Stable Carbonium Ions. Part III.[1] Reactions involving 1,3-Diarylallyl and 1-Ferrocenyl-3-arylallyl Cations

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Equilibrium constants have been measured for the acid-catalysed equilibration of a series of 1,3-diarylpropenols (chalcols) and 1(3)-ferrocenyl-3(1)-arylallyl ethers. The thermodynamic stability of the styryl system is increased by substitution in the aromatic ring of groups exerting either a positive or a negative resonance effect (*e.g.*, *p*-OMe, *p*-NO_2) or a positive inductive effect (*e.g.*, *p*-Me). The styryl system is destabilised by the introduction of groups exerting a negative inductive effect (*e.g.*, *p*-Cl, *m*-NO_2). Conjugation of a carbon–carbon double bond with a ferrocenyl group confers greater thermodynamic stability than that provided by conjugation with an aryl group. In all of these cases, the effects are small. The rate of acid-catalysed chalcol equilibration is accelerated by electron-donating substituents and retarded by electron-withdrawing substituents in the aromatic rings. Analysis of the isomeric chalcol mixtures formed under kinetic control in the solvolysis (80% aqueous acetone) of a series of 1,3-diarylallyl *p*-nitrobenzoates has shown that positive charge distribution in the intermediate 1,3-diarylallyl cations is moderately sensitive to the nature of the substituents present in the aromatic rings.

DESPITE the large volume of work which has been devoted to the study of the properties of unsymmetrically substituted allylic cations,[2] the factors which control the distribution of products by way of the alternative reaction pathways are still incompletely understood. Several reactions are known, however, which lend support to the idea [3,4] that the energy requirements associated with the capture of a nucleophile at each terminal carbon atom of the allylic system will be related in some measure to the relative concentrations of positive charge at these reactive centres.[5]

In order to gain insight into the importance or otherwise of such a relationship, several optimum requirements can be specified for the substrate. First, the substitution pattern should be such that a significant and, if possible, predictable imbalance in positive charge allocation to the terminal allylic carbon atoms should result. Secondly, the cation should possess sufficient thermodynamic stability such that its formation is assured and its reaction with a nucleophile is selective. Parenthetically, it can be argued that increased cation stability would lead to a beneficial decrease in the importance of specific solvation and ion-pair effects.[4,6] Thirdly, steric shielding at each of the reactive centres in the cation by the attached substituents should be of a similar magnitude. Finally, the product composition obtained from the reaction of the cation with a nucleophile should be controlled solely by kinetic factors.

These conditions are admirably satisfied by cations of the type (I) in which the terminal aryl substituents exert a powerful stabilising effect upon the allylic system.† In this paper, we report the results of a series of reactions involving such 1,3-diarylallyl cations and related experiments involving 1-ferrocenyl-3-arylallyl cations.

Synthetic Methods.—The compounds required in this study were obtained as outlined in the Scheme. A series of *trans*-1,3-diarylpropenones (chalcones) (IIa—f; IIIa—f) were prepared by the Claisen–Schmidt condensation of appropriately substituted acetophenone and benzaldehyde derivatives. Reduction of these unsaturated ketones to the corresponding *trans*-1,3-diarylpropenols (chalcols) (IVa—f; Va—f) was achieved either by the Meerwein–Ponndorf method or, more conveniently, by use of sodium borohydride in methanol. As noted previously,[8] the isomeric *p*-methoxychalcols (IVa and Va) were found to be rather unstable and these alcohols were freshly prepared each time before use. Repeated attempts to prepare their *p*-nitrobenzoyl derivatives (VIa and VIIa) were unsuccessful. The *p*-nitrobenzoates (PNB) (VIb—d; VIIb—d) of other chalcols were readily obtained, however, by reaction with *p*-nitrobenzoyl chloride in pyridine. The spectral characteristics of all the compounds prepared were in accord with the assigned structures.

Equilibration Studies.—In order to obtain information regarding the relative ground-state energies of the allylic systems employed in this study, a series of acid-catalysed equilibration experiments was carried out. Each of the chalcols (IVa—f; Va—f) was allowed to equilibrate with its allylic isomer in aqueous acidic dioxan solution and the equilibrium product composition was determined in each case by u.v. spectroscopy (see Experimental section). Within experimental error, the same equilibrium mixture of chalcols was formed irrespective of the identity of the particular isomer [(IV) or (V)] used as

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† The 1,3-diphenylallyl cation itself has been isolated as a stable tetrafluoroborate salt.[7]

[1] Part II, M. J. A. Habib, J. Park, and W. E. Watts, *J. Chem. Soc.* (*C*), 1970, 2556.

[2] (*a*) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 753; (*b*) P. B. D. de la Mare in 'Molecular Rearrangements Part 1,' ed. P. de Mayo, Interscience, New York, 1963; (*c*) R. H. DeWolfe and W. G. Young, in 'Chemistry of the Alkenes,' ed. S. Patai, Interscience, New York, 1964.

[3] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[4] R. A. Sneen, *J. Amer. Chem. Soc.*, 1960, **82**, 4261; R. A. Sneen and A. M. Rosenberg, *ibid.*, 1961, **83**, 895, 900.

[5] A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, p. 379.

[6] W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1958; H. L. Goering and E. F. Silversmith, *ibid.*, 1955, **77**, 1129, 6249; H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *ibid.*, p. 5026.

[7] K. Hafner and H. Pelster, *Angew. Chem.*, 1961, **73**, 342.

