15. *Free-radical Phenylation of Phenanthrene.*

By A. L. J. Beckwith and M. J. Thompson.

Phenyl radicals, produced by thermal decomposition of diazoaminobenzene, react with phenanthrene to yield a mixture of phenylphenanthrenes which has been analysed by chromatography on partially acetylated cellulose and by measurement of ultraviolet absorption. The yields of isomeric phenylphenanthrenes are in accord with modern theories of reactivity in aromatic hydrocarbons. The physical properties and ultraviolet absorption spectra of all the phenylphenanthrenes are recorded herein.

Recent extensive investigations have proved the relative rates of reaction of unsubstituted aromatic hydrocarbons with free radicals to be substantially in accord with earlier predictions.[1] For instance, appropriate maximum or minimum values of free-valency number and localisation energy for alternant hydrocarbons may be correlated with their rates of reaction with methyl,[2-4] trichloromethyl,[3,5] and benzoylperoxy-radicals.[4,6]

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[1] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900; Dewar, *ibid.*, 1952, **74**, 3357; Daudel and Daudel, *J. Chem. Phys.*, 1948, **16**, 639; Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553.

[2] Coulson, *J.*, 1955, 1435.

[3] Dewar, Mole, and Warford, *J.*, 1956, 3581.

[4] Pullman and Effinger, " Colloque International sur le Calcul des Fonctions d'Onde Moleculaires," C.N.R.S., Paris, 1958, p. 329.

[5] Kooyman and Farenhorst, *Trans. Faraday Soc.*, 1953, **49**, 58.

[6] Turner and Waters, *J.*, 1956, 879.

Within any one hydrocarbon there should be a similar relation between the relative rates of free-radical substitution at various positions and the respective theoretical indices, but this hypothesis has not yet been tested rigorously, for in most investigations of this type of reaction either no accurate determination of isomer distribution was attempted or one position in the molecule was so reactive as completely to overshadow other positions (*e.g.*, the reaction of anthracene with methyl [7] or phenyl [8] radicals). In those cases where an accurate analysis of the products was carried out (naphthalene with methyl [9] or phenyl radicals [10]) the number of available positions (two) was not sufficient to test the theory adequately.

Phenanthrene, which has five positions available for substitution, provides an ideal substrate for studies of isomer distribution, particularly as the range in reactivity between the most and the least reactive position is predicted to be similar to that between the 1- and the 2-position of naphthalene.

There have been few previous attempts to bring phenanthrene into reaction with free radicals. With benzyl radicals, produced by reaction of di-t-butyl peroxide with toluene, it yielded an unidentified dibenzyl derivative; [11] with the acetoxy-radicals from manganese triacetate it was converted in small yield into 9-acetoxyphenanthrene.[12] Phenanthrene in chlorobenzene was reported [13] not to react with benzoyl peroxide, but 15% of the starting material was not recovered and the yields of carbon dioxide and benzoic acid strongly suggest that some reaction did, in fact, occur.

For our initial experiments diazoaminobenzene was employed as a source of free radicals. Its thermal decomposition produces both phenyl and anilino-radicals; [14] the latter act as acceptors for hydrogen atoms and so minimise the formation of addition products and the tars which may result therefrom. The reaction was carried out by heating diazoaminobenzene with phenanthrene, which was present in considerable excess to eliminate as far as possible the production of disubstituted compounds. It was essential to eliminate anthracene from our phenanthrene owing to the very rapid reaction of the former.

Analysis of the reaction mixture proved very difficult. Considerable quantities or unchanged phenanthrene were removed by distillation under reduced pressure, and aniline and diphenylamine were isolated by extraction with acid. Treatment of the reaction mixture with acid also precipitated a dark amorphous substance, which contained nitrogen and showed NH absorption in the infrared region. Its formation may indicate that anilino-radicals can react directly with suitable aromatic molecules. The determination of the constituents of the hydrocarbon residue required considerable use of chromatography. Adsorption chromatography on alumina yielded two fractions, the first consisting of phenanthrene, and 9- and 1-phenylphenanthrene, and the second of 2- and 3-phenylphenanthrene. The latter fraction was readily separated into its constituents by fractional crystallisation, since the 2- and 3-phenylphenanthrene are the least and the most soluble respectively of all the isomers. In some cases their proportions in the mixtures were also determined by the ultraviolet-spectrographic method of Dewar and Urch.[15]

The chromatographic procedures recently developed by Spotswood,[16] using acetylated cellulose, facilitated the analysis of the fraction containing phenanthrene and 1- and 9-phenylphenanthrene. Identification and quantitative determination were by ultraviolet

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[7] Beckwith and Waters, *J.*, 1956, 1108.

