

10. *Anionotropic Systems. Part VII.* Reversible Rearrangements of the 1-Naphthyl-3-phenylallyl Alcohols. A Kinetic Determination of the Conjugation Energies of the α - and β -Vinyl-naphthalene Systems.*

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The two pairs of 1 : 3-diarylallyl alcohols (I) and (II) where X = α - and β -naphthyl have been synthesised and their reversible, acid-catalysed inter-conversion has been studied spectrokinetically by a microtechnique. The



rearrangement of the α -naphthyl derivatives is slightly slower than that of the β -naphthyl derivatives and has slightly higher energies and entropies of activation.

The equilibria lie on the side of the vinyl-naphthalene derivatives (II), in the sequence X = α -naphthyl > β -naphthyl > phenyl. The free energies of rearrangement, which are a measure of the resonance energies of the α - and β -vinyl-naphthalene relative to the styrene system, are 205 and 35 cal./mole respectively. These values may be compared with those of 760 and 120 cal./mole derived from Coulson and Longuet-Higgins's molecular-orbital calculations. It is apparent that an ethylenic bond conjugates more strongly with a naphthyl than with a phenyl group, but that the observed conjugation energies are rather smaller than those predicted. Possible reasons for this are discussed and it is suggested that steric effects may be a contributory factor in accounting for the relatively low reactivity and conjugation stabilisation of the α -naphthyl derivatives.

In a previous paper,¹ it was shown that the reversible rearrangement of 1 : 3-disubstituted allyl alcohols $\text{HO}\cdot\text{CHX}\cdot\text{CH}=\text{CHY} \rightleftharpoons \text{CHX}=\text{CH}\cdot\text{CHY}\cdot\text{OH}$ provides an excellent basis for a quantitative comparison of the conjugating properties of X and Y. By using Y = Ph as a standard of reference and varying X, the electronic effects of X relative to phenyl can be assessed from the rates of the forward and the reverse reaction, while from the equilibrium constants the conjugation energy of the system X·CH=CH relative to the styryl system Ph·CH=CH can be determined since the difference will be equal, as a close approximation, to the free energy of the isomerisation. Thus, it was shown¹ that the conjugation energy

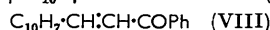
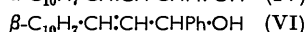
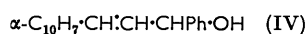
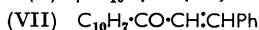
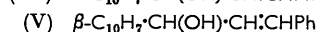
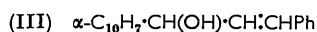
* Part VI, *J.*, 1958, 2404.

¹ Part I, Braude and Waight, *J.*, 1953, 419.

(arising from interaction of the π -electrons of an aryl group with those of $\text{CH}=\text{CH}$, in the ground state) of the *p*-nitrostyryl system exceeds that of the styryl system by 120 ± 2 cal./mole. This example illustrated two advantages of such a kinetic method of determining resonance energies: the method can be used to increase quite small interactions which could not be accurately deduced from heats of combustion, and it can be employed with systems where alternative thermochemical methods (*e.g.*, heats of hydrogenation) are not readily applicable.

The kinetic approach is particularly suited to the study of condensed aromatic systems and the present work deals with the α - and β -naphthyl derivatives. Several recent rate comparisons are already available, including one based on the irreversible rearrangement² of the methyl-naphthylallyl alcohols ($\text{X} = \text{C}_{10}\text{H}_7$, $\text{Y} = \text{Me}$), but no previous attempt has been made to determine the conjugation energies of the naphthylvinyl system experimentally, though precise values of these quantities have been predicted from molecular-orbital calculations.

Syntheses.—The 1-naphthyl-3-phenylallyl alcohols were synthesised by standard methods. The alcohol (III) was obtained directly from cinnamaldehyde and α -naphthylmagnesium bromide in 75% yield. This method fails with β -naphthylmagnesium bromide although normal reactions of this Grignard reagent with other carbonyl compounds have been reported.^{3,4} The alcohol (V) was therefore synthesised by another route from β -acetylnaphthalene. Condensation with benzaldehyde under acidic or basic conditions gave the same β -naphthyl styryl ketone (VII) (evidently the *trans*-isomer) which was converted into the alcohol (V) by reduction with lithium aluminium hydride at -20° ; β -naphthyl phenethyl ketone, formed by 1:4-reduction⁵ or by prototropic rearrangement⁶ of the alcohol, is obtained as a side-product.



The isomers (IV) and (VI) were synthesised from the naphthaldehydes. β -Naphthaldehyde was conveniently prepared from 2-naphthonitrile by controlled reduction with lithium aluminium hydride at 0° , after an experiment with benzonitrile had afforded benzaldehyde in good yield. This method has been previously employed for preparing few aliphatic examples⁷ but has not been widely used; it appears to work well generally for aromatic derivatives. Since condensation of the naphthaldehydes with acetaldehyde to give the α -naphthylacraldehydes presents difficulties,³ the aldehydes were converted instead into the 2-naphthylvinyl phenyl ketones (VIII) by reaction with acetophenone: again the same (*trans*-)isomer was obtained under acidic or basic conditions. Reduction of the α -naphthyl derivative (VIII) with lithium aluminium hydride at 0° and -20° gave, not the alcohol (IV), but mainly 3- α -naphthyl-1-phenylpropan-1-ol and 2- α -naphthylethyl phenyl ketone, respectively; at -30° , however, a product estimated spectroscopically to contain not less than 75% of the alcohol (IV) was obtained. Reduction of the β -naphthyl derivative (VIII) at -20° gave the alcohol (VI) in good yield.

