85. *Anionotropic Systems. Part I.* The Effect of a Nitro-substituent on Equilibrium and Mobility in the* 1 : 3-*Diphenylallyl Alcohol System.*

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Rate and equilibrium constants have been determined for the interconversion of 3-*p*-nitrophenyl-1-phenyl- (III) and 1-*p*-nitrophenyl-3-phenyl-allyl alcohol (IV) under the influence of hydrochloric acid in aqueous dioxan. The equilibrium mixture contains 55% of (III) and 45% of (IV); the equilibrium constant ($K = 0{\cdot}83 \pm 0{\cdot}01$) varies less than the experimental error over the temperature range 30—80°. The free-energy change ($\Delta G = 0{\cdot}12$ kcal./mole), representing the difference between the conjugation energies of an ethylenic bond with a phenyl and a *p*-nitrophenyl group, is unexpectedly small.

The rate and activation energy of the rearrangement of (III) are very similar to those of 1-phenylallyl alcohol (V), showing that the effect of the *p*-nitrophenyl group on mobility is practically nil. This indicates that the deactivating, electron-attractive influence of the nitro-substituent is compensated by an electromeric effect of the phenyl ring in the opposite direction.

HITHERTO, quantitative studies on three-carbon anionotropic systems of the type (I) $\rightleftharpoons$ (II) have mainly been concerned with examples in which X is a strongly conjugating group (*e.g.*, C:C, C:C, Ph, etc.) and Y is a weakly conjugating group (*e.g.*, H, Me, etc.), and in which the equilibrium consequently lies far on the side of the more highly conjugated isomer (II). As has been shown previously, such systems provide an excellent basis for investigating the electronic properties of substituents by means of rate measurements, but the equilibrium constants are too large to be determined. Added interest, therefore, attaches to examples in which X and Y have sufficiently similar conjugating properties to render the equilibrium measurable. The free-energy change of the reaction (I) $\rightleftharpoons$ (II)

$$\text{(I)}\quad \text{A·CHX·CH:CHY} \rightleftharpoons \text{CHX:CH·CHYA}\quad \text{(II)}$$

will correspond closely to the difference in resonance energies of X·C:C and Y·C:C, thus providing a kinetic method of determining such quantities. This method is capable of greater precision than is attainable in the evaluation of resonance energies from thermochemical data, particularly when small differences are involved, and is less subject to uncertainties of interpretation. The only assumption which has to be made is the very reasonable one that any stabilisation due to hyperconjugation of the C–A bond will be the same in (I) and (II).

We now report the results for a model system, the reversible isomerisation of (III) and (IV). This was chosen because the nitro-group is one of the most strongly polar of common substituents; if the equilibrium point is suitable in this case, as it has been found to be, a wide applicability for the method is assured.

$$\text{(III)}\quad \text{Ph·CH(OH)·CH:CH·}C_6H_4\text{·}NO_2 \rightleftharpoons \text{Ph·CH:CH·CH(OH)·}C_6H_4\text{·}NO_2\quad \text{(IV)}$$

The two alcohols were conveniently prepared in good yields by Ponndorf reduction of the corresponding ketones, as crystalline solids of almost identical, but mutually depressed, melting points, and each formed its own *p*-nitrobenzoate under appropriate conditions. The two alcohols are characterised by distinct ultra-violet light absorption properties (see Figure); (III) exhibits an intense band at 3110 Å associated with the *p*-nitrostyryl chromophore (cf. Pestemer, Langer, and Manchen, *Monatsh.*, 1936, **68**, 326), while (IV) exhibits a wide band with a maximum at 2515 Å arising from superposition of the absorption due to the nitrophenyl and the styryl chromophore. Mixtures of (III) and (IV) are readily analysed by this means, and it is found that, under the influence of acids, both alcohols isomerise to give the same equilibrium mixture containing about 55% of (III) and 45% of (IV). The composition of the equilibrium mixture is scarcely affected by the experi-