[8] Norman and Waters, *J.*, 1958, 167.

[9] Kent and Norman, *J.*, 1959, 1724.

[10] Marshall and Waters, *J.*, 1959, 381; Huisgen and Grashey, *Annalen*, 1957, **607**, 46; Davies, Hey, and Williams, *J.*, 1958, 1878.

[11] Beckwith, D.Phil. Thesis, Oxford, 1956.

[12] Zonis, *Sbornik Statey po obshchei Khim.*, 1953, **2**, 1091; *Chem. Abs.*, 1955, **49**, 5414.

[13] Roitt and Waters, *J.*, 1952, 2695.

[14] Hardie and Thomson, *J.*, 1958, 1286.

[15] Dewar and Urch, *J.*, 1957, 345.

[16] Spotswood, *J. Chromatog.*, 1960, **3**, 101.

absorption measurements. For mixtures of authentic compounds the method was found to be reproducible and accurate. Infrared spectrography could not be applied to the quantitative analysis of the complex mixtures encountered here because of similarity of the spectra of the components, but proved useful for the qualitative identification of the constituents in various fractions. Chromatography on acetylated paper was employed for the same purpose.[17]

The relative yields of phenylphenanthrenes produced in our experiments are shown in Table 1 together with other relevant data. A notable feature is the absence of 4-phenylphenanthrene: evidently the 4-position is too sterically hindered to allow it to be attacked by phenyl radicals. The results show that the reactivities of the positions in phenanthrene towards substitution by phenyl radicals are in the order $9 > 1 > 3 > 2$. The order of reactivities predicted by all the methods of calculation (see Table 1) is $9 > 1 > 3 > 2$. Our analytical techniques, particularly with regard to 2- and 3-phenylphenanthrene, are not sufficiently accurate to allow a quantitative comparison of reactivities with theoretical indices, but superficially it appears that Dewar's " reactivity numbers " [13] are in better agreement with experiment than others listed in Table 1.

TABLE 1. *Relative yields of substitution products, and theoretical indices of reactivity for phenanthrene.*

	Relative yields of substituted phenanthrenes				Theoretical indices of reactivity			
	Phenylation *							
Position	D.A.B.	B.P.	Nitration [19]	Alkylation [20]	$F_{V.B.}$	$F_{M.O.}$	E	R
1–	4·1	4·6	3·9	0·85	0·197	0·450	2·30	1·86
2–	1·0	1·0	1·0	1·0	0·163	0·402	2·50	2·18
3–	1·0	1·3	3·2	1·57	0·172	0·407	2·41	2·04
4–	0	0	0·8	0	0·184	0·440	2·39	1·96
9–	6·7	6·3	5·3	2·0	0·200	0·451	2·30	1·80

* D.A.B., phenylation with diazoaminobenzene; B.P., phenylation with benzoyl peroxide. $F_{V.B.}$, free-valency number calculated by the valency-bond method (Daudel and Daudel, *J. Chem. Phys.*, 1948, **16**, 639); $F_{M.O.}$ and E, free valency number and atom-localisation energy respectively, calculated by the molecular orbital method (Coulson and Daudel, " Dictionary of Values of Molecular Constants," 1955, Vol. II, p. 20); R, Dewar's " reactivity numbers " (ref. 18).

The results reported here may be compared with similar studies of electrophilic substitution in phenanthrene. Nitration of phenanthrene [19] shows an order of reactivities $9 > 1 > 3 > 2$, and the isomer distribution, except for the 3-position, is very close to that for free-radical phenylation. This agreement is in accord with the accepted theory that free-valency numbers and similar numerical magnitudes provide a measure of reactivity towards all types of chemical reagent, both ionic and free-radical, in unsubstituted alternant hydrocarbons. Electrophilic alkylation of phenanthrene with cyclohexyl benzenesulphonate [20] yields isomeric cyclohexylphenanthrenes in the order $9 > 3 > 2 > 1$. It was suggested that this order differed from that predicted theoretically because of the low selectivity of the attacking reagent.[20] However, decrease in the selectivity of an attacking reagent should lower the total range of reactivity rather than change the order,[21] and we therefore suggest that the low reactivity of the 9- and the 1-position (1-naphthalenic) compared with the 2- and the 3-position (2-naphthalenic) may be ascribed to steric hindrance. The high reactivity of the 3-position towards nitration has been similarly explained.[19] Alternatively, the high yields of 2- and 3-cyclohexylphenanthrenes obtained by Rule and Hickinbottom [20] may be due to the fact that the alkylation is not truly irreversible. It is noteworthy that reversible acylation of phenanthrene yields the 2- and the 3-isomer.[22]