Kinetic Measurements.—The two pairs of alcohols (III \rightleftharpoons IV) and (V \rightleftharpoons VI) are rapidly interconverted in the presence of dilute mineral acid and the reactions were studied

² Braude and Fawcett, *J.*, 1950, 800.

³ Braude, Fawcett, and Newman, *J.*, 1950, 793.

⁴ See Kharash and Reinmuth, "Grignard Reactions of Non-metallic Substances," Constable and Co., London, 1954, for other examples.

⁵ Cf. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, New York, 1956, for references to other examples.

⁶ Tiffeneau, *Bull. Soc. chim. France*, 1907, 1, 1209; Nomura, *ibid.*, 1925, 37, 1245; Burton and Ingold, *J.*, 1928, 904.

⁷ Henne, Pelley, and Alm, *J. Amer. Chem. Soc.*, 1950, 72, 3370; Vandick and Larsen, *ibid.*, 1951, 73, 3534; Smith and Rogier, *ibid.*, p. 4048; cf. Braude and Wheeler, *J.*, 1955, 320; Soffer and Katz, *J. Amer. Chem. Soc.*, 1956, 78, 1705.

under the standard conditions (0.01M-hydrogen chloride in 60% aqueous dioxan) used previously.² Although the differences in ultraviolet light absorption between the isomers are smaller than for the aryl-methylallyl alcohols,³ owing to superposition of absorption due to the aryl and the arylvinyl chromophore, the rearrangements could be followed quantitatively by the spectrokinetic technique. By using a specially designed cell-holder in a thermostat, the reactions could be carried out directly in the absorption cell. In this way, high accuracy was attained on a micro-scale, only a few milligrams of each alcohol being required for investigation at five temperatures. The overall rate constants, determined separately for both members of each pair, were in excellent agreement; thus, for the rearrangement ($V \rightleftharpoons VI$) at 30°, the values 0.243 ± 0.029 and 0.249 ± 0.019 min.⁻¹ were obtained from measurements at 2490 Å, and the values 0.249 ± 0.009 and 0.263 ± 0.004 min.⁻¹ from measurements at 3000 Å. The absorption curves of the equilibrium

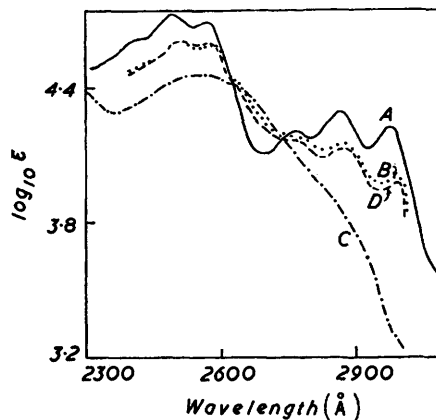


FIG. 1.

A (—), 3-β-Naphthyl-1-phenylallyl alcohol (VI).
 B (.....), Rearranged (VI).
 C (- · - · - ·), 1-β-Naphthyl-3-phenylallyl alcohol (V).
 D (----), Rearranged (V).

mixture obtained from either isomer were identical within experimental error (see Fig. 1) and the equilibrium constants calculated from the extinction coefficients at different wavelengths coincided closely.

RESULTS AND DISCUSSION

The results are collected in Tables 1 and 2. The rates of rearrangement are slightly greater, and the energy of activation is slightly lower, for the β- than for the α-derivative.

TABLE 1. First-order rate-constants (k in min.⁻¹) for the rearrangements in dioxan-water (6 : 4) containing 0.01M-hydrogen chloride.

Temp.	X = α-Naphthyl			X = β-Naphthyl		
	k	k_1	k_{-1}	k	k_1	k_{-1}
30°	0.177	0.103	0.074	0.257	0.132	0.125
35	0.307	0.180	0.127	0.445	0.228	0.217
40	0.540	0.316	0.224	0.749	0.385	0.364
45	0.938	0.549	0.389	1.300	0.668	0.532
50	1.580	0.923	0.657	2.170	1.120	1.050

TABLE 2. Equilibrium constants (K), free energies, and activation parameters (at 30°) for the rearrangements.

