Kinetics of Reduction of 1,5-Diarylpenta-1,4-dien-3-ones with Sodium Borohydride in Propan-2-ol

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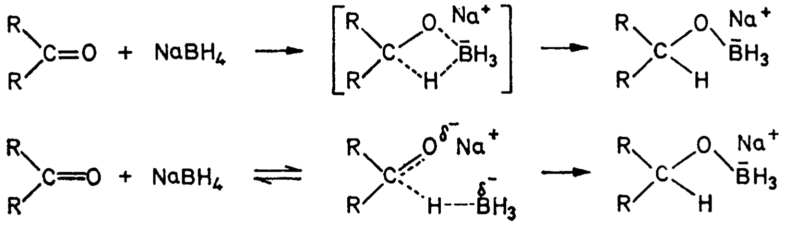
Symmetrically disubstituted 1,5-diarylpenta-1,4-dien-3-ones undergo quantitative 1,2-addition with sodium borohydride in propan-2-ol. The rate coefficients for reduction of the *para*- and *meta*-substituted compounds correlate with the Hammett equation, yielding a ρ value of 0·913 at 40 °C. The influence of *ortho*-, *meta*-, and *para*-substituents on the rate of reduction are linearly related to the hydrolytic reactivities of the corresponding ethyl *trans*-cinnamates.

THE mechanism and rate of reaction of a number of ketones and aldehydes with sodium borohydride in propan-2-ol have been investigated by Brown and his co-workers.[1-4] The reaction is considered to proceed with a rate-determining hydride transfer from the borohydride to the carbonyl carbon by either of two mechanisms (1) and (2), and should be promoted by electron-withdrawing substituents which increase the electrophilic nature of the carbonyl carbon. Correlations of reaction rates with the Hammett equation support this view, ρ values of $+3{\cdot}06$ (30 °C) and $+3{\cdot}11$ (25 °C) being



(1)

(2)

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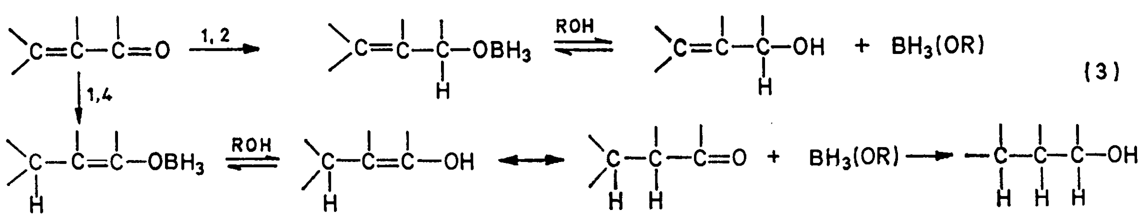
[1] H. C. Brown, O. H. Wheeler, and K. Ichikawa, *Tetrahedron*, 1957, **1**, 214.

[2] H. C. Brown and K. Ichikawa, *Tetrahedron*, 1957, **1**, 221.

[3] H. C. Brown and K. Ichikawa, *J. Amer. Chem. Soc.*, 1961, **83**, 4372.

[4] H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Amer. Chem. Soc.*, 1965, **87**, 1280.

observed for the reduction of substituted acetophenones[5] and substituted fluorenones[6] respectively. The reaction of αβ-unsaturated ketones with sodium borohydride is slightly more complex, both 1,4- and 1,2-addition being possible (3). The change in orientation with the reaction conditions and substrate structure can be explained in terms of steric and electronic factors.[7,8] However, to our knowledge, there is not at present a study of the quantitative influence of substituents on the rates of reduction by either 1,4- or 1,2-addition. We therefore have measured the rate coefficients for the reduction of a series of substituted 1,5-diarylpenta-1,4-dien-3-ones with sodium borohydride in propan-2-ol. The reaction products under these conditions are those solely of 1,2-addition (4), a result in marked contrast to the corresponding reduction of the closely related benzylideneacetone, which undergoes both 1,2- and 1,4-addition (5).[7]



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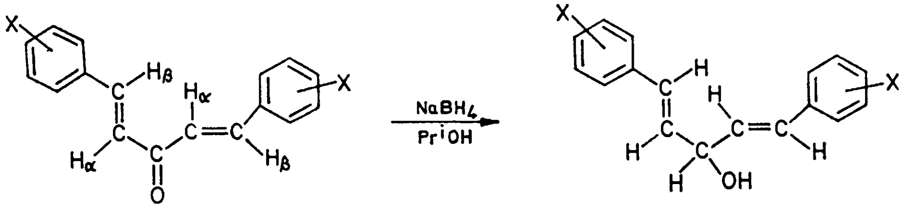