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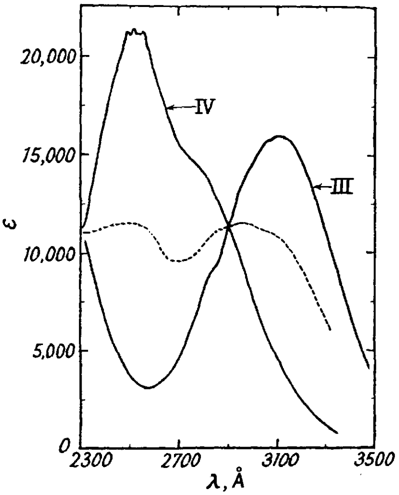
* Continuation of two separate series [" Studies on Molecular Rearrangement " Part IX, *J.*, 1952, 4155) and " The Kinetics of Anionotropic Rearrangement " (Part X, *J.*, 1952, 4158)] which will now be merged.

mental conditions (*e.g.*, solvent, temperature, and catalyst concentration), but no interconversion takes place in the absence of acid catalyst under the conditions examined.

A quantitative spectrometric investigation of the system (III)–(IV) was carried out in 60% aqueous dioxan–0·1M-hydrochloric acid. The reactions exhibit normal first-order kinetics; first-order rate constants and equilibrium constants are given in Table 1. The equilibrium constant, $K = 0{\cdot}83$, changes by less than 2% over the temperature range 30—80°. The derived value for the free-energy change is $\Delta G = 0{\cdot}12$ kcal./mole; the enthalpy change ΔH must be of the same order or smaller, and the entropy change ΔS must be less than 0·5 cal. mole^{-1} deg.$^{-1}$.

TABLE 1. *First-order rate constants (in min.*$^{-1}$*) and equilibrium constants for the system* (III) $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ (IV) *in* 60% *aqueous dioxan–*0·1M*-hydrochloric acid:* $k = k_1 + k_{-1}$; $K = k_1/k_{-1}$.

Temp.	K	10^4k	10^4k_{-1}	10^4k_1	Temp.	K	10^4k	10^4k_{-1}	10^4k_1
30°	0·83	10·2	5·6	4·6	60°	0·83	322	176	146
40	0·82	36·6	20·2	16·4	70	0·84	950	516	434
50	0·83	103	56	47	80	0·83	2370	1300	1070



Ultra-violet light absorption of (III), (IV), *and their equilibrium mixture (broken curve) in ethanol solution.*

It is instructive to compare the system (III) $\rightleftharpoons$ (IV) with, on the one hand, the irreversible rearrangement of 1-phenylallyl alcohol (V) to cinnamyl alcohol (VI) (Braude, Jones, and Stern, *J.*, 1946, 396) and, on the other, with the symmetrical system, 1 : 3-diphenylallyl alcohol (VII), in which the two isomers are identical and the equilibrium constant has the value $K = 1$.

$$\text{(V)}\quad HO\cdot CHPh\cdot CH{:}CH_2 \rightleftharpoons CHPh{:}CH\cdot CH_2\cdot OH \quad \text{(VI)}$$

$$\text{(VII)}\quad HO\cdot CHPh\cdot CH{:}CHPh \rightleftharpoons CHPh{:}CH\cdot CHPh\cdot OH$$

The reaction rate in the latter case obviously cannot be determined directly, but it can be accurately extrapolated from measurements (to be published) by Mr. P. H. Gore on analogues in which one of the phenyl groups is replaced by a naphthyl group, in conjunction with data previously obtained for 1-aryl-3-methylallyl alcohols (Braude and Fawcett, *J.*, 1950, 800). Comparison of the data (Table 2) for (III) and (V) shows that a *p*-nitrophenyl group has a large effect on equilibrium, but only a negligible effect on mobility, the rate constants and energies of activation being very similar. By contrast, comparison of the data for (III) and (VII) shows that a *p*-nitro-substituent has a small effect on equilibrium, but a large effect on mobility, decreasing the rate constant by a factor of *ca.* 200 and increasing the energy of activation by *ca.* 2 kcal./mole.