	K	$-\Delta G$ (cal./mole)	ΔE_A (cal./mole)	ΔS^\ddagger (e.u.)
α-C ₁₀ H ₇	1.41	205	21,400	+3
β-C ₁₀ H ₇	1.06	35	20,800	0

This is the reverse of the usual sequence of reactivity, but the differences are too small to be of much significance. Of the 3-methyl-1-naphthylallyl alcohols,² the β -derivative rearranged more slowly than the α below 50°, but faster above 50°. Another familiar example is the sulphonation of naphthalene, which is slower at 80°, but faster at 160° in the β - than in the α -position, while the reverse applies to the hydrolysis of the corresponding sulphonic acids. Somewhat similar observations have been made for the bromination of naphthalene.⁹ In all these cases, the energies of activation of α - and β -derivatives have closely similar values and the Arrhenius plots evidently have a cross-over point within the range of measurements, so that the isomer which is more reactive will depend on the temperature chosen for comparison. As had previously been pointed out,² these facts are in accord with simple valence-bond theory, which predicts a relatively small difference between the polarisability of the α - and the β -position of naphthalene, but are quantitatively in disagreement with molecular-orbital calculations which predict a larger difference between the two positions in naphthalene than between naphthalene and benzene.

For both α - and β -naphthylphenylallyl alcohols, the equilibria lie on the side of the 3-naphthyl-1-phenylallyl isomers, *i.e.*, those in which the naphthyl group is conjugated with the double bond. The equilibrium constants are larger for the α - than for the β -isomer, and the values of the free energy changes $-\Delta G_{30}$ are 205 and 35 cal./mole, respectively. The equilibrium constants decrease slightly with increasing temperature, but over the range studied (30—60°), the differences are almost within experimental error and do not justify a separate estimate of the enthalpy changes $-\Delta H$; these must be of the same order as, or smaller than, $-\Delta G$. The present results show that an ethylenic bond conjugates more strongly with a naphthyl than with a phenyl group, and more strongly in the α - than in the β -position, *i.e.*, in the sequence $\text{Ph} < \beta\text{-C}_{10}\text{H}_7 < \alpha\text{-C}_{10}\text{H}_7$.

Previous equilibrium studies in the naphthalene field¹⁰ comprise the reversible prototropic rearrangements of 1-phenyl-3-arylmethyleneazomethines,^{10a} in which conjugation of an aryl nucleus with $\text{CH}=\text{N}$ was shown to increase in the sequence $\alpha\text{-C}_{10}\text{H}_7 < \text{Ph} < \beta\text{-C}_{10}\text{H}_7$ (but in which the equilibrating species presumably is anionic), and the reversible solvolysis of aryl chloromethyl derivatives,^{10b} which is not significant for the present investigation. The only other relevant experiments appear to be those by Badger¹¹ who inferred from a study of rates of hydroxylation that in 1:2-diarylethylenes there is greater conjugation between an ethylenic bond and an α - than a β -naphthyl group. This is in agreement with the calculated bond orders¹¹ of the ethylenic linkage, which are an *inverse* measure of the conjugating effect of the aryl group and decrease in the sequence Ph (1.820) $>$ β -naphthyl (1.814) $>$ α -naphthyl (1.792).

The conjugating properties of the α - and the β -positions in naphthalene were first discussed theoretically by Hückel¹² in 1932 and then by many other authors, particularly during recent years. The most precise calculations of the conjugation energies for the α - and the β -vinylnaphthalene system are those by Coulson and Longuet-Higgins,¹³ which lead to (rounded) values of 7530 and 6890 cal./mole, to be compared with 6770 for the styryl system. The differences of 760 and 120 cal., respectively, are qualitatively, though not quantitatively, in agreement with the present results. It will be noted that the calculated figures are larger than the experimental ones by about the same factor (3.7, 3.4) in each case. The possibility that the molecular-orbital approximation exaggerates the difference in conjugating properties of the α - and the β -position in naphthalene cannot be excluded, but it seems probable that the lack of quantitative agreement is, at least partly, inherent in the particular features of the equilibrium system on which the experimental data are based. Thus, the free-energy difference between the two isomers may deviate

⁸ Spryskov, *J. Gen. Chem. (U.S.S.R.)*, 1947, **17**, 59; cf. Braude, *Ann. Reports*, 1949, **46**, 137.

⁹ Sixma, *Rec. trav. chim.*, 1949, **68**, 925; Sixma and Wibaut, *ibid.*, 1950, **69**, 577.

¹⁰ (a) Shoppee, *J.*, 1933, 37; (b) Dewar and Sampson, *J.*, 1956, 2789.

¹¹ Badger, *Nature*, 1950, **165**, 647; Coulson, *J.*, 1950, 2252.

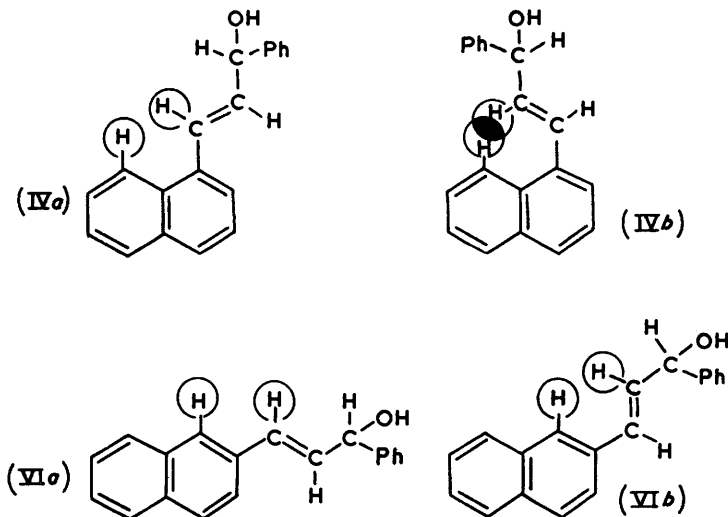
¹² Hückel, *Z. Physik*, 1932, **76**, 636.