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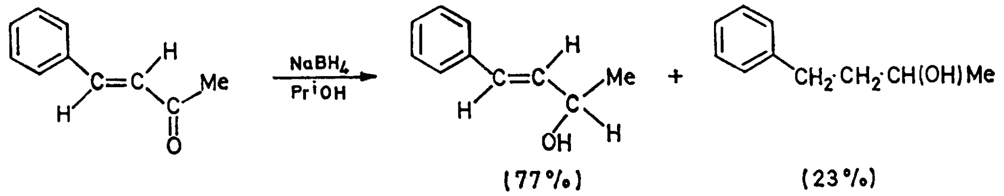

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EXPERIMENTAL

Substrates.—The 1,5-diarylpenta-1,4-dien-3-ones were prepared by the condensation of the appropriate benzaldehyde with acetone [9a] or, as in the case of the *p*-nitro-derivative, with acetonedicarboxylic acid,[9b] by methods described previously. Purification was effected by column chromatography followed by recrystallisation. All the samples had satisfactory spectral properties (i.r., n.m.r.) and m.p.s in close agreement with literature values. The 3,5-*dimethoxy-derivative* had m.p. 124·5—125·5 °C (Found: C, 71·0; H, 6·45. $C_{21}H_{22}O_5$ requires C, 71·19; H, 6·21%).

Sodium Borohydride.—A commercial sample was recrystallised from diglyme as described by Brown and his co-workers.[10]

Propan-2-ol.—This solvent was distilled from sodium and then from calcium hydride. Both propan-2-ol and sodium borohydride were stored continually in a dry-box. Fresh solutions of sodium borohydride in propan-2-ol for kinetic runs were prepared daily, although it has been established that these solutions show no decomposition at 60 °C during 24 h.[10]

Characterisation of Reaction Products.—In a typical small-scale preparation, 1,5-bis-(*p*-chlorophenyl)penta-1,4-dien-3-one was reduced quantitatively by sodium borohydride in propan-2-ol to 1,5-bis-(*p*-chlorophenyl)penta-1,4-dien-3-ol, m.p. 98—100 °C (lit.,[11] 99—101 °C). The n.m.r. spectrum was clear of even trace resonances due to methylene hydrogens expected for the saturated product arising from an initial 1,4-addition. The u.v. spectrum was identical to that of the product obtained in kinetic experiments in which the borohydride : substrate ratio was greater than 1000. Typical changes in the u.v. spectrum of the reaction solution during a kinetic run are illustrated in Figure 1. All the substrates behaved in a similar qualitative manner to the *p*-chloro-substrate except the *p*-nitro-derivative, which was too insoluble in propan-2-ol to allow kinetic studies.

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[5] K. Bowden and M. Hardy, *Tetrahedron*, 1966, **22**, 1169.

[6] J. A. Parry and K. D. Warren, *J. Chem. Soc.*, 1965, 4049.

[7] K. Iqbal and W. R. Jackson, *J. Chem. Soc. (C)*, 1968, 616.

[8] W. R. Jackson and A. Zurquiyah, *J. Chem. Soc.*, 1965, 5280.

[9] (*a*) C. R. Conrad and M. A. Dolliver, *Org. Synth.*, Coll. Vol. II, 1943, 167; (*b*) P. Petrenko-Kritschenko, *Ber.*, 1898, **31**, 1511.

[10] H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1955, **77**, 6209.

[11] G. Hesse and P. Thieme, *Annalen*, 1965, **686**, 64.

Kinetic Measurements.—The rate of reduction of a pentadienone by sodium borohydride in propan-2-ol was monitored spectrophotometrically by observing the reduction in the absorbance with time, at the u.v. wavelength of maximum absorption of the substrate. All the reactions were carried out in stoppered 1 cm silica cells in the thermostatted (±0·1 °C) cell compartment of a Unicam SP 700 spectrophotometer. Solutions of the reactants were allowed to equilibrate to the desired reaction temperature in a two-limbed glass vessel, which fitted flushly into the silica cell. The reaction was initiated by inverting the apparatus rapidly. To simplify the kinetics, a large excess of borohydride over substrate was always employed. The pseudo-first-order rate coefficients, obtained graphically from a plot of log (D_t − D_∞) against time, where D_∞ is the absorbance of the reaction solution at 10 half-lives and D_t at time *t*, were converted into second-order rate coefficients by division by the borohydride concentration. Most reactions were run at least in duplicate, the reproducibility being ±2—3%.