The large effect of the *p*-nitrophenyl group on equilibrium is to be expected, since the conjugating properties of such a group will be very different from that of a hydrogen atom. Similarly, the large effect of the *p*-nitro-substituent on mobility is also as expected, for it

TABLE 2. *Effects of substituents in the rearrangement*

$$\text{HO·CHPh·CH:CHX} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{CHPh:CH·CHX·OH.}$$

X	K	$-\Delta G_{30^\circ}$ (kcal./mole)	k'_1 (min.$^{-1}$) *	$E_{\text{Arr.}}$ (kcal./mole)	$\log_{10} A$ †
H (V) ‡	>10	>2	0·0038	24·5	14·6
Ph (VII) §	1	0	0·70	21·5	14·7
$C_6H_4{\cdot}NO_2$ (III)	0·83	−0·12	0·0046	23·7	14·1

* Specific rate constant (k_1/acid concentration) at 30° for 60% aqueous dioxan–hydrochloric acid.

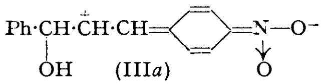
† Defined by log k' (sec.$^{-1}$) $= A\mathrm{e}^{-E_{\text{Arr.}}/\boldsymbol{RT}}$.

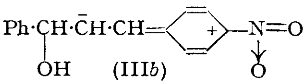
‡ Part V, *J.*, 1946, 396. The value for the activation energy is a revised one, based on new measurements.

§ Extrapolated values based on unpublished measurements by Mr. P. H. Gore.

is known that anionotropic rearrangements are very sensitive to electronic influences, being strongly facilitated by electron-donating, and strongly retarded by electron-attracting substituents (Braude, *Quart. Reviews*, 1950, **4**, 404).

On the other hand, the effects of the *p*-nitro-substituent on equilibrium and of a *p*-nitrophenyl group on mobility are unexpectedly small, obviously owing to some common factor which causes the mobilities (k_1 and k_{-1}) of both (III) and (IV) to differ little from that of (V), and hence the ratio k_1/k_{-1} to differ little from unity. The extra conjugation present in the nitrostyrene system of (III) evidently contributes only little resonance stabilisation additional to that of the styrene system (IV), and the retarding influence of the nitro-substituent must be compensated by an independent accelerating influence of the phenyl ring to which it is attached. It is as if the allyl grouping competes successfully with the nitro-substituent for the benzenoid π-electrons; in terms of the valency-bond representation of mesomeric electron displacements, we must conclude that contribution from structures of type (III*b*) can equal the combined effects of contributions of type (III*a*) and of the negative inductive effect of the nitro-substituent.


(III*a*)


(III*b*)

Very little information is available concerning the relative strength of conjugation of an ethylenic bond with a substituted and an unsubstituted phenyl group. Theoretically, one might expect a strongly polar substituent, independently of the sign of its mesomeric effect, to assist the π-electron interaction. This is borne out by the recent calculations by Pullmann (*Compt. rend.*, 1948, **226**, 486) and Coulson and Jacobs (*J.*, 1949, 1983) for *p*-aminostilbene, which indicate that the aminophenyl group interacts more strongly than the unsubstituted phenyl group with the central ethylenic link. The difference between the conjugation energies of an ethylenic bond with an aminophenyl and a phenyl group can be estimated from Coulson and Jacobs's results as *ca.* 300 cal.* This is of the same order as, but somewhat larger than, the value of 120 cal. obtained here for the difference between the conjugation energies of an ethylenic bond with a nitrophenyl and a phenyl group.

$$\text{(VIII)}\quad \text{HO·CHPh·CH:CH·}C_6H_4\text{Cl-}p \rightleftharpoons \text{CHPh:CH·CH(OH)·}C_6H_4\text{Cl-}p\quad \text{(IX)}$$

$$\text{(X)}\quad \text{Ph·}CH_2\text{·N:CH·}C_6H_4\text{·}NO_2\text{-}m \rightleftharpoons \text{Ph·CH:N·}CH_2\text{·}C_6H_4\text{·}NO_2\text{-}m\quad \text{(XI)}$$

Empirically, the nearest analogies come from Burton and Ingold's work (*J.*, 1928, 904) on the 3-*p*-chlorophenyl-1-phenylallyl alcohol system (VIII) ⇌ (IX) and from Shoppee's work (*J.*, 1932, 696) on the reversible prototropic isomerisation of the azomethines (X) and (XI). Burton and Ingold did not make quantitative measurements, but concluded