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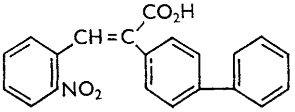
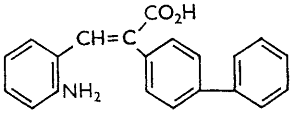
[17] Spotswood, *J. Chromatog.*, 1959, **2**, 90.
[18] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3357.
[19] Dewar and Warford, *J.*, 1956, 3570.
[20] Rule and Hickinbottom, *J.*, 1959, 2517.
[21] Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.
[22] Mosettig and van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3704.

In order to compare diazoaminobenzene as a source of phenyl radicals with the customary reagents, the reaction of phenanthrene with benzoyl peroxide has also been examined. The yield of phenylphenanthrenes from this reaction was low, and the analytical results are accordingly less accurate than those recorded above. Nevertheless, the isomer distribution (Table 1) agrees well with that obtained by using diazoaminobenzene. Though accurate determination of the other reaction products was beyond the scope of this investigation, some points of interest are apparent. The yield of phenols, isolated after hydrolysis of the product mixture, is much greater than that of phenylphenanthrenes, a fact which accords with observations elsewhere[23] that the ratio of benzoyloxylation to phenylation increases with increasing reactivity of the aromatic hydrocarbon. After hydrolysis, the reaction mixture also yielded a neutral gum, insoluble in benzene, which we tentatively suggest is a mixture of dihydrophenanthrenediols, a hypothesis supported by the amount of benzoic acid produced during the hydrolysis. The addition of two benzoyloxy-radicals to an aromatic molecule should be particularly favoured by the presence of two adjacent reactive positions, such as the 9- and the 10-position in phenanthrene.

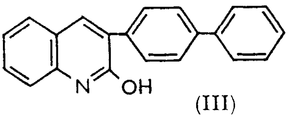
In order to develop our analytical procedure authentic specimens of all the phenylphenanthrenes were required. 1-, 4-, and 9-Phenylphenanthrenes were prepared by routes similar to those described in the literature, and the 2-isomer was obtained pure from the free-radical phenylation and its identity confirmed by the preparation of derivatives. 3-Phenylphenanthrene,[24] which had not been described when this work was undertaken, was synthesised by Pschorr's method. Condensation of *p*-biphenylylacetic acid with *o*-nitrobenzaldehyde yielded *cis*- and *trans*-α-4-biphenylyl-*o*-nitrocinnamic acid (I). The two isomers, which could be interconverted by irradiation with ultraviolet light, were differentiated by reduction; the *trans*-compound yielded a *trans*-amino-acid (II) whereas the *cis*-isomer was converted into 3-(4-biphenylyl)quinolin-2-ol (III). The quinolinol was also produced by irradiation of *trans*-isomer (II). Cyclisation of acid (II) and decarboxylation of the product yielded 3-phenylphenanthrene.



(I)



(II)



(III)

TABLE 2. *Infrared spectra* (μ) *of phenanthrene * and phenylphenanthrenes in Nujol*

	Substituted phenanthrenes				
Phenanthrene	1-Phenyl-	2-Phenyl-	3-Phenyl-	4-Phenyl-	9-Phenyl-
10·53s	11·55w	11·21s	11·35s	12·05vs	10·59w
11·45s	11·94w	11·50vw	11·61w	12·50s	11·01vw
11·53s	12·01s	12·26s	12·90vs	12·96w	11·27s
12·25vs	12·35vs	13·46vs	12·50vs	13·13s	11·58w
13·68vs	13·00s	13·81vw	13·16s	13·27s	11·78vw
14·05s	13·15s	14·00w	13·48vs	13·50vs	12·87s
	13·25s	14·45s	14·10vw	13·87vs	13·06s
	13·40s		14·55s	14·30vs	13·50s
	14·18s				13·84s
	14·27s				14·05w
					14·32s

* Anthracene as an impurity in phenanthrene can be detected by its characteristic absorption at 11·25 μ.