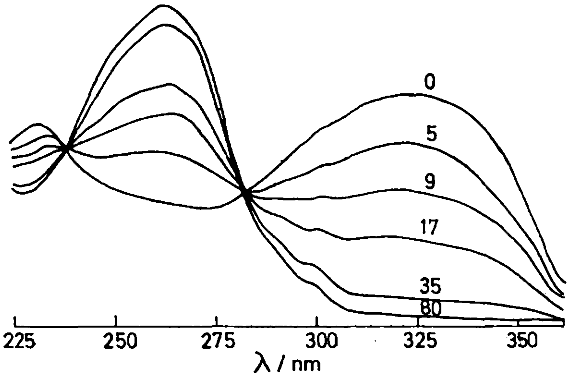


FIGURE 1 U.v. absorbance change in reaction solution during the reduction of 1,5-bis-(*p*-chlorophenyl)penta-1,4-dien-3-one ($\lambda_{max.}$ 324 nm) to 1,5-bis-(*p*-chlorophenyl)penta-1,4-dien-3-ol ($\lambda_{max.}$ 262 nm) by NaBH$_4$ in propan-2-ol at 40 °C (numbers on Figure are reaction times in minutes)

RESULTS AND DISCUSSION

The Structure of 1,5-*Diarylpenta*-1,4-*dien*-3-*ones*.—The olefinic double bonds in all the pentadienones were shown to have a *trans*-configuration by n.m.r. spectroscopy. The vinylic proton pattern was analysed as an AB spin system and by analogy with model compounds,[12] the doublet (*J* 16 Hz) at low field was assigned to the benzylic hydrogen and that at higher field to the hydrogen α to the carbonyl group. With changes in the aromatic substituents, the chemical shift of the benzylic proton is hardly affected, but a noticeable variation in that of the other vinylic proton is observed (Table 1). In fact the chemical shift of the latter proton correlates excellently with the $\sigma_R{}^0$ value of the *para*-substituent (see Figure 2).[13] The $\sigma_R{}^\circ$ value represents the disturbance of the substituent on the π-electron system of the benzene ring and presumably this relates to the shielding effect of the aromatic nucleus on the hydrogen α to the carbonly group.*

TABLE 1

N.m.r. parameters of substrates and $\sigma_R{}^0$ values [13]

	^{1}H N.m.r. shift/Hz [a]		
p-X [b]	α to carbonyl	Benzylic	$\sigma_R{}^0$
NMe$_2$	414·2	462·0	−0·53
OEt	416·9	461·0	−0·44
OMe	418·4	462·2	−0·43
Cl	422·2	461·0	−0·22
Me	423·4	464·0	−0·10
H	426·0	465·0	0·00
NO$_2$	429·1	469·8	0·17

[a] Solutions were 2·5% (w/v) in CDCl$_3$ measured on a Varian A-60A instrument with tetramethylsilane as internal reference (δ = 0·0 Hz). Error ±0·1 Hz. [b] See equation (4).

Dipole moment studies have been used to show that in 1,5-bis-(*p*-chlorophenyl)penta-1,4-dien-3-one, when the olefinic bonds are both *trans*, the molecule exists as a mixture of the *s-cis*, *s-trans* (I), and *s-cis*, *s-cis* (II) forms.[14]

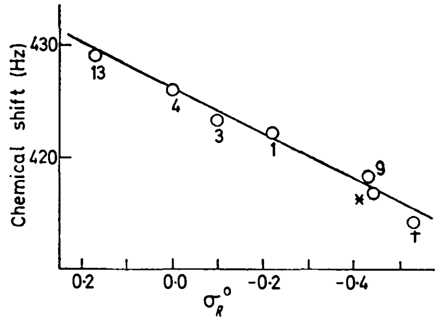
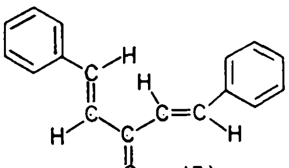


