158. *Studies in Molecular Rearrangement. Part II.* Oxotropic Rearrangements in the Polycyclic Aromatic Series.*

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The 1-aryl-3-methylallyl alcohols (I), where X = 1-naphthyl, 2-naphthyl, 9-anthryl, and 9-phenanthryl, have been prepared. They readily undergo the expected oxotropic rearrangements in the presence of dilute acids to give the corresponding 3-aryl-1-methylallyl alcohols (II). The structure of the latter was proved by Oppenauer oxidation to the ketones (III)

X·CH(OH)·CH:CHMe (I.) ⟶ X·CH:CH·CH(OH)Me (II.) ⟶ X·CH:CH·COMe (III.)

which were also obtained by condensation of the appropriate aryl aldehydes with acetone. The various derivatives have been characterised by their ultra-violet light-absorption properties which exhibit a number of interesting features.

In two earlier papers (Braude, Jones, and Stern, *J.*, 1946, 396; 1947, 1087) the oxotropic rearrangements of phenylpropenylcarbinol (I; X = Ph) and of a number of nuclear-substituted phenylpropenylcarbinols (I; X = C_6H_4R) to the corresponding styrylmethylcarbinols (II) have been described. The rearrangements take place very readily in the presence of dilute acids, and at room temperature proceed either to completion or to equilibrium mixtures containing more than 90% of the conjugated isomers (II), as would be expected since the latter are stabilised by the considerable additional resonance energy of the styryl or substituted styryl system (Braude and Stern, *J.*, 1947, 1096). It was of interest to extend the range of this reaction to polycyclic aromatic derivatives in order to obtain some evidence concerning the conjugating properties of polycyclic aromatic groups. Moreover, a kinetic study

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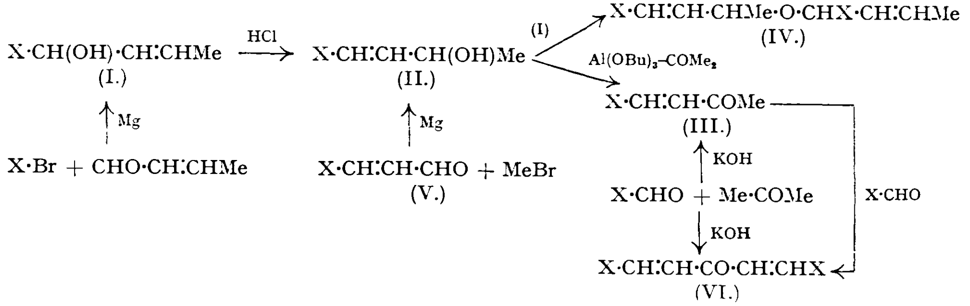
* A paper by Braude, Jones, and Stern, *J.*, 1947, 1087, is regarded as Part I.

of such rearrangements and a comparison with the data for phenylpropenylcarbinol would provide some quantitative information, which has been almost entirely lacking hitherto, regarding the effects of polycyclic aryl groups on reactivity.

The four *arylpropenylcarbinols* (1-*aryl*-3-*methylallyl alcohols*) (I), where X = 1-naphthyl, 2-naphthyl, 9-anthryl, and 9-phenanthryl, were prepared by the Grignard condensation of the appropriate aryl bromides with crotonaldehyde. After careful purification by fractionation in high vacuum or chromatography, the carbinols were obtained as low-melting crystalline solids, with the exception of the 1-naphthyl derivative which is a viscous liquid at room temperature.



On treatment with dilute hydrochloric acid in aqueous acetone at room temperature, the arylpropenylcarbinols were readily converted into the higher-melting *methyl*-2-*arylvinylcarbinols* (3-*aryl*-1-*methylallyl alcohols*) (II), which were also characterised by their *p*-*nitrobenzoates*. The isomerisations takes place practically quantitatively under suitable conditions and in sufficiently dilute solution. At high carbinol concentrations some self-etherification may occur; thus, a 7% solution of 1-naphthylpropenylcarbinol in 90% aqueous acetone–0·1M-hydrochloric acid afforded the rearranged carbinol in only 30% yield, together with a 55% yield of a higher-boiling product, which from its analytical data, its light absorption properties, and the absence of " active " hydrogen, must be formulated as the " half-rearranged " *ether* (IV) derived from one molecule of unrearranged, and one molecule of rearranged carbinol. On carrying out the rearrangement with a more dilute, 2·5%, solution of the carbinol in 60% aqueous acetone under otherwise identical conditions, the rearranged carbinol is obtained in 90% yield, and hardly any of the ether is formed. Self-etherification in the course of oxotropic rearrangement has previously been observed with ethynylpropenylcarbinol (I; X = CH⋮C) (Heilbron, Jones, and Weedon, *J.*, 1945, 81), but in this case the resulting ether was fully rearranged. These reactions are analogous to the easy cross-etherification of propenylcarbinols with methanol or ethanol which have also been shown to occur both with and without rearrangement in aqueous-alcoholic solution in the presence of dilute acids (Heilbron, Jones, and Weedon, *loc. cit.*; Braude, Jones, and Stern, *locc. cit.*; Braude and Stern, *loc. cit.*).