Ultraviolet spectrographic measurements were extensively used for the qualitative and quantitative analysis of reaction mixtures. The spectra of phenanthrene and 1-, 4-, and

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[23] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 165.

[24] Anderson, Campbell, Leaver, and Stafford, *J.*, 1959, 3992.

9-phenylphenanthrenes show low-intensity absorption bands of characteristic fine structure, but those of 2- and 3-phenylphenanthrenes are relatively featureless. All the phenylphenanthrenes have characteristic infrared absorption bands and these are recorded in Table 2.

EXPERIMENTAL

Ultraviolet spectra were measured with an Optica Recording Spectrophotometer for solutions in 95% ethanol. Infrared spectra were measured on a Grubb–Parsons S4 double-beam recording spectrophotometer as Nujol mulls with a sodium chloride prism. Analyses were carried out by the C.S.I.R.O. and University of Melbourne Microanalytical Laboratory.

Materials.—Phenanthrene was a commercial sample purified by treatment with maleic anhydride in xylene.[25] It crystallised from ethanol in plates, m. p. 97·5—98°, and then showed ultraviolet absorption almost identical with that of a specimen prepared by the Pschorr method. The synthetic sample had $\lambda_{\text{max.}}$ 310, 316, 324, 332, 339, and 346 mμ (ε 172, 209, 236, 288, 242, and 271, respectively). Diazoaminobenzene was purified by chromatography on alumina, and benzoyl peroxide was crystallised from chloroform. Adsorption chromatography was carried out on Spence-type U.G. 1 alumina, with hexane and benzene as eluting solvents.

Chromatography on Partially Acetylated Cellulose.—Cellulose powder was acetylated by Spotswood's method [16] and the quality of the product was tested as follows. The acetylated cellulose was packed in a column 1″ × 12″ with ethanol–toluene–water (17 : 4 : 1), and 2 mg. of an equimolar mixture of perylene and 3,4-benzopyrene were eluted through it with the same solvent mixture until the tail of the perylene band (detected by its fluorescence under ultraviolet light) was 10″ from the top of the column. With satisfactory acetylated cellulose the distance between the tail of the perylene band and the front of the benzopyrene band was then 6·5—7″. Inferior batches, which gave a smaller separation of perylene and benzopyrene, were of no use for the analysis of mixtures of phenylphenanthrenes. For the separation of phenylphenanthrenes the above solvent system was satisfactory but the eluate from the column always showed a weak, featureless, but variable ultraviolet absorption and it was more convenient to use methanol–ether–water (4 : 4 : 1) which gave equally good separation with less background absorption. Mixtures containing phenanthrene and 1- and 9-phenylphenanthrene were separated on a column of acetylated cellulose (1″ × 40″). Constant-volume fractions (7 ml.) were collected and the concentration of hydrocarbon in each tube was determined from the ultraviolet absorption. The intensity at a chosen wavelength was plotted against the tube number, and the area under the curve was obtained by weighing the paper. The percentage composition of the mixture was determined by comparison of these areas after correction by factors derived from the extinction coefficients at the appropriate wavelengths. The total amount of each compound eluted from the column was also determined from the ultraviolet absorption of the combined fractions containing that compound. There was good agreement between results obtained by the two methods. The accuracy of analyses carried out by chromatography on acetylated cellulose was established by test experiments using standard mixtures of pure synthetic hydrocarbons. The most convenient sample size was 12—18 mg. The wavelengths employed for the determination of hydrocarbons in the eluate were phenanthrene, 346 mμ; 1-phenylphenanthrene, 350 mμ; and 9-phenylphenanthrene, 350 mμ.