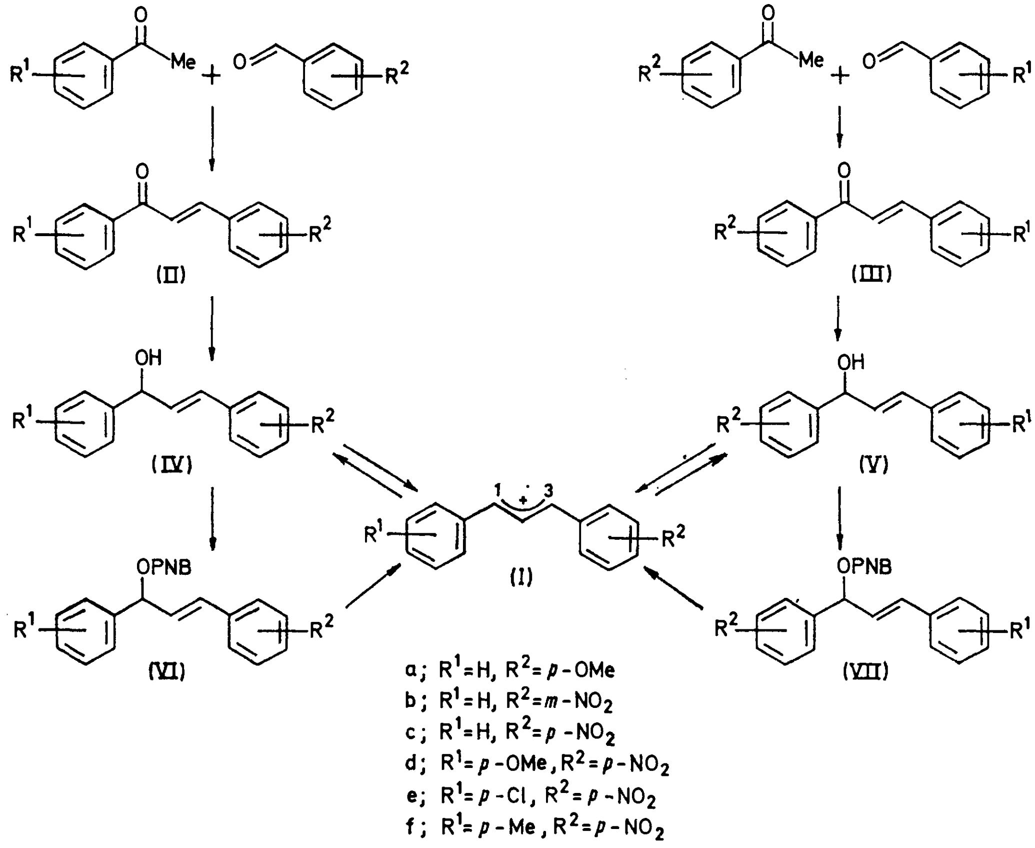
[8] S. C. Bernstein, *J. Org. Chem.*, 1968, **33**, 3486.

starting material. It may be reasonably concluded, therefore, that these acid-catalysed isomerisations proceed *via* 1,3-diarylallyl cation intermediates (I), generated by loss of a water molecule from the conjugate acids of the chalcols.

The equilibrium constants, K_{eq}, determined by this method for the equilibration of the six pairs of isomeric chalcols, are given in Table 4 together with the results obtained in previous investigations [8,9] for the *p*-methoxy- and *p*-nitro-systems. In agreement with the conclusion of the earlier studies, the results show clearly that the position of equilibrium in the chalcol isomerisations (IV) $\rightleftharpoons$ (V) is influenced only to a small extent by the presence in the aromatic rings of *meta*- or *para*-substituents, irrespective of their electronic character. All of the equilibrium constants obtained lie in the range 0·6—1·6.

If it is assumed that hyperconjugative interactions between the ethylenic bond and the groups attached to the allylic carbon atom provide a relatively insignificant contribution to the ground-state stability of these chalcols, the derived free-energy differences ($\Delta G°$) in Table 4 reflect changes in conjugation energy between a carbon–carbon double bond and a series of aryl groups. Although the effects are small (<2 kJ mol^{-1}) the results establish that the styryl system (PhCH=CH–) is slightly stabilised by *para*-substituents which extend conjugation by a resonance effect operating either in a positive (*e.g.*, *p*-OMe) or a negative direction (*e.g.*, *p*-NO_2). A small stabilising influence is also provided by groups exerting a positive inductive effect [*e.g.*, *p*-Me; see (IVf) $\rightleftharpoons$ (Vf)]. The styryl system is slightly destabilised, on the other hand, by groups which exert a negative inductive effect (*e.g.*, *m*-NO_2, *p*-Cl), presumably inhibiting release of π-electron density from the aromatic ring to the ethylenic bond.

Similar conclusions were reached in a parallel study [10] of the acid-catalysed equilibration of a series of ferrocenyl(aryl)allyl ethers (VIII and IX; R = H, *o*-, *m*-, and *p*-OMe, *p*-Cl, and *p*-Me). The preparation and characterisation of these compounds were described in Part II.[1] In each example, treatment of either ether of an isomeric pair in methanol solution with a trace of aqueous sulphuric acid promotes very fast equilibration to produce the same mixture of isomeric ethers whose composition was unchanged with time. These mixtures were readily analysed by u.v. spectroscopy (see Experimental section), the large separation between the styryl and ferrocenylvinyl chromophores of the components being used. The equilibrium constants, K_{eq}, and the free-energy differences, $\Delta G°$, calculated for each system are in Table 5.



SCHEME

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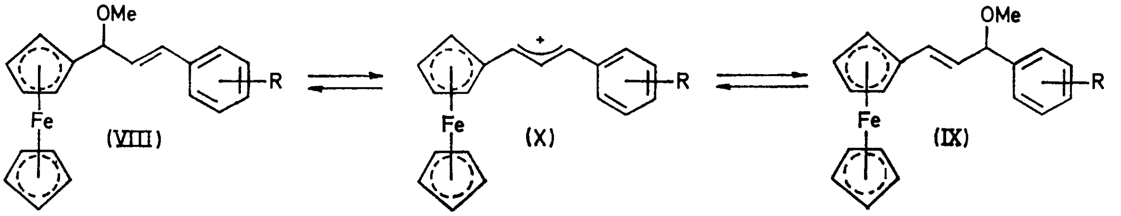
[9] E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1953, 419.

[10] Preliminary communication, M. J. A. Habib, J. Park, and W. E. Watts, *J. Organometallic Chem.*, 1970, **21**, P59.

