcohol, ethanol, and methanol) and ethyl acetate, acetone, and dimethyl sulphoxide, were considered a suitable range to test a relationship between the rates and the ANs.

The kinetic data reported in Table 1 are the average of at least 3–5 kinetic runs, each with a different reagent ratio.

The solvent effect, which was 30 for (**2d**) in acetic acid *vs.* cyclohexane,[1] was again significant, since it ranged from 10 (**2a**) to 26 (**2c**) for the same solvents. Again, every attempt to correlate the kinetic data of the DA reactions of (**2a**–**c**) with polar parameters failed. However, when log $k$ values were plotted *vs.* ANs, three hyperbolic relationships were obtained (Figure 1). If we compare these with the data of the parent 1,4-naphthoquinone (**2d**),[1] the following order of reactivity is obtained for the DA reaction with 2,3-dimethylbutadiene:

5-H (**2d**) < 5-OMe (**2b**) ≃ 5-COMe (**2c**) < *syn* 5-OH (**2a**)

Our expectations from Houk's data[7] of the LUMO energies were slightly different.

Simple FMO reasoning rationalizes the order of reactivity found for 5-H (**2d**) < 5-COMe (**2c**) < *syn* 5-OH (**2a**), with the order of the energy of each, respective LUMO. Since an acetyl group is less electron-attracting than a formyl group, the gap between (**2a**) and (**2c**) seemed to be fully justified. The unexpectedly fast rate found for 5-OMe (**2b**) is, on the other hand, hard to rationalize. Perhaps a twisting from the planar *anti* conformation of the methoxy group could increase its electron-attracting character, but the question is certainly still open.

The hyperbolic shape of these correlations was rationalized as being derived from a relation between the stabilization energy and the AN given[1] by equation (1) ($a$, $b$, $c$, and $d$ being constants), assuming that $\Delta E$ is a linear function of log $k$. This

$$\Delta E = \frac{a - b\text{AN}}{c - d\text{AN}} \qquad (1)$$

last assumption requires the entropy to be a constant within the series of the solvents. This was tested for (**2a**–**d**) in four significant solvents: benzene, dimethyl sulphoxide, isopropyl alcohol, and acetic acid, and the results are reported in Table 2. The values of $\Delta S^{\ddagger}$ fall (−31, −44 e.u.) in the range found[9] for DA reactions, in which a highly ordered transition state is assumed. Even if some values [*e.g.* −31 e.u. for the reaction of (**2a**) in acetic acid] suggest a specific solvation (in the above case a competition between the intramolecular OH ··· O=C hydrogen bond and the intermolecular effect of $MeCO_2H$), the $\Delta S^{\ddagger}$ contribution can be considered to be constant. Thus equation (1) can be changed into equation (2), $a'$, $b'$, $c'$, and $d'$ being new constants.

$$\log k = \frac{a' - b'\text{AN}}{c' - d'\text{AN}} \qquad (2)$$

In order to evaluate whether the solvent effect is independent of the nature of the substituent, the different curves must be compared quantitatively. Thus, equation (2) was changed from a hyperbolic to a linear relation by taking AN = $x$ and factorising equation (2) which becomes equation (3).

$$\log k = \frac{a'}{c'} \times \frac{(1 - b'x/a')}{(1 - d'x/c')} \qquad (3)$$

If $a'/c' = A$; $b'/a' = B$; $d'/c' = C$ and $\log k = y$, equation (3) becomes equation (4):

$$y = A\,\frac{(1 - Bx)}{(1 - Cx)} \qquad (4)$$

**Table 2.** Activation parameters of the DA reaction between 2,3-dimethylbutadiene and 1,4-naphthoquinones (**2a–d**).[a]

| Naphthoquinone | Parameter | Solvent | | | |
|---|---|---|---|---|---|
| | | Benzene | Dimethyl sulphoxide | Isopropyl alcohol | Acetic acid |
| **(2a)** | $\Delta S^{\ddagger b}$ | 13.1 ± 0.5 | 11.3 ± 0.3 | 11.9 ± 0.3 | 13.4 ± 0.3 |
| | $\Delta S^{\ddagger c}$ | 36 ± 2 | 35 ± 1 | 36 ± 1 | 31 ± 1 |
| **(2b)** | $\Delta H^{\ddagger}$ | 14.7 ± 0.4 | 12.8 ± 0.4 | 12.6 ± 0.4 | 11.2 ± 0.3 |
| | $\Delta S^{\ddagger}$ | 34 ± 1 | 36 ± 1 | 36 ± 1 | 38 ± 1 |
| **(2c)** | $\Delta H^{\ddagger}$ | 11.2 ± 0.9 | 12.3 ± 0.4 | 12.1 ± 0.4 | 12.2 ± 0.6 |
| | $\Delta S^{\ddagger}$ | 44 ± 2 | 36 ± 1 | 36 ± 1 | 36 ± 2 |
| **(2d)** | $\Delta H^{\ddagger}$ | 12.5 ± 0.8 | 12.9 ± 0.3 | 11.7 ± 0.3 | 11.2 ± 0.3 |
| | $\Delta S^{\ddagger}$ | 41 ± 1[d] | 36 ± 1 | 39 ± 1 | 38 ± 1[d] |

[d] The rate constants at different temperatures are reported in the experimental part (Table 5). [b] kcal mol$^{-1}$. [c] cal K$^{-1}$ mol$^{-1}$. [d] Values taken from ref. 1.