Reaction of Phenanthrene with Diazoaminobenzene.—An intimate mixture of phenanthrene (200 g.) and diazoaminobenzene (16 g., 0·08 mole) was heated at 152° for 24 hr. There was initially a vigorous evolution of nitrogen, but this ceased after 6 hr. While still molten, the mixture was poured into light petroleum (b. p. 40—60°; 3 l.), and the resultant solution was heated almost to the b. p. and then extracted with hot concentrated hydrochloric acid (2 × 250 ml.). The precipitated tar was collected, washed, and dried, and there was obtained a dark purple solid (3·4 g.), which gave a positive test for nitrogen and ionic chlorine, and showed NH absorption in the infrared spectrum. When the acid extract was evaporated to a small bulk and diluted with water, diphenylamine (0·5 g.) crystallised. It was filtered off and the filtrate was made alkaline and steam-distilled to recover aniline (5·0 g., 66%). The petroleum solution was washed with aqueous alkali, dried, and evaporated. The residual hydrocarbon mixture was distilled under reduced pressure and the distillate (116 g.; b. p. 146—147°/0·5 mm.) was fractionally crystallised from ethanol to yield phenanthrene (113 g., m. p. and

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[25] Feldman, Pantages, and Orchin, *J. Amer. Chem. Soc.*, 1951, **73**, 4341.

mixed m. p. 97—98°) and a mixture (A, 2·7 g.). When the distillation residue was crystallised from light petroleum (500 ml.) a further quantity (45 g.) of substantially pure phenanthrene was obtained. The material dissolved in the mother-liquor was chromatographed on a column (4·5 × 40 cm.) of alumina and eluted with petroleum. The first fraction (4 l.) contained impure phenanthrene (36·5 g.), which was separated by fractional crystallisation from light petroleum into pure phenanthrene (16·7 g.) and a hydrocarbon mixture (B; 5·4 g.). When the mother-liquor and the second chromatographic fraction (11 l.) were combined and evaporated, a mixture (C; 19·8 g.) containing a high proportion of phenylphenanthrenes was obtained. Elution of the column with light petroleum–benzene yielded a mixture (D; 1·9 g.) of 2- and 3-phenylphenanthrene, and a further quantity (1·5 g.) of unidentifiable material was eluted with benzene and ethanol. The mixture (D) was separated into 2- (0·9 g; m. p. 194°) and 3-phenylphenanthrene (0·9 g.; m. p. and mixed m. p. 74°) by fractional crystallisation from ethanol. Mixture (B) was analysed by chromatography on acetylated cellulose (see above) and was found to contain phenanthrene (4·8 g.) and 9- (0·4 g.) and 1-phenylphenanthrene (0·2 g.). A similar determination showed the constituents of (C) to be phenanthrene (10·6 g.) and 9- (5·7 g.) and 1-phenylphenanthrene (3·5 g.). Mixture A contained phenanthrene (1·5 g.) and 9- (0·6 g.), 1- (0·4 g.), 2- (0·1 g.), and 3-phenylphenanthrene (0·1 g.). Yields of phenylphenanthrenes were as follows: 1-, 4·1 g. (0·016 mole); 2-, 1·0 g. (0·004 mole); 3-, 1·0 g. (0·004 mole); and 9-, 6·7 g. (0·026 mole); total yield of phenylphenanthrenes, 12·8 g. (0·05 mole, 62%).

Reaction of Phenanthrene with Benzoyl Peroxide.—Benzoyl peroxide (22·6 g., 0·093 mole) was added slowly (0·5 hr.) to molten phenanthrene (100 g.). During the addition the temperature was allowed to fall from 105° to 90° and it was then kept at 90° for 17 hr.; there appeared to be very little carbon dioxide evolved. The reaction mixture was then dissolved in light petroleum—benzene (1 l.), and the brown solution extracted with aqueous potassium carbonate. Acidification of the aqueous extract yielded benzoic acid (7·3 g.), m. p. 120—121°. The hydrocarbon layer, after drying ($MgSO_4$), was evaporated, and the residue was boiled under reflux with 10% ethanolic potassium hydroxide (300 ml.) for 17 hr. The solvent was removed under reduced pressure, and the residue treated with water (500 ml.) and benzene (1 l.). The aqueous solution was filtered from a gum (9 g.; dihydrophenanthrenediols?) and saturated with carbon dioxide. The phenanthrols (4·5 g., 25%) which were precipitated were extracted with ether. The aqueous solution was then acidified with hydrochloric acid and extracted with ether to yield slightly impure benzoic acid (11·7 g., 0·096 mol.), m. p. 114—118°. The benzene solution was evaporated, and the residue distilled under reduced pressure. The distillate (44·1 g.; b. p. 146—147°/0·5 mm.), on crystallisation from ethanol, yielded pure phenanthrene (40·3 g.). The solvent was removed from the mother-liquor and the residue, combined with that from the distillation, was dissolved in light petroleum and chromatographed on alumina. Thereafter the separation and determination of isomeric phenylphenanthrenes were carried out as described for the earlier experiments. The yields of phenylphenanthrenes were as follows: 1-, 1·4 g. (0·005 mole); 2-, 0·3 g. (0·0012 mole); 3-, 0·4 g. (0·0016 mole); 9-, 1·9 g. (0·0075 mole); total, 4·0 g. (0·016 mole, 17%).