FIGURE 2 Plot of chemical shift of H$_\alpha$ against $\sigma_R{}^0$ for substituted 1,5-bis-(*p*-phenyl)penta-1,4-dien-3-ones. For definition of H$_\alpha$ see equation (4). Numbers on Figure refer to Table 2. Additionally * indicates *para*-ethoxy- and † *para*-*NN*-dimethylamino-substituents. Equation of the line is: $\delta_X = 20{\cdot}09\,(\sigma_R{}^0)_X + 425{\cdot}9$, correlation coefficient = 0·9891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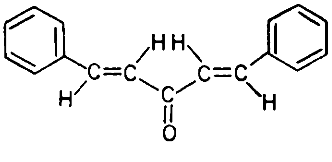
(II)

The Reduction of 1,5-*Diarylpenta*-1,4-*dien*-3-*ones with Sodium Borohydride in Propan*-2-*ol*.—*Products*. Benzylideneacetone undergoes 1,2-addition about three times as

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* A similar observation has been made in a series of *trans*-styrylimidazole derivatives (A. F. Cockerill, N. C. Franklin, and D. M. Rackham, unpublished work).

[12] High-resolution N.m.r. Spectra Catalog, ed. N. J. Bhacca, L. F. Johnson, and E. A. Pier, Varian Associates, 1963.

[13] A. R. Katritzky and R. D. Topson, *Angew. Chem. Internat. Edn.*, 1970, **9**, 87.

[14] B. A. Arbuzov, L. K. Yuldasheva, I. V. Anonimova, R. R. Shagidulin, A. V. Chernova, and D. F. Fazilev, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1969, 1485.

rapidly as 1,4-addition with sodium borohydride in propan-2-ol [see equation (5)].[7] However, despite the presence of two potential sites for 1,4-addition, we find that only the product of 1,2-addition is formed in the reduction of 1,5-diarylpenta-1,4-dien-3-ones. The origin of this change in orientation must lie in the greater electrophilic character of the carbonyl carbon relative to the β-carbon of the olefinic bond in our series. This does not seem unreasonable as a *trans*-β-styryl substituent is more electron-withdrawing than a methyl group as shown by the greater acidity of *trans*-cinnamic acid ($\mathrm{p}K_a$ 4·44) [15] than acetic acid ($\mathrm{p}K_a$ 4·75) [16] in aqueous media.

Kinetic studies. The second-order rate coefficients for the reduction of the substituted pentadienones with sodium borohydride in propan-2-ol are listed in Table 2. Most of the results refer to 40 °C, but in the case of substrates possessing electron-releasing substituents, the reactions were too slow for convenient measurement and interpolated values were derived, from measurements performed at higher temperatures, by use of the Arrhenius equation.

TABLE 2

Second-order rate coefficients for the reduction of 1,5-diarylpenta-1,4-dien-3-ones by sodium borohydride in propan-2-ol

Temp. 40 °C unless indicated

Substnt. No.	Substnt. X [a]	10^3k_2/l mol^{-1} s^{-1}	10^2[NaBH$_4$]/M
1	*p*-Cl	150·3	0·491
		140·3	1·26
		125·7	1·81
		117·1	2·46
		114·2	2·77
		101·9	3·68
		110·5 [b]	3·00

10^2[NaBH$_4$] = 3·00M;

Substnt. No.	2	3	4	5
Substnt. X	*m*-Cl	*p*-Me	H	*o*-Cl
10^3k_2/l mol^{-1} s^{-1}	196 [b]	19·7 [b]	40·1	183

Substnt. No.	6	7	8
Substnt. X	*o*-Me	3,5-(OMe)$_2$	3,4-(OMe)$_2$
10^3k_2/l mol^{-1} s^{-1}	26·3	49·9	10·6

Substnt. No.	Substnt. X [a]	10^3k_2/l mol^{-1} s^{-1}	t/°C
9	*p*-OMe	13·8 [b]	40·0
		23·8	50·1
		29·9	55·1
		39·0	60·0
10	*o*-OMe	8·36 [b]	40·0
		18·0	50·0
		25·8	55·1
		39·4	60·3
11	*o*-Et	5·91 [b]	40·0
		15·6	50·0
		25·3	54·9
		40·4	60·3
12	2,4,5-(OMe)$_3$	3·20 [b]	40·0
		9·18	50·0
		16·8	54·9
		26·4	60·3
13	*p*-NO$_2$ [c]		

[a] For definition of X, see equation (1). [b] Interpolated values from rate data at different NaBH$_4$ concentration or different reaction temperatures. All rate coefficients not designated by *b* are accurate to ±2—3%. and are the mean of at least two experiments. [c] Insufficiently soluble in propan-2-ol for kinetic data.