**Table 3.** Optimized values of $A$, $B$ and $C$; $\chi^2$ of the fits; calculated parameters $M$ and $N$ and correlation coefficient ($r$) for linear correlations obtained by plotting $X$ *vs.* the experimental $y$ values (Figure 2).

| Values | Naphthoquinones | | | |
|---|---|---|---|---|
| | **(2a)**[a] | **(2b)** | **(2c)** | **(2d)**[b] |
| $A$ | −5.71 | −3.79 | −3.83 | −4.08 |
| $B \times 10^3$ | −102 | −3 | −2 | −4 |
| $C \times 10^2$ | −28 | −1.5 | −1.6 | −17 |
| $\chi^2$ | 116 | 186 | 57 | 33 |
| $M$ | 3.6 | 2.9 | 3.2 | 3.0 |
| $N$ | −2.1 | −0.8 | −0.5 | −1.1 |
| $r$ | 0.985 | 0.963 | 0.962 | 0.985 |

[a] Cyclohexane value excluded. [b] Calculation was performed on values taken from ref. 1 for the ten solvents investigated in this paper.

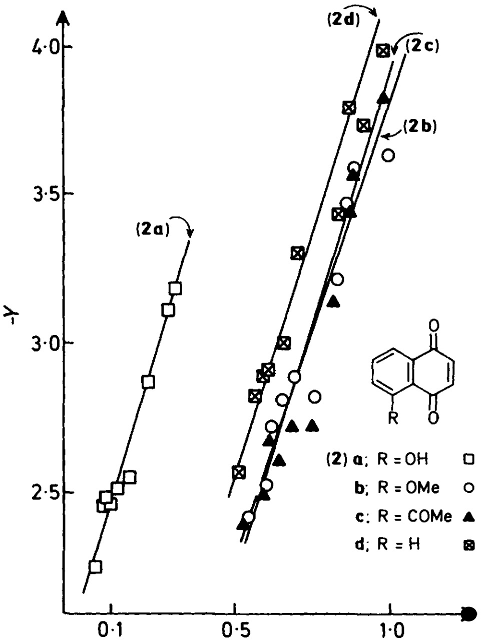

Figure 2. Graphic representation of equation (6) for (**2a–d**).

which can be rearranged in the form of equation (5) dividing the numerator by the denominator:

$$y = \frac{AB}{C} + \frac{A\left(\frac{B}{C} - 1\right)}{Cx - 1} \qquad (5)$$

**Table 4.** Wavelengths/in nm used for the kinetic runs.

| Solvent | **(2a)** | **(2b)** | **(2c)** |
|---|---|---|---|
| Cyclohexane | 430 | 384 | 335 |
| Benzene | 430 | 394 | 337 |
| Ethyl acetate | 420 | 391 | 340 |
| Acetone | 420 | 392 | 338 |
| Dimethyl sulphoxide | 420 | 398 | 340 |
| t-Butyl alcohol | 425 | 398 | 340 |
| Isopropyl alcohol | 424 | 395 | 340 |
| Ethanol | 425 | 395 | 340 |
| Methanol | 445 | 395 | 338 |
| Acetic acid | 430 | 398 | 337 |

If $AB/C = N$; $A(B/C - 1) = M$ and $1/(Cx - 1) = X$, equation (5) becomes the desired first-degree equation (6):

$$y = MX + N \qquad (6)$$

In order to determine $M$ (the slopes of the lines to be compared for (**2a–d**) [for (**2d**) using the data taken from ref. 1], $A$, $B$, and $C$ are required, so they were roughly derived from graphs log $K$ *vs.* AN since

$$A = a'/c' = \log k \text{ for AN} = 0$$
$$1/C = c'/d' = \text{AN for } \log k \longrightarrow \infty$$
$$B = b'/a' = Cb'/Ad' \text{ with } b'/d' = \log k \text{ for AN} \longrightarrow \infty$$

To obtain the best fit with equation (4) the raw values of $A$, $B$, and $C$ were optimized using the program MINUIT.[10] These values, together with the calculated parameters $M$ and $N$ of equation (6) for each naphthoquinone are reported in Table 3.