* This estimate has been obtained as follows. According to Coulson and Jacobs, the charge migration in aniline confers a charge of 0·090*e* on the nitrogen atom: this is associated with a resonance energy of *ca.* 5000 cal. (Wheland, " The Theory of Resonance," Wiley, New York, 1944). In 4-aminostilbene, the charge on the nitrogen atom is increased to 0·096*e*; the difference of 0·006*e* will be approximately equivalent to an additional stabilisation of 5000 × 6/90 = 300 cal. We are indebted to Professor C. A. Coulson, F.R.S., for pointing out to us that this estimate does not take explicit account of the change in bond orders with substitution, but that the bond-order energy term is likely to be small compared with the Coulomb energy term.

from qualitative evidence that (VIII) "is the main isomeride;" if this is correct, the much more strongly polar *p*-nitro-substituent might be expected to result in a considerably larger displacement of the equilibrium. In the prototropic system studied by Shoppee, the equilibrium mixture was found to contain 68% of (X) at 82°; again, a *p*-nitro-substituent might be expected to have an even larger effect. However, the direct comparison between the anionotropic and prototropic systems is not necessarily valid; in the former, the entities actually undergoing equilibrium are the oxonium ions formed by addition of a proton to a hydroxyl group and in which the positive charge will have little influence on the conjugated system, whereas in prototropy the entities undergoing equilibration are probably the mesomeric carbanions formed by loss of a proton from the methylene group and in which the negative charge forms an integral part of the conjugated system (cf. Braude and Forbes, *J.*, 1951, 1755).

We now turn to the effect of the *p*-nitrophenyl group on mobility and to the opposing electronic influences of the phenyl group and the nitro-substituent which it indicates. It is well known that an unsubstituted phenyl group can exert an electron-donating or electron-attracting influence by the electromeric mechanism according to the demands of the reaction, and the accelerating effect of phenyl on anionotropy is shown by comparing the data for (V) and (III); but, in the presence of a strongly polar nuclear substituent, it is usual for the substituent to take control even when it hinders the reaction. The situation is reminiscent of that encountered in the electrophilic substitution of *p*-nitrodiphenyl and β-nitrocinnamic acid, in which the *p*-nitrophenyl and β-nitrovinyl groups cause overall deactivation coupled with *op*-direction (cf. Gull and Turner, *J.*, 1929, 491; Hartman and Robertson, *J.*, 1945, 891; Bordwell and Rohde, *J. Amer. Chem. Soc.*, 1948, **70**, 1191). This has also been ascribed to the $+T$ effects of the phenyl and vinyl groups acting in opposition to the $-I,-T$ effects of the nitro-substituent. Unlike the present case, however, the activating effect of the phenyl ring is heavily outweighed by the deactivating effect of the nitro-substituent; thus the rates of nuclear halogenation of the *p*-nitrophenyl derivatives are decreased by factors of *ca.* 10^2 with respect to the unsubstituted compounds (Hartman and Robertson, *loc. cit.*). Similarly, the electrophilic addition of halogens to acrylic acid is facilitated by a phenyl group but strongly retarded by a nitrophenyl group (relative rates of chlorine addition under standard conditions are: acrylic acid 0·018, cinnamic acid 4·9, methyl *p*-nitrocinnamate 0·0011; cf. de la Mare, *Quart. Reviews*, 1949, **3**, 126). The most probable reason for the difference between the effects of a *p*-nitrophenyl group on the rates of acid-catalysed anionotropy and of electrophilic halogenation is that the former involves initial attack by a positively charged ion (H^+),* whereas the latter involves attack by an essentially neutral reagent (Cl_2, Br_2): the ion will be much more effective than a neutral molecule in bringing into play the compensating $+T$ effect of the phenyl ring.

EXPERIMENTAL

(M. p.s are uncorrected. Light-absorption data were determined on a Hilger Spekker photographic instrument except where otherwise stated.)