¹³ Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, **192**, A, 16.

somewhat from the resonance-energy difference owing to secondary structural effects due to the allyl alcohol grouping.

The possibility of special steric effects in the α -vinylnaphthalene derivatives must also be considered. Whereas in the β -vinylnaphthalene derivative both uniplanar conformations (VIa and VIb) are essentially free from strain and will be similar in energy content, in the α -vinylnaphthalene derivative one uniplanar conformation (IVb) is subject to severe steric interference between the 8-hydrogen atom of the aromatic ring and one of the hydrogen atoms attached to the vinyl group, so that the other unhindered uniplanar conformation (IVa), in which maximum resonance-stabilisation is not off-set by repulsion forces, will be preferred. In the anionotropic rearrangement, the initial conformation of the product will depend on that of the reactant, and it can easily be seen that of two

FIG. 2.



possible types of conformation of the starting alcohol, one will lead to the unhindered and the other to the hindered conformation of the isomer. This is tantamount to a decrease in resonance stabilisation in the transition state, as well as an increased loss in rotational freedom accompanying the rearrangement, and will result in a larger energy of activation and a smaller free energy gain. Both the relatively low rate of formation (k_1), and the relatively low rate of disappearance (k_{-1}), of the α -vinylnaphthalene system may thus be accounted for.

EXPERIMENTAL

Analytical data were determined in the organic microanalytical laboratory of this Department (Mr. F. H. Oliver and his staff). Some of the spectroscopic data were determined by Mrs. A. I. Boston using Hilger-Spekker and Unicam instruments. The spectrometric work on the naphthyl-phenylallyl alcohols was carried out with a Beckman instrument (see below).

1- α -Naphthyl-3-phenylallyl Alcohol (III) (with J. S. FAWCETT).—Freshly distilled cinnamaldehyde (66 g.) in ether (300 ml.) was added during 3 hr. to a stirred solution of 1-naphthylmagnesium bromide [from magnesium (12 g.) and 1-bromonaphthalene (103 g.)] in ether (500 ml.) under nitrogen at 10°. Stirring was continued for a further 3 hr., excess of saturated aqueous ammonium chloride was added, and the ether layer was separated, washed with water, dried ($\text{Na}_2\text{SO}_4 + \text{K}_2\text{CO}_3$), and evaporated under reduced pressure. Naphthalene (2 g., 3%) was separated from the solid product by sublimation in a vacuum and the residue (98 g., 75%) was crystallised from light petroleum, giving the *alcohol*, m. p. 66–67°, λ_{max} . 2240, 2510, 2580, 2820, and 2910 Å (ϵ 85,000, 20,000, 22,400, 13,800, and 9900, respectively) in ethanol (Found: C, 87.4; H, 6.3. $\text{C}_{18}\text{H}_{16}\text{O}$ requires C, 87.7; H, 6.2%).

2- α -Naphthylvinyl Phenyl Ketone (VIII).— α -Naphthaldehyde¹⁴ was stored as the hydrogen sulphite derivative.¹⁵ The 2 : 4-dinitrophenylhydrazone had m. p. 251°, λ_{\max} . 3910 Å (ϵ 30,000) in chloroform (Coles and Dodds¹⁶ give m. p. 254°).

A mixture of the aldehyde (8.5 g.), acetophenone (5.7 g.), ethanol (200 ml.), and 10% aqueous sodium hydroxide (25 ml.) was kept for 18 hr. at room temperature. The solution was acidified with dilute hydrochloric acid and extracted with benzene. The solvent was distilled off and a small amount of a solid *product*, which appears to be derived from the condensation of 2 molecules of acetophenone and 1 molecule of naphthaldehyde with the elimination of 1 molecule of water, was separated; it crystallised from methanol in colourless needles, m. p. 120° (Found: C, 85.4; H, 5.8. $C_{27}H_{22}O_2$ requires C, 85.7; H, 5.9%). The bulk of the reaction product was an oil which was chromatographed in benzene on alumina and then crystallised from benzene-light petroleum, giving pale yellow crystals (11.7 g.), m. p. 56–68°. After two recrystallisations from ethanol, the bulk of the material still melted over a range and appeared to show a double melting point, 72–77° and 84–88° (Gheorghiu and Matei¹⁷ give m. p. 88° and state that the ketone is phototropic); it had λ_{\max} . 2650 (ϵ 19,000) and 3520 Å (ϵ 14,500) in ethanol. The 2 : 4-dinitrophenylhydrazone formed red crystals, m. p. 45°, λ_{\max} . 4030 Å. (ϵ 30,000) in chloroform.