The graphic representation of the linear relationships of equation (6) for (**2a–d**) is given in Figure 2 and, at a first approximation, is a set of parallel lines.

A comparison of their slopes ($M$ values of Table 3) suggests that the lines can be considered similar if $\chi^2$ values ($\chi^2$ being a measure of the deviations between observed and calculated values), are taken into account. Hence the substituent in position 5 of 1,4-naphthoquinone has a small influence on the solvent effect of the DA reaction.

In conclusion, the above reported results suggest that the solvent effect exerted on reactions between weak polar reagents giving weak, polar products through weak, polar transition states, is the result of the interaction between the solvent, acting as an electrophile, and a donor reagent. The close analogy of the mechanism of the solvent effect in the DA reaction with the corresponding Lewis-acid catalysed reaction will be discussed in future research.

**Table 5.** Rate constants for the determination of the activation parameters.

| | Benzene | | Dimethyl sulphoxide | | Isopropyl alcohol | | Acetic acid | |
|---|---|---|---|---|---|---|---|---|
| Naphthoquinones | $T$/°C | $10^4 k$[b] | $T$/°C | $10^4 k$[b] | $T$/°C | $10^4 k$[b] | $T$/°C | $10^4 k$[b] |
| **(2a)** | 35 | 0.36 ± 0.03 | 35 | 3.36 ± 0.09 | 35 | 2.51 ± 0.07 | 35 | 2.73 ± 0.03 |
| | 50 | 1.01 ± 0.03 | 50 | 9.30 ± 0.05 | 50 | 6.71 ± 0.05 | 50 | 9.0 ± 0.2 |
| | 65 | 2.66 ± 0.09 | 65 | 20.7 ± 0.3 | 65 | 15.1 ± 0.5 | 65 | 23.9 ± 0.3 |
| | 80 | 6.31 ± 0.05 | 80 | 40.5 ± 0.5 | 80 | 35.2 ± 0.3 | 80 | 51.6 ± 0.2 |
| **(2b)** | 50 | 0.28 ± 0.01 | 35 | 0.85 ± 0.03 | 35 | 0.96 ± 0.03 | 35 | 2.83 ± 0.01 |
| | 65 | 0.76 ± 0.04 | 50 | 2.51 ± 0.02 | 50 | 3.03 ± 0.07 | 50 | 7.49 ± 0.03 |
| | 80 | 1.93 ± 0.05 | 65 | 6.19 ± 0.07 | 65 | 7.49 ± 0.07 | 65 | 17.2 ± 0.3 |
| | 95 | 5.36 ± 0.07 | 80 | 14.0 ± 0.2 | 80 | 14.8 ± 0.8 | 80 | 33.1 ± 0.4 |
| **(2c)** | 35 | 0.23 ± 0.03 | 35 | 1.44 ± 0.05 | 35 | 1.77 ± 0.04 | 35 | 2.28 ± 0.03 |
| | 50 | 0.70 ± 0.04 | 50 | 4.08 ± 0.05 | 50 | 4.81 ± 0.06 | 50 | 6.58 ± 0.09 |
| | 65 | 1.13 ± 0.05 | 65 | 9.85 ± 0.08 | 65 | 11.3 ± 0.2 | 65 | 14.7 ± 0.1 |
| | 80 | 3.00 ± 0.05 | 80 | 21.4 ± 0.7 | 80 | 25.3 ± 0.9 | 80 | 33.5 ± 0.4 |
| **(2d)** | 60[a] | 0.51 ± 0.02 | 35 | 0.81 ± 0.03 | 35 | 0.94 ± 0.03 | 22[a] | 0.94 ± 0.04 |
| | 70[a] | 0.93 ± 0.06 | 50 | 2.27 ± 0.03 | 50 | 2.63 ± 0.08 | 38.2[a] | 2.83 ± 0.03 |
| | 80[a] | 1.54 ± 0.07 | 65 | 5.86 ± 0.09 | 65 | 6.11 ± 0.04 | 60[a] | 9.2 ± 0.3 |
| | 90[a] | 2.62 ± 0.11 | 80 | 13.4 ± 0.2 | 80 | 12.1 ± 0.2 | 80[a] | 26.2 ± 1.1 |

[a] Values taken from ref. 1. [b] mol dm$^{-3}$ s$^{-1}$.

## Experimental

*General.*—Melting points were determined by the capillary method on a Tottoli apparatus (Büchi). Elemental analyses were carried out with a Carlo Erba model 1106 CHN analyser. $^1$H N.m.r. spectra were recorded on a Bruker WP 80SY spectrometer in $CDCl_3$ solutions, $SiMe_4$ being the standard.