3-p-*Nitrophenyl*-1-*phenylallyl Alcohol* (III).—*p*-Nitrobenzaldehyde (25 g.) was condensed with acetophenone (20 g.) in the presence of methanolic potassium hydroxide (5%; 125 ml.) at room temperature, giving *p*-nitrostyryl phenyl ketone (38 g., 90%), m. p. 163° (cf. Sorge, *Ber.*, 1902, **35**, 1068; Wieland, *ibid.*, 1904, **37**, 1149). The ketone (5 g.), aluminium *iso*propoxide (32 g.), *iso*propanol (30 ml.), and benzene (120 ml.) were heated under partial reflux until formation of acetone ceased (about 4 hours). After cooling, excess of 2N-sodium hydroxide was added, the benzene layer separated, and the aqueous layer extracted with benzene. Evaporation of the combined benzene solutions afforded 3-p-*nitrophenyl*-1-*phenylallyl alcohol* (4·2 g., 84%), which crystallised from benzene–light petroleum (b. p. 60—80°) in pale yellow plates, m. p. 84—85° (Found: C, 70·2; H, 5·4; N ,5·5. $C_{15}H_{13}O_3N$ requires C, 70·6; H, 5·1; N, 5·5%). Light absorption in ethanol: $\lambda_{max.}$ 3110 Å; ε 16,450 (cf. Fig.). The p-*nitrobenzoate*, obtained from the alcohol and *p*-nitrobenzoyl chloride in dry pyridine at 0°, separated from methanol–ethyl

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* The addition of the proton to the hydroxyl group is, of course, reversible and not rate-determining, but the equilibrium concentration of the oxonium ion enters the rate equation (cf. Braude, *J.*, 1948, 794).

acetate–water as almost colourless crystals, m. p. 135—136° (Found: C, 64·9; H, 4·3; N, 7·0. $C_{22}H_{16}O_6N_2$ requires C, 65·3; H, 4·0; N, 6·9%). Light absorption in chloroform: $\lambda_{max.}$ 2570, 2680, 2800, and 3040 Å; ε 18,000, 18,000, 18,000, and 22,000, respectively.

1-p-*Nitrophenyl*-3-*phenylallyl Alcohol* (IV).—*p*-Nitroacetophenone (25 g.; Walker and Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 1368) and benzaldehyde (16 g.) in the presence of methanolic potassium hydroxide (5%, 125 ml.) gave *p*-nitrophenyl styryl ketone (25 g., 65%), m. p. 145° after recrystallisation from ethanol–benzene (cf. Weygand and Günther, *Annalen*, 1927, **459**, 115). Reduction of the ketone (5 g.) with aluminium *iso*propoxide (16 g.) and *iso*propanol (100 ml.) as above afforded 1-p-*nitrophenyl*-3-*phenylallyl alcohol* (3·7 g., 74%), which crystallised from benzene–light petroleum (b. p. 60—80°) as plates, m. p. 83—84°, depressed on admixture with the isomer above (Found: C, 70·6; H, 5·1; N, 5·4%). Light absorption in ethanol: $\lambda_{max.}$ 2515 and 2800 Å; ε 21,300 and 12,700 (cf. Fig.). The p-*nitrobenzoate*, crystallised from methanol–ethyl acetate–water, had m. p. 151° (Found: C, 65·4; H, 4·2; N, 7·2%; *M*, in camphor, 395. $C_{22}H_{16}O_6N_2$ requires C, 65·3; H, 4·0; N, 6·9%; *M*, 404). Light absorption in chloroform: $\lambda_{max.}$ 2590 and 2660 Å; ε 40,000 and 36,000.

Interconversion of the Two Alcohols.—A solution of the alcohol (III) (1 g.) in 0·1M-hydrochloric acid–60% aqueous dioxan (100 ml.) was kept at 78° for 1 hour, then neutralised by potassium carbonate, and most of the solvent removed at 0·1 mm. The residue was diluted with water and extracted with ether, and the extract dried (Na_2SO_4) and evaporated under reduced pressure. The oily residue (0·95 g.) solidified when stirred under light petroleum (b. p. 40—60°) and then had m. p. 61—71°. The light absorption of this product corresponded to that of a mixture of 55% of (III) and 45% of (IV). An artificial mixture of the two alcohols in these proportions had m. p. 61—71°, unaltered on admixture with the rearrangement product. A similar experiment with the alcohol (IV) gave an identical result.

