801. *Syntheses of* 1-*Phenylfluorene and* 1- *and* 3-*Phenylphenanthrene.*

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and (the late) W. H. Stafford.

The syntheses of these hydrocarbons and of *m*-terphenyl are reported. The spectra of these and related compounds are discussed.

2-Benzylideneindan-1-one (I) and ethyl acetoacetate with one mole of sodium ethoxide failed to yield the expected ethyl 1,2,3,9a-tetrahydro-3-oxo-1-phenylfluorene-2-carboxylate (a derivative of III), but gave instead an ester in which the 4,4a double bond had moved to the 4a,9a-position. An infrared band at 1670 cm.$^{-1}$ was shown not to be due to a conjugated carbonyl group [1] by the absence of an absorption band at 280—300 mμ such as is found in the spectrum of 3,5-diphenylcyclohex-2-en-1-one (XI). The structure of this and related esters will be discussed later.

The ester when heated with sulphuric acid, acetic acid, and water afforded 1,2,3,4-tetrahydro-3-oxo-1-phenylfluorene (II), whose constitution follows from the similarity of its ultraviolet spectrum to those of β-methylstyrene and indene,[2a, b] and from a single infrared band at 1716 cm.$^{-1}$ denoting an unconjugated carbonyl group.[3] Slightly different conditions but no distillation yielded the isomeric 1,2,3,9a-tetrahydro-3-oxo-1-phenylfluorene (III), whose constitution follows from the similarity of its ultraviolet spectrum to that of benzylideneacetone [4a] and from infrared bands at 1650 cm.$^{-1}$ (with shoulder at 1670 cm.$^{-1}$ which is resolved into a peak at 1672 cm.$^{-1}$ by the use of hexachlorobutadiene) and 1622 cm.$^{-1}$. These are attributed to the conjugated carbonyl and ethylenic groups in the fragment CH:CH·CO· and are comparable with the carbonyl absorption band at 1650 cm.$^{-1}$ in benzylideneacetophenone and the ethylenic band at 1620 cm.$^{-1}$ in benzylideneindanone.[5] Similar instances of isomerism of unsaturated cyclic ketones have been reported,[4a, b] but whereas in some of these at least, double-bond migration is effected by alkali we found that mere distillation was sufficient to convert the αβ-isomer (III) partially into the βγ-isomer (II). Reduction of the ketone (III) with lithium aluminium hydride gave 1,2,3,9a-tetrahydro-3-hydroxy-1-phenylfluorene (IV),[6] which yielded 1-phenylfluorene (V; CH_2 instead of CO) by dehydration and dehydrogenation with sulphur. The structure of this compound was confirmed by oxidising it to 1-phenylfluorenone (V) [absorption at 1706 cm.$^{-1}$ comparable to 1718 cm.$^{-1}$ in fluorenone [7]].

By a similar series of reactions 2-benzylidenetetral-1-one yielded 1,2,3,9,10,10a-hexahydro-3-oxo-1-phenylphenanthrene (VI; R = Ph), absorbing at 1660 cm.$^{-1}$, reduced by

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[1] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1956, p. 118.

[2] (*a*) Campbell, Linden, Godshalk, and Young, *J. Amer. Chem. Soc.*, 1947, **69**, 880; (*b*) Ramart-Lucas and Amagat, *Bull. Soc. chim. France*, 1932, **51**, 119.

[3] Ref. 1, p. 116.

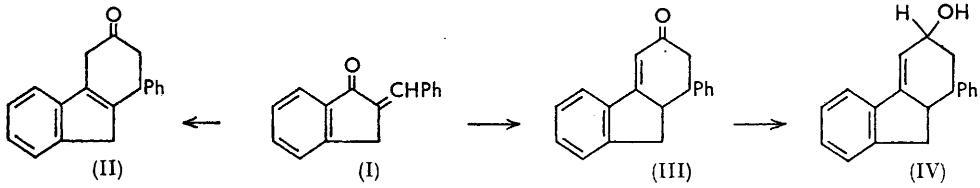
[4] (*a*) Robinson *et al.*, *J.*, 1936, 752, 759; (*b*) Köster, *Ber.*, 1944, **77**, 553.