3- α -Naphthyl-1-phenylallyl Alcohol (IV).—(a) The foregoing ketone (1 g.) in ether (150 ml.) was treated with lithium aluminium hydride (0.36 g.) at –30°. After 1.5 hr., ethyl acetate (10 ml.) was added, followed by aqueous ammonium chloride. The organic layer was separated and dried (Na_2SO_4), the ether was removed under reduced pressure, and the residue was taken up in hot benzene-light petroleum (b. p. 60–80°). On cooling, the impure *alcohol* separated as a pale yellow oil (0.9 g.), b. p. 150° (bath temp.)/10^{–4} mm., which was chromatographed in benzene on neutral alumina; it did not solidify at room temperature and had λ_{\max} . 2900 (ϵ 9300) and 2970 Å (ϵ 10,000), $\lambda_{\text{inf.}}$ 2560 Å (ϵ 8000) in 60% aqueous dioxan (Found: C, 87.8; H, 6.4. $C_{19}H_{16}O$ requires C, 87.7; H, 6.2%). It gave no precipitate on treatment with Brady's reagent and on rearrangement with hydrochloric acid afforded about 80% of the equilibrium mixture of the α -naphthyl-phenylallyl alcohols, as determined spectrometrically (see below). The oil thus contains ca. 80% of 3- α -naphthyl-1-phenylallyl alcohol, probably admixed with 3- α -naphthyl-1-phenylpropan-1-ol.

(b) *2- α -Naphthylvinyl phenyl ketone* (3.6 g.) in ether (100 ml.) was treated with lithium aluminium hydride (0.5 g.) at –20°. Aqueous ammonium chloride was added and the product was worked up as above, giving *2- α -naphthylethyl phenyl ketone* as a pale yellow oil (3.0 g., 83%), b. p. 120° (bath-temp.)/10^{–4} mm., λ_{\max} . 2240, 2510, 2580, 2810, and 2900 Å (ϵ 55,000, 9500, 9500, 8000, and 8000, respectively) in ethanol (Found: C, 87.6; H, 6.4. $C_{19}H_{16}O$ requires C, 87.7; H, 6.2%). The 2 : 4-dinitrophenylhydrazone crystallised from pyridine-ethyl acetate in orange needles, m. p. 227–228°, λ_{\max} . 3840 Å (ϵ 26,500) in chloroform (Found: C, 65.6; H, 5.0; N, 12.7. $C_{25}H_{20}O_4N_4$ requires C, 68.2; H, 4.6; N, 12.7%).

(c) (With J. S. FAWCETT.) *2- α -Naphthylvinyl phenyl ketone* (5 g.) in ether (25 ml.) and benzene (25 ml.) was treated with lithium aluminium hydride (0.4 g.) in ether (50 ml.) at 0°. Isolation of the product as above gave *3- α -naphthyl-1-phenylpropan-1-ol* (2.5 g.), b. p. 120° (bath-temp.)/10^{–4} mm. (Found: C, 86.8; H, 7.2. $C_{19}H_{18}O$ requires C, 87.0; H, 6.9%). The *p-nitrobenzoate* had m. p. 123–125° [from light petroleum (b. p. 100–120°)] (Found: C, 76.2; H, 5.2; N, 3.5. $C_{26}H_{21}O_4N$ requires C, 75.9; H, 5.1; N, 3.4%).

2-Acetylnaphthalene.—2-Cyanonaphthalene (9.5 g.) in ether (100 ml.) was added to methylmagnesium iodide [from magnesium (1.6 g.) and methyl iodide (9.3 g.)] in ether (65 ml.), and the mixture was refluxed for 1 hr. under nitrogen. After cooling, excess of 2N-hydrochloric acid was added, and the ether layer was separated, washed, and evaporated. The dark brown solid product was chromatographed on alumina in benzene and then crystallised from light petroleum (b. p. 60–80°), giving the colourless ketone (6.6 g., 63%), m. p. 48° (Stobbe¹⁸ gives m. p. 51.5°). The mother-liquors, with Brady's reagent, gave the 2 : 4-dinitrophenylhydrazone (2.2 g., corresponding to a further 10% yield of ketone), m. p. 231°, which after chromatography on alumina in benzene-ethyl acetate and crystallisation from ethyl acetate-carbon tetrachloride formed bright red needles, m. p. 251–252°, λ_{\max} . 3850 Å (ϵ 30,000) in chloroform (Found: C, 61.4; H, 4.1; N, 15.6. $C_{18}H_{14}O_4N_4$ requires C, 61.7; H, 4.0; N, 16.0%).

¹⁴ Angyal, Tetaz, and Wilson, *Org. Synth.*, 1950, **30**, 67.

¹⁵ Cf. Bamberger and Looter, *Ber.*, 1888, **21**, 259.

¹⁶ Coles and Dodds, *J. Amer. Chem. Soc.*, 1938, **60**, 853.