Kinetic Measurements.—Weighed amounts of alcohol (approx. 20 mg.) were added to 25 ml. of reaction medium contained in a reaction vessel of the type previously described (*J.*, 1946, 396), in a thermostat. 1-Ml. samples were withdrawn at appropriate intervals and added to 95% aqueous ethanol containing sufficient potassium hydroxide to neutralise the hydrochloric acid. The absorption intensities at the maxima of the two isomers were determined by using a Beckman photoelectric spectrophotometer provided with special cells of 0·1-cm. thickness. The intensity values, expressed as $E^{1\%}_{1\,\text{cm.}}$, of the separate isomers are 139 at 2515 Å and 645 at 3110 Å for (III), and 842 at 2515 Å and 154 at 3110 Å for (IV). First-order rate constants for (III) were calculated from $k = (2{\cdot}3/t)\log_{10}[(a - 139)/(a - x)]$, where x is the intensity at time t and a the final intensity at 2515 Å, and those for (IV) were calculated from $k = (2{\cdot}3/t)\log_{10}[(b - 154)/(b - x)]$, where b is the final intensity at 3110 Å. Equilibrium constants were calculated from $K = [\text{IV}]/[\text{III}] = (a - 139)/(842 - a)$ and from $K = (645 - b)/(b - 154)$. The results obtained for the two isomers were in good agreement; four typical runs at the lowest and the highest temperature employed are reproduced below. The reaction medium was prepared by mixing 61 ml. of dioxan and 10 ml. of M-hydrochloric acid, and adding water to give a total volume of 100 ml.

(i) Rearrangement of (III) at 30°. Alcohol concn. 0·0030M.

Time (min.)	0	150	300	470	725	1345	3200
$E^{1\%}_{1\,\text{cm.}}$ (2515 Å)	139	184	224	257	303	375	458
$E^{1\%}_{1\,\text{cm.}}$ (3110 Å)	645	—	—	—	—	—	428
10^4k (min.$^{-1}$)	—	10·1	10·3	9·9	10·0	10·0	—

K (mean) = 0·82; k (mean) = 10·1, k_1 = 5·5, k_{-1} = 4·6.

(ii) Rearrangement of (IV) at 30°. Alcohol concn. 0·0028M.

Time (min.)	0	150	300	470	725	1345	3200
$E^{1\%}_{1\,\text{cm.}}$ (2515 Å)	842	—	—	—	—	—	459
$E^{1\%}_{1\,\text{cm.}}$ (3110 Å)	154	196	222	252	300	348	423
10^4k (min.$^{-1}$)	—	11·3	9·7	9·6	10·8	9·5	—

K (mean) = 0·83; k (mean) = 10·2, k_1 = 5·6, k_{-1} = 4·6.

(iii) Rearrangement of (III) at 80°. Alcohol concn. 0·0026M.

Time (min.)	0	1	2	3	4	5	110
$E^{1\%}_{1\,\text{cm.}}$ (2515 Å)	139	209	262	305	337	363	458
$E^{1\%}_{1\,\text{cm.}}$ (3110 Å)	645	—	—	—	—	—	426
10^4k (min.$^{-1}$)	—	2480	2440	2440	2420	2420	—

K (mean) = 0·82; k (mean) = 2440, k_1 = 1340, k_{-1} = 1100.

(iv) Rearrangement of (IV) at 80°. Alcohol concn. 0·0030M.

Time (min.)	0	1	2	3	4	5	110
$E^{1\%}_{1\,\text{cm.}}$ (2515 Å)	842	—	—	—	—	—	460
$E^{1\%}_{1\,\text{cm.}}$ (3110 Å)	154	211	253	289	315	336	424
10^4k (min.$^{-1}$)	—	2410	2280	2320	2270	2250	—

K (mean) = 0·83; k (mean) = 2310, k_1 = 1260, k_{-1} = 1050.

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