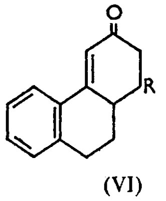
[5] Hassner and Cromwell, *J. Amer. Chem. Soc.*, 1958, **80**, 896.

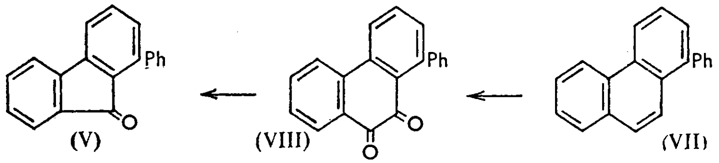
[6] Cf. Keene and Schofield, *J.*, 1958, 1080.

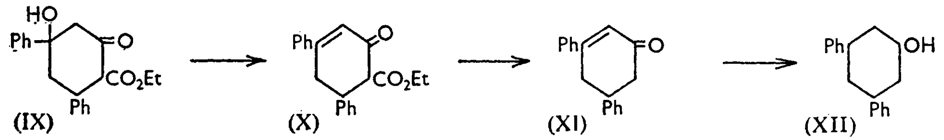
[7] Bergmann and Pinchas, *J. Chim. Phys.*, 1952, **49**, 537; Josien and Fuson, *Bull. Soc. chim. France*, 1952M, 389.

lithium aluminium hydride to the alcohol (VI; R = Ph, with CH·OH for CO), whose ultraviolet spectrum resembled that of cinnamyl alcohol.[2a] The ketone was converted by sulphur into 1-phenylphenanthrene (VII).[8]


(II) (I) (III) (IV)


(VI)


(V) (VIII) (VII)


(IX) (X) (XI) (XII)

The Mannich base 2-morpholinomethyltetral-1-one was methylated and condensed with ethyl acetoacetate. The resulting keto-ester when distilled under reduced pressure gave 1,2,3,9,10,10a-hexahydro-3-oxophenanthrene (VI; R = H), with a broad band at 1660 cm.$^{-1}$, which with phenylmagnesium bromide gave the corresponding alcohol. Dehydration and dehydrogenation of the alcohol with sulphur yielded 3-phenylphenanthrene. All the monophenylphenanthrenes have now been synthesised.

Chalkone and ethyl acetoacetate interact in the presence of bases to give, according to the experimental conditions,[9] a 1,5-diketone, the isomeric ethyl 4-hydroxy-2-oxo-4,6-diphenylcyclohexanoate (IX), absorbing at 1706 cm.$^{-1}$ (6-membered ring ketone), 1748 cm.$^{-1}$ (non-enolised β-keto-ester), and 3390 cm.$^{-1}$ (OH with bonding), and ethyl 2-oxo-4,6-diphenylcyclohex-3-enoate (X), absorbing at 1735 cm.$^{-1}$ (ethoxycarbonyl group), 1663 cm.$^{-1}$ (αβ-unsaturated ketone), and 287 mμ ($\text{Ph·CH⁚CH·CO·CH}_2\text{·}$ grouping). Hydrolysis and decarboxylation of the ester (X) gave 3,5-diphenylcyclohex-2-en-1-one (XI),[10] shown to be an αβ-unsaturated ketone by absorption at 285 mμ (log ε 4·27) and by an infrared band at 1657 cm.$^{-1}$. The compound (XI) when reduced to the alcohol (XII) and heated with sulphur yielded *m*-terphenyl.[11]

The absorption spectra of the phenylated hydrocarbons were compared with those of the parent hydrocarbons. The spectrum of 1-phenylfluorene resembles that of *m*-terphenyl but differs markedly from that of fluorene and 9-phenylfluorene (Fig. 1).[12] The spectra of fluorenone and 1-phenylfluorenone, however, display considerable similarity (Fig. 2). In the absence of data for other phenylated fluorenes and fluorenones discussion is not attempted.