The second-order rate coefficients for the bis-*p*-chloro-substrate decrease linearly with increasing borohydride concentration $\{\log (k_2)_{p\text{-Cl}}^{40°} = -0{\cdot}795 - 5{\cdot}400[\mathrm{NaBH_4}]$, correlation coefficient $= 0{\cdot}9950\}$. This observation contrasts markedly with an earlier report that the rate coefficients for reduction of substituted fluorenones in propan-2-ol were invariant with the borohydride concentration.[17] Our variation is most probably due to a medium effect, arising either from increased association of borohydride with increasing concentration (*i.e.*, changes in aggregation or the type of ion pair) or a salt effect on the rate coefficient.[18] For comparative purposes, all measurements were made with a borohydride concentration of $3{\cdot}00 \pm 0{\cdot}01 \times 10^{-2}$M.

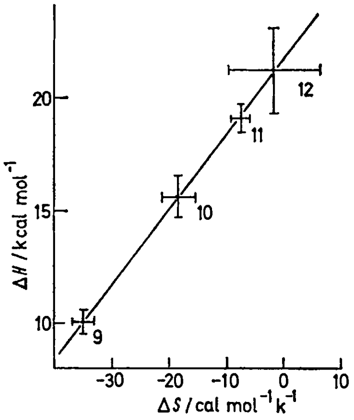

FIGURE 3 Graph of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ for the reduction of some 1,5-diarylpenta-1,4-dien-3-ones with NaBH$_4$ in propan-2-ol at 40 °C. Numbers on Figure refer to Table 2. Equation of the line is: $\Delta H^{\ddagger} = 0{\cdot}338\Delta S^{\ddagger} + 21{\cdot}87$; $r = 0{\cdot}9998$. For each point the mean position and standard deviation on each axis is shown (see Table 3)

Activation parameters were only measured for a few substrates (Table 3). However, as noted previously in the reduction of fluorenones,[6] an increase in the activation energy is observed with an increase in $\log_{10}k$,

TABLE 3

Activation parameters for the reduction of 1,5-diarylpenta-1,4-dien-3-ones by sodium borohydride in propan-2-ol [a]

Substnt. X [b]	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
2-OMe	15·7 ± 0·9	−18·1 ± 2·65
4-OMe	10·1 ± 0·6	−34·9 ± 1·82
2-OEt	19·1 ± 0·6	−7·68 ± 1·75
2,4,5-(OMe)$_3$	21·3 ± 2·2	−1·97 ± 6·85

[a] Calculated from the least-squares slope of a plot of log k_2 (Table 2) against $1/T$. Temperature for calculation of $\Delta H^{\ddagger}$ from E_a and $\Delta S^{\ddagger}$ from log A was 40·0 °C. [b] For definition of X see equation (4).

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[15] J. F. Dippy and F. R. Williams, *J. Chem. Soc.*, 1934, 1888.

[16] J. F. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1937, 1008.

[17] G. G. Smith and R. P. Bayer, *Tetrahedron*, 1962, **18**, 323.

[18] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, p. 150.

and $-\Delta S^\ddagger$ increases as $\Delta H^\ddagger$ decreases. In fact the relationship between the last two variables is remarkably good (Figure 3) in view of the wide range of substitution pattern compared. Although this relationship can be explained in terms of varying degrees of solvation, a more modern view is to attribute it to the invariant shapes of the potential energy surfaces for a series of similar reactants.[19]

The rate coefficients for reduction of the 4,4′- and 3,3′-disubstituted 1,5-diarylpenta-1,4-dien-3-ones are correlated excellently by the Hammett equation (6).[20] In the present case, as each substrate carries two substituents, a plot of log k_X/k_0 against 2σ[21] was used (see

$$\log (k_X/k_0) = \rho\sigma \qquad (6)$$

Figure 4). The reaction constant ρ, which is positive, demonstrates that the reaction is promoted by electron-withdrawing substituents and apparently follows a similar mechanism to that of the simple ketones [equation (1) or (2)].