¹⁷ Gheorghiu and Matei, *Gazzetta*, 1943, **73**, 65; *Chem. Abs.*, 1947, **41**, 2719.

¹⁸ Stobbe, *Annalen*, 1911, **380**, 95.

β -Naphthyl Styryl Ketone (VII).—(a) A solution of the foregoing ketone (2.6 g.) and benzaldehyde (1.6 g.) in 85% ethanol (55 ml.) containing sodium hydroxide (0.5 g.) was kept at room temperature. A first crop (3.0 g., 75%), m. p. 102°, was collected after 2 hr. and a second (0.2 g., 5%), m. p. 97°, after a further 2 hr. The two crops were combined and after one crystallisation from ethanol formed pale yellow needles, m. p. 102°, λ_{\max} . 2510 (ϵ 14,700), 2580 (ϵ 14,700), and 3130 Å (ϵ 19,300) in dioxan (Matei¹⁹ gives m. p. 104°).

(b) A solution of 2-acetylnaphthalene (6.6 g.) and benzaldehyde (4.2 g.) in dry ethyl acetate (60 ml.) was saturated with dry hydrogen chloride. After 42 hr., during which considerable darkening occurred, the solvent was removed under reduced pressure and the residue dissolved in benzene. The benzene solution was thoroughly washed with aqueous sodium hydrogen sulphite, water, dilute aqueous potassium hydroxide, and again water, dried (Na₂SO₄), and passed through alumina. The eluate was evaporated and the solid residue was fractionally sublimed at 100° (bath-temp.)/10⁻⁴ mm. Unchanged 2-acetylnaphthalene (3.5 g., 53%) sublimed first, followed by β -naphthyl styryl ketone which was crystallised from ethanol, giving pale yellow needles (1.1 g., 23%), m. p. 102°, undepressed on admixture with the specimen obtained as under (a).

1- β -Naphthyl-3-phenylallyl Alcohol (V).—Lithium aluminium hydride (0.28 g.) in ether (100 ml.) was added during 20 min. to a stirred solution of the foregoing ketone (3.7 g.) in ether (200 ml.) and benzene (60 ml.) at -20°. After a further 30 min., excess of aqueous ammonium chloride was added, the upper layer was separated, and the aqueous layer extracted with ether. The combined ether-benzene solutions were washed with water, dried (Na₂SO₄), and evaporated under reduced pressure. The solid residue was crystallised once from benzene-light petroleum, giving the alcohol as colourless needles (1.9 g., 51%), m. p. 78°, λ_{\max} . 2510 (ϵ 27,000) and 2640 Å (ϵ 26,000) in ethanol (Found: C, 87.5; H, 6.3. C₁₉H₁₆O requires C, 87.7; H, 6.2%). The mother-liquors deposited more of the alcohol (0.5 g., 14%) as fluffy needles, m. p. 75°, together with colourless flakes of β -naphthyl phenethyl ketone (0.55 g., 15%). The latter were separated manually and after one crystallisation from benzene-light petroleum had m. p. 92–93°, λ_{\max} . 2480, 2800, 2900, 3280, and 3370 Å (ϵ 52,000, 10,500, 8900, 1200, and 1200, respectively) in chloroform (Found: C, 87.1; H, 6.0. C₁₉H₁₆O requires C, 87.7; H, 6.2%). The ketone gave an immediate precipitate with Brady's reagent and its m. p. was depressed to 74–76° on admixture with β -naphthyl styryl ketone.

An attempt to prepare the alcohol from cinnamaldehyde and β -naphthylmagnesium bromide, under conditions similar to those used above with α -naphthylmagnesium bromide, gave only 2 : 2'-dinaphthyl, m. p. 178° (Meyer and Hofman²⁰ give m. p. 181°), together with intractable, high-boiling products.²¹

β -Naphthaldehyde.—Lithium aluminium hydride (0.9 g.) in ether (80 ml.) was added during 20 min. to a stirred solution of 2-cyanonaphthalene (10 g., m. p. 64–66°, prepared analogously to *o*-toluonitrile²²) in ether (100 ml.) at 0°. After a further 80 min., the buff-coloured precipitate was dissolved by adding 2N-sulphuric acid (200 ml.). Stirring was continued for 30 min. and the ethereal layer was then separated, washed with water, dried (Na₂SO₄), and evaporated. The product was purified *via* the sodium hydrogen sulphite derivative and by crystallisation from aqueous alcohol, giving β -naphthaldehyde (6.7 g., 65%), m. p. 62–63° (Shoppee^{10a} gives m. p. 59°). The bright red 2 : 4-dinitrophenylhydrazone, after chromatography on alumina in benzene-ethyl acetate and crystallisation from ethyl acetate, had m. p. 262°, λ_{\max} . 3840 Å (ϵ 32,000) in chloroform (Pickering and Smith²³ give m. p. 270°).

