

980. *The Synthesis of 1,7-Diphenylnaphthalene, 7-Phenyl-1-o-tolylnaphthalene, and 1,8-Diphenylnaphthalene.*

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The three hydrocarbons named in the title have been synthesised and shown to form solid complexes with benzotrifuroxan.

THE most effective organic reagents (acceptors) for the formation of charge-transfer complexes with aromatic compounds (donors) are those which are completely planar.¹ Suppression of complex formation can also occur because of an unfavourable steric arrangement in the donor molecule. *ortho*-Substituted dimethylanilines form less stable complexes than dimethylaniline,² and hexaethylbenzene forms very unstable complexes, association constants for this hydrocarbon being smaller than those for toluene.³ 1-Phenylnaphthalene, a non-planar molecule,^{4,5} has only given a solid complex with benzotrifuroxan,^{1,5} and 1,5-diphenylnaphthalene (Ia) failed to complex with this reagent.⁶ In order to extend these observations the preparation of 1,7-diphenylnaphthalene (Ib), 7-phenyl-1-*o*-tolylnaphthalene (Ic), and 1,8-diphenylnaphthalene (Id) was undertaken. After the completion of this work the syntheses of compounds (Ib) and (Id) were reported by House and his co-workers.⁷

¹ Bailey and Case, *Tetrahedron*, 1958, **3**, 113; Bailey, Henn, and Langdon, *ibid.*, 1963, **19**, 161.

² Ley and Pfeiffer, *Ber.*, 1921, **54**, 367; Ley and Grau, *ibid.*, 1925, **58**, 1765.

³ Foster, Hammick, and Parsons, *J.*, 1956, 555; Merrifield and Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

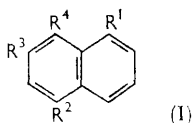
⁴ Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.

⁵ Orchin and Friedel, *J. Amer. Chem. Soc.*, 1949, **71**, 3002.

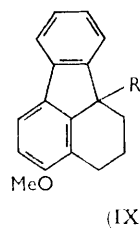
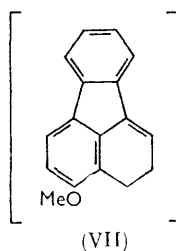
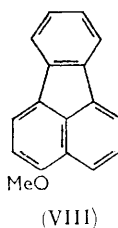
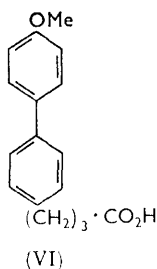
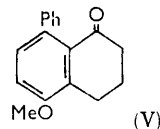
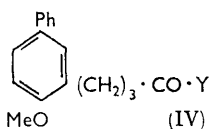
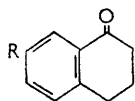
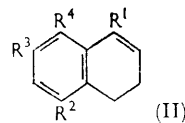
⁶ Bailey, *Canad. J. Chem.*, 1959, **37**, 541.

⁷ House, Magin, and Thompson, *J. Org. Chem.*, 1963, **28**, 2403.

1,7-Diphenylnaphthalene (Ib) was prepared from the known⁸ ketone (III; R = Ph) by reaction with phenylmagnesium bromide followed by dehydration, to give compound (IIb), and dehydrogenation;⁷ compound (Ic) was prepared similarly. 1,7-Diphenylnaphthalene appears to be polymorphic, the compound melting at 85° and at 93°; it is also the lowest melting of the ten diphenylnaphthalenes. In these properties it resembles 1,7-dimethylnaphthalene.⁹



- (a: R¹ = R² = Ph, R³ = R⁴ = H)
 (b: R¹ = R³ = Ph, R² = R⁴ = H)
 (c: R¹ = *o*-tolyl, R³ = Ph, R² = R⁴ = H)
 (d: R¹ = R⁴ = Ph, R² = R³ = H)
 (e: R¹ = R⁴ = Ph, R² = OMe, R³ = H)