Although the 3-aryl-1-methylallyl alcohols (II) differ from the 1-aryl-3-methylallyl alcohols in their ultra-violet light-absorption properties, the spectral data do not in every case provide conclusive evidence for the structure of the rearranged carbinols (see below). The structures of the latter were unambiguously proved, however, by Oppenauer oxidation to the methyl 2-arylvinyl ketones (III) which were obtained in good yields. The ketones were synthesised independently by condensation of the appropriate aryl aldehydes with acetone and characterised by their 2 : 4-*dinitrophenylhydrazones*. The preparation of methyl 2-1′- and methyl 2-2′-naphthylvinyl ketone has been previously described (Gibson, Hariharan, Menon, and Simonsen, *J.*, 1926, 2247; Wilds, Beck, Close, Djarassi, Johnson, Johnson, and Shunk, *J. Amer. Chem. Soc.*, 1947, **69**, 1985). The reaction between 9-anthraldehyde and acetone in acid or alkaline solution was found to give largely the high-melting di-condensation product *di*-(2-9′-*anthrylvinyl*) *ketone* (VI; X = 9-anthryl) unless a large excess of acetone was employed. As might be expected in view of this result, the mono-condensation product, *methyl* 2-9′-*anthrylvinyl ketone* (III; X = 9-anthryl) condenses very readily with 9-anthraldehyde to give the di-condensation product. The condensation of 9-phenanthraldehyde with aqueous acetone in the presence of dilute sodium hydroxide also gave a mixture of products, which was separated by chromatography into (i) the desired *methyl* 2-9′-*phenanthrylvinyl ketone*, m. p. 85°, (ii) the hydroxy-ketone, 3-*keto*-1-9′-*phenanthrylbutan*-1-*ol*, m. p. 119°, and (iii) a high-melting *dimer* of methyl 2-9′-phenanthrylvinyl ketone, m. p. 274°, probably to be formulated as a *cyclo*butane derivative by analogy with similar dimers obtained from substituted styryl methyl ketones (Heilbron *et al.*, *J.*, 1927, 1888; 1928, 2323).

An alternative route to the 3-aryl-1-methylallyl alcohols is represented by the condensation of methylmagnesium bromide with the β-arylacraldehydes (V). The latter should be accessible *via* the arylaldehydes, but the reaction of acetaldehyde with both 1-naphthaldehyde and 9-anthraldehyde proved very sluggish. This is somewhat surprising in view of the high reactivity of the aryl aldehyde towards acetone (see above). In another attempt to prepare β-9′-anthrylacraldehyde (VI; X = 9-anthryl) *via* β-9′-anthrylacrylic acid, it was found that treatment of the acid with excess of thionyl chloride gave, not the required acid chloride, but a dichlorinated product which was readily hydrolysed to a monochloro-acid formulated as β-(10-*chloro*-9-*anthryl*)*acrylic acid.* This approach was not pursued.

The ultra-violet light-absorption data for the various derivatives are given in the table and n Figs. 1—4, and exhibit a number of interesting features. The absorptions of the 1-aryl-3-methylallyl alcohols (I) in this region are very similar to those of the unsubstituted polycyclic hydrocarbons, and practically identical with those of 1- and 2-methylnaphthalene, 9-methylanthracene and 9-methylphenanthrene severally, as far as these have been recorded (De Laszlo, *Z. physikal. Chem.*, 1925, **118**, 369; Jones, *Chem. Reviews*, 1947, **41**, 353; Askew, *J.*, 1935, 509). The spectral data thus provide very little evidence for any interaction between the aryl groups and the unconjugated ethylenic bond, such as observed (Braude, *J.*, 1949, 1902) in allylbenzene and certain related systems.

Ultra-violet light-absorption properties of 1-*aryl*-3-*methylallyl alcohols* (I), 3-*aryl*-1-*methylallyl alcohols* (II), *and methyl* 2-*arylvinyl ketones* (III) *in ethanol solution.*

(c = Concn. of absorbent in g.-mols./l. Cell thickness = 1 cm. throughout, except for X = Ph.)

X.	c.	I.		II.		III.	
		$\lambda_{\text{max.}}$, A.†	ε.	$\lambda_{\text{max.}}$, A.†	ε.	$\lambda_{\text{max.}}$, A.†	ε.
Phenyl [1, 2]	—	2510	450	2480	19,000	2850	23,000
		2580	450	2510	19,500	—	—
		—	—	2810	2,000	—	—
		—	—	2910	1,550	—	—
1-Naphthyl	0·000021	2240	69,000 *	2280	51,000 *	2240	30,000
		2700	5,900	2960	10,000	2500	15,000
		2800	7,200	—	—	3300	11,500
		2900	5,200	—	—	—	—
	0·00021	3130	320	—	—	—	—
2-Naphthyl	0·000014	2260	95,000 *	*2390*	45,000 *	2370	16,500
		2740	6,300	2460	55,000 *	2450	16,500
		—	—	2540	50,000 *	*2650*	29,000
		—	—	*2750*	13,500	2720	32,000
		—	—	2840	16,500	3100	28,000
		—	—	2950	13,500	—	—
9-Anthryl	0·000012	2200	14,000	2200	10,500	2170	23,500
		2540	130,000 *	2550	115,000 *	2540	110,000
		3300	3,500	*3500*	6,000	3520	6,000
		3450	6,750	3600	8,500	3650	8,300
		3630	9,300	3820	8,000	3830	8,700
		3820	8,500	—	—	—	—
9-Phenanthryl	0·000021	*2440*	44,500	2400	34,500	2500	46,000
		2530	60,000	2570	48,000	3340	14,000
		2770	12,500	3010	13,500	—	—
		2950	11,000	*3050*	12,500		