*Materials.*—5-Hydroxy-1,4-naphthoquinone (**2a**) and 2,3-dimethylbutadiene (**1**) were recrystallized (resp. redistilled) Fluka pure reagents.

5-*Methoxy*-1,4-*naphthoquinone* (**2b**).—This was prepared from (**2a**) as reported in the literature.[11] It was recrystallized first from benzene and then from methanol as orange needles m.p. 187 °C (lit.,[11] 187 °C).

5-*Acetyl*-1,4-*naphthoquinone* (**2c**).—This was prepared from 1-acetylnaphthalene as reported in the literature.[12] M.p. 141 °C (from methanol) (lit.,[12] 141.5 °C).

2,3-*Dimethyl*-5-*hydroxy*-1,4,4a,10a-*tetrahydro*-9,10-*anthraquinone* (**3a**).—Compounds (**2a**) (1 mmol) and (**1**) (10 mmol) were heated together for 3 days in a sealed quartz vial at 60 °C. The excess of (**1**) was then evaporated off and the residue was crystallized from ethanol to give (**3a**) as white crystals m.p. 139–140 °C in nearly quantitative yield (lit.,[13] 141–142 °C).

2,3-*Dimethyl*-5-*methoxy*-1,4,4*a*,10*a*-*tetrahydro*-9,10-*anthraquinone* (**3b**).—Compounds (**2a**) (1 mmol) and (**1**) (10 mmol) were heated together for 24 h in a sealed quartz vial at 80 °C. The excess of (**1**) was then evaporated off and the residue gave (**3b**) as white crystals, m.p. 114–115 °C (from ethanol–water) (82% yield) (Found: C, 74.4; H, 6.8. $C_{17}H_{18}O_3$ requires C, 74.5; H, 6.7%); $\delta_H$ 1.65 (6 H, s), 2.25 (4 H, d), 3.30 (2 H, m), 4.00 (3 H, s), and 7.2–7.8 (3 H, m).

5-*Acetyl*-2,3-*dimethyl*-1,4,4a,10a-*tetrahydro*-9,10-*anthraquinone* (**3c**).—Compounds (**2c**) (1 mmol) and (**1**) (15 mmol) were heated together under an argon atmosphere in a sealed quartz vial at 80 °C for 1 h. The excess of (**1**) was then evaporated off and the residue gave (**3c**) as white crystals, m.p. 130 °C (from ethanol–water) (79% yield) (Found: C, 76.4; H, 6.4. $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4%); $\delta_H$ 1.65 (6 H, s), 2.25 (4 H, t), 2.50 (3 H, s), 3.40 (2 H, m), and 7.3–8.1 (3 H, m).

*Solvents.*—Solvents for the kinetic runs were freshly distilled reagent grade (u.v. spectroscopic grade when available).

*Kinetics.*—The overall reaction rates were measured by following the disappearance of (**2a–c**) on a Perkin-Elmer Lambda 5 spectrophotometer; solutions were measured in 1.00 cm OS Hellma cells of 3 cm$^3$ capacity. Measurements were made for the different solvents at the wavelengths given in Table 4. A sample (*ca.* 1 mg) of the 5-substituted-1,4-naphthoquinone (**2**) was weighed accurately into a 10 cm$^3$ volumetric flask and dissolved in the required solvent. 2,3-Dimethylbutadiene (*ca.* 0.05–0.5 cm$^3$) was added to an accurately weighed 25 cm$^3$ volumetric flask containing *ca.* 10 cm$^3$ of the required solvent. After the addition of (**1**), the flask was again weighed and the amount of dimethylbutadiene was accurately determined. The naphthoquinone solution (5.00 cm$^3$) was added to the solution of dimethylbutadiene and the solvent was added up to 25 cm$^3$ (1 cm$^3$ of ethanol was added to t-butyl alcohol to prevent crystallization of this solvent at room temperature). After vigorous mixing of the solution, *ca.* 3 cm$^3$ portions of the homogeneous solution were placed into quartz* tubes which were sealed. About seven samples were prepared for each run. At time zero the samples were placed into an ultrathermostat at the required temperature and the absorbance of the solution was determined on a further sample. At appropriate time intervals [from 3 to 100 min depending on the reaction rate of (**2**), the temperature, the solvent, and the concentration of (**1**)] the reaction was quenched with ice and the residual absorbance of (**2**) was measured. In order to measure the activation parameters, kinetic determinations at four different temperatures were performed (Table 5). The rates at 35 °C were determined by placing the samples (up to six) in the thermostatted cell of the spectrophotometer and measuring the absorbance using the 'automatic multicell programmer' of the P.E. Lambda 5. The reactions were followed to 60–80% completion and 10–15 measurements for each run were programmed.

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* Glass must be avoided otherwise the results obtained are not reproducible.

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