Models show that the coplanarity of the rings in 1- and 9-phenylphenanthrene is opposed by steric interference and it might be expected that the spectra of these compounds [8,12]

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[8] Fuson and Tomboulian, *J. Amer. Chem. Soc.*, 1957, **79**, 956.
[9] Dieckmann and v. Fischer, *Ber.*, 1911, **44**, 966.
[10] Petrov, *Ber.*, 1929, **62**, 642.
[11] Gillam and Hey, *J.*, 1939, 1170.
[12] Bradsher and Wissow, *J. Amer. Chem. Soc.*, 1946, **68**, 2149.

would be similar to one another and to that of phenanthrene[13] but differient from those of 2- and 3-phenylphenanthrene.[14] There is indeed such similarity if allowance is made for the lack of fine structure in the phenyl-phenanthrenes (see Table), but this cannot be used as evidence for lack of conjugation since the spectra of 1- and 3-phenylphenanthrene (Fig. 3) are not very different. Evidently we are dealing with an instance of spectral conjugation without coplanarity.[15] The spectrum of 1-phenylphenanthraquinone[8] differs, however, from that of 3-phenylphenanthraquinone (Fig. 4).

FIG. 1.

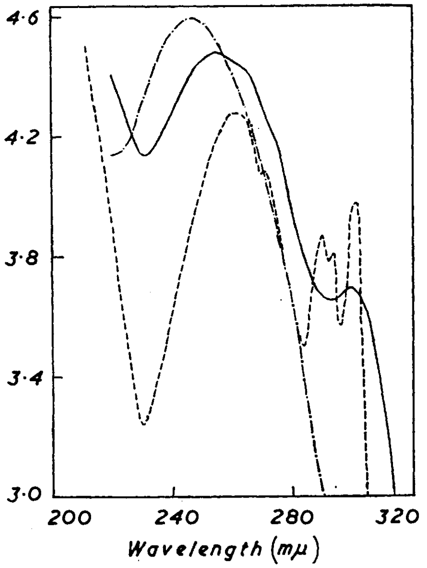

FIG. 2.

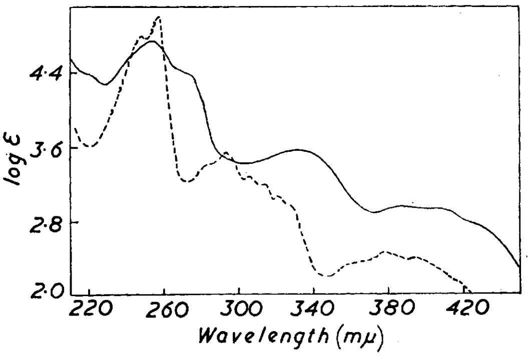

FIG. 1. *Ultraviolet absorption spectra, in ethanol, of fluorene* (– – – –), *1-phenylfluorene* (——), *and* m-*terphenyl* (— · — · —).

FIG. 2. *Ultraviolet absorption spectra, in ethanol, of fluorenone* (– – – –) *and 1-phenylfluorenone* (——).

FIG. 3.

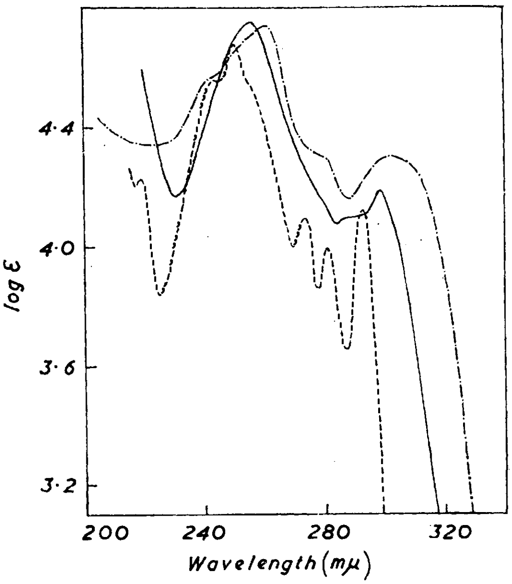

FIG. 4.