* Strongly concentration-dependent.

† Figures in italics refer to inflections.

[1] Braude, Jones, and Stern, *J.*, 1946, 396.

[2] Lowry, Moureu, and MacConkey, *J.*, 1928, 3167.

With the 3-aryl-1-methylallyl alcohols (II), the bands are generally displaced towards longer wave-lengths, and the data for the naphthyl derivatives are very similar to those of 1-propenylnaphthalene (Pestemer and Manchen, *Monatsh.*, 1936, **68**, 92) and 2-vinylnaphthalene (Laitinen, Miller, and Parks, *J. Amer. Chem. Soc.*, 1947, **69**, 2707), respectively. The displacements are considerably smaller than those observed in comparing styrene with toluene, or cinnamyl alcohol with phenylvinylcarbinol. This is not unexpected since the additional conjugation due to the side-chain ethylenic group will be relatively smaller in the polycyclic systems. An exact comparison of the data for the unconjugated and conjugated derivatives is complicated by the vibrational structure of the bands, but for the purpose of discussion the highest of the vibrational peaks may be taken as the centre of the particular band system. The bands of all the polycyclic derivatives fall into two groups, a high-intensity system (subsequently denoted by " E ") in the 2300—2600 A. region, and a low-intensity system (subsequently denoted by " B ") in the 2900—3600 A. region. With the conjugated 1-naphthyl derivatives, the displacements of the E bands are smaller than those of the B bands, whereas the reverse applies in the case of the 2-naphthyl derivatives. Somewhat related observations

FIG. 1.

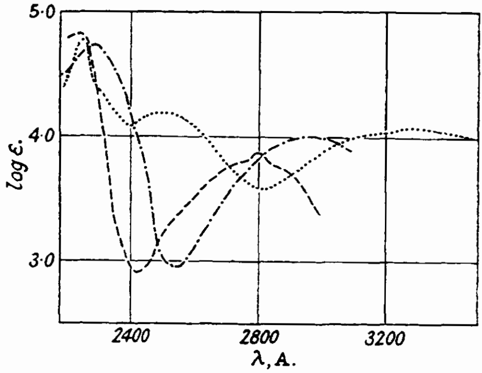


FIG. 2.

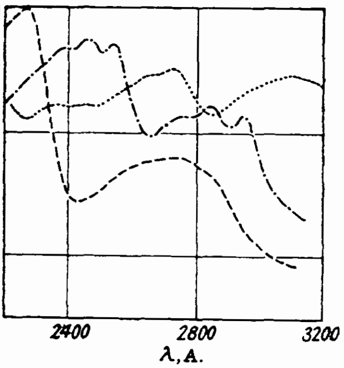


FIG. 1.—*Light absorption in ethanol of :* — — — — 1-(1-*Naphthyl*)-3-*methylallyl alcohol.*
— · — · — 3-(1-*Naphthyl*)-1-*methyllalyl alcohol.*
- - - - - - - *Methyl* 2-1′-*naphthylvinyl ketone.*

FIG. 2.—*Light absorption in ethanol of :* — — — — 1-(2-*Naphthyl*)-3-*methylallyl alcohol.*
— · — · — 3-(2-*Naphthyl*)-1-*methylallyl alcohol.*
- - - - - - - *Methyl* 2-2′-*naphthylvinyl ketone.*

FIG. 3.

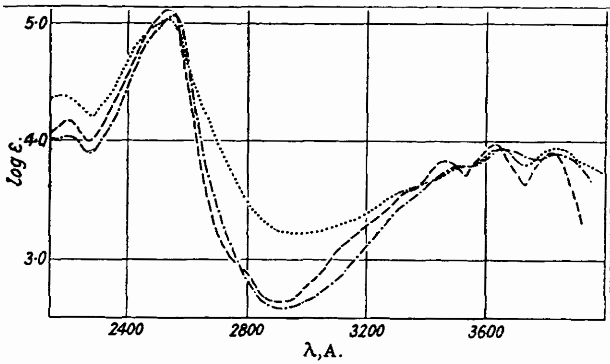


FIG. 4.