Preparation of Reference Compounds.—*1-Phenylphenanthrene.* γ-1-Naphthyl-γ-oxobutyric acid [26] was reduced by Huang-Minlon's modification of the Wolff–Kishner method [27] to γ-1-naphthylbutyric acid which was cyclised by treatment with phosphorus pentachloride and stannic chloride.[28] The resultant 1,2,3,4-tetrahydro-1-oxophenanthrene (9·7 g.), dissolved in ether, was added to ethereal phenyl-lithium, prepared from bromobenzene (11 g.) and lithium (1 g.), and the mixture was stirred at room temperature for 1·5 hr. then decomposed with ammonium chloride solution. After being washed with water and dried ($MgSO_4$), the ether layer was evaporated, and the residue crystallised from benzene–hexane. 1,2,3,4-Tetrahydro-1-hydroxy-1-phenylphenanthrene (10·7 g., 79%) occurred in prisms, m. p. 112—115° (lit.,[29] m. p. 115—115·5°). When heated under reduced pressure the carbinol was dehydrated to 3,4-dihydro-1-phenylphenanthrene (10·2 g.), b. p. 264°/10 mm., which was fused with sulphur (1·4 g.) at 300° for 1 hr. The crude product was chromatographed in hexane on alumina.

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[26] Newman, Taylor, Hodgson, and Garrett, *J. Amer. Chem. Soc.*, 1947, **69**, 1784.

[27] Wilds and Werth, *J. Org. Chem.*, 1952, **17**, 1154; Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

[28] Wilds, quoted by W. S. Johnson, *Org. Reactions*, 1944, **2**, 114.

[29] Bachmann and Wilds, *J. Amer. Chem. Soc.*, 1938, **60**, 624.

Evaporation of the first fractions (4 × 100 ml.) yielded 1-phenylphenanthrene which crystallised from ethanol in needles (7·2 g., 73% from the alcohol), m. p. 79·5—80·5° (lit.,[29] m. p. 79—79·5°), $\lambda_{max.}$ 258, 300, 334, 343, and 350 mμ (ε 60,090, 15,500, 390, 250, and 287 respectively). The *trinitrobenzene complex* crystallised from ethanol in bright yellow needles, m. p. 134—136° with a transition into a second crystal form, m. p. 139—140° (Found: N, 9·1. $C_{26}H_{17}N_3O_6$ requires N, 9·0%). A complex was also obtained with 2,4,7-trinitrofluorenone. When oxidised with chromium trioxide in acetic acid, 1-phenylphenanthrene was converted in good yield into 1-phenylphenanthra-9,10-quinone, orange plates (from acetic acid), m. p. 228° (lit.,[30] m. p. 230—231°) (Found: C, 84·0; H, 4·4. Calc. for $C_{20}H_{12}O_2$: C, 84·5; H, 4·3%).

2-*Phenylphenanthrene.* Because of its strong adsorption on alumina and its relatively low solubility, pure 2-phenylphenanthrene was readily isolated from the free-radical reaction mixture. It crystallised from ethanol in plates, m. p. 194° (lit.,[31] m. p. 196·6—197·2°), $\lambda_{max.}$ 270 (ε 65,700) and 292 mμ (ε 26,000). The trinitrobenzene complex formed yellow plates (from ethanol), m. p. 154·5—155·5° (lit.,[31] m. p. 156—157°), and 2-phenylphenanthraquinone crystallised from acetic acid in deep red plates, m. p. 218° (lit.,[31] m. p. 220—221°).