2- β -Naphthylvinyl Phenyl Ketone (VIII).—(a) Dry hydrogen chloride was passed for 30 min. through a solution of β -naphthaldehyde (4.3 g.) and acetophenone (2.8 g.) in dry ethyl acetate (100 ml.). The solution was then kept in a closed flask at room temperature for 42 hr., during which there was copious separation of pale yellow crystals. The solvent was removed under reduced pressure and the product crystallised from benzene, giving 2- β -naphthylvinyl phenyl ketone (5.3 g., 76%), m. p. 154°, λ_{\max} . 2800 (ϵ 20,000) and 3280 Å (ϵ 24,000) in ethanol (Found: C, 88.5; H, 5.8. C₁₉H₁₄O requires C, 88.3; H, 5.5%).

¹⁹ Matei, *Ann. Sci. Univ. Jassy*, 1943, **29**, 17.

²⁰ Meyer and Hofman, *Monatsh.*, 1916, **37**, 708.

²¹ Cf. Lovenich and Loesser, *Ber.*, 1927, **60**, 320; Gilman, Zoellner, and Didsey, *J. Amer. Chem. Soc.*, 1929, **51**, 1579.

²² *Org. Synth.*, Coll. Vol. I, 1941, p. 514.

²³ Pickering and Smith, *Rec. Trav. chim.*, 1950, **69**, 535.

(b) 10% Aqueous sodium hydroxide (10 ml.) was added to a solution of β -naphthaldehyde (3.3 g.) and acetophenone (2.2 g.) in ethanol (100 ml.). After 2 hr. at room temperature the crystalline precipitate was filtered off. The filtrate was kept for a further 15 hr. and diluted with water, and the precipitate was collected. The combined solid products were chromatographed on alumina in benzene and finally crystallised from ethanol, giving the ketone as very pale yellow crystals (2.2 g., 40%), m. p. and mixed m. p. 154°.

3- β -Naphthyl-1-phenylallyl Alcohol (VI).—Lithium aluminium hydride (0.3 g.) in ether (150 ml.) was gradually added, with stirring, to the foregoing ketone (4 g.) in ether (90 ml.) and benzene (40 ml.) at -20° . Stirring was continued for 30 min., excess of saturated aqueous ammonium chloride was added, and the ether layer was separated, washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The solid product (4.0 g.) crystallised from benzene–light petroleum in colourless tufts (2.6 g., 65%), m. p. 76° , λ_{max} . 2490, 2570, 2770, 2870, and 2980 Å (ϵ 53,000, 49,000, 16,000, 19,500, and 17,000, respectively) in ethanol–dioxan (20 : 1) (Found: C, 88.0; H, 6.3. $\text{C}_{19}\text{H}_{16}\text{O}$ requires C, 87.7; H, 6.2%).

Conversion of Benzonitrile into Benzaldehyde.—65% Lithium aluminium hydride (2.9 g., 0.25 mol.) was added gradually to a stirred solution of benzonitrile (21.1 g.) in dry ether (200 ml.) at -5° . Ethyl acetate (1 ml.) was then added to destroy excess of hydride, followed by 2*N*-sulphuric acid (200 ml.), and the whole stirred for 30 min. at room temperature. The ether layer was separated, the aqueous layer was extracted with ether, and the combined ether solutions were shaken with saturated aqueous sodium metabisulphite, all these operations being conducted under nitrogen. The bisulphite compound (22.7 g., 50%; 73% on unrecovered benzonitrile) was filtered off, and a portion was converted by Brady's reagent into benzaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 233° . Distillation of the ether solution yield unchanged benzonitrile (7.0 g.), b. p. $68^\circ/13$ mm., n_D^{18} 1.5300.

Kinetic Measurements.—These were carried out with a Beckman D.U. spectrophotometer, provided with a mounting block and a specially constructed cell-holder both in a thermostat. The temperature inside the absorption cells was within $\pm 0.05^\circ$ between room temperature and 50° .

The reaction medium was prepared from 59 ml. of dioxan and 10.2 ml. of 0.1*N*-hydrochloric acid, made up to 100 ml. with water. The composition of this medium is such that, after addition of 0.15 ml. of dioxan to 2.45 ml., it becomes 60% (by vol.) aqueous dioxan–0.01*M*-hydrogen chloride. Stock solutions of the allyl alcohols were prepared by weighing out an appropriate amount (usually 2–20 mg.) and dissolving it in 10 ml. of dioxan. Dioxan was purified by prolonged refluxing over sodium, followed by fractionation; only cuts with an extinction of less than 0.5 at 2550 Å in a 1 cm. cell (corresponding to a benzene content of less than 0.02%) were used. All vessels were very thoroughly cleaned with chromic acid, washed with conductivity water and then redistilled spectroscopically pure ethanol, and dried at 100° ; these precautions were essential to eliminate effects which appear to be due to traces of alkali adhering to the surfaces.

