1246. *The Reversible Prototropic Isomerisation of* 1,3-*Arylphenylpropenes. The Relative Conjugating Power of Aryl Substituents*

By D. R. Ross and E. S. Waight

Rate and equilibrium constants and derived free-energy changes (ΔG) have been obtained for the base-catalysed isomerisation of 1,3-arylphenylpropenes. The values of ΔG are discussed in terms of the relative conjugating power of the various aryl groups and of steric inhibition of resonance in those groups having *peri*-hydrogen atoms.

Braude and his co-workers [1] attempted to compare the conjugating power of various aryl groups with phenyl by measuring the equilibrium constants (K) for the acid-catalysed interconversion of the allylic alcohols (I and II; X = OH). Whilst these data do provide a measure of the free-energy difference between isomeric alcohols, a better measure of the conjugating power of the various groups would, in our opinion, be obtained by determining the equilibrium constants (K^+) for the interconversion of the oxonium ions, the species that actually undergo isomerisation.[2] Values of K^+ differ from those of K by the ratio, not necessarily unity, of unknown equilibrium constants for the formation of the oxonium ions from the respective alcohols. In the base-catalysed rearrangement of 1,3-arylphenylpropenes (I and II; X = H) this complication is removed; on the other hand, steric factors in the two systems should be similar. Shoppee [3] has already studied the equilibration of the 1,3-arylphenylmethyleneazomethines but the isomerisation of the related propenes has received scant attention in the literature.[4]

The propenes were prepared by acid-catalysed dehydration of 1,3-arylphenylpropanols (III) and (IV). Infrared spectra indicated that *trans*-isomers were formed. To check this, in one instance the *cis*-isomer of 3-(1-naphthyl)-1-phenylprop-1-ene was prepared by partial hydrogenation of the appropriate propyne and its infrared spectrum compared with that of the product of dehydration of the propanol (III; Ar = 1-naphthyl); the dehydration products contained not more than 3% of the *cis*-propene.

$\mathrm{Ar{\cdot}CHX{\cdot}CH{:}CHPh}$ (I) $\quad$ $\mathrm{Ar{\cdot}CH{:}CH{\cdot}CHX{\cdot}Ph}$ (II)

$\mathrm{Ar{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}Ph}$ (III) $\quad$ $\mathrm{Ar{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2Ph}$ (IV)

The isomerisations were conducted in solution in methanol containing sodium methoxide, within the temperature range 45—95°. No side reactions could be detected, apart from some decomposition of the reaction medium, so that the concentration of each isomer could be determined by ultraviolet spectrophotometry.

Experimental

Analyses were by Miss J. Cuckney and the staff of the Organic Microanalytical Laboratories. Infrared spetra were determined by Dr. R. L. Erskine with a Grubb–Parsons DB1/S4 spectrometer. Ultraviolet spectra were determined for solutions in methanol by using a Beckman DU spectrophotometer.

Aromatic aldehydes were prepared by standard literature methods.

1-(1-*Naphthyl*)-3-*phenylpropan*-1-*ol*.—1-(1-Naphthyl)-3-phenylallyl alcohol (6·5 g.; prepared by Dr. P. H. Gore [1]) in ether (20 ml.) was added over 20 min. to excess of lithium aluminium hydride (0·95 g.) in ether (13 ml.). The mixture was refluxed (4½ hr.), cooled, and decomposed with saturated aqueous ammonium chloride. The organic layer was separated, combined with

---

[1] E. A. Braude and E. S. Waight, *J.*, 1953, 419; E. A. Braude and P. H. Gore, *J.*, 1959, 41; P. H. Gore, Ph.D. Thesis, London, 1953.

[2] E. A. Braude, *Ann. Reports*, 1949, **46**, 114; *Quart. Rev.*, 1950, **4**, 404.

[3] C. W. Shoppee, *J.*, 1933, 37.

[4] C. K. Ingold and C. W. Shoppee, *J.*, 1929, 447; C. K. Ingold and H. A. Piggott, *J.*, 1922, 2381.

ether extracts (2 × 100 ml.) of the aqueous layer, washed with water, dried (Na_2SO_4), and evaporated, giving 1-(1-*naphthyl*)-3-*phenylpropan*-1-*ol*, m. p. 60—63° (6·0 g., 91%). Recrystallisation from benzene–light petroleum (b. p. 60—80°) gave rosettes of colourless needle-shaped crystals m. p. 64·5—65·5° (Found: C, 87·0; H, 7·1. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%).

1-(1-*Naphthyl*)-3-*phenylpropene*.—Potassium hydrogen sulphate (0·2 g.; freshly fused, finely powdered) was added to 1-(1-napthyl)-3-phenylpropan-1-ol (4·7 g.), heated to 140° in a distillation flask. The pressure was cautiously reduced and, after the dehydration was complete, the product was distilled to give 1-(1-*naphthyl*)-3-*phenylpropene* (3·0 g., 70%) as a colourless oil, b. p. 159—164°/0·02 mm., n_D^{22} 1·6523, which crystallised on the addition of methanol. Recrystallisation from methanol gave colourless needles, m. p. 31—32° (Found: C, 93·3; H, 6·8. $C_{19}H_{16}$ requires C, 93·4; H, 6·6%), $\lambda_{max.}$ 227, 298 mμ (ε 53,500, 12,600), $\nu_{max.}$ (liquid film) 1645 (C:C conj.), 965s cm.$^{-1}$ (*trans*-CH:CH).