Three routes to the 1,8-disubstituted naphthalene were examined. First, an attempt was made to utilise the method used for 1,8-dimethylnaphthalene.⁹ *o*-Phenylbenzotrile¹⁰ was converted into 2-biphenyl cyclohexyl ketone by treatment with cyclohexylmagnesium bromide. An attempt to prepare this ketone by reacting *o*-phenylbenzoyl chloride with cyclohexylzinc chloride¹¹ failed, fluorenone being formed by cyclisation of the acid chloride. 2-Biphenyl cyclohexyl ketone failed to react with ethyl bromoacetate (Reformatsky), with the lithium derivative of ethoxyacetylene,¹² and with ethynylmagnesium bromide.¹³ This approach was, therefore, abandoned.

Fieser¹⁴ reported the preparation of 1,2,3,4-tetrahydro-5-methoxy-1-oxo-8-phenylnaphthalene (V) in 15% yield by cyclisation of the acid (IV; Y = OH) with hydrogen fluoride. We have obtained this compound (m. p. 10° higher than reported by Fieser) in 4% yield only. The infrared spectrum of this ketone (see Experimental section) was in agreement with structure (V); the ultraviolet spectrum [λ_{max} . 206 (ϵ 31,300), 233 (ϵ 29,000), 323 (ϵ 4050); λ_{min} . 219 (ϵ 21,400), 287 (ϵ 920)] showed that there must be some interaction between the benzene nuclei of compound (V) [*m*-methoxyacetophenone has λ_{max} . 244 (ϵ 8500), 298 (ϵ 2800)].¹⁵ Since the yield of ketone was very small and the melting point of the product 10° different from the reported value, we considered the possibility that the acid (IV; Y = OH) was contaminated with some of the higher-melting isomer

⁸ Hey and Wilkinson, *J.*, 1940, 1030.

⁹ Bailey, Bryant, Hancock, Morrell, and Smith, *J. Inst. Petroleum*, 1947, **33**, 503; Evans and Smith, *ibid.*, 1953, **39**, 717.

¹⁰ Goldschmidt and Veer, *Rec. Trav. chim.*, 1948, **67**, 502.

¹¹ Shirley, *Org. Reactions*, 1954, **8**, 28.

¹² Arens, *Adv. Org. Chem.*, 1960, **2**, 202.

¹³ Jones, Skattebol, and Whiting, *J.*, 1956, 4765.

¹⁴ Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272.

¹⁵ Dearden and Forbes, *Canad. J. Chem.*, 1959, **37**, 1305.

(VI),¹⁶ and that the ketone obtained in small quantity was compound (III; R = *p*-methoxyphenyl) produced from compound (VI). A specimen of compound (VI) was prepared¹⁶ and cyclised (polyphosphoric acid) to give the ketone (III; R = *p*-methoxyphenyl) which was different from the ketone obtained from the acid (IV; Y = OH). The acid (IV; Y = OH) was unaffected by polyphosphoric acid¹⁷ at 120°; at higher temperatures¹⁸ a solid was obtained which melted over a range of 20°, contained no carbonyl group (infrared spectrum), and fluoresced strongly in solution. The material was probably a mixture of 3-methoxyfluoranthene (VIII) and the corresponding tetrahydro-derivative (IX; R = H) formed by cyclisation of compound (V) followed by disproportionation of compound (VII). Evans and Smith¹⁸ have observed similar reactions. The presence of 3-methoxyfluoranthene (VIII) in the material was indicated by the characteristic ultraviolet spectrum¹⁹ and the mixture was dehydrogenated to compound (VIII) identical (infrared spectrum) with an authentic sample. In another approach the acid chloride (IV; Y = Cl) was treated with diphenylcadmium forming the ketone (IV; Y = Ph). This compound was cyclised with polyphosphoric acid giving a small quantity of a compound which analysed for (IIe). The ultraviolet spectrum of compound (IIe) ought to have some relationship to that of 7,8-dihydro-1-methoxynaphthalene (II; R² = OMe, R¹ = R³ = R⁴ = H) [λ_{max} , 265 (ϵ 7820), 298 (ϵ 2130)],²⁰ with slight interaction between the benzene rings. The spectrum of the compound obtained was very similar to that of 2-methoxyfluorene (λ_{max} , 268, 301, and 310)²¹ and the compound is thought to be 4,5,6,6a-tetrahydro-3-methoxy-6a-phenylfluoranthene (IX; R = Ph) formed from compound (IIe) by a Bogart-Cook cyclisation.²² Structure (IX; R = Ph) is supported by the nuclear magnetic resonance spectrum of the compound, which shows the absence of an olefinic proton ($\tau = 4-6$) as required for structure (IIe). The compound contains 11 aromatic protons ($\tau = 2.4-3.2$) including one phenyl group (sharp peak at $\tau = 2.9$; 5H); 1 methoxy group ($\tau = 6.2$); 2 benzylic protons ($\tau = 6.9-7.6$, complex); and 4 aliphatic protons ($\tau = 8.0-8.8$, complex).