Comparison of the reaction constants for the ionisation of substituted benzoic acids ($\rho = 1{\cdot}00$) with that for *trans*-cinnamic acids[22] ($\rho = 0{\cdot}418$) shows that the transmission of the substituent effect is reduced by *ca.* 60% by insertion of the olefinic double bond between the reaction site and substituent. The difference between our reaction constant (0·92 at 40 °C) and that for reduction of the substituted acetophenones[5] (3·06 at 30 °C) in the same solvent again indicates a similar order of reduction in transmission by the olefinic double bond (substituted chalcones would be a more appropriate model but relevant kinetic data are not available).

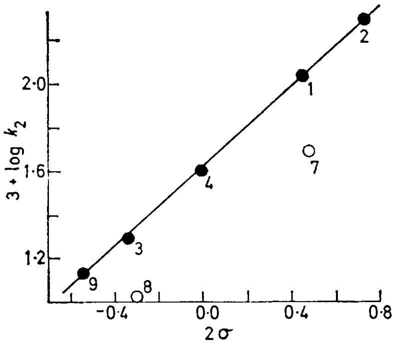

FIGURE 4 Plot of log (k_X/k_0) against 2σ for the reduction of 1,5-diarylpenta-1,4-dien-3-ones by $NaBH_4$ in propan-2-ol at 40 °C. Numbers in Figure refer to Table 2. Equation of the line for ● points is: $\log k_X = -1{\cdot}3844 + 0{\cdot}9135\ (2\sigma)_X$; $r = 0{\cdot}9997$. Values of σ from C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1965, **3**, 334. Values of σ for points 7 [3,5-$(OMe)_2$] and 8 [3,4-$(OMe)_2$] calculated by summation of the appropriate σ_m and σ_p values

We now turn our attention to the *ortho*- and multi-substituted methoxy-substrates. Additional to the polar and resonance effects exerted by *meta*- and *para*-substituents, which are adequately described by the Hammett equation, *ortho*-substituents can display a variable steric effect. When the proximity permits, direct steric interaction between the substituent and the reaction site can influence the reactivity of the substrate. In our case, the *ortho*-substituent is too distant from the reaction site to exert a direct steric effect, but interaction with the adjacent olefinic bond could cause a deformation between the planes of the aromatic π-system and the olefinic π-system. Such an indirect steric effect could drastically reduce the transmission of mesomeric effects.

Recently, Charton listed 32 different sets of *ortho*-substituent constants,[23] most of which had been defined from a knowledge of the reaction constant derived from *meta*- and *para*-reactivities, and the log k_0 value. Use of this approach, which combines the steric and electronic properties into the substituent constant, σ_{ortho} gives the following values from our results at 40 °C: Cl, 0·35; Me, −0·11; OMe, −0·38; OEt, −0·46. These values of course have very limited application, referring only to our reaction. However, the values for methyl and methoxy-groups are similar to those reported for the detritiation of phenylacetylenes,[24] acid and alkaline hydrolysis of ethyl benzoates,[25] and n.m.r. shifts of phenols.[26] Our value for Cl is an average figure, but the reported values for this electronegative atom vary widely with the reaction. Our figure for *p*-OEt is the most negative value yet reported.[23]

Taft and his co-workers have recently favoured the dual-substituent parameter approach for estimating the reactivities of *ortho*-substituents [equation (7)].[27] The reaction constant is split into polar and resonance contributions and values of σ_I and σ_R for the *para*-substituent are used.[23] Alternatively, if the *ortho*-substituent simply distorts the coplanarity of the benzene and olefin systems, a reduction in transmission of the resonance effect can be made by using equation (8). However, neither of these equations describes the re-

$$\log (k_X/k_0) = \rho_I\sigma_I + \rho_R\sigma_R \qquad (7)$$

$$\log (k_X/k_0) = \rho(\sigma_I + n\sigma_R) \qquad (8)$$

activity of *ortho*-substituents in the pentadienone reduction. The failure can be explained in terms of the inequality of *ortho*- and *para*-electrical effects,[23] or in varying steric contributions for each substituent.

The simplest method of correlating our results for *ortho*- and multi-substituted substrates is to compare the reactivities in the borohydride reduction with those of

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[19] (*a*) J. Leffler, *J. Org. Chem.*, 1955, **20**, 1202; (*b*) A. V. Willi, *Chimia* (*Switz.*), 1961, **15**, 558; (*c*) K. J. Laidler, *Trans. Faraday Soc.*, 1959, **55**, 1725.