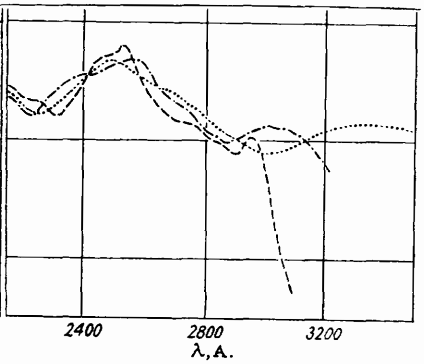


FIG. 3.—*Light absorption in ethanol of :* — — — — 1-(9-*Anthryl*)-3-*methylallyl alcohol.*
— · — · — 3-(9-*Anthryl*)-1-*methylallyl alcohol.*
- - - - - - - *Methyl* 2-9′-*anthrylvinyl ketone.*

FIG. 4.—*Light absorption in ethanol of :* — — — — 1-(9-*Phenanthryl*)-3-*methylallyl alcohol.*
— · — · — 3-(9-*Phenanthryl*)-1-*methylallyl alcohol.*
- - - - - - - *Methyl* 2-9′-*phenanthrylvinyl ketone.*

have been made by Jones (*loc. cit.*), who found that in anthracene derivatives, conjugating substituents in the 9-position produce smaller displacements of the E than of the B bands, whereas the reverse applies in the case of conjugating substituents in the 2-position. Jones put forward a tentative explanation of his observations in terms of the linear electronic oscillator model (Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273), assuming that the E and B bands arise from transitions polarised along the longer and shorter axis of the molecule, respectively. This assignment is in agreement with that deduced by Coulson (*Proc. Physical Soc.*, 1948, **60**, 257) from molecular-orbital calculations. The present observations on the spectral effects of an ethylenic substituent in the 1- and the 2-position of naphthalene may be explained in a similar way.* Another effect shown by the polycyclic derivatives in contrast to their phenyl analogues is that only the intensity of the B bands is increased, whilst that of the E bands is reduced, by the conjugated ethylenic group.

The absorption of 3-9′-phenanthryl-1-methylallyl alcohol exhibits bathochromic displacements similar to those of the 1-naphthyl derivative. 3-9′-Anthryl-1-methylallyl alcohol, on the other hand, differs from the other members of the series in that the wave-length locations of the maxima are practically identical with those of the unconjugated isomer, 1-9′-anthryl-3-methylallyl alcohol; moreover, the intensities of all the bands are considerably reduced as compared with the unconjugated isomer. A similar lack of spectral interaction has been observed by Jones (*loc. cit.*) in 9-phenylanthracene, and ascribed to the non-coplanarity of the phenyl and the anthryl groups owing to steric interference between the *o*-hydrogen atoms of the former and the 1- and 8-hydrogen atoms of the latter. Many other examples of the manifestation of steric inhibition of resonance in spectral properties have been described (for a summary and discussion, see Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890) and there can be little doubt that the anomalous absorption of 3-9′-anthryl-1-methylallyl alcohol also arises in this way. It will be observed that 3-9′-phenanthryl-1-methylallyl alcohol appears to exhibit normal absorption although free rotation should again be hindered; in this case, however, interference will only occur with the 8-hydrogen atom on one " side " of the molecule and a coplanar configuration is possible when the end of the side chain is inclined towards the 10-position.

The absorptions of the methyl 2-arylvinyl ketones (III) exhibit relationships similar to those shown by the 3-aryl-1-methylallyl alcohols and need not be discussed in detail. As would be expected, the bathochromic displacements are somewhat greater with the ketones than with the alcohols, but very much smaller than those shown by the phenyl analogue, styryl methyl ketone. The absorption of the 9-anthryl derivative again shows an almost complete lack of bathochromic displacements, probably owing to steric hindrance. The same effect is observed in the structurally related *oo*′-dimethylstyryl methyl ketone (Braude, Jones, and Sondheimer, forthcoming publication).

Another interesting feature associated with the spectra of the polycyclic derivatives is that the intensity of some of the bands appears to be strongly concentration-dependent (see Table I). This phenomenon is also shown in varying degrees by the parent hydrocarbons and is due to the superposition of absorption and fluorescence-emission (Braude, Fawcett, and Timmons, *J.*, in the press). The fluorescence activity of the different bands varies greatly; it is particularly marked in the high-intensity (E) bands of the anthryl derivatives and naphthylcarbinols, but almost absent in the phenanthryl derivatives and the methyl 2-naphthylvinyl ketones. Solutions of 3-9′-anthryl-1-methylallyl alcohol exhibit strong visible fluorescence in daylight.

EXPERIMENTAL.

(Light-absorption data are only given when not included in Table I.)