In each case studied, the ferrocenylvinyl ether (IX) proved to be thermodynamically slightly more stable than its styryl isomer (VIII). In the parent system (VIII $\rightleftharpoons$ IX; R = H), a free-energy difference of *ca.* 1·15 kJ mol^{-1} between the isomers was found. With the proviso mentioned previously, this value represents the difference between the conjugation energies of an ethylenic bond with a ferrocenyl and a phenyl group. The interaction of the former confers the greater thermodynamic stability. Substitution in the phenyl ring exerts only a small effect upon the position of equilibrium between the ethers. As found for the chalcol isomerisations, the styryl system is slightly destabilised by the presence of a substituent which exerts a negative inductive effect (*e.g.*, *m*-OMe). The preponderance of the ferrocenylvinyl isomer (IX; R = *m*-OMe) in the equilibrium mixture is correspondingly increased. A small destabilisation of the styryl system is also caused by the presence of an *o*-methoxy-substituent. Steric repulsion between this group and the vinylic hydrogen atoms raises the energy of the all-planar conformations of the styryl group in the ether (VIII; R = *o*-OMe) and $p\pi$–$p\pi$ conjugation between the aryl ring and the double bond is accordingly reduced. Extra stabilisation of the styryl system in the ethers (VIII) by electron-donating groups (*e.g.*, *p*-OMe, *p*-Me) is minimal.



(VIII) (X) (IX)

Although the equilibrium constants for these isomerisations [(IV) $\rightleftharpoons$ (V) and (VIII) $\rightleftharpoons$ (IX)] are only slightly sensitive to the presence of substituents in the benzene rings, the rates of equilibration are very sensitive to substituent effects. For example, the *p*-methoxychalcols (IVa) $\rightleftharpoons$ (Va) equilibrate very much more rapidly (probably $>10^4$ times; see below) than the *p*-nitrochalcols (IVc) $\rightleftharpoons$ (Vc) yet the equilibrium constants for these reactions are of similar magnitude. The rates of equilibration of the *p*-methoxychalcols and of the ferrocenyl(aryl)allyl ethers proved too fast to be measured by conventional techniques. However, the presence of a *p*-nitro-group depresses the rate and, in such systems, the rate constants for the forward and reverse reactions (k_1 and k_{-1} respectively) can be readily measured by u.v. spectroscopic analysis (see Experimental section).

The rate constants obtained for the equilibration of those chalcols incorporating a *p*-nitrophenyl group (*i.e.*, IVc—f, Vc—f) are in Table 4. The influence of substitution in the second aromatic ring upon the equilibration rate can then be assessed from these data. The results show that the substituent effect acts to increase the equilibration rate through the series: *p*-Cl < *p*-H < *p*-Me < *p*-OMe. A Hammett plot of the eight log k_1 and log k_{-1} values against $\Sigma\sigma_p{}^+$ (*i.e.* the sum of the appropriate $\sigma_p{}^+$ values [11] for the aryl substituents present in each case) gives a good linear relationship (correlation coefficient = 0·985). Standard least-squares refinement of the data gives the slope of the best line as —2·46 (standard deviation = 0·15), which corresponds to the reaction constant ρ. From this relationship, a rate constant of *ca.* 83 l mol^{-1} min^{-1} can be calculated for the equilibration of the *p*-methoxychalcols (IVa) $\rightleftharpoons$ (Va).

It is clear from these results that the transition state for the acid-catalysed equilibration of isomeric chalcols must be well advanced towards the 1,3-diarylallyl cation (I). Strongly electron-donating groups (*e.g.*, *p*-OMe) stabilise this transition state and correspondingly accelerate the rate of reaction. Build-up of positive charge is resisted by the presence of strongly electron-withdrawing groups (*e.g.*, *p*-NO$_2$) on the other hand, and much slower rates are observed. Similarly, the very fast rates of equilibration of the ethers (VIII) and (IX) may be attributed to the exceptional ability of the ferrocenyl group to stabilise carbonium ions.[12] Previous work [1] has established that cations of the type (X) are indeed very stable.

Solvolysis Studies.—Each *p*-nitrobenzoate (VIb—d; VIIb—d) was quantitatively hydrolysed in refluxing aqueous acetone solution, affording a mixture of the corresponding isomeric chalcols (IV) and (V). The product composition from each solvolysis was analysed as before from the u.v. spectrum of the total chalcol mixture after removal of the *p*-nitrobenzoic acid formed as equimolar by-product. It was independently established that this acid, unlike mineral acids (see above), does not catalyse rearrangement of the individual chalcols under the solvolysis conditions. The solvolysis of each ester was carried out at least twice and reproducible results were obtained. Within experimental error, the same mixture of chalcols was formed for a given pattern of substitution in the aromatic rings, irrespective of the identity of the ester used as starting material. The results of these experiments are in Table 6.

Rearrangement of allylic *p*-nitrobenzoates is often observed under solvolysis conditions.[13] However, when

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

[12] E. A. Hill and R. Wiesner, *J. Amer. Chem. Soc.*, 1969, **91**, 509; E. A. Hill, *J. Organometallic Chem.*, 1970, **24**, 457.

[13] H. L. Goering and R. W. Greiner, *J. Amer. Chem. Soc.*, 1957, **79**, 3464.

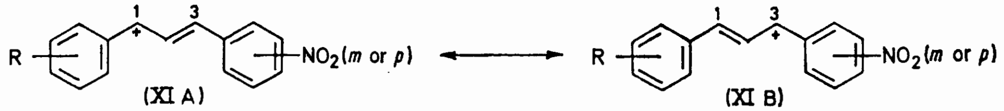
the above solvolyses were interrupted before ester hydrolysis was complete and the unconsumed *p*-nitrobenzoate recovered, no indication of the presence of rearranged ester was found. Similarly, the esters involved were recovered unchanged after heating for prolonged periods in dry acetone solution. Since it is highly improbable that a combination of S_N2 and S_N2' mechanisms would produce the same chalcol mixture from both isomeric ester precursors, as found experimentally, it may be inferred that these reactions proceed by an S_N1 mechanism involving formation of a common intermediate, the 1,3-diarylallyl cation (I). Product formation then occurs by capture of a water molecule at the 1- or 3-position of this intermediate, the distribution being kinetically controlled.