Phenyl 2-(1-*Naphthyl*)*vinyl Ketone*.—A solution of potassium hydroxide (2·5 g.) in ethanol (13 ml.) was added slowly to a mixture of 1-naphthaldehyde [5] (11·6 g.) and acetophenone (8·9 g.) in ethanol (25 ml.). After 1 hr. the product, which initially separated as an oil, solidified and was removed by filtration and recrystallised from benzene–light petroleum (b. p. 60—80°) to give phenyl 2-(1-naphthyl)vinyl ketone (11·5 g., 59%), m. p. 86—87°.

3-(1-*Naphthyl*)-1-*phenylpropan*-1-*ol*.—Phenyl 2-(1-naphthyl)vinyl ketone (11·5 g.) in tetrahydrofuran (40 ml.) was added dropwise (1 hr.) to a boiling solution of lithium aluminium hydride (1·5 g.) in ether (50 ml.). An intense emerald green colour, which persisted throughout the reduction, developed during the addition. The mixture was refluxed (8 hr.), cooled, and treated with saturated ammonium chloride solution. The colourless ethereal layer was separated, and the aqueous layer extracted with ether (2 × 100 ml.). The combined extracts were dried (Na_2SO_4) and evaporated, giving 3-(1-naphthyl)-1-phenylpropan-1-ol (11·3 g.).

3-(1-*Naphthyl*)-1-*phenylpropene*.—3-(1-Naphthyl)-1-phenylpropan-1-ol (10·4 g.; crude), treated at 150° with potassium hydrogen sulphate (0·75 g.) as for the isomeric compound, gave 3-(1-*naphthyl*)-1-*phenylpropene*, b. p. 158—162°/0·02 mm., m. p. 65—68°. Recrystallisation from benzene–methanol gave needles, m. p. 74—75° (Found: C, 93·4; H, 6·7. $C_{19}H_{16}$ requires C, 93·4; H, 6·6%), $\lambda_{max.}$ 223, 254, 270, 282, 292, 313, 317 mμ (ε 76,400, 20,100, 12,800, 11,600, 8400, 503, 251), $\nu_{max.}$ (CS_2) 965s (*trans*-CH:CH), 794s, 787s, 776s, 744m, 732m, 704m, 689s cm.$^{-1}$.

1-*Naphthylmethyl Toluene*-p-*sulphonate*.[6]—A solution of 1-naphthylmethanol (42 g.) in ether (300 ml.) was added dropwise (1 hr.) to a stirred suspension of finely powdered sodium hydride (6·6 g.) in boiling ether (100 ml.). The stirred mixture was boiled under reflux (15 hr.) during which time the sodium salt separated. The mixture was cooled to −20° and a solution of pure *p*-toluenesulphonyl chloride [7] (50·4 g.) in ether (30 ml.) was added (1 hr.). The solution was stirred for 1 hr. longer. The mixture was filtered with the minimum exposure to the atmosphere, concentrated to 500 ml., and cooled to −60°. The toluene-*p*-sulphonate crystallised and was collected. Further quantities were obtained by concentration of ethereal extracts of the residue from the first filtration. This gave 1-*naphthylmethyl toluene*-p-*sulphonate* (40 g., 48%) decomposing at 56—58°. The analytical specimen was recrystallised twice from light petroleum (b. p. 40—60°) at −40°; it then decomposed at 60° (Found: C, 69·6; H, 5·4; S, 10·1. $C_{18}H_{16}O_3S$ requires C, 69·2; H, 5·2; S, 10·2%).

3-(1-*Naphthyl*)-1-*phenylpropyne*.—2-Phenylethynylmagnesium bromide [8] (0·063 mole, from 7·5 g. ethyl bromide, 2·1 g. magnesium, and 6·4 g. phenylacetylene) was added dropwise (1 hr.) to 1-naphthylmethyl toluene-*p*-sulphonate (40 g., 0·125 mole) suspended in benzene–ether (1 : 1; 180 ml.). The stirred mixture was boiled under reflux (8 hr.), cooled, and decomposed with dilute hydrochloric acid (300 ml.). The layers were separated and the aqueous layer was extracted with ether. The combined ethereal solutions were washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated. The residual oil was treated with pyridine (200 ml.) (to remove the 1-naphthylmethyl bromide), diluted with water, and extracted with ether. The extracts were washed with hydrochloric acid and with water, dried, and evaporated to give 3-(1-naphthyl)-1-phenylpropyne (13 g.), m. p. 55—60°. This was purified by rapid chromatography in light petroleum (b. p. <40°) on acid-washed alumina, to give a solid, m. p.

---

[5] C. V. Gheorgiu and V. Mattei, *Gazzetta*, 1943, **73**, 65.

[6] Cf. J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 3443.

[7] S. W. Pelletier, *Chem. and Ind.*, 1953, 1034.

[8] J. W. Kroegger and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 1861.