A synthesis of 1,8-diphenyl-naphthalene (Id) was finally accomplished from 1,4,5,8,9,10-hexahydro-1,4-dioxo-5-phenyl-naphthalene (X).²³ This compound was prepared as previously described from phenylbutadiene and *p*-benzoquinone;²³ on one occasion, instead of the expected compound (X), 5,8-dihydro-5-phenyl-1,4-naphthaquinone (XII) was obtained. The quinone (XII) was probably formed by oxidation of compound (X) with *p*-benzoquinone.²⁴ The spectral properties of the compound were in good agreement²⁴ with structure (XII) and this was confirmed by the reduction of compound (XII) to the known²⁵ quinol. During another preparation of compound (X) the anthraquinone (XIII)²⁶ was isolated, being formed by addition of phenylbutadiene to the naphthaquinone (XII). Reduction of compound (X) gave compound (XI) in good yield.²³ It was expected that the two carbonyl groups of compound (XI) would differ in reactivity and that the group at C-1 could be removed selectively, differences of this type being well known.^{23,27,28} With an excess of ethanedithiol the bis-adduct (XIV) was formed; using one equivalent of thiol and boron trifluoride-ether as catalyst,^{29,30} the monoadduct

¹⁶ Fieser and Bradsher, *J. Amer. Chem. Soc.*, 1936, **58**, 1738.

¹⁷ Uhlig and Snyder, *Adv. Org. Chem.*, 1960, **1**, 35.

¹⁸ Evans and Smith, *J.*, 1954, 798.

¹⁹ Stubbs and Tucker, *J.*, 1954, 227.

²⁰ Eastham and Larkin, *J. Amer. Chem. Soc.*, 1958, **80**, 2887.

²¹ Neish, *J. Org. Chem.*, 1951, **16**, 694; Korte and Behner, *Annalen*, 1959, **621**, 51.

²² Bergmann, *Chem. Rev.*, 1941, **29**, 531; Bergel and Morrisson, *Quart. Rev.*, 1948, **2**, 378.

²³ Robins and Walker, *J.*, 1958, 409.

²⁴ Strumza and Ginsburg, *J.*, 1961, 1505.

²⁵ Weizmann, Bergmann, and Haskelberg, *J.*, 1939, 391.

²⁶ Braude, Fawcett, and Webb, *J.*, 1954, 1049.

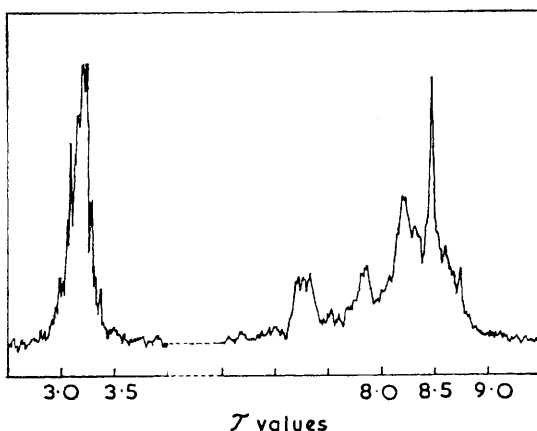
²⁷ Cole, Johnson, Robins, and Walker, *J.*, 1962, 244.