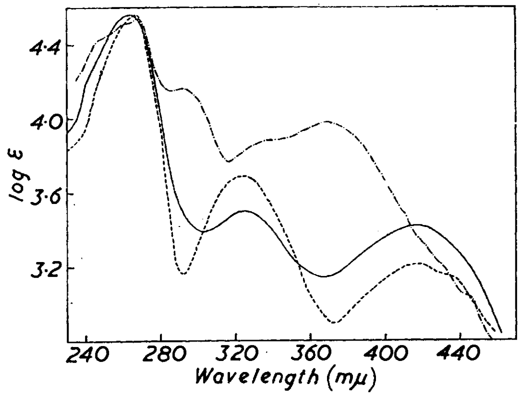

FIG. 3. *Ultraviolet absorption spectra, in ethanol, of phenanthrene* (– – – –), *1-phenylphenanthrene* (——), *and 3-phenylphenanthrene* (— · — · —).

FIG. 4. *Ultraviolet absorption spectra, in chloroform, of phenanthraquinone* (– – – –), *1-phenylphenanthraquinone* (——), *and 3-phenylphenanthraquinone* (— · — · —).

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[13] Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2021.

Spectra of Phenylphenanthrenes.

Position of Ph group	Unsub.[12] *	1[8]	2[14]	3	4[13]	9[11]
$\lambda_{max.}$ (mμ)	252	256	276	261	230	254
	293	298	291	302	258	298
	330					

* Highest peak.

4-Phenylphenanthrene[16] has a band at 230 mμ not observed in phenanthrene or the other phenylphenanthrenes, possibly a reflection of molecular overcrowding, and there are marked differences between the spectra of 2- and 3-phenylphenanthrenes although in these compounds the phenyl groups are free from steric interference.

EXPERIMENTAL

Ultraviolet spectra were measured with a Unicam SP. 500 quartz spectrophotometer and infrared spectra were obtained in Nujol mulls with a Hilger H 800 double-beam spectrometer. Ether extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The light petroleum had b. p. 60—80°.

1,2,3,4-*Tetrahydro*-3-*oxo*-1-*phenylfluorene*.—2-Benzylideneindan-1-one (50 g.), ethyl acetoacetate (30 g.), and ethanol (250 ml.) containing sodium ethoxide (from 5 g. of sodium) were boiled for 3 hr. and poured into water (1 l.) containing acetic acid (15 ml.). Extraction with ether and evaporation gave a syrup (*A*) and an *ester* (46 g.), m. p. 133—134° after crystallisation from light petroleum (Found: C, 79·5; H, 6·0. $C_{22}H_{20}O_3$ requires C, 79·5; H, 6·1%); $\lambda_{max.}$ 218 and 253 mμ (log ε 4·40 and 4·34), ν 1670, 1637, and 1600 cm.$^{-1}$. The ester (2 g.) was boiled for 3 hr. with acetic acid (10 g.), sulphuric acid (8 g.), and water (8 g.) and the mixture then poured into water. The resulting yellow oil when triturated with ether yielded a polymer of 2-benzylideneindan-1-one probably the *dimer*, m. p. 244—245° (Found: C, 87·3; H, 5·8. $C_{32}H_{24}O_2$ requires C, 87·3; H, 5·5%). Evaporation of the ether extract gave a residue which when distilled at 230°/0·1 mm. yielded 1,2,3,4-*tetrahydro*-3-*oxo*-1-*phenylfluorene* as plates, m. p. 115°, from light petroleum; $\lambda_{max.}$ 261 mμ (log ε 4·12) in ethanol (Found: C, 87·5; H, 6·3. $C_{19}H_{16}O$ requires C, 87·7; H, 6·2%). The 2,4-*dinitrophenylhydrazone* formed red prisms, m. p. 236—237°.

1,2,3,9*a*-*Tetrahydro*-3-*oxo*-1-*phenylfluorene*.—The above ester (45 g.) was boiled (40 min.) with acetic acid (180 ml.), sulphuric acid (90 ml.), and water (45 ml.), and the mixture poured into water. Extraction with ether and evaporation of the ether gave 1,2,3,9*a*-*tetrahydro*-3-*oxo*-1-*phenylfluorene* (25 g.) as elongated plates (from light petroleum), m. p. 117—118° (depressing the m. p. of the isomer); $\lambda_{max.}$ 235, 291, and 313 mμ (log ε 3·98, 4·24, and 4·24) in ethanol (Found: C, 87·7; H, 6·2%). Some of the compound was obtained by similar hydrolysis and decarboxylation of the syrup (*A*). The 2,4-*dinitrophenylhydrazone* had m. p. 236—237°, not depressed when admixed with the dinitrophenylhydrazone obtained from the isomer (Found: C, 68·4; H, 4·5. $C_{25}H_{20}O_4N_4$ requires C, 68·2; H 4·4%). Distillation of the oxo-compound at 250°/0·01 mm. and recrystallisation of the distillate from ethanol–light petroleum gave mainly unchanged compound, but evaporation of the mother liquors yielded rectangular and hexagonal plates. The latter were separated by extraction with a little ether and afforded the isomeric βγ-unsaturated ketone, m. p. and mixed m. p. 115°.