58—63° (12 g., 75%), which crystallised from cold (—10°) light petroleum as colourless prisms, m. p. 67—68° (Found: C, 94·0; H, 6·1. $C_{19}H_{14}$ requires C, 94·2; H, 5·8%) $\lambda_{max.}$ 222, 238, 250, 270, 280, 288, 291, 313 mμ (ε 77,900, 23,100, 20,900, 7770, 9090, 5780, 5890, 360), $\nu_{max.}$ (CCl_4) 2254w (R·C⋮C·R′), 1595s, 1572w, 1502m, 1483s, 1441m, 1418m, 1397s, 1299m, 1266m, 1029m, 1019m, 914m cm.$^{-1}$.

cis-3-(1-*Naphthyl*)-1-*phenylpropene*.—The propyne (2·42 g.) was hydrogenated in the presence of Lindlar catalyst (2·40 g.) and quinoline (0·5 g.) in ethyl acetate (170 ml.). The initially rapid uptake of hydrogen decreased abruptly at 0·95 moles. Recrystallisation of the product from benzene–methanol gave prisms of cis-3-(1-*naphthyl*)-1-*phenylpropene*, m. p. 51·5—52·5° (Found: C, 93·2; H, 6·6. $C_{19}H_{16}$ requires C, 93·4; H, 6·6%), $\lambda_{max.}$ 223, 271, 282, 288, 291, 313, 317 mμ (ε 73,900, 9040, 9800, 6630, 6530, 503, 301), $\nu_{max.}$ (CCl_4) 1595s, 1503s, 1488s, 1446s, 1396s, 1078m, 916m cm.$^{-1}$, $\nu_{max.}$ (CS_2) 796s, 791s, 787s, 758m, 734m, 702s cm.$^{-1}$.

1-(2-*Naphthyl*)-3-*phenylpropan*-1-*ol*.—2-Naphthaldehyde [9] (7·8 g.) in a mixture of ether and tetrahydrofuran (14 and 40 ml., respectively) was added dropwise (45 min.) to a cooled solution of phenethylmagnesium bromide [from phenethyl bromide (11·6 g.)] in ether, and the mixture stirred overnight at room temperature. The intermediate was decomposed with 2N-hydrochloric acid, the layers separated, and the aqueous layer extracted with ether (2 × 100 ml.). The combined extracts were dried ($MgSO_4$) and distilled giving 1-(2-*naphthyl*)-3-*phenylpropan*-1-*ol* (12·8 g.), which after crystallisation from benzene–light petroleum (b. p. 40—60°) formed colourless needles, m. p. 62·5—64° (Found: C, 86·6; H, 7·0. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%).

1-(2-*Naphthyl*)-3-*phenylpropene*.—The propanol (9·4 g.) was dehydrated with potassium hydrogen sulphate (0·5 g.) giving 1-(2-*naphthyl*)-3-*phenylpropene* (6·1 g., 70%), b. p. 168—172°/0·02 mm., which was crystallised from methanol giving needles, m. p. 63—64° (Found: C, 93·7; H, 6·8. $C_{19}H_{16}$ requires C, 93·4; H, 6·6%), $\lambda_{max.}$ 250, 276, 286, 294 mμ (ε 49,700, 15,100, 19,100, 15,500), $\nu_{max.}$ (Nujol) 1621w, 1595m, 965s cm.$^{-1}$ (*trans*-CH⁚CH).

Phenyl 2-(2-*Naphthyl*)*vinyl Ketone*.—Condensation of 2-naphthaldehyde (8·6 g.) and acetophenone (6·4 ml.) in ethyl acetate (200 ml.) saturated with dry hydrogen chloride yielded the ketone (8·3 g., 59%), which on recrystallisation from benzene–light petroleum (b. p. 60—80°) had m. p. 154—155°.

3-(2-*Naphthyl*)-1-*phenylpropan*-1-*ol*.—A suspension of phenyl 2-(2-naphthyl)vinyl ketone (8·0 g.) in a tetrahydrofuran–benzene (75 : 40 ml.) was added (45 min.) to lithium aluminium hydride (1·0 g.) in ether (25 ml.). The greenish-black solution was refluxed (3 hr.), cooled, and 2N-sulphuric acid cautiously added. The organic layer was separated, and the aqueous layer extracted with ether (2 × 100 ml.). The ethereal solutions were washed with water, dried ($MgSO_4$–Na_2CO_3), and distilled giving 3-(2-naphthyl)-1-phenylpropan-1-ol (7·7 g.).

3-(2-*Naphthyl*)-1-*phenylpropene*.—The propanol (7·4 g., crude) was dehydrated with potassium hydrogen sulphate (0·4 g.), giving 3-(2-*naphthyl*)-1-*phenylpropene* (3·4 g., 50%), b. p. 152—160°/0·005 mm., n_D^{22} 1·6525, m. p. 34—36°, which after crystallisation from methanol formed colourless plates, m. p. 39—40° (Found: C, 93·3; H, 6·7. $C_{19}H_{16}$ requires C, 93·4; H, 6·6%). $\lambda_{max.}$ 255, 305 mμ (ε 32,400, 690). $\nu_{max.}$ (Nujol) 1626w, 1597m, 1488m, 964s cm.$^{-1}$ (*trans*-CH⁚CH).

Phenyl 2-(1-*Phenanthryl*)*vinyl Ketone*.—1-Phenanthraldehyde [10] (5·0 g.) and acetophenone (3·0 g.) were dissolved in a mixture of tetrahydrofuran (20 ml.) and methanol (10 ml.), and a solution of potassium hydroxide in methanol (2 g. in 6 ml.) was added. The product started to separate within a few minutes and was collected after 1 hr. Further solid was obtained by diluting the filtrate with methanol. Recrystallisation from benzene–light petroleum (b. p. 60—80°; 1 : 1) gave the chalcone (6·5 g.) as lemon-yellow plates, m. p. 181—182°.