²⁸ Woodward, Bader, Bickel, Frey, and Kierstead, *Tetrahedron*, 1958, **2**, 1.

²⁹ Fieser and Romero, *J. Amer. Chem. Soc.*, 1953, **75**, 4716.

³⁰ Herz and Caple, *J. Amer. Chem. Soc.*, 1962, **84**, 3517.

(XV) was obtained in good yield. It softened at 153° and had m. p. $157\text{--}160^\circ$. In spite of the melting point range it appears to be free from the isomeric 4-ethylenethioketal. If this compound was an impurity in the 1-ethylenethioketal (XV) the 1,8-diphenylnaphthalene (Id) would have been contaminated with the high-melting 1,5-diphenylnaphthalene (Ia).⁶ An example of a thioketal softening and melting over a 5° range has been reported.³¹ The thioketal was desulphurised³² with W-2 Raney nickel³³ forming *cis-syn*-8-phenyl-1-decalone (XVI); the compound contained no olefinic protons (n.m.r. spectrum) and was identical (infrared spectrum) with the compound prepared by House and Thompson³⁴ from $\Delta^{8,9}$ -octal-1-one. This identity was confirmed by converting compound (XVI) into the known³⁴ *trans-anti*-8-phenyl-1-decalone. Examples of C:C reduction during



Nuclear magnetic resonance spectrum.

Raney nickel desulphurisation are known.^{32,35} Phenyl-lithium reacted with compound (XVI) to give a good yield of 1(*trans*)-hydroxy-*cis-syn*-1,8-diphenyldecalin (XVII). Phenyl-lithium would attack the "convex" face²⁸ of compound (XVI) giving (XVII) rather than the isomer (XVIII). This structure (XVII) is supported by the infrared spectrum of the compound which contained a very sharp band at 3570 cm.^{-1} ($\cdot\text{OH}$ group) in the solid (Nujol) showing the absence of hydrogen bonding; the n.m.r. spectrum (see Figure) contained a strong band (complex), $\tau = 3.15$ showing that the phenyl groups of compound (XVII) were shielding each other. 1,8-Diphenylnaphthalene (Id) has $\tau = 3.15$ for the aromatic protons.⁷ The hydroxyl group of compound (XVII) gave a sharp signal ($\tau = 8.48$) indicating an axial conformation.³⁶ Dehydration and dehydrogenation of the alcohol then gave 1,8-diphenylnaphthalene (Id), long (2 cm.) colourless needles, m. p. $150\text{--}151^\circ$; House⁷ describes the compound as pale yellow needles, m. p. $149.5\text{--}150.5^\circ$.

The ultraviolet spectra of compounds (Ib) and (Id) have been discussed.⁷ Comparison of the ultraviolet spectrum of compound (Ic) with that of compound (Ib) (see Experimental section) shows the greater steric hindrance to a planar configuration of an *o*-tolyl group in the 1-position of naphthalene as compared with a phenyl group.⁴

1,5-Diphenylnaphthalene (Ia) has not yielded any solid complex. Hot solutions of (Ia) and benzotrifuroxan (XIX) are yellow in colour but, on cooling, the hydrocarbon separates. The non-formation of a solid adduct must be caused by the two phenyl groups hindering the approach of the acceptor molecule to the naphthalene nucleus and by the fact that 1,5-diphenylnaphthalene (Ia) is very insoluble and highly crystalline.

³¹ Ireland and Schiess, *J. Org. Chem.*, 1963, **28**, 6.

³² Pettit and van Tamelen, *Org. Reactions*, 1962, **12**, 356.