1-*Phenylfluorene*.—Lithium aluminium hydride (1·4 g.) in ether was added to the ketone (III) (13·4 g.) in ether (250 ml.) and benzene (50 ml.), and the mixture was boiled (5 min.). Ammonium chloride solution was added; the ethereal layer on evaporation gave 1,2,3,9*a*-*tetrahydro*-3-*hydroxy*-1-*phenylfluorene* (11·5 g.) as needles, m. p. 100—101°, after trituration with light petroleum and crystallisation from benzene (Found: C, 87·2; H, 6·8. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%). This had a broad hydroxyl band at 3400—3100 cm.$^{-1}$ due to considerable hydrogen bonding. The alcohol (5·2 g.) was heated at 220° with sulphur (0·75 g.) for 3 hr., and the residue was chromatographed in light petroleum–benzene on alumina (200 g.). Development with light petroleum–benzene yielded 1-*phenylfluorene* (3·3 g.) as needles (from ethanol–light petroleum), m. p. 48° (Found: C, 94·2; H, 5·6. $C_{19}H_{14}$ requires C, 94·2; H, 5·8%); $\lambda_{max.}$

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[14] Miller and Mann, *J.*, 1951, **73**, 45.

[15] Turner *et al.*, *J.*, 1952, 854.

[16] Campbell, *J.*, 1954, 3659.

255 and 300 mμ (log ε 4·49 and 3·70) in ethanol. 1-Phenylfluorene (0·5 g.) was oxidised by chromium trioxide and acetic acid to 1-*phenylfluorenone* (0·1 g.), yellow needles (from ethanol), m. p. 120° (Found: C, 88·7; H, 4·7. $C_{19}H_{12}O$ requires C, 89·0; H, 4·7%); $\lambda_{max.}$ 253, 330, 385—390 mμ (log ε 4·74, 3·56, and 2·95) in 95% ethanol.

1,2,3,9,10,10*a-Hexahydro*-3-*oxo*-1-*phenylphenanthrene*.—A solution of 2-benzylidenetetral-1-one (100 g.) and ethyl acetoacetate (58·9 g.) in ethanol (600 ml.) containing sodium ethoxide (from 10 g. of sodium) was boiled for 4 hr. and worked up as above to give a syrup (B) and an *ester* (85 g.), pale yellow prisms, m. p. 141°, from light petroleum–ethyl acetate (Found: C, 79·5; H, 6·5. $C_{23}H_{22}O_3$ requires C, 79·7; H, 6·4%); $\lambda_{max.}$ 220 and 254 mμ (log ε 4·46 and 4·32); ν 1675, 1647, and 1627 cm.$^{-1}$. The ester (85 g.), acetic acid (320 g.), sulphuric acid (160 ml.), and water (80 ml.) were boiled (15 min.) and treatment as above yielded 1,2,3,9,10,10a-*hexahydro*-3-*oxo*-1-*phenylphenanthrene* (47 g.), also obtained (13 g.) by the hydrolysis and decarboxylation of syrup B; it formed pale yellow rhombs (from light petroleum–benzene), m. p. 99° (Found: C, 87·7; H, 6·8. $C_{20}H_{18}O$ requires C, 87·6; H, 6·6%); $\lambda_{max.}$ 229 and 300 mμ (log ε 4·03 and 4·32) in ethanol. The 2,4-*dinitrophenylhydrazone* formed red prisms, m. p. 272—274° (Found: C, 68·9; H, 4·9; N, 12·4. $C_{26}H_{22}O_4N_4$ requires C, 68·7; H, 4·9; N, 12·3%). A solution of the ketone (30 g.) in ether (400 ml.) and benzene (100 ml.) was boiled (10 min.) with lithium aluminium hydride (1·5 g.) in ether (100 ml.) yielding the *hexahydro*-3-*hydroxyphenanthrene* (30 g.), needles (from benzene), m. p. 120°, which loses benzene when heated (Found: C, 87·8; H, 7·4. $C_{20}H_{20}O,C_6H_6$ requires C, 88·1; H, 7·4%); $\lambda_{max.}$ 257, 288 (infl.), and 298 mμ (infl.) (log ε 4·12, 3·35, and 3·20).