3-(1-*Phenanthryl*)-1-*phenylpropan*-1-*ol*.—Phenyl 2-(1-phenanthryl)vinyl ketone (6·0 g.) was reduced with lithium aluminium hydride (0·6 g.) in tetrahydrofuran (35 ml.), a Soxhlet extractor being used. The mixture was refluxed (5 hr.), cooled, and saturated aqueous ammonium chloride solution added. The organic layer was separated, the aqueous layer extracted with ether (2 × 50 ml.), and the combined organic solutions were dried ($MgSO_4$) and distilled, giving 3-(1-phenanthryl)-1-phenylpropan-1-ol.

3-(1-*Phenanthryl*)-1-*phenylpropene*.—The propanol (2·6 g.) was dehydrated with potassium hydrogen sulphate (0·1 g.) in the normal fashion, and the crude propene dissolved in ether and

---

[9] H. M. Doukas, *J. Chem. Educ.*, 1954, **31**, 12.

[10] W. E. Bachmann and C. H. Boatner, *J. Amer. Chem. Soc.*, 1936, **58**, 2097; P. H. Gore, *J. Org. Chem.*, 1957, **22**, 135.

separated from the catalyst. Distillation of the ethereal solution gave 3-(1-*phenanthryl*)-1-*phenylpropene* which, after vacuum distillation and recrystallisation from benzene–methanol, gave colourless crystals, m. p. 138—139° (1·7 g., 69%) (Found: C, 93·4; H, 6·3. $C_{23}H_{18}$ requires C, 93·8; H, 6·2%), $\lambda_{max.}$ 213, 248, 256, 276, 287, 299 (ε 56,000, 62,900, 77,900, 21,500, 17,900, 20,600), $\nu_{max.}$ (CCl_4) 1653w (C=C conj.), 1597s, 1577w, 1495s, 1458s, 1445s, 975s cm.$^{-1}$ (*trans*-CH:CH).

1-(1-*Phenanthryl*)-3-*phenylpropan*-1-*ol*.—To the Grignard reagent prepared from phenethyl bromide (5·8 g.) in ether (30 ml.) was added 1-phenanthraldehyde (5·2 g.) in tetrahydrofuran–benzene (40 : 10 ml.). The mixture was refluxed (1 hr.), and stirred at room temperature (2 hr.). Saturated ammonium chloride solution was added and the product extracted with ether. The ethereal solution was dried ($MgSO_4$) and distilled, giving the propanol as a colourless solid, m. p. 97—100° (7 g., 89%).

1-(1-*Phenanthryl*)-3-*phenylpropene*.—The propanol (5·0 g.) was dehydrated with potassium hydrogen sulphate (0·6 g.) and the crude propene purified as above. Recrystallisation from benzene–methanol gave 1-(1-*phenanthryl*)-3-*phenylpropene* (4·0 g., 85%) as colourless crystals, m. p. 95—96° (Found: C, 93·7; H, 6·4. $C_{23}H_{18}$ requires C, 93·8; H, 6·2%), $\lambda_{max.}$ 218, 259, 300 mμ (ε 60,100, 46,500, 18,000), $\nu_{max.}$ (CCl_4) 1647w (C:C conj.), 1600m, 1592m, 1493s, 1453s, 1429m, 970s cm.$^{-1}$ (*trans*-CH:CH).

2-*Phenanthryl Styryl Ketone*.—2-Phenanthryl methyl ketone (9·9 g.) [11] and benzaldehyde (5·0 g.) in tetrahydrofuran (80 ml.) and methanol (30 ml.) were treated with a solution of potassium hydroxide (5 g.) in methanol (15 ml.). An immediate yellow colour was produced, and after 10 min. an additional 20 ml. of methanol was added and the mixture allowed to stand (1 hr.). After recrystallisation from chloroform–methanol, the chalcone (8·3 g., 60%) had m. p. 152·5—153·5° (Asselineau and Willemart [12] give 125°; Gore [1] gives 148—150°), $\nu_{max.}$ (CCl_4) 1668s (C:O conj.), 1647w (infl.) (C:C conj.); 1605s, 1572w, 1490m (aromatic); 1332s; 1173s; 976m cm.$^{-1}$ (*trans*-CH:CH).

1-(2-*Phenanthryl*)-3-*phenylpropan*-1-*ol*.—2-Phenanthryl styryl ketone (7·5 g.) was reduced with lithium aluminium hydride (1·25 g.) in tetrahydrofuran (40 ml.), a Soxhlet extractor being used. The mixture was boiled (5 hr.), cooled, and then decomposed with aqueous ammonium chloride, and extracted with ether. Distillation of the dried extract gave 1-(2-phenanthryl)-3-phenylpropan-1-ol (7·3 g.).