1-1′-*Naphthyl*-3-*methylallyl Alcohol* (I; X = 1-Naphthyl).—Freshly distilled crotonaldehyde (35 g.) in ether (100 ml.) was added to 1-naphthylmagnesium bromide (from magnesium, 12 g., and 1-bromonaphthalene, 104 g.) in ether (500 ml.) during 2 hours at 0° in an atmosphere of nitrogen. Stirring was continued for 2 hours and excess of saturated ammonium chloride solution was then added during ½ hour at 0°. The ethereal layer was separated, dried (Na_2SO_4), and distilled in a high vacuum from a trace of anhydrous potassium carbonate. A small amount of naphthalene (*ca.* 0·5 g.) sublimed first and then 1-1′-*naphthyl*-3-*methylallyl alcohol* (61 g., 62%) distilled as viscous oil, b. p. 110° (bath)/10^{-5} mm., n_D^{19} 1·6218 (Found: C, 85·0; H, 7·1. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%). Shurakowski (*J. Phys. Chem. Russia*, 1909, **41**, 1687) gives b. p. 204—206°/22 mm. The p-*nitrobenzoate* separated from light petroleum (b. p. 60—80°) in colourless crystals, m. p. 118—119° (Found: N, 4·1. $C_{21}H_{17}O_4N$ requires N, 4·0%). Light absorption in ethanol: Maxima, 2230 and 2640 A., ε = 87,000 and 19,000, respectively. On prolonged storage in contact with air, the carbinol is slowly converted into the conjugated isomer (below), as a result of the formation of small amounts of acidic oxidation products.

3-1′-*Naphthyl*-1-*methylallyl Alcohol* (II; X = 1-Naphthyl).—(*a*) 1-1′-Naphthyl-3-methylallyl alcohol (5 g.) was dissolved in 60% aqueous acetone–0·1M-hydrochloric acid (200 ml.), and the solution kept for 24 hours at room temperature. On dilution with water 3-1′-*naphthyl*-1-*methylallyl alcohol* (4·5 g.) separated as an oil, which was distilled at 95° (bath)/10^{-5} mm. It solidified on storage at 0° and crystallised from pentane in colourless plates, m. p. 41—42° (Found: C, 85·1; H, 7·3. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%). The p-*nitrobenzoate* crystallised from light petroleum (b. p. 60—80°) in very pale yellow needles, m. p. 93° (Found: C, 73·0; H, 5·0; N, 4·1. $C_{21}H_{17}O_4N$ requires C, 72·6; H, 4·9; N, 4·0%). Light absorption in ethanol: Maxima, 2280, 2600, and 2910 A., ε = 61,000, 17,500, and 14,000, respectively.

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* Since this paper was written, a longitudinal polarisation of the 2300 A. band and a transverse polarisation of the 2900 A. band of naphthalene have also been deduced by Klevens and Platt (*J. Chem. Physics*, 1949, **17**, 470).

(*b*) 1-1′-Naphthyl-3-methylallyl alcohol (5 g.) was dissolved in 90% aqueous acetone–0·1M-hydrochloric acid (75 ml.), and the solution kept for 24 hours at room temperature. On dilution with water an oil separated, which was distilled at 10^{-5} mm., giving 3-1′-naphthyl-1-methylallyl alcohol, b. p. 95° (bath) (1·5 g., 30%), and a high-boiling fraction, b. p. 250° (bath) (2·75 g., 55%). On cooling, the high-boiling fraction set to a glassy solid which failed to react with sodium or methylmagnesium iodide in ether. On the basis of this evidence and the analytical and light-absorption data it is formulated as 1-1′-*naphthyl*-3-*methylallyl* 3-1′-*naphthyl*-1-*methylallyl ether* (Found : C, 88·4; H, 6·9. $C_{28}H_{26}O$ requires C, 88·8; H, 6·9%). Light absorption in ethanol : Maxima, 2260 and 2820 A., ε = 130,000 and 17,000, respectively.

Methyl 2-1′-*Naphthylvinyl Ketone* (III; X = 1-Naphthyl).—(*a*) 1-Naphthaldehyde (4 g.; Hinkel, Ayling, and Beynon, *J.*, 1936, 342), acetone (30 ml.), and 1% sodium hydroxide (100 ml.) were stirred together at 40° for 24 hours. Ether extraction and distillation yielded the ketone (4 g., 80%), b. p. 142°/5 × 10^{-4} mm., $n_{\rm D}^{20}$ 1·6670 (Wilds *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 1985, give b. p. 163—173°/0·9 mm., $n_{\rm D}^{25}$ 1·6665). The 2 : 4-*dinitrophenylhydrazone* crystallised from pyridine in needles, m. p. 261° (Found: C, 64·0; H, 4·4; N, 15·0. $C_{20}H_{16}O_4N_4$ requires C, 63·8; H, 4·3; N, 14·9%). Light absorption in chloroform : Maxima, 2560, 3230, and 3970 A., ε= 32,500, 16,000, and 37,500, respectively.

(*b*) 3-1′-Naphthyl-1-methylallyl alcohol (2 g.), aluminium *tert.*-butoxide (2·5 g.), dry acetone (20 ml.), and benzene (20 ml.) were refluxed together for 24 hours. Decomposition with excess of sulphuric acid, ether-extraction, and distillation yielded 1-naphthylmethyleneacetone, b. p. 85°/10^{-5} mm., $n_{\rm D}^{22}$ 1·6580 (1·3 g., 65%), which gave a 2 : 4-dinitrophenylhydrazone, m. p. 261°, undepressed on admixture with the authentic specimen.