2.50 ml. of medium were introduced into the comparison cell and 2.45 ml. into the solution cell, a lid was placed on the solution cell, both cells were placed in position, and a thermometer was inserted into the comparison cell through a hole provided in the cover slide. When the desired temperature had been reached, the instrument was balanced with the comparison cell in the light beam, the thermometer was withdrawn, and the lid was transferred to the comparison cell. 0.05 ml. of stock solution was next added to the solution cell from an "Agla" microsyringe, the solution was mixed by ten rapid up-and-down strokes with a small pre-warmed glass stirrer, and the initial reading was immediately taken with the solution cell in the beam. Further readings were taken at appropriate intervals; if the half-time of the rearrangement exceeded 10 min., the contents of the cells were later transferred to stoppered flasks immersed in the thermostat bath to allow the reaction equilibrium to be reached, and then returned to the pre-warmed cells for the final reading.

The concentrations of alcohol were so chosen as to give a final E value of 0.5–0.7 at the wavelength employed. In general, the 3000 Å region where the alcohols exhibit maxima with ϵ ca. 10,000 was found the most convenient; in the 2500 Å region where the maxima are of higher intensity (ϵ ca. 50,000), fluorescence effects are marked²⁴ and the stronger solvent absorption reduces the total light flux and consequently lowers the accuracy. Under optimum conditions, E readings were reproducible to about ± 0.002 .

First-order rate-constants were calculated from $k = (2.3/t) \log [(a - x_0)/(a - x)]$ where x_0

²⁴ Braude, Fawcett, and Timmons, *J.*, 1950, 1019.

and a are the initial and the final reading and x is the reading at time t ; the estimated accuracy is $\pm 2\%$. Equilibrium constants were calculated from $K = (a - x_0)a'/(x_0' - a)a$ where x_0' and a' are the initial and the final readings for the isomeric alcohol at a comparable concentration. Energies of activation were computed graphically; the plots of k against $1/T$ were satisfactorily linear in each case. Entropies of activation were calculated from $\Delta S = 2.3R \log k + (E_A - RT)/T - 2.3R \log (RT/Nh) = 4.6 \log k + (E_A - RT)/T - 59$ after conversion of k 's (in min.^{-1} and for 0.01M-acid solutions) into specific k 's (in sec.^{-1} and for M-acid solutions).

Six representative runs at 30° are recorded.

(i) Rearrangement of (III) ($0.1474 \times 10^{-4}\text{M}$).														
Time (min.)	0	13.1	18.1	20.5	26.7	29.3	34.5	38.3	45.5	54.2	64.9	1200		
E at 3180 Å	0.062	0.174	0.210	0.228	0.270	0.284	0.314	0.331	0.365	0.401	0.436	0.609		
10^4k (min.^{-1})	—	175	174	177	179	178	179	177	177	178	177	—		
												Mean = 177		
(ii) Rearrangement of (IV) ($0.1461 \times 10^{-4}\text{M}$).														
Time (min.)	0	14.4	17.2	20.8	26.2	28.7	31.9	34.5	41.5	52.7	930			
E at 3180 Å	0.800	0.734	0.720	0.711	0.690	0.681	0.671	0.661	0.648	0.619	0.488			
10^4k (min.^{-1})	—	165	172	162	166	167	167	171	161	165	—	Mean = 166		
(iii) Rearrangement of (V) ($0.156 \times 10^{-4}\text{M}$).														
Time (min.)	0	10.9	12.1	13.3	15.8	17.1	18.3	20.6	24.9	27.8	300			
E at 2490 Å	0.435	0.477	0.481	0.486	0.494	0.499	0.501	0.507	0.518	0.521	0.618			
10^4k (min.^{-1})	—	240	240	246	247	251	245	243	243	228	—	Mean = 243		
(iv) Rearrangement of (V) ($0.508 \times 10^{-4}\text{M}$).														
Time (min.)	0		9.4		11.5		15.2		18.1		22.2	25.2	28.2	
E at 3000 Å		0.121		0.190		0.203		0.226		0.242		0.262	0.275	0.286
10^4k (min.^{-1})		—		260		259		264		265		264	263	259
Time (min.)		35.2		38.0		42.1		45.1		49.0		1020		
E at 3000 Å		0.314		0.322		0.334		0.342		0.353		0.439		
10^4k (min.^{-1})		265		263		263		263		267		—	Mean = 263	
(v) Rearrangement of (VI) ($0.156 \times 10^{-4}\text{M}$).														
Time (min.)	0	14.2	14.9	16.3	18.0	21.8	25.2	32.0	33.1	310				
E at 2490 Å	0.729	0.691	0.689	0.687	0.684	0.679	0.669	0.659	0.655	0.602				
10^4k (min.^{-1})	—	250	254	246	243	230	254	250	264	—		Mean = 249		
(vi) Rearrangement of (VI) ($0.508 \times 10^{-4}\text{M}$).														
Time (min.)	0		8.3		10.8		12.1		15.4		17.5	19.5	22.6	
E at 3000 Å		0.704		0.650		0.634		0.631		0.612		0.602	0.596	0.581
10^4k (min.^{-1})		—		251		259		243		251		251	242	248
Time (min.)		24.9		28.5		30.5		37.0		42.4		1080		
E at 3000 Å		0.572		0.559		0.530		0.530		0.516		0.417		
10^4k (min.^{-1})		248		247		247		252		251		—	Mean = 249	

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