1-(2-*Phenanthryl*)-3-*phenylpropene*.—The propanol (2·0 g.) was dehydrated with potassium hydrogen sulphate (0·2 g.), and distilled under high vacuum, giving 1-(2-*phenanthryl*)-3-*phenylpropene* (1·0 g., 53%). Recrystallisation from benzene–methanol gave colourless needles, m. p. 97·5—99° (Found: C, 93·7; H, 6·4. $C_{23}H_{18}$ requires C, 93·8; H, 6·2%), $\lambda_{max.}$ 260 (infl.), 270, 291, 304 mμ (ε 82,500, 107,000, 35,900, 27,700), $\nu_{max.}$ (CCl_4) 1653w (C:C conj.), 1621m, 1603w, 1488s, 1464m, 1456m, 1429m, 967s (*trans*-CH:CH), 891s cm.$^{-1}$.

3-*Phenanthryl Styryl Ketone*.—3-Phenanthryl methyl ketone [11] (16·5 g.) and benzaldehyde (7·9 g.) in tetrahydrofuran (40 ml.) and methanol (20 ml.), were treated with a solution of potassium hydroxide (4·0 g.) in methanol (12 ml.). An immediate yellow colour was produced. When the solution was cooled to 0°, the product separated as a solid, m. p. 103—107°. Recrystallisation from chloroform–methanol gave light yellow crystals, m. p. 110—111° (13·7 g., 65%), mixed m. p. with material prepared by Dr. P. H. Gore 110—111°, $\nu_{max.}$ (CCl_4) 1672s (C:O conj.), 1605s, 1575w, 1488m, 1330s, 1208s, 976s (*trans*-CH:CH), 843s cm.$^{-1}$.

1-(3-*Phenanthryl*)-3-*phenylpropan*-1-*ol*.—3-Phenanthryl styryl ketone (11 g.) in tetrahydrofuran (40 ml.) was added slowly to a boiling solution of lithium aluminium hydride (2 g.) in tetrahydrofuran (20 ml.). After 5 hr. the mixture was cooled, decomposed with aqueous ammonium chloride, and extracted with ether. Distillation of the dried ($MgSO_4$) solution gave 1-(3-phenanthryl)-3-phenylpropan-1-ol (10·4 g.).

1-(3-*Phenanthryl*)-3-*phenylpropene*.—The propanol (7·4 g.) was dehydrated with potassium hydrogen sulphate (0·7 g.), the crude propene dissolved in ether, and the solution filtered. Vacuum distillation gave 1-(3-*phenanthryl*)-3-*phenylpropene* which, on recrystallisation from benzene–methanol, formed colourless plates, m. p. 92·5—94° (Found: C, 93·7; H, 6·0. $C_{23}H_{18}$ requires C, 93·8; H, 6·2%), $\lambda_{max.}$ 254, 262, 281, 290, 302, 316 mμ (ε 56,700, 62,700, 29,800, 16,100, 28,400, 26,900), $\nu_{max.}$ (CCl_4) 1647w (C:C conj.), 1603m, 1502w, 1488s, 1453s, 1429s, 976s (*trans*-CH:CH), 844s cm.$^{-1}$.

---

[11] E. Mossetig and J. Van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3704.

[12] J. Asselineau and A. Willemart, *Bull. Soc. chim. France*, 1947, 116.

1-(9-*Phenanthryl*)-3-*phenylpropan*-1-*ol*.—1-(9-Phenanthryl)-3-phenylallyl alcohol (4·6 g.; prepared by Dr. J. S. Fawcett) in tetrahydrofuran (11 ml.) was added dropwise (50 min.) to a stirred, boiling solution of lithium aluminium hydride (0·35 g.) in ether (5 ml.). The mixture was boiled for a further 5 hr., cooled, and a saturated solution of ammonium chloride slowly added. The layers were separated, the aqueous layer extracted with ether, and the ethereal solutions washed and dried ($MgSO_4$). Removal of the solvent gave 1-(9-phenanthryl)-3-phenylpropan-1-ol (4·2 g.).

1-(9-*Phenanthryl*)-3-*phenylpropene*.—The propanol (2·2 g.) was dehydrated with potassium hydrogen sulphate (0·1 g.) in the usual manner and gave 1-(9-*phenanthryl*)-3-*phenylpropene*, b. p. 205—210°/0·005 mm., m. p. 71—74° (1·2 g., 50%); crystallisation from benzene–methanol gave long needles, m. p. 83—84° (Found: C, 93·6; H, 6·2. $C_{23}H_{18}$ requires C, 93·8; H, 6·2%), $\lambda_{max.}$ 258, 273, 301 mμ (ε 52,000, 21,000, 15,200), $\nu_{max.}$ (Nujol) 972s cm.$^{-1}$ (*trans*-CH⁚CH).

Phenyl 2-(9-*Phenanthryl*)*vinyl Ketone*.—This was prepared by the condensation of 9-phenanthraldehyde [13] with acetophenone according to the method of Dr. J. S. Fawcett given by Gore.[1] The ketone had m. p. 136—137°.

3-(9-*Phenanthryl*)-1-*phenylpropan*-1-*ol*.—A solution of phenyl 2-(9-phenanthryl)vinyl ketone (7·7 g.) in tetrahydrofuran (30 ml.) was added dropwise (45 min.) to a stirred suspension of lithium aluminium hydride (0·75 g.) in boiling tetrahydrofuran (10 ml.). The intermediate was golden yellow in colour. After being boiled under reflux (4 hr.) the mixture was decomposed with saturated ammonium chloride solution and extracted with ether (2 × 50 ml.). The ethereal solution was dried ($MgSO_4$) and evaporated, giving 3-(9-phenanthryl)-1-phenylpropan-1-ol (7·5 g.).