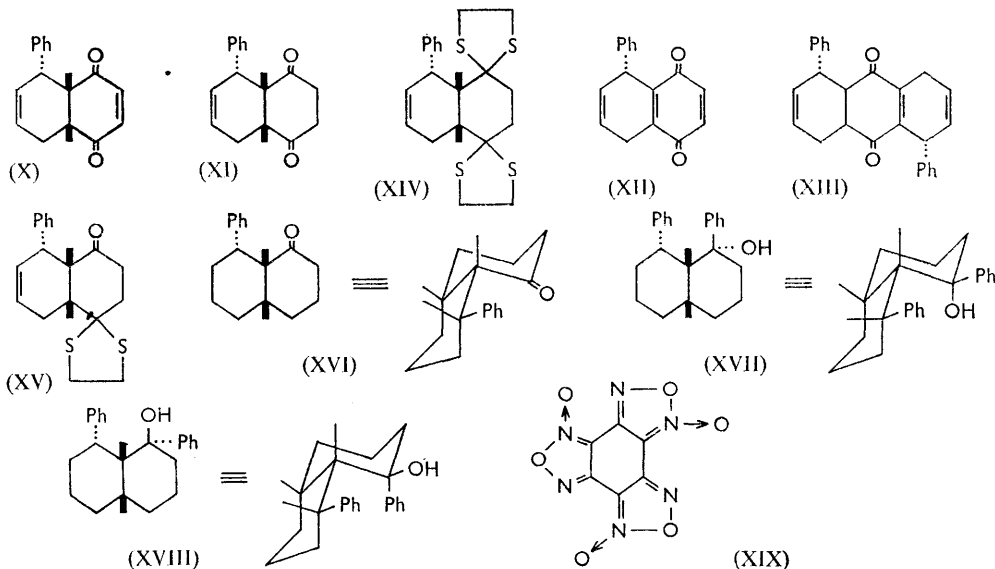
³³ Mozingo, *Org. Synth.*, Coll. Vol. III, p. 181.

³⁴ House and Thompson, *J. Org. Chem.*, 1963, **28**, 360.

³⁵ Hill and Martin, *Proc. Chem. Soc.*, 1959, 390.

³⁶ Garbisch and Patterson, *J. Amer. Chem. Soc.*, 1963, **85**, 3228.

1,7-Diphenylnaphthalene (Ib), 7-phenyl-1-*o*-tolyl-naphthalene (Ic) and 1,8-diphenylnaphthalene (Id) all gave crystalline 1:1 adducts with benzotrifuroxan (XIX). It is interesting that compound (Id), a hydrocarbon with both phenyl groups occupying α positions of the naphthalene nucleus, gives a complex whilst the isomer (Ia) also having phenyl groups attached to α positions of the naphthalene ring does not readily complex. It must be much easier for the acceptor to approach the naphthalene ring of (Id) as compared with that of (Ia).



Only 1,7-diphenylnaphthalene (Ib) formed a solid complex with 1,3,5-trinitrobenzene. This contained two molecules of trinitrobenzene to one of the hydrocarbon. In this respect 1,7-diphenylnaphthalene (Ib) is similar to 2-phenylnaphthalene (I; $R^3 = \text{Ph}$, $R^1 = R^2 = R^4 = \text{H}$) which forms a 1:1 adduct with benzotrifuroxan (XIX)¹ and a complex containing 2 trinitrobenzene:1 hydrocarbon.⁴

This difference in the ratio of acceptor to donor for compound (XIX) and TNB with derivatives of β -phenylnaphthalene is strange since molecules of compound (XIX) and trinitrobenzene must be similar in area. We hope to examine equilibrium constants for complex formation in solution to clarify this problem. This difference between compound (XIX) and trinitrobenzene in complex formation is known with other compounds. For example copper oxinate gives a 1:1 complex with benzotrifuroxan (XIX)³⁷ and complexes containing 2 molecules of acceptor with picryl azide, trinitrobenzene,³⁸ and benzotrifurazan.³⁹

The hydrocarbons (Ia), (Ib), and (Id) were examined on a Pye "Argon" chromatograph using a column of Q.F.1 on Gas-Chrom P at 135° (10 lb./sq. in. pressure) and showed the following relative retention times: (Id) 1.0; (Ia) 2.0; (Ib) 3.5. The thioketal (XV) gave a single peak on this column (retention time 31 min., temperature of column 158°).