1-*Phenylphenanthrene*.—The alcohol (5·5 g.) was heated at 220° (3 hr.) with sulphur (1·4 g.); the residue when chromatographed in light petroleum–benzene on alumina (200 g.) afforded 1-phenylphenanthrene (3·5 g.), plates, m. p. 79° (lit.,[17] m. p. 79—79·5°); $\lambda_{max.}$ 256 and 298 mμ (log ε 4·75 and 4·19). The picrate had m. p. 117° (lit.,[17] m. p. 117—117·5°), the quinone, m. p. 230—231° (lit.,[8] m. p. 230—231°); $\lambda_{max.}$ 264, 325, and 415 mμ (log ε 4·56, 3·50, and 3·42) in chloroform, whose azine absorbed at 255, 280 (infl.), 298, 311, 365, and 382 mμ (log ε 4·85, 4·63, 4·06, 4·06, 4·07, and 4·11). The quinone (0·5 g.) was heated with 10% aqueous ethanolic potassium hydroxide in a stream of air until it dissolved. The solution was acidified, extracted with ether, and the ethereal layer shaken with sodium carbonate solution. The aqueous layer with hydrochloric acid yielded 9-hydroxy-1-phenylfluorene-9-carboxylic acid, which was heated at 220—230° until evolution of gas ceased. The resulting brown oil was heated (1 min.) with chromium trioxide ("AnalaR"; 0·4 g.) in acetic acid and the solvent then evaporated under reduced pressure. The residue was shaken with ether and water; evaporation of the ethereal layer gave a yellow oil which after chromatographic purification gave 1-phenylfluorenone, m. p. and mixed m. p. with the above sample, 120°.

3-*Phenylphenanthrene*.—A solution of α-tetralone (25 g.), morpholinium chloride (22 g.), and paraformaldehyde (8 g.) in ethanol (35 ml.) was boiled (2 hr.). Addition of ether precipitated 2-*morpholinomethyltetral*-1-*one hydrochloride* (39 g.), prisms (from ethanol), m. p. 153—154° (Found: C, 63·9; H, 7·1. $C_{15}H_{20}O_2NCl$ requires C, 64·0; H, 7·2%). The hydrochloride (42 g.) was treated with 4N-sodium hydroxide (150 ml.) saturated with potassium chloride. Extraction with ether and evaporation of the solvent afforded the free base which with acetone (50 ml.) and methyl iodide yielded the *methiodide* (37 g.), plates (from aqueous ethanol), m. p. 200—202° (Found: C, 49·9; H, 5·8. $C_{16}H_{22}O_2NI$ requires C, 49·8; H, 5·5%). A solution of the methiodide (10 g.) and ethyl acetoacetate (3·5 g.) in ethanol (50 ml.) containing sodium ethoxide (from 1·25 g. of sodium) was boiled for 3 hr. and then poured into water (150 ml.) containing acetic acid (3 ml.). Extraction with ether, evaporation of the solvent, and distillation at 180—190°/0·1 mm. gave a syrup which eventually partially crystallised. Separation of the solid and crystallisation from light petroleum gave 1,2,3,9,10,10a-*hexahydro*-3-*oxophenanthrene*, needles (0·5 g.), m. p. 80—81° (Found: C, 84·1; H, 7·2. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%); $\lambda_{max.}$ 228 and 297 mμ (log ε 4·04 and 4·33) in ethanol, ν 1660 cm.$^{-1}$. The 2,4-*dinitrophenylhydrazone* formed red prisms, m. p. 234—236° (Found: C, 63·8; H, 4·9; N, 14·4. $C_{20}H_{18}O_4N_4$ requires C, 63·5; H, 4·8; N, 14·8%). The ketone (3·5 g.) in ether (20 ml.) was added to phenylmagnesium bromide (from 4·5 g. of bromobenzene) in ether (20 ml.) and the mixture boiled (15 min.). The solution was poured onto ice and 2N-sulphuric acid; the ethereal layer on evaporation gave a syrup (3·9 g.) which was heated with sulphur (1·1 g.) at 220° for 2 hr. The residue in benzene–light petroleum was chromatographed on alumina (200 g.); elution with