3-(9-*Phenanthryl*)-1-*phenylpropene*.—Dehydration of 3-(9-phenanthryl)-1-phenylpropan-1-ol in the usual fashion gave 3-(9-*phenanthryl*)-1-*phenylpropene*. This crystallised from benzene–light petroleum (b. p. 60—80°) as colourless needles m. p. 113—114° (Found: C, 94·1; H, 6·4. $C_{23}H_{18}$ requires C, 93·8; H, 6·2%), $\lambda_{max.}$ 246, 253, 285, 296 mμ (ε 66,800, 79,200, 15,000, 14,700), $\nu_{max.}$ (CCl_4) 1653w (C⁚C conj.), 1600m, 1577w, 1490s, 1449s, 1435s, 965m cm.$^{-1}$ (*trans*-CH⁚CH).

1-(9-*Anthryl*)-3-*phenylpropan*-1-*ol*.—A solution of 9-anthraldehyde [14] (3·1 g.) in tetrahydrofuran (20 ml.) was slowly added (30 min.) to phenethylmagnesium bromide (from 3·5 g. phenethyl bromide and 0·38 g. magnesium) in ether (15 ml.). The mixture was stirred overnight at room temperature, and then decomposed by the addition of saturated ammonium chloride solution. The layers were separated, the aqueous layer extracted with ether (2 × 50 ml.), and the combined ethereal solutions dried ($MgSO_4$) and distilled, giving 1-(9-anthryl)-3-phenylpropan-1-ol (4·4 g.).

1-(9-*Anthryl*)-3-*phenylpropene*.—The crude propanol (2·3 g.) was dehydrated with potassium hydrogen sulphate (0·2 g.), and the mixture distilled, giving 1-(9-*anthryl*)-3-*phenylpropene*, b. p. 215—225°/0·1 mm. Recrystallisation from benzene–methanol gave light yellow needles (0·050 g.), m. p. 96—97°, which showed a strong blue fluorescence in daylight in dilute solution (Found: C, 94·1; H, 6·3%; *M* (Rast), 285. $C_{23}H_{18}$ requires C, 93·8; H, 6·2%; *M*, 294), $\lambda_{max.}$ (methanol) 255, 333, 348, 367, 386 mμ (ε 112,000, 22,700, 45,400, 64,400, 58,300), $\nu_{max.}$ (CCl_4) 1656w (C⁚C conj.), 1621m, 1603m, 1488m (aromatic), 1451m, 1441m, 972s (*trans*-CH⁚CH), 884s, 842s cm.$^{-1}$.

3-(9-*Anthryl*)-1-*phenylpropan*-1-*ol*.—A solution of phenyl 2-(9-anthryl)vinyl ketone [15] (3·4 g.) in tetrahydrofuran (20 ml.) was added dropwise to a stirred, boiling solution of lithium aluminium hydride (0·35 g.) in tetrahydrofuran (10 ml.). The mixture was boiled (4 hr.), cooled, and decomposed with saturated ammonium chloride solution. The aqueous layer was separated, extracted with ether, and the combined ethereal solutions were dried and distilled, giving 3-(9-anthryl)-1-phenylpropan-1-ol.

Attempted Dehydration of 3-(9-*Anthryl*)-1-*phenylpropan*-1-*ol*.—The propanol formed an involatile polymeric compound when heated with potassium hydrogen sulphate.

Isomerisation of 1,3-*Arylphenylpropenes*.—*Reaction medium*. Standard sodium methoxide solution was prepared by dissolving sodium in anhydrous methanol (purified by distillation from magnesium methoxide) and diluting to 4M. This solution was standardised by titration (after admixture with water) with hydrochloric acid.

---

[13] *Org. Synth.*, 1950, **28**, 82.
[14] E. Campaigne and W. L. Archer, *J. Amer. Chem. Soc.*, 1953, **75**, 989.
[15] A. Russell and W. B. Happoldt, jun., *J. Amer. Chem. Soc.*, 1942, **64**, 1101.

Isomerisation products. 1-(2-Naphthyl)-3-phenylpropene (0·500 g.) in methanolic sodium methoxide (2M; 50 ml.) was heated in a sealed, thick-walled, flask at 90° for 1 hr. The cooled, colourless solution was poured into water and the mixture, after neutralisation with hydrochloric acid (2N), extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and distilled at 10^{-2} mm., yielding a solid (0·474 g., 95%). The infrared spectrum of this (in carbon disulphide and in carbon tetrachloride) was practically identical with that of a mixture of 1-(2-naphthyl)-3-phenylpropene (55% w/w) and 3-(2-naphthyl)-1-phenylpropene (45% w/w) determined under the same conditions.