EXPERIMENTAL

Ultraviolet spectra were measured in ethanol (λ in μ), n.m.r. spectra in deuteriochloroform. Petroleum refers to the fraction, b. p. 60–80°, unless otherwise stated.

3,4-Dihydro-1,7-diphenylnaphthalene (IIb).— β -*p*-Phenylbenzoylpropionic acid (m. p. 185–186°, reported⁸ m. p. 185°) was reduced by the Huang-Minlon method to γ -4-biphenylbutyric acid (m. p. 116–118°, reported⁸ m. p. 118–119°). The latter was cyclised with polyphosphoric acid (150°, 5 min.)¹⁷ and the neutral fraction chromatographed on alumina (grade H). Elution

³⁷ Bailey, Powell, Prout, Williams, and Wright, unpublished results.

³⁸ Bailey, Williams, and Wright, *J.*, in the press.

³⁹ Bailey and Evans, *Chem. and Ind.*, 1964, 1424.

with benzene-petroleum (1 : 1) gave the ketone (III; R = Ph) (80% yield, m. p. 68.5—69°, reported⁸ m. p. 69°). The 2,4-dinitrophenylhydrazone formed red plates from 2-methoxyethanol (m. p. 265—268° decomp.) (Found: C, 65.9; H, 4.4; N, 14.3. $C_{22}H_{18}N_4O_4$ requires C, 65.7; H, 4.5; N, 13.9%). 1,2,3,4-Tetrahydro-1-oxo-7-phenylnaphthalene (20 g.) in ether (200 ml.) was added to a solution of phenylmagnesium bromide (from 20 ml. of bromobenzene) and the mixture heated for 1 hr. The reaction was worked up in the usual way, the crude carbinol heated (water-bath) for 30 min. with formic acid (100 ml.; 95%), the formic acid evaporated *in vacuo*, and the residue steam-distilled for 1 hr. The non-volatile solid was collected, dried, and crystallised from petroleum (b. p. 100—120°). 3,4-Dihydro-1,7-diphenylnaphthalene formed rods, m. p. 132—133° (81% yield) Found: C, 93.3; H, 6.4. $C_{22}H_{18}$ requires C, 93.6; H, 6.4%, λ_{\max} . 250 (ϵ 48,600), λ_{\min} . 222 (ϵ 24,300). The trinitrobenzene adduct formed orange-red needles, m. p. 116°, from propanol (Found: C, 67.9; H, 4.2. $C_{26}H_{21}N_3O_6$ requires C, 67.9; H, 4.3%).

1,7-Diphenylnaphthalene (Ib).—3,4-Dihydro-1,7-diphenylnaphthalene (10 g.) was heated with palladium-charcoal (1 g., 30%)⁴⁰ at 200° (silicone bath) for 30 min. A slow stream of hydrogen was passed through the apparatus.⁹ The temperature of the bath was then raised to 250° for 30 min. The product was dissolved in chloroform, the catalyst filtered off, the solvent removed, and the residue crystallised from ethanol-benzene (1 : 1) giving white needles (8.1 g.) m. p. 80—81°. Two more crystallisations gave stout rods, m. p. 85—85.5°, resolidifying and having m. p. 91°. Recrystallisation from hexane gave needles, m. p. 93—93.5° (in agreement with House⁷) (Found: C, 94.3; H, 5.8. Calc. for $C_{22}H_{16}$: C, 94.25; H, 5.75%). The compound had λ_{\max} . 253 (ϵ 64,340), 300 (ϵ 13,400); λ_{\min} . 224 (ϵ 27,030), 276 (ϵ 8622).