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

light petroleum–benzene gave 3-*phenylphenanthrene*, m. p. 73° (Found: C, 94·3; H, 5·3. $C_{20}H_{14}$ requires C, 94·5; H, 5·5%); $\lambda_{max.}$ 261 and 302 mμ (log ε 4·74 and 4·30), after purification through the *dipicrate*, m. p. 120—121° (Found: C, 56·0; H, 2·9; N, 11·5. $C_{32}H_{20}O_{12}N_6$ requires C, 56·1; H, 2·9; N, 12·3%). Oxidation of the hydrocarbon with chromium trioxide and acetic acid gave the *quinone*, orange needles (from acetic acid), m. p. 210° (Found: C, 84·7; H, 4·5. $C_{20}H_{12}O_2$ requires C, 84·5; H, 4·3%); $\lambda_{max.}$ 268, 293, and 368 mμ (log ε 4·54, 4·16, and 3·99) in chloroform, which with *o*-phenylenediamine yielded the *quinoxaline*, pale yellow needles (from benzene–light petroleum), m. p. 227—228° (Found: C, 87·1; H, 4·7; N, 7·1. $C_{26}H_{16}N_2$ requires C, 87·8; H, 4·5; N, 7·9%); $\lambda_{max.}$ 262, 285, 303, 316, 379, and 399 mμ (log ε 4·80, 4·73, 4·42, 4·36, 4·29, and 4·37) in ethanol.

m-*Terphenyl*.—3,5-Diphenylcyclohex-2-en-1-one, $\lambda_{max.}$ 285 mμ (log ε 4·27), $\lambda_{min.}$ 245 mμ (log ε 3·51) [2,4-*dinitrophenylhydrazone*, red needles (from acetic acid), m. p. 223° (Found: N, 12·8. $C_{24}H_{20}O_4N_4$ requires N, 13·1%), and *hydrazone*, needles (from ethanol), m. p. 163° (Found: C, 81·3; H, 6·8. $C_{18}H_{18}N_2$ requires C, 82·4; H, 6·9%)], was reduced at room temperature by hydrogen (40 lb./sq. in.) to 3,5-diphenylcyclohexanol, needles (from light petroleum), m. p. 111° (lit.,[10] m. p. 127°) (Found: C, 85·4; H, 8·0. Calc. for $C_{18}H_{20}O$: C, 85·7; H, 8·0%), absorbing at 3260 cm.$^{-1}$ (OH with strong hydrogen bonding). This was oxidised by chromic acid and acetic acid to the diphenylcyclohexanone, m. p. 140°, (lit.,[10] m. p. 139—140°) and yielded *m*-terphenyl when dehydrated by phosphoric oxide in boiling xylene, and the xylene layer heated with chloranil. *m*-Terphenyl was advantageously prepared by boiling the diphenylcyclohexenone (5·6 g.) in ether (100 ml.) and benzene (20 ml.) for 10 min. with lithium aluminium hydride (1 g.) in ether (90 ml.). Ammonium chloride solution was added; the ether layer on evaporation yielded an oil (4·4 g.) which was heated with sulphur (1 g.) at 220° for 3 hr. The residue in light petroleum was chromatographed on alumina (200 g.); elution with the same solvent afforded *m*-terphenyl (3·3 g.), m. p. 86°, $\lambda_{max.}$ 247 mμ (log ε 4·60), identical with a sample kindly supplied by Professor D. H. Hey, F.R.S.

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