Kinetics.—The rate of isomerisation was very low at room temperature, and negligible at 0°. A mixture of a solution of the propene of known concentration in anhydrous methanol and standard sodium methoxide solution (4M) was diluted with methanol to an appropriate concentration (2M with respect to the catalyst), and then transferred to 2 ml. ampoules, which were sealed and stored in a refrigerator. Eight to twelve ampoules were immersed in a thermostcontrolled oil-bath and allowed to reach thermal equilibrium (5—10 min.). The first ampoule was removed at a noted time and cooled to −40° (chloroform–carbon dioxide bath) to stop the reaction. The other ampoules were removed at appropriate intervals, the last two after at least ten reaction half-lives, and treated similarly. The contents of each ampoule were allowed to reach room temperature and a sample (1 ml.) was withdrawn and diluted to 25 ml. with methanol. The optical density (E) of the solution was measured at a wavelength chosen so that the maximum possible change in E occurred during the isomerisation. In general, measurements were made in the less intense regions of absorption (>300 mμ). Values of E were corrected for decomposition of the reaction medium determined separately; this was only appreciable after very long periods of heating, *i.e.*, when equilibrium was nearly reached.

Total rate constants, $k_1 + k_{-1}$, (min.$^{-1}$) were estimated graphically from the plot of $\log_{10}(E_e - E_t)$ against time, t (min.), which was linear over at least 85% of the reaction, and equilibrium constants ($K = k_1/k_{-1}$), which were reproducible to ±2·5%, were calculated from the expression:

$$K = (E_e - E_{\text{I}})/(E_{\text{II}} - E_e)$$

where E_{I} and E_{II} are the optical densities before heating of solutions of propenes (I) and (II), respectively, of the same concentration, E_e is the optical density at equilibrium, and E_t the optical density at time t. ΔH was estimated graphically by using the van't Hoff reaction isochore; ΔG was given by $-\boldsymbol{R}T\ln K$, where T is the absolute temperature.

Examples of kinetic runs. Stock solutions of the 1-naphthylphenylpropenes (151·9 mg.) in methanol (50 ml.) were prepared. A portion (5 ml.) was mixed with methanolic sodium methoxide (4·0M; 12·5 ml.), diluted with methanol to 25 ml., and sealed into ampoules. Optical densities were measured at 310 mμ.

1-(1-*Naphthyl*)-3-*phenylpropene*, 2·49 × 10^{-3} mole/l.; 60°; E_{II}, 0·910.

t (min.)	0	6	12	30	42	50	70	∞	∞
E	0·810	0·790	0·775	0·718	0·695	0·674	0·633	0·314	0·314

$10^4k = 65·0$ min.$^{-1}$; $K = 0·39$.

3-(1-*Naphthyl*)-1-*phenylpropene*, 2·49 × 10^{-3} mole/l.; 60°; E_{I}, 0·083.

t (min.)	0	6	14	25	49	84	∞	∞
E	0·136	0·143	0·154	0·165	0·186	0·213	0·314	0·314

$10^4k = 60·6$ min.$^{-1}$; $K = 0·39$.

RESULTS AND DISCUSSION

The results summarised in the Table apply at 80° to the system:

$$\text{(I) Ar·CH}_2\text{·CH:CHPh} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Ar·CH:CH·CH}_2\text{Ph (II)}$$

where $K = k_1/k_{-1}$ and $k = k_1 + k_{-1}$.

Ar	K	ΔG (cal./mol.)	ΔH (cal./mol.)	K †	10^4k (min.$^{-1}$)	$E_{\text{Arr.}}$ (kcal./mole)
2-Naphthyl	1·18	−115	∼−100	0·96	722	24·0
2-Phenanthryl ...	1·3	−195	∼−200	2·18	1203	24·1
3-Phenanthryl ...	1·4	−225	∼−300	3·72	1420	23·5
1-Naphthyl	0·44 *	570	1300	1·37	462 *	23·8
1-Phenanthryl ...	0·48	510	1000	∼0·7	591	24·0
9-Phenanthryl ...	0·365	700	1100	1·04	643	23·9
9-Anthryl	0·62	340	∼−200	—	263	24·7

* Interpolated. † Values for the isomerisation of arylphenylpropenols at 50°.[1]

Where Ar = 2- and 3-phenanthryl, only the isomer (II) was prepared, the light absorption of the propene (I) being assumed to be the same as for the arylphenylpropenol[1] with the same chromophore. This assumption is thought to give a systematic error not exceeding ±5% in the value of K. A similar uncertainty exists in the figure for Ar = 9-anthryl. In this case, only the propene (II) could be prepared, and the light absorption of the isomer (I) was taken as approximately that of 1-(9-anthryl)-3-methylallyl alcohol.[16]

Although the mechanism of rearrangement is largely irrelevant to the discussion of conjugating powers of aryl substituents, a consideration of the rate constants, energies of activation ($E_{\text{Arr.}}$), and non-exponential factors ($\log_{10} A_{\text{Arr.}}$), which range from 13·4 to 14·0 min.$^{-1}$, makes it clear that the same mechanism is involved for all the propenes, probably that which is also involved in the rearrangement of the arylphenylazomethines,[17]* namely

Dewar[18,19] has stated that there is no first-order perturbation to the original π-energy when two even alternant hydrocarbons, *e.g.*, benzene and ethylene, are joined together, and that the second-order perturbation is small and approximately constant. This means that the conjugation energies of various aryl groups with C=C should be very similar, and they have in fact been neglected by Dewar and Sampson[19] in their estimation of the change in π-energy when C^+ is joined to aryl to form an arylcarbonium ion. Such π-energy changes have also been estimated by Mason[20] and reviewed by Streitwieser.[21]