α-(4-*Biphenylyl*)-o-*nitrocinnamic acid.* 4-Biphenylylacetic acid[32] (7 g.; m. p. 161—162°), triethylamine (4·6 ml.; redistilled), *o*-nitrobenzaldehyde (5 g.), and acetic anhydride (20 ml.) were boiled under reflux for 1·5 hr. The excess of anhydride was decomposed by addition of water (6 ml.) in acetic acid (20 ml.) to the hot reaction mixture, which was then set aside in the refrigerator overnight. The mother-liquor was decanted, and the crude residue (A) washed with acetic acid. The liquors deposited a yellow powder (1·8 g.). The residue (A) was washed with hot toluene to remove a dark brown impurity and then crystallised from acetic acid, a crude product (5·1 g.), m. p. 195—215°, being obtained. When the combined solids were dissolved in a large volume of acetic acid and allowed to crystallise very slowly there was precipitated a mixture of light and dark yellow crystals which were separated by hand-picking. The mother-liquor on slow evaporation yielded further batches of light yellow material. Recrystallisation of the dark yellow material from toluene and from acetic acid yielded prisms (3·6 g., 32%), m. p. 231°, of cis-α-(4-*biphenylyl*)-o-*nitrocinnamic acid* (Found: C, 73·1; H, 4·7; N, 4·0. $C_{21}H_{15}NO_4$ requires C, 73·0; H, 4·4; N, 4·1%), $\lambda_{max.}$ 277 mμ (ε 21,650). The trans-*acid* (3·0 g., 26%) crystallised from toluene or acetic acid in pale yellow prisms, m. p. 231° (Found: C, 72·8; H, 4·5; N, 4·2%); $\lambda_{max.}$ 250 mμ (ε 25,000).

Both isomers when separately irradiated in ethanolic solution with ultraviolet light were converted into the same equilibrium mixture containing mainly the *cis*-acid. In subsequent experiments the two isomers were separated by preparation of the ammonium salts. The salt of the *cis*-acid is readily soluble in water whereas that of the *trans*-acid is relatively insoluble.

trans-o-*Amino*-α-(4-*biphenylyl*)*cinnamic acid.* The foregoing *trans*-nitro-acid (0·95 g.) was dissolved in hot aqueous 0·2N-ammonia (70 ml.), and a solution of ferrous sulphate (7 g.) in water (30 ml.) was stirred in. The mixture was then immersed in a water-bath at 90° and stirred vigorously while concentrated aqueous ammonia (15 ml.) was added dropwise. After 1 hr. the hot solution was filtered through Celite, and the crude product was precipitated by acidification of the cooled filtrate with acetic acid. Further quantities of amino-acid were obtained by extraction of the residue with hot ethanol. The combined solids were purified *via* the ammonium salt, and crystallised from methanol. trans-o-*Amino*-α-(4-*biphenylyl*)-*cinnamic acid* formed pale yellow plates (0·59 g., 68%), m. p. 216—217° (Found: C, 80·0; H, 5·5; N, 4·5. $C_{21}H_{17}NO_2$ requires C, 80·0; H, 5·4; N, 4·4%).

3-(4-*Biphenylyl*)*quinolin*-2-*ol.* (*a*) *cis*-α-(4-Biphenylyl)-*o*-nitrocinnamic acid (0·50 g.) was reduced as above with ferrous sulphate (5 g.) and concentrated aqueous ammonia (13 ml.). After filtration of the mixture the residue was washed with hot water, then dissolved in hot glacial acetic acid containing a drop of sulphuric acid. Dilution of the solution with water yielded the crude product, which was crystallised from acetic acid (charcoal) and from dioxan. The *quinolinol* (0·38 g., 89%) formed needles, m. p. 334° (Found: C, 85·0; H, 5·0; N, 4·6. $C_{21}H_{15}NO$ requires C, 84·8; H, 5·1; N, 4·7%).

(*b*) The quinolinol was precipitated quantitatively when a hot ethanolic solution of the *trans*-amino-acid was irradiated with ultraviolet light.

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[30] Fuson and Tomboulian, *J. Amer. Chem. Soc.*, 1957, **79**, 956.

[31] Newman, *J. Org. Chem.*, 1944, **9**, 518.

[32] Long and Henze, *J. Amer. Chem. Soc.*, 1941, **63**, 1939; Schwenk and Papa, *J. Org. Chem.*, 1946, **11**, 798.