1-2′-*Naphthyl*-3-*methylallyl Alcohol* (I; X = 2-Naphthyl).—2-Bromonaphthalene (52 g., Newman and Wise, *J. Amer. Chem. Soc.*, 1941, **63**, 2847) in ether (200 ml.) was added slowly to a suspension of magnesium (6 g.) in ether (200 ml.) containing ethyl bromide (0·5 g.), and the mixture was stirred for 2 hours in an atmosphere of nitrogen. Freshly distilled crotonaldehyde (18 g.) in ether (30 ml.) was then added slowly at 0°, and stirring continued for a further 3 hours. Decomposition of the Grignard complex with ammonium chloride solution, isolation of the product in the usual manner, and distillation from a trace of anhydrous potassium carbonate afforded 2 : 2′-dinaphthyl, m. p. 175° (0·5 g.), and 1-2′-*naphthyl*-3-*methylallyl alcohol* (27 g., 55%), b. p. 90° (bath)/10^{-5} mm., $n_{\rm D}^{22}$ 1·6190, which solidified when kept and crystallised from pentane in fine needles, m. p. 43—44° (Found : C, 84·8; N, 7·1. $C_{14}H_{14}O$ requires C, 84·8: H, 7·1%).

3-2′-*Naphthyl*-1-*methylallyl Alcohol* (II; X = 2-Naphthyl).—1-2′-Naphthyl-3-methylallyl alcohol (5 g.) was dissolved in 60% aqueous acetone–0·1M-hydrochloric acid (200 ml.), and the solution kept for 24 hours at room temperature. On dilution with water, 3-2′-*naphthyl*-1-*methylallyl alcohol* (4·8 g.) separated. It crystallised from light petroleum (b. p. 40—60°) in fine needles, m. p. 94° (Found : C, 85·1; H, 7·1. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%). The p-*nitrobenzoate* separated from light petroleum (b. p. 80—100°) in crystals, m. p. 113° (Found : C, 72·7; H, 5·1; N, 4·0. $C_{21}H_{17}O_4N$ requires C, 72·6; H, 4·9; N, 4·0%). Light absorption in chloroform : Maxima, 2510, 2570, 2700, 2780, 2890, 2990, and 3410 A., ε = 55,500. 28,000, 21,500, 19,000, 15,500, and 1,100, respectively.

Methyl 2-2′-*Naphthylvinyl Ketone* (III; X = 2-Naphthyl).—3-2′-Naphthyl-1-methylallyl alcohol (2·5 g.), aluminium *tert.*-butoxide (3 g.), dry acetone (30 ml.), and benzene (30 ml.) were refluxed together for 24 hours. Decomposition with sulphuric acid gave the ketone (1·5 g.), which separated from methanol as crystals, m. p. 103—104° (Wilds *et al.*, *loc. cit.*, give m. p. 104°). The 2 : 4-*di-nitrophenylhydrazone* crystallised from pyridine in needles, m. p. 268° (Found: C, 64·1; H, 4·5; N, 14·9. $C_{20}H_{16}O_4N_4$ requires C, 63·8; H, 4·3: N, 14·9%). Light absorption in chloroform : Maxima, 3160 and 3980 A., ε = 19,000 and 37,500, respectively.

1-9′-*Anthryl*-3-*methylallyl Alcohol* (I; X = 9-Anthryl).—9-Bromoanthracene (26 g., Barnett and Cook, *J.*, 1924, **125**, 1084) in ether (200 ml.) was refluxed with ethyl bromide (11 g.) and magnesium (4·9 g.) for 24 hours. Freshly distilled crotonaldehyde (14 g.) in ether (50 ml.) was then added slowly to the ice-cold suspension, and stirring continued for 1 hour. Decomposition of the Grignard complex with ammonium chloride, and isolation of the product afforded 1-9′-*anthryl*-3-*methylallyl alcohol* (17 g., 68%), which crystallised from hot ethyl acetate–light petroleum (b. p. 40—60°) in very pale yellow crystals, m. p. 114° (Found : C, 87·0; H, 6·4. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%).

3-9′-*Anthryl*-1-*methylallyl Alcohol* (II; X = 9-Anthryl).—1-9′-Anthryl-3-methylallyl alcohol (5 g.) was dissolved in 60% aqueous acetone–0·1M-hydrochloric acid, and the solution kept for 24 hours at room temperature. On dilution with water, 3-9′-*anthryl*-1-*methylallyl alcohol* (4·9 g.) separated. It crystallised from light petroleum (b. p. 40—60°) in yellow needles, m. p. 116° (Found : C, 86·9; H, 6·65. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%). The p-*nitrobenzoate* crystallised from light petroleum (b. p. 80—100°) in orange needles, m. p. 150° (Found : C, 75·6; H, 5·0; N, 3·6. $C_{25}H_{19}O_4N$ requires C, 75·6; H, 4·8; N, 3·5%). Light absorption in ethanol : Maxima, 2560, 3510, 3670, and 3860 A., ε = 155,000, 6,500, 8,500, and 7,100, respectively.