The order (ΔE_ω values) quoted by Streitwieser[21] is phenyl < 2-naphthyl < 2-phenanthryl < 3-phenanthryl < 9-phenanthryl < 1-naphthyl < 1-phenanthryl (<9-anthryl[19]). The order of conjugating power as measured by ΔG for the isomerisation of the propenes is 9-phenanthryl < 1-naphthyl < 1-phenanthryl < 9-anthryl < phenyl < 2-naphthyl < 2-phenanthryl < 3-phenanthryl. This is the same order as obtained in the limited investigation by Shoppee[3] of the methyleneazomethine isomerisation (9-phenanthryl < 1-naphthyl < phenyl < 2-naphthyl), but very different from that found by Gore[1] from the acid-catalysed rearrangement of arylphenylpropenols, namely: 1-phenanthryl < 2-naphthyl ∼ phenyl ∼ 9-phenanthryl < 1-naphthyl < 2-phenanthryl < 3-phenanthryl. The considerable differences between propenols and propenes and the theoretical predictions support the view that free-energy differences between isomeric propenols do not provide a satisfactory measure of the conjugating power of the various aryl groups, and that it might be preferable to consider the free-energy differences between isomeric oxonium ions.

When the order of conjugating power found from the propenes is considered, it is

---

* (*Added in proof.*—However see D. J. Cram and R. D. Guthrie, *J. Amer. Chem. Soc.*, 1965, **87**, 397.)

[16] E. A. Braude, J. S. Fawcett, and D. D. E. Newman, *J.*, 1950, 793.

[17] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 572.

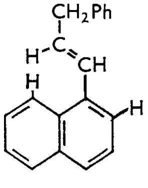
[18] M. J. S. Dewar, *J.*, 1952, 3532.

[19] M. J. S. Dewar and R. J. Sampson, *J.*, 1956, 2789.

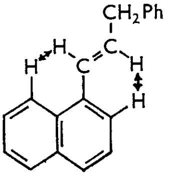
[20] S. F. Mason, *J.*, 1958, 808.

[21] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, London and New York, 1961, p. 373.

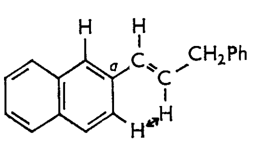
immediately obvious that 2-naphthyl-type substituents, *i.e.*, 2- and 3-phenanthryl, conjugate more effectively with C=C than do 1-naphthyl-type substituents, *i.e.*, 9-anthryl and 1- and 9-phenanthryl, but that, within the two groups, the theoretical order given above is followed. This kind of division has been noted before in aromatic side-chain reactions, and has been attributed to steric hindrance by the *peri*-hydrogen in the 1-naphthyl-type groups.[1,19,22-25] Steric effects in the 1- and 2-vinylnaphthalene systems have been discussed before [1] but it is worth noting the following points: in the 1-vinylnaphthalene system, one conformation (Va) is strongly hindered and is unlikely to be near-planar, while the other conformation (Vb) exhibits two 1,4-hydrogen interactions. In the 2-vinylnaphthalene system, and also in the styryl system, both possible conformations (VIa and b) exhibit one 1,4-hydrogen interaction which may be minimised by in-plane bending of the bond (*a*). Such interactions may be small, but are clearly not negligible, and appear to be more important than electronic effects in determining the relative stability of isomers. This is, of course, in agreement with Dewar's theoretical conclusion [18] that there should be little difference in the conjugating power of various aromatic hydrocarbons with ethylene. The case of the 9-anthryl system is peculiar in that ΔH is of opposite sign to ΔG, a fact consistent with a small decrease in entropy in forming the 9-anthrylvinyl system; in all other cases, ΔH and ΔG are of the same sign and magnitude. Molecular models show that the 9-anthrylvinyl system cannot be planar without considerable distortion of ethylenic and aromatic C–H bonds and the observed value of ΔG suggests that the loss of conjugation energy is about 2 kcal./mole.



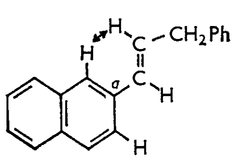
(Va)



(Vb)



(VIa)



(VIb)

While the explanation of the results in terms of steric inhibition of resonance seems obvious, it must be borne in mind that the energy change for the equilibration can be considered as the sum of two energy differences, between Ar·CH:CH· and Ph·CH:CH·, and between Ar·CH_2· and Ph·CH_2. In the foregoing discussion, the latter has been taken as negligible in comparison with the former, an assumption which may only be valid if the molecular environments of the methylene groups in the two isomers are reasonably similar.

ORGANIC CHEMISTRY LABORATORIES, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
IMPERIAL INSTITUTE ROAD, LONDON S.W.7.
[*Received, November* 18*th*, 1964.]

---

[22] M. J. S. Dewar and R. J. Sampson, *J.*, 1957, 2947, 2952.

[23] P. J. C. Fierens, H. Hannaert, J. Van Rysselberge, and R. H. Martin, *Helv. Chim. Acta*, 1955, **38**, 2009; M. Adam-Briers, P. J. C. Fierens, and R. H. Martin, *ibid.*, p. 2022; P. J. C. Fierens and J. Berkowitch, *Tetrahedron*, 1957, **1**, 129.

[24] F. L. J. Sixma, *Rec. Trav. chim.*, 1955, **74**, 168.

[25] E. Berliner and N. Shieh, *J. Amer. Chem. Soc.*, 1957, **79**, 3849.