(*c*) *trans-o*-Amino-α-(4-biphenylyl)cinnamic acid (0·15 g.) was refluxed in acetic acid (2 ml.) and sulphuric acid (0·2 ml.) for 1 hr., cooled, and poured into water. Crystallisation of the precipitate from acetic acid yielded pure 3-(4-biphenylyl)quinolin-2-ol (60 mg., 43%), m. p. and mixed m. p. 334°.

3-*Phenyl*-10-*phenanthroic acid*. *trans-o*-Amino-α-(4-biphenylyl)cinnamic acid (1·2 g.) in ethanol (100 ml.) and concentrated hydrochloric acid (2·0 ml.) was stirred at room temperature while isopentyl nitrite (0·6 ml.) was added dropwise. There was a deep yellow coloration, and the formation of the diazonium salt was confirmed by the production of a pink azo-dye with alkaline, aqueous β-naphthol. After 5 min. the solution was treated with copper bronze (2 g.), and there was an immediate evolution of nitrogen. The mixture was warmed to complete the reaction and the product was separated by formation of the soluble sodium salt. 3-*Phenyl*-10-*phenanthroic acid* (1·0 g., 88%), which was precipitated as a white solid, m. p. 233°, by the addition of hydrochloric acid, crystallised from acetic acid in needles, m. p. 235—236° (Found: C, 83·8; H, 4·8. $C_{21}H_{14}O_2$ requires C, 84·5; H, 4·7%).

3-*Phenylphenanthrene*. The foregoing acid (1·1 g.) was refluxed in quinoline (100 ml.) with copper bronze (2 g.) for 1 hr., and the mixture was cooled, diluted with ether, and filtered. The quinoline was removed by extraction with acid, and the crude product isolated by evaporation of the ethereal solution. 3-Phenylphenanthrene (0·85 g., 91%) crystallised from ethanol in long, flat needles, m. p. 70°, raised by recrystallisation to m. p. 76° (lit.,[24] m. p. 73°) (Found: C, 94·4; H, 5·6. Calc. for $C_{20}H_{14}$: C, 94·5; H, 5·5%), $\lambda_{max.}$ 262 (ε 53,900) and 304 mμ (ε 19,700). It formed a *complex* with trinitrobenzene which crystallised from ethanol in orange needles, m. p. 125—126°, with a transition to a second form, m. p. 129—130° (Found: N, 9·1. $C_{26}H_{17}N_3O_6$ requires N, 9·0%). 3-Phenylphenanthraquinone, obtained by oxidation of the hydrocarbon with chromium trioxide in acetic acid, crystallised from acetic acid in yellow needles, m. p. 207—208° (lit.,[24] m. p. 210°) (Found: C, 84·9; H, 4·3. Calc. for $C_{20}H_{12}O_2$: C, 84·5; H, 4·3%).

4-*Phenylphenanthrene*. γ-2-Naphthyl-γ-oxobutyric acid[26,33] was converted into 1,2,3,4-tetrahydro-4-oxophenanthrene as described for the 1-oxo-compound, and 4-phenylphenanthrene was then prepared according to Campbell's method.[34] The product, which was purified by chromatography on alumina, crystallised from ethanol in fine needles, m. p. 80·5—81·5° (lit.,[34] m. p. 80—81°). It had ultraviolet light absorption in ethanol identical with that recorded by Campbell,[34] and formed a complex in ethanol solution with 2,4,7-trinitrofluorenone but not with picric acid or trinitrobenzene. 4-*Phenylphenanthraquinone*, obtained by oxidation of the hydrocarbon with chromium trioxide in acetic acid, crystallised from aqueous acetic acid in orange plates, m. p. 196—197° (Found: C, 84·4; H, 4·4. $C_{20}H_{12}O_2$ requires C, 84·5; H, 4·3%).

9-*Phenylphenanthrene*. A sample of 9-cyclohex-1′-enylphenanthrene (kindly given by Dr. T. M. Spotswood) was dehydrogenated by heating with sulphur. 9-Phenylphenanthrene crystallised from ethanol in plates, m. p. 106°, $\lambda_{max.}$ 257, 288, 299, 335, 343, and 350 mμ (ε 58,700, 12,200, 13,370, 383, 262, and 308, respectively). The *trinitrobenzene complex* crystallised from ethanol in bright yellow needles, m. p. 108·5—109·5° (Found: N, 9·1. $C_{21}H_{17}N_3O_6$ requires N, 9·1%).

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