[20] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[21] G. Schott and S. Kuhla, *Z. Chem.*, 1969, **9**, 430.

[22] K. Bowden, *Canad. J. Chem.*, 1963, **41**, 2781.

[23] M. Charton, *J. Amer. Chem. Soc.*, 1969, **91**, 6649.

[24] C. Eaborn, G. A. Skinner, and D. R. M. Walton, *J. Chem. Soc.*, 1966, 922.

[25] R. W. Taft, jun., in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, p. 619.

[26] M. T. Tribble and J. G. Traynham, *J. Amer. Chem. Soc.*, 1969, **91**, 379.

[27] P. R. Wells, S. Ehrensen, and R. W. Taft, jun., *Prog. Phys. Org. Chem.*, 1968, **6**, 223.

other cinnamoyl derivatives. This approach overcomes the difficulty of having to allow for varying steric effects for some substituents. Two reactions series, the dissociation of substituted *trans*-cinnamic acids and the hydrolysis of the corresponding ethyl esters, have been well characterised. Of these, we prefer to relate our results to the latter, as the small reaction constant [22] for the cinnamic acid dissociation means that differences between pK values of some substituted acids are of similar magnitude to the uncertainties in the individual values. We observe a close relationship between the rate of our borohydride reductions and the hydrolysis of ethyl *trans*-cinnamates [28,29] (Figure 5) for *ortho*-substituted derivatives and the 3,4-dimethoxy-substrate. Hydrolysis data were not available for the 3,5-dimethoxy-substituted *trans*-cinnamate, but the reactivity of the pentadienone relates to the hydrolysis of the corresponding ethyl benzoate (Figure 5).[30] The success of the latter correlation however could be fortuitous as the 3,4-dimethoxy-point deviates markedly from the graph.

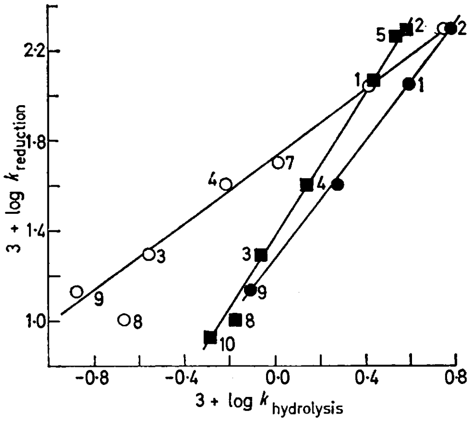

FIGURE 5 Plot of log k for reduction against log k for hydrolysis. Reduction: 1,5-diarylpenta-1,4-dien-3-ones by $NaBH_4$. Hydrolysis: ○ Hydrolysis of ethyl benzoates in 85% aqueous ethanol at 25 °C (ref. 30) (slope = 0·756, r = 0·9946, excluding point 8); ■ hydrolysis of ethyl *trans*-cinnamates in 85% aqueous ethanol at 24·8 °C (ref. 28) (slope = 1·638, r = 0·9984); ● hydrolysis of ethyl *trans*-cinnamates in 87·8% aqueous ethanol at 30 °C (ref. 29) (slope = 1·314 r = 0·9995). Numbers on Figure refer to Table 2

Unless steric interactions between substituents limit free rotation, reactivities of disubstituted aromatic compounds should be predictable from a simple summation of the constituent substituent constants. In the hydrolysis of ethyl *trans*-cinnamates, Jones and Watkinson [28] found this to be the case, but their changes in reactivity were manifested mainly by changes in the activation energy, the entropy of activation being constant for a wide range of substituents. The reactivities of our multisubstituted substrates cannot be predicted by simple summation of the σ_{ortho}, σ_m, and σ_p constants (see Figure 4), even in the absence of direct 1,2-interactions (*e.g.*, 3,5-dimethoxy). In fact, when 1,2-interaction might be expected to decrease the resonance electron-releasing effect from the 4-methoxy-substituent, the rate of reaction is actually slower than in the absence of this interaction. Possibly the explanation lies in differences in the relative contributions of conformations (I) and (II) to the overall structure of the substituted 1,5-diarylpenta-1,4-dien-3-one, when the substitution pattern is changed from mono- to multisubstitution with highly polar substituents.

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