Methyl 2-9′-*Anthrylvinyl Ketone* (III; X = 9-Anthryl).—(*a*) A mixture of 9-anthraldehyde (2 g.: Fieser, Hartwell, and Jones, *Org. Synth.*, **20**, 11), acetone (20 ml.), and 10% sodium hydroxide (1 ml.) was kept at room temperature for 24 hours. Filtration yielded 1 : 5-*di*-9′-*anthrylpenta*-1 : 4-*dien*-3-*one* (0·4 g., 18%). which crystallised from pyridine in orange plates, m. p. 293° (Found : C, 91·2; H, 4·9. $C_{33}H_{22}O$ requires C, 91·2; H, 5·1%). Light absorption in chloroform : Maxima, 2520, 2560, and 3850 A., ε = 14,500, 14,500, and 13,500, respectively. Addition of water to the filtrate gave *methyl* 2-9′-*anthrylvinyl ketone* (1·4 g., 56%), which crystallised from ethanol in yellow needles, m. p. 113° (Found : C, 88·0; H, 5·8. $C_{18}H_{14}O$ requires C, 87·8; H, 5·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised from pyridine in needles, m. p. 244° (Found : C, 67·5; H, 4·2; N, 13·1. $C_{24}H_{18}O_4N_4$ requires C, 67·6; H, 4·3; N, 13·1%). Light absorption in chloroform : Maxima, 4080 A., ε = 22,500. On one occasion, a different di-condensation product, probably a stereoisomeric 1 : 5-*di*-9′-*anthrylpenta*-1 : 4-*dien*-3-*one*, m. p. 268°, was obtained (Found : C, 91·4; H, 5·4. $C_{33}H_{22}O$ requires C, 91·2; H, 5·1%). Light absorption in chloroform : Maxima 2510, 2560, and 3680 A., ε = 110,000, 105,000, and 7,200 respectively.

(*b*) 3-9′-Anthryl-1-methylallyl alcohol (0·8 g.), aluminium *tert.*-butoxide (2 g.), dry acetone (10 ml.), and benzene (10 ml.) were refluxed together for 24 hours. Decomposition with sulphuric acid and ether extraction gave a viscous oil, which crystallised from ethanol to give methyl 2-9′-anthrylvinyl ketone, m. p. 112°, undepressed on admixture with the authentic specimen.

1 : 5-*Di*-9′-*anthrylpenta*-1 : 4-*dien*-3-*one*.—A solution of 9-anthrylmethyleneacetone (0·5 g.) and 9-anthraldehyde (0·5 g.) in dry ethyl acetate (10 ml.) was saturated with dry hydrogen chloride and kept for 2 hours. The 1 : 5-di-9′-anthrylpenta-1 : 4-dien-3-one (0·8 g.) was filtered off, and crystallised from pyridine in orange plates, m. p. 291°, undepressed on admixture with the specimen obtained above.

1-9′-*Phenanthryl*-3-*methylallyl alcohol* (I; X = 9-Phenanthryl).—9-Bromophenanthrene (21 g.; Austin, *J.*, 1908, **93**, 1763) and ethyl bromide (9 g.) in a mixture of benzene (100 ml.) and ether (100 ml.) were added slowly to a suspension of magnesium (4 g.) in ether (100 ml.), stirred for 1 hour and then refluxed for 7 hours. Freshly distilled crotonaldehyde (11·5 g.) in ether (50 ml.) was added slowly at 0°, and stirring continued for 2 hours. Decomposition of the Grignard complex with ammonium chloride, isolation of the product, and vacuum distillation gave an oil which did not solidify. This was chromatographed from benzene solution on an alumina column, a mixture of benzene and ethanol being used as eluent, to give solid 1-9′-*phenanthryl*-3-*methylallyl alcohol* (15 g., 75%), which crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 88—89° (Found: C, 86·8; H, 6·4. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%).

3-9′-*Phenanthryl*-1-*methylallyl Alcohol* (II; X = 9-Phenanthryl).—1-9′-Phenanthryl-3-methylallyl alcohol (3 g.) was dissolved in 60% aqueous acetone–0·1M-hydrochloric acid (200 ml.), and the solution set aside for 24 hours at room temperature. On dilution with water 3-9′-*phenanthryl*-1-*methylallyl alcohol* (2·7 g.) separated. It crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 103° (Found: C, 87·3; H, 6·6. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%). The p-*nitrobenzoate* crystallised from *cyclo*hexane in colourless needles, m. p. 122° (Found: C, 75·9; H, 4·8; N, 3·7. $C_{25}H_{19}O_4N$ requires C, 75·6; H, 4·8; N, 3·5%). Light absorption in ethanol: Maxima, 2550 and 3050 A., ε = 53,500 and 15,000, respectively.