The benzotrifuoxan complex, prepared in ethanol-acetic acid (4 : 1), formed lemon-yellow needles m. p. 152—154° (Found: C, 63.1; H, 3.1; N, 15.7. $C_{23}H_{16}N_6O_6$ requires C, 63.2; H, 3.0; N, 15.8%); the nitrobenzodifuoxan complex formed dark red needles, m. p. 122—122.5° (Found: C, 64.5; H, 3.4; N, 13.3. $C_{23}H_{17}N_5O_6$ requires C, 64.7; H, 3.3; N, 13.5%); the trinitrobenzene adduct (prepared in ethanol) formed yellow prisms, m. p. 96—97° (Found: C, 58.4, 58.1; H, 3.3, 3.3; N, 11.3, 11.8. $C_{22}H_{16} \cdot 2C_6H_3N_3O_6$ requires C, 57.8; H, 3.1; N, 11.9%).

3,4-Dihydro-7-phenyl-1-o-tolylnaphthalene (IIc).—1,2,3,4-Tetrahydro-1-oxo-7-phenylnaphthalene (10 g.) in benzene (100 ml.) was added to a solution of *o*-tolylmagnesium bromide (from *o*-bromotoluene, 11 g.) in ether (60 ml.). Ether was allowed to distil from this mixture until the temperature of the distillate reached 65°. The solution was refluxed and stirred for 20 hr., cooled, decomposed with ice and hydrochloric acid. The crude carbinol was dehydrated with formic acid and the product chromatographed on alumina (grade H, 300 g.). Elution with petroleum-benzene (1 : 1) gives the olefin, free from unchanged ketone (infrared spectrum). The compound formed prisms, m. p. 75°, from petroleum (54% yield) (Found: C, 93.2; H, 6.7. $C_{23}H_{20}$ requires C, 93.2; H, 6.8%), λ_{\max} . 248 (ϵ 48,030), λ_{\min} . 223 (ϵ 21,400).

7-Phenyl-1-o-tolylnaphthalene (Ic).—Dehydrogenation of the dihydro-compound gave the naphthalene as prisms (m. p. 59—60°) from ethanol (Found: C, 93.7; H, 6.2. $C_{23}H_{18}$ requires C, 93.8; H, 6.2%), λ_{\max} . 252 (ϵ 52,110) and 294 (ϵ 11,750), λ_{\min} . 227 (ϵ 24,890) and 273 (ϵ 8233). The benzotrifuoxan complex formed yellow needles, m. p. 134—135° (Found: C, 63.8; H, 3.5; N, 15.6. $C_{29}H_{18}N_6O_6$ requires C, 63.8; H, 3.3; N, 15.4%).

2-Biphenyl cyclohexyl Ketone.—*o*-Phenylbenzoic acid was converted into the corresponding cyanide,¹⁰ b. p. 168—170°/10 mm., m. p. 36° (von Braun⁴¹ reports m. p. 36°). *o*-Phenylbenzotrile (100 g.) dissolved in benzene (700 ml.) was slowly added to an ethereal solution of cyclohexylmagnesium bromide (170 ml. of cyclohexyl bromide; 500 ml. of ether). The ether was distilled from the reaction mixture, benzene (250 ml.) added, and the solution stirred and heated for 9 hr. To the cold mixture was added glacial acetic acid (250 ml.) and water (100 ml.), and the liquid was boiled (30 min.), cooled, and the organic layer separated. The aqueous phase was extracted with benzene, the benzene extracts combined, washed with sodium hydroxide solution, and dried ($MgSO_4$). Distillation afforded the ketone b. p. 135—140°/0.01 mm. (103 g.) (Found: C, 86.1; H, 7.6. $C_{19}H_{20}O$ requires C, 86.3; H, 7.6%); the infrared spectrum had a strong band at 1680 cm^{-1} (liquid film). The 2,4-dinitrophenylhydrazone formed orange prisms, m. p. 196—198°, from acetic acid (Found: C, 66.9; H, 5.6; N, 12.6. $C_{25}H_{24}N_4O_4$ requires C, 67.6; H, 5.4; N, 12.6%).

⁴⁰ Linstead, Millidge, Thomas, and Walpole, *J.*, 1937, 1146.

⁴¹ von Braun and Manz, *Annalen*, 1929, 468, 273.

A solution of cyclohexylmagnesium bromide was prepared from cyclohexyl