The results in Table 6 can be interpreted as follows. Consider the 1,3-diphenylallyl cation (I; $R^1 = R^2 = H$). On symmetry grounds, the terminal allylic carbon atoms C(1) and C(3) must be equally reactive towards addition of a nucleophile and must bear an equal proportion of the total positive charge. Introduction of a substituent into one of the aromatic rings removes the symmetry of the system. In the case of the *m*- and *p*-nitro-substituted cations (I; $R^1 = H$, $R^2 = m$- and p-NO_2 respectively), it is found experimentally that the position adjacent to the phenyl ring, C(1), is more reactive towards nucleophilic addition of water than the position adjacent to the nitrophenyl ring, C(3). The chalcols (IVb and IVc respectively) containing a nitrostyryl group accordingly predominate in the product mixtures from the ester solvolyses.

Since there should be no steric preference for nucleophilic addition to either of the reactive sites, this reactivity difference can be sensibly attributed only to unsymmetrical charge distribution across the allylic system in these cations, C(1) bearing a higher proportion than C(3) in each case. This interpretation is in accord with the known relative capacities of the aryl groups in question to stabilise an adjacent electron-deficient atom by a resonance effect, *i.e.*, phenyl > *m*-nitrophenyl > *p*-nitrophenyl (*cf.* Hammett σ substituent constants[11]). In other words, the relative heights of the free-energy barriers associated with addition of a particular nucleophile to C(1) and C(3) in these cations are influenced by the positive charge concentrations at these sites, an increase in charge concentration leading to a lowering of the barrier. In fact, rather small free-energy differences ($\Delta\Delta G^\ddagger$) of *ca.* 1·8 and 3·3 kJ mol^{-1} between the heights of these barriers are derived for the addition of water to the *m*- and *p*-nitro-substituted cations respectively, with reaction at the phenyl substituted terminus, C(1), favoured in each case.

The effect of a *p*-methoxy-substituent upon the relative reactivities of C(1) and C(3) in the cation (I; $R^1 = H$, $R^2 = p$-OMe) could not be investigated directly because of synthetic problems. In the *p*-nitro-*p'*-methoxy-substituted cation (I; $R^1 = p$-NO_2, $R^2 = p$-OMe), however, unsymmetrical charge distribution again produces a greater reactivity towards nucleophilic addition at C(1), the allylic site furthest removed from the nitrophenyl ring. The associated free-energy difference ($\Delta\Delta G^\ddagger = ca.$ 2·4 kJ mol^{-1}), surprisingly, is calculated to be smaller than that produced by a *p*-nitro-substituent itself, although the discrepancy in the values is close to the estimated limits of experimental accuracy. However, it may be inferred that the additional effect of a *p*-methoxy-substituent is minimal in this situation.

For these mesomeric cations, therefore, it appears that the canonical structure (XIA; R = H or *p*-OMe) makes a larger contribution to the electronic character of the species than the alternative (XIB; R = H or *p*-OMe). Since it was shown previously that the *m*-nitrostyryl system is thermodynamically less stable than the styryl system, the principal factor controlling the relative contributions of these canonical structures cannot be simply a styryl conjugation effect. The actual distribution of π-electron density in 1,3-diarylallyl cations (I) may well reflect a balancing of aryl substituent effects upon benzylic cation (ArC^+) stabilisation and styryl (ArC=C) conjugation energy.



(XI A) (XI B)

EXPERIMENTAL

For general remarks, see Part I.[14] U.v. spectra were recorded on a Unicam SP 800A spectrometer calibrated against holmium film. ^1H N.m.r. spectra were obtained for deuteriochloroform solutions on a Perkin-Elmer R10 spectrometer with tetramethylsilane as internal reference.

Preparation of Chalcones (II) *and* (III).—These ketones were prepared by Claisen–Schmidt condensation of appropriate acetophenone and benzaldehyde derivatives by use of either potassium hydroxide (method A) or sodium methoxide (method B) as base catalyst. Only one example of each procedure is described. The chalcones prepared are listed in Table 1. The magnitude (*ca.* 16 Hz) of the vinylic coupling constants in the ^1H n.m.r. spectra of these compounds established a *trans*-stereochemistry for the carbon–carbon double bond in each structure.

Method A.—trans-1-p-*Methoxyphenyl*-3-p-*nitrophenylpropenone* (IId). A solution of potassium hydroxide (0·56 g, 0·01 mol) in water (5 ml) was mixed with a solution of *p*-methoxyacetophenone (15 g, 0·10 mol) in ethanol (100 ml) and then a solution of *p*-nitrobenzaldehyde (15·1 g, 0·10 mol) in ethanol (200 ml) was added slowly with stirring. The mixture was left for several hours at room temperature.

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[14] M. J. A. Habib and W. E. Watts, *J. Chem. Soc.* (*C*), 1970, 2552.

The chalcone (IId) (25 g, 83%) was filtered off and crystallised as pale yellow needles, m.p. 168—169 °C (from chloroform–ethanol).

TABLE 1

Chalcones [a]

Compound	Method of prepn.[b]	M.p. (°C)	Lit. m.p. (°C)	Ref.
(IIa)	A	76—77	77—78	*c*
(IIIa)	A	104—105	105—106	*d*
(IIb)	A	146—148	145—146	*e*
(IIIb)	B	125—127	125—127	*f*
(IIc)	A	164—165	163	*g*
(IIIc)	B	148—150	145	*g*
(IId)	A	168—169	167—168	*h*
(IIId)	B	177—178	176—177	*i*
(IIe)	A	162—163	164	*j*
(IIIe)	B	147—148	143	*k*
(IIf)	A	160—162	162—163	*j*
(IIIf)	B	163—164	163—164	*k*

[a] The presence of a *trans*-double bond in these compounds is indicated by the magnitude (*ca.* 16 Hz) of the vinylic coupling constant in their ^{1}H n.m.r. spectra ($CDCl_3$ solutions). [b] See text. [c] F. J. Pond and A. S. Shoffstall, *J. Amer. Chem. Soc.*, 1900, **22**, 666. [d] P. Pfeiffer, *J. prakt. Chem.*, 1925, **109**, 5156. [e] R. Sorge, *Ber.*, 1902, **1**, 1065. [f] R. P. Barnes and L. B. Dodson, *J. Amer. Chem. Soc.*, 1943, **65**, 1587. [g] Ref. 9. [h] P. Pfeiffer, *Annalen*, 1925, **441**, 240. [i] W. Dilthey, *J. prakt. Chem.*, 1929, **123**, 238. [j] G. V. Grinev, G. I. Chervenyuk, and A. V. Dombrovskii, *Zhur. obshchei Khim.*, 1968, **38**, 225 (*Chem. Abs.*, 1968, **69**, 26,941). [k] V. F. Lavrushin, L. M. Kutsenko, L. M. Grin, and I. Y. Litvin, *Ukrain. khim. Zhur.*, 1968, **34**, 413 (*Chem. Abs.*, 1968, **69**, 76,794).

Method B.—trans-3-p-*Methoxyphenyl*-1-p-*nitrophenylpropenone* (IIId). A solution of *p*-methoxybenzaldehyde (13·6 g, 0·10 mol) in methanol (50 ml) was added slowly to a stirred solution of *p*-nitroacetophenone (16·5 g, 0·10 mol) and sodium methoxide [from sodium (1·0 g, 0·04 g-atom)] in methanol (50 ml), cooled in an ice-bath. The mixture was stirred at 0 °C for several hours and then left overnight in a refrigerator. The chalcone (IIId) (20·4 g, 72%) was filtered off and crystallised as pale yellow needles, m.p. 177—178 °C (from chloroform–ethanol).

TABLE 2

Chalcols [a]

Compound	Method of prepn.[b]	M.p. (°C)	Lit. m.p. (°C)	Styryl chromophore [c] $\lambda_{max.}$/nm	Styryl chromophore [c] $10^{-4}\varepsilon$/l mol^{-1} cm^{-1}	Ref.[d]
(IVa)	D	50—52	52·5	266	2·29	*e*
(Va)	D	54—55	55—56	257	2·15	*f*
(IVb)	C	69—71		251	2·73	
(Vb)	C	46—47		256	2·45	
(IVc)	D	83—84	84—85	313	1·74	*g*
(Vc)	D	85—86	83—84	253	2·07	*g*
(IVd)	C	82—83	79—80	315	1·72	*h*
(Vd)	C	93—94	94—95	265	2·69	*h*
(IVe)	D	103—104	104—105	312	1·64	*i*
(Ve)	D	133—134	132—133	259	2·45	*i*
(IVf)	D	54—56	56—57	310	1·70	*i*
(Vf)	D	123—125	124—125	257	2·90	*i*

[a] From their method of preparation and their ^{1}H n.m.r. spectra, the double bond in these compounds is assigned a *trans*-stereochemistry. [b] See text. [c] In absolute ethanol; values quoted are the average of at least three determinations. [d] Unless present work. [e] W. Davey and J. A. Hearne, *J. Chem. Soc.*, 1968, 4978. [f] Ref. 8. [g] Ref. 9. [h] V. F. Lavrushin, L. M. Kutsenko, and L. M. Grin, *Zhur. org. Khim.*, 1967, **3**, 72 (*Chem. Abs.*, 1967, **66**, 94,751). [i] Ref. *k*, Table 1.

Preparation of Allylic Alcohols and Ethers.—The chalcols (IV) and (V) were prepared by reduction of the corresponding chalcones with either aluminium isopropoxide (method C) or sodium borohydride (method D). Only one example of each procedure is described. The chalcols prepared are listed in Table 2. The method of preparation of the ferrocenyl(aryl)allyl ethers (VIII) and (IX) was described in Part II.[1]

Method C.—trans-1-m-*Nitrophenyl*-3-*phenylprop*-2-*enol* (Vb). The chalcone (IIIb) (5·0 g, 0·02 mol) was added to a stirred suspension of aluminium isopropoxide (32 g, 0·16 mol) in a mixture of dry benzene (120 ml) and freshly distilled isopropyl alcohol (40 ml). The mixture was heated under partial reflux until the distillate was acetone-free (Brady's reagent test). This usually required at least 6 h. The bulk of the solvent was then evaporated under reduced pressure and the residue was diluted with an excess of aqueous sodium hydroxide solution (2M). The organic layer was separated and combined with several benzene extracts of the aqueous layer. The total extract was washed (H_2O), dried (Na_2SO_4), and evaporated. The residual gum was triturated with light petroleum giving the *chalcol* (Vb) (2·8 g, 54%) which crystallised as a white solid, m.p. 46—47 °C (from light petroleum–ether) (Found: C, 70·65; H, 5·25; N, 4·95. $C_{15}H_{13}NO_2$ requires C, 70·05; H, 5·1; N, 5·5%).

By a similar method, the chalcone (IIb) was reduced to the isomeric *chalcol* (IVb) which crystallised as a white solid, m.p. 69—71 °C (from light petroleum–ether) (Found: C, 70·4; H, 5·15; N, 4·9%).

Method D.—trans-1-p-*Nitrophenyl*-3-*phenylprop*-2-*enol* (Vc). Sodium borohydride (0·7 g, 0·02 mol) was added in portions to a stirred suspension of the chalcone (IIIc) (5·0 g, 0·02 mol) in methanol (30 ml). The mixture was stirred and gently heated until a clear solution resulted. This was diluted with saturated aqueous sodium chloride solution (100 ml) and extracted thoroughly with ether. The extract was washed (H_2O), dried (Na_2SO_4), and evaporated giving the chalcol (Vc) (4·0 g, 80%) which crystallised as buff needles, m.p. 84—86 °C (from light petroleum–benzene).

Preparation of p-*Nitrobenzoates* (VI) *and* (VII).—A slurry of *p*-nitrobenzoyl chloride (0·94 g, 5 mmol) in dry benzene (1 ml) was added to a solution of the appropriate chalcol (IV) or (V) (5 mmol) in dry pyridine (10 ml) at 0 °C. The mixture was stirred for 2 h at 0 °C and then poured with stirring into ice–water (100 ml). The pasty solid which was precipitated was quickly separated and dissolved in methylene dichloride. The solution was quickly washed (H_2O), dried (Na_2SO_4), and evaporated. The residual crude ester was crystallised from methylene dichloride–ether.

Details of the *p*-nitrobenzoates prepared are in Table 3.

Repeated attempts to prepare these derivatives of the *p*-methoxychalcols (IVa) and (Va) were unsuccessful.

Acid-catalysed Equilibration of Chalcols.—Each of the chalcols (IVa—f; Va—f) was equilibrated with its allylic isomer in aqueous acidic solution. Details of two such experiments are given. For each chalcol, the equilibration experiment was carried out at least twice and consistent results were obtained. The equilibrium mixtures were analysed by u.v. spectroscopy (see below). The results are in Table 4.

Equilibration of m-*Nitrochalcols* (IVb) $\rightleftharpoons$ (Vb).—A solution of the chalcol (IVb) (0·26 g, 1 mmol) in aqueous acidic dioxan (100 ml) was allowed to stand for 24 h at 20 ± 1 °C. (The solvent was prepared by diluting concentrated hydrochloric acid (8·13 ml) to 600 ml with freshly distilled dioxan and then making the total volume up to 1000 ml with distilled water. An acid concentration of 0·100M was thus obtained.) The acid was then neutralised by addition of aqueous potassium carbonate solution (*ca.* 1M) and the bulk of the solvent was evaporated under reduced pressure. The residue was diluted with distilled water and extracted thoroughly with ether. The total ether extract was washed (H_2O), dried (Na_2SO_4), and evaporated under reduced pressure until no further weight loss occurred. The residual mixture of chalcols (IVb) + (Vb) (0·24 g, 96%) was analysed by u.v. spectroscopy (absolute ethanol solution).

Equilibration of p-*Methoxychalcols* (IVa) $\rightleftharpoons$ (Va).—Direct spectroscopic investigation of this extremely easy equilibration was possible. The u.v. spectrum of a solution of accurately known concentration (*ca.* 0·06 g l^{-1}) of each chalcol in dioxan–water (3 : 2; 100 ml) at 20 ± 1 °C was recorded over the range 280—300 nm. One drop of aqueous sulphuric acid (5M) was then mixed with each solution and the spectra were redetermined. Very fast equilibration occurred and the spectra of the equilibrium mixtures were recorded when no further spectral change was established. The composition of these equilibrium mixtures of chalcols (IVa) and (Va) was calculated from the changes in absorbance of the solutions at 292 nm (see below). In each case, the same equilibrium mixture was formed.

Rate Experiments.—Bernstein's procedure was adopted.[8] The aqueous acidic dioxan solvent employed was the same as that described previously. An accurately weighed amount (*ca.* 20 mg) of the chalcol was dissolved in this solvent (100 ml) thermostatted at 30 ± 0·1 °C in a volumetric flask. The clock was started and aliquot portions (1·00 ml) of the solution were withdrawn at appropriate intervals and quenched by dilution to 100 ml with ethanolic potassium hydroxide solution (0·14 g KOH per 1000 ml 95% EtOH). The u.v. spectra of these diluted aliquot portions were recorded. The reference (solvent) cell was filled with a solution prepared by diluting 1·00 ml of the acidic dioxan solution to 100 ml with the ethanolic potassium hydroxide solution. Each reaction was followed until no further spectral change was noted, *i.e.*, equilibrium had been attained. Each chalcol of an isomeric pair was equilibrated by this procedure and at least three separate

TABLE 3

p-Nitrobenzoates

Compound	M.p. (°C)	Lit. m.p. (°C)	Found (%)			Required (%)		
			C	H	N	C	H	N
(VIb)	139—140		65·15	3·85	6·75	65·35	4·0	6·95
(VIIb)	112—114		65·5	4·15	6·75	65·35	4·0	6·95
(VIc)	133—134	135—136 [a]	65·2	3·8	6·6	65·35	4·0	6·95
(VIIc)	151—152	151 [a]	65·45	4·05	6·7	65·35	4·0	6·95
(VId)	118—119		63·85	4·45	6·25	63·6	4·2	6·45
(VIId)	128—130		63·55	4·4	6·5	63·6	4·2	6·45

[a] Ref. 9.

TABLE 4

Equilibrium and rate constants for the acid-catalysed equilibration of the chalcols (IV) and (V) in 60% aqueous dioxan [a]

Substituents		t/°C	$K_{eq.}$ [b]	k_1 [c] / l mol⁻¹ min⁻¹	k_{-1} [c] / l mol⁻¹ min⁻¹	ΔG^0 [d] / kJ mol⁻¹	Ref.[e]
R¹	R²						
H	*p*-OMe	20 ± 1	0·6 ± 0·2	(83) [h]	(83) [h]	+1·4 ± 0·8	
		29·66 ± 0·07	0·71 ± 0·18			+0·88 ± 0·62	*f*
H	*m*-NO_2	20 ± 1	1·6 ± 0·2			−1·15 ± 0·30	
H	*p*-NO_2	30·0 ± 0·1	0·83 ± 0·05	(4·62 ± 0·40) × 10^{-3}	(5·58 ± 0·15) × 10^{-3}	+0·47 ± 0·15	
		30	0·83 ± 0·01	4·6 × 10^{-3}	5·6 × 10^{-3}	+0·50 ± 0·04	*g*
		29·57 ± 0·01	0·805 ± 0·05	(4·75 ± 0·47) × 10^{-3}	(5·87 ± 0·21) × 10^{-3}	+0·54 ± 0·17	*f*
p-OMe	*p*-NO_2	30·0 ± 0·1	1·06 ± 0·05	(2·35 ± 0·30) × 10^{-1}	(2·22 ± 0·10) × 10^{-1}	−0·15 ± 0·10	
p-Cl	*p*-NO_2	30·0 ± 0·1	0·67 ± 0·08	(1·51 ± 0·25) × 10^{-3}	(2·25 ± 0·10) × 10^{-3}	+1·01 ± 0·30	
p-Me	*p*-NO_2	30·0 ± 0·1	1·12 ± 0·05	(2·58 ± 0·35) × 10^{-2}	(2·30 ± 0·10) × 10^{-2}	−0·30 ± 0·10	

[a] The constants given for the systems investigated in this study are the average of those calculated for the equilibration of each chalcol of an isomeric pair. [b] $K_{eq} = k_1/k_{-1} = \%(V)/\%(IV)$ at equilibrium. [c] k_1 and k_{-1} are the specific rate constants for the forward reaction (IV) $\longrightarrow$ (V) and the reverse reaction (V) $\longrightarrow$ (IV) respectively; they are obtained by dividing the pseudo-first-order rate constants by the acid concentration (0·100M). [d] $\Delta G^0 = -RT \ln K_{eq}$. [e] Unless present work. [f] Ref. 8. [g] Ref. 9. [h] Estimated from Hammett plot (see text).

runs were carried out for each chalcol. Within experimental error, the same equilibrium mixture was formed, irrespective of the identity of the isomer used as starting material.

The progress of each equilibration was followed by monitoring the decrease in extinction coefficient at the wavelength of maximum absorbance due to the styryl chromophore of the starting material and the increase in extinction coefficient at the wavelength of maximum absorbance of the styryl chromophore of its isomer. The wavelength of maximum absorbance ($\lambda_{max.}$) and the extinction coefficient (ε) for these styryl chromophores are given in Table 2. The equilibrium constant (K_{eq}) and the first-order rate constants for the forward and reverse reactions (k_1 and k_{-1} respectively) were calculated conventionally (see ref. 8). Good agreement was found between the set of constants calculated for the equilibration starting with one chalcol and the set derived starting with its isomer. The results are in Table 4.

TABLE 5

Equilibrium constants for the acid-catalysed equilibration of the ethers (VIII) and (IX) in absolute methanol [a]

Substituent R	Ether equilibrated	Equilibrium mixture [b]		K_{eq} [c]	ΔG^0 [d] kJ mol^{-1}
		(VIII) (%)	(IX) (%)		
H	(VIII)	39	61	1·6 ± 0·2	−1·15 ± 0·3
H	(IX)	38	62		
o-OMe	(VIII)	30	70	2·3 ± 0·2	−2·0 ± 0·2
o-OMe	(IX)	30	70		
m-OMe	(VIII)	30	70	2·4 ± 0·3	−2·1 ± 0·3
m-OMe	(IX)	29	71		
p-OMe	(VIII)	39	61	1·5 ± 0·2	−1·0 ± 0·3
p-OMe	(IX)	40	60		
p-Cl	(VIII)	36	64	1·75 ± 0·2	−1·35 ± 0·3
p-Cl	(IX)	37	63		
p-Me	(VIII)	43	57	1·35 ± 0·15	−0·7 ± 0·3
p-Me	(IX)	42	58		

[a] At 20 ± 1 °C. In these solutions, the concentration of the cations (X), which have distinctive electronic spectra (ref. 1), is below the level of detection. [b] Analysed spectroscopically (details in Experimental section); values given are the average of at least three separate experiments and are considered accurate to ±2%. [c] K_{eq} = %(IX)/%(VIII). [d] $\Delta G^0 = -RT \ln K_{eq}$.

Acid-catalysed Equilibration of Ferrocenyl(aryl)allyl Ethers.—Since these ethers (VIII) and (IX) equilibrate very rapidly in methanol solution in the presence of a trace of acid, a direct investigation by u.v. spectroscopy was possible. One such experiment is described in detail. For each ether, the equilibration was carried out at least three times. Consistent results were obtained. The results are in Table 5.

Equilibration of Ethers ($VIII \rightleftharpoons IX$; R = *p*-OMe).—The u.v. spectrum of a solution of accurately known concentration (*ca.* 0·025 g l^{-1}) of the ether (VIII; R = *p*-OMe) in absolute methanol (100 ml) at 20 ± 1 °C was recorded. One drop of aqueous sulphuric acid (1M) was then mixed thoroughly with the solution and the u.v. spectrum immediately redetermined. After *ca.* 30 min the spectrum of the solution was recorded once more and found to be superimposable upon the previous spectrum (*i.e.*, the spectrum of the equilibrium mixture). The procedure was then repeated with the isomeric ether (IX; R = *p*-OMe). Formation of the same equilibrium mixture was observed. The composition of this mixture was calculated as described below.

Ester Solvolyses.—Each of the *p*-nitrobenzoates (VIb—d) and (VIIb—d) was hydrolysed to a mixture of isomeric chalcols (IV) + (V) by refluxing in 80% aqueous acetone solution (*i.e.*, at 65 ± 1 °C). The reflux time required to effect complete hydrolysis varied from several days for the *p*-nitro-substrates (VIc) and (VIIc) to a few hours for the *p*-methoxy-*p*′-nitro-substrates (VId) and (VIId). The solvolysis of each ester was carried out at least twice and consistent results were obtained. Product composition was analysed by u.v. spectroscopy. Within experimental error, the same mixture of isomeric chalcols was formed, irrespective of the identity of the ester starting material. Only one such experiment is described. Results are summarised in Table 6.

Solvolysis of p-*Nitrobenzoate* (VId).—A solution of this ester (0·30 g, 0·7 mmol) in acetone–water (4 : 1; 50 ml) was refluxed (65 ± 1 °C) for 3 h. Aqueous potassium carbonate solution (*ca.* 1M; 5 ml) was then added and the volume of the mixture evaporated to *ca.* 15 ml by evaporation under reduced pressure. The residual solution was extracted thoroughly with ether. The extract was washed (aqueous K_2CO_3, then H_2O), dried (Na_2SO_4), and evaporated under reduced pressure until no further weight loss occurred. The i.r. spectrum of the residue showed the absence of ester (no carbonyl absorption). The mixture of chalcols (IVd) + (Vd) (0·13 g, 99%) was analysed spectroscopically. Acidification of the previous aqueous solutions and extraction with ether gave *p*-nitrobenzoic acid (0·075 g, 94%).

TABLE 6

Product composition from the solvolysis of the *p*-nitrobenzoates (VI) and (VII) in 80% aqueous acetone [a]

Substituents		Ester solvolysed	Product composition [b]		$\Delta\Delta G^{\ddagger}$ [c] kJ mol^{-1}
R^1	R^2		(IV)(%)	(V)(%)	
H	*m*-NO_2	(VIb)	66	34	+1·8 ± 0·3
H	*m*-NO_2	(VIIb)	65	35	
H	*p*-NO_2	(VIc)	76	24	+3·3 ± 0·4
H	*p*-NO_2	(VIIc)	77	23	
p-OMe	*p*-NO_2	(VId)	71	29	+2·4 ± 0·3
p-OMe	*p*-NO_2	(VIId)	70	30	

[a] At 65 ± 1 °C. [b] Determined spectroscopically (see Experimental section); values given are the average of at least two experiments and are considered accurate to ±2%. [c] $\Delta\Delta G^{\ddagger} = -RT \ln[\%(V)/\%(IV)]$; values given are the average of those obtained independently for the esters of an isomeric pair.

Interrupted Ester Solvolysis.—The ester (VIIc) was hydrolysed as in the preceding experiment but reaction was terminated when only about half of the ester had been consumed. This was recovered and found to be identical with the starting material. No evidence for the presence of rearranged ester (VIc) was found by spectroscopic analysis.

Similarly, interrupted solvolysis of the other *p*-nitrobenzoates gave no indication of ester isomerisation under the reaction conditions.

Attempted Thermal Isomerisation of Esters.—Solutions of the *p*-nitrobenzoates (VIb—d) and (VIIb—d) in dry acetone were refluxed for prolonged periods and the solvent was then evaporated. The recovered ester in each case was identical with the starting material.

TABLE 7

Styryl and ferrocenylvinyl chromophores of ethers (VIII) and (IX)

Compound	Styryl chromophore [a]		Ferrocenylvinyl chromophore [a]	
	$\lambda_{\max.}$/nm	$10^{-4}\varepsilon$/l mol^{-1} cm^{-1}	$\lambda_{\max.}$/nm	$10^{-4}\varepsilon$/l mol^{-1} cm^{-1}
(VIII; R = H)	253	1·95		
(IX; R = H)			281	1·14
(VIII; R = *o*-OMe)	254	1·61		
(IX; R = *o*-OMe)			280	1·00
(VIII; R = *m*-OMe)	256	1·66		
(IX; R = *m*-OMe)			281	1·01
(VIII; R = *p*-OMe)	265	2·04		
(IX; R = *p*-OMe)			280	1·07
(VIII; R = *p*-Cl)	259	2·35		
(IX; R = *p*-Cl)			280	1·04
(VIII; R = *p*-Me)	258	2·14		
(IX; R = *p*-Me)			281	1·09

[a] In absolute methanol; values given are the average of at least three determinations.

Attempted Chalcol Isomerisation by Use of p-*Nitrobenzoic Acid.*—The chalcol (IVd) (100 mg, 0·35 mmol) was dissolved in 80% aqueous acetone (100 ml) containing *p*-nitrobenzoic acid (58 mg, 0·35 mmol) and the solution was refluxed for 3 h. The reaction was worked-up as in the solvolysis experiments. The chalcol recovered (92 mg, 92%) was identical with the starting material and the absence of the isomeric chalcol (Vd) was established by u.v. spectral analysis.

Product Analysis.—The percentage composition of the various mixtures of isomeric chalcols (IV) + (V) was calculated in most cases from the u.v. extinction coefficients (average of at least three determinations) of the mixture in absolute ethanol solution at the wavelengths of maximum absorbance for the two particular styryl chromophores present (see Table 2). The extinction coefficients at these wavelengths were similarly calculated for each of the pure constituents. By application of the Beer–Lambert law, the proportion of each isomer present in a given mixture could thus be calculated by simple proportionality (see ref. 1). By use of the two styryl chromophores present in each mixture, an independent internal check on the calculated composition was possible. Good agreement was found in all cases.

A similar method was used to analyse mixtures of isomeric ferrocenyl(aryl)allyl ethers (VIII) + (IX) except that absolute methanol was used as solvent. The wavelength of maximum absorbance ($\lambda_{\max.}$) and the extinction coefficient (ε) for the styryl and ferrocenylvinyl chromophores of these ethers are in Table 7.

In the case of the *p*-methoxychalcols (IVa) + (Va) and the *m*-nitrochalcols (IVb) + (Vb), the wavelengths and intensities of the styryl chromophores of the isomers are closely similar (Table 2). Accordingly, these mixtures were analysed at suitable wavelengths corresponding to a large difference in extinction coefficient between the isomers. For the *p*-methoxychalcols in 60% aqueous dioxan, the extinction coefficient at 292 nm was used ($\varepsilon_{\text{IVa}} = 4{\cdot}85 \times 10^3$; $\varepsilon_{\text{Va}} = 1{\cdot}85 \times 10^3$). For the *m*-nitrochalcols in absolute ethanol, the extinction coefficient at 292·5 nm was used ($\varepsilon_{\text{IVb}} = 1{\cdot}70 \times 10^3$; $\varepsilon_{\text{Vb}} = 4{\cdot}25 \times 10^3$).

Independently, all of these mixtures of isomers in predetermined proportions were shown to give u.v. spectra in excellent accord with the Beer–Lambert law. The analyses obtained by this method are considered accurate to ±2%.

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