Methyl 2-9′-*Phenanthrylvinyl Ketone* (III; X = 9-Phenanthryl).—3-9′-Phenanthryl-1-methylallyl alcohol (1 g.) and aluminium *tert*.-butoxide (2 g.) in dry acetone (10 ml.) and benzene (10 ml.) were refluxed for 24 hours. Decomposition with sulphuric acid and ether extraction gave a viscous oil, which crystallised from ethanol to give the ketone (0·6 g., 60%). The 2 : 4-dinitrophenylhydrazone crystallised from pyridine in needles, m. p. 268°, undepressed on admixture with the authentic specimen obtained below.

Reaction between 9-*Phenanthraldehyde and Acetone*.—A mixture of 9-phenanthraldehyde (3 g.; Miller and Bachman, *J. Amer. Chem. Soc.*, 1935, **57**, 766), acetone (40 ml.), and 10% sodium hydroxide (1 ml.) was kept at room temperature for 24 hours. Addition of water to the mixture gave a viscous gum which did not solidify. This was chromatographed from benzene solution on an alumina column to give 3 products as follows.

(i) *Methyl* 2-9′-*phenanthrylvinyl ketone* (1·5 g., 40%), which crystallised from aqueous acetone in pale yellow crystals, m. p. 85° (Found: C, 87·5; H, 5·8%; *M*, in camphor, 251. $C_{18}H_{14}O$ requires C, 87·8; H, 5·7%; *M*, 246). The 2 : 4-*dinitrophenylhydrazone* crystallised from pyridine in needles, m. p. 269° (Found: C, 67·7; H, 4·4; N, 12·9. $C_{24}H_{18}O_4N_4$ requires C, 67·6; H, 4·3; N, 13·1%). Light absorption in chloroform: Maxima, 2560, 3240, and 2980 A., ε = 57,000, 14,500, and 36,000, respectively.

(ii) 3-*Keto*-1-9′-*phenanthrylbutan*-1-*ol* (0·96 g., 25%), which crystallised from light petroleum (b. p. 80—100°) in colourless needles, m. p. 119° (Found: C, 82·1; H, 6·3. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%). Light absorption in ethanol: Maxima, 2530, 2970, 3250, 3320, 3410, and 3480 A., ε = 71,000, 13,000, 290, 330, 260, and 290, respectively. The 2 : 4-*dinitrophenylhydrazone* separated from aqueous pyridine in orange crystals, m. p. 256° (Found: C, 65·0; H, 4·7; N, 12·8. $C_{24}H_{20}O_5N_4$ requires C, 64·9; H, 4·5; N, 12·6%). Light absorption in chloroform: Maxima, 2560, 2900, 2990, and 3600 A., ε = 67,000, 13,500, 14,500, and 22,000, respectively.

(iii) A *dimer* of methyl 2-9′-phenanthrylvinyl ketone (0·4 g., 10%), which separated from pyridine as colourless plates, m. p. 274° (Found: C, 87·7; H, 6·0; *M*, in camphor, 450. $C_{36}H_{28}O_2$ requires C, 87·8; H, 5·7%; *M*, 492). Light absorption in chloroform: Maxima, 2560, 2800, 2910, and 3010 A., ε = 125,000, 27,000, 23,000, and 28,000, respectively.

Reaction between Anthrylacrylic Acid and Thionyl Chloride.—Anthrylacrylic acid (2 g.; Davis and Carmack, *J. Org. Chem.*, 1947, **12**, 76) was refluxed with thionyl chloride (1·7 g.) for 30 minutes. The product solidified on cooling and crystallised from benzene in yellow-brown needles, m. p. 204° (1·8 g., 75%), and is formulated as β-(9-*chloro*-10-*anthryl*)*acryloyl chloride* (Found: C, 67·4; H, 3·5. $C_{17}H_{10}OCl_2$ requires C, 67·8; H, 3·3%). The acid chloride (1·8 g.) was refluxed with 10% potassium hydroxide (20 ml.) for 30 minutes. The reaction mixture was acidified, and crystallisation of the product from nitrobenzene gave a chloro-acid, m. p. 264° (1·6 g., 95%), formulated as β-(9-*chloro*-10-*anthryl*)*acrylic acid* (Found: C, 72·1; H, 4·2. $C_{17}H_{11}O_2Cl$ requires C, 72·2; H, 3·9%). Light absorption in ethanol: Maxima, 2580, 3770, and 3970 A., ε = 155,000, 9,600, and 9,400, respectively.

Reaction between 1-*Naphthaldehyde and Acetaldehyde*.—Acetaldehyde (2 g.) was slowly added to a stirred solution of 1-naphthaldehyde (2 g.) and 10% sodium hydroxide (2 ml.) in aqueous methanol (20 ml.). Ether extraction of the reaction mixture gave an oil, which on distillation gave unchanged 1-naphthaldehyde (0·5 g.) and a high-boiling fraction which did not solidify. Similar results were obtained when using piperidinium acetate as a catalyst.

Reaction between 9-*Anthraldehyde and Acetaldehyde*.—Acetaldehyde (2 g.) was caused to react with 9-anthraldehyde (2 g.) under similar conditions to the above. Ether extraction gave a gum which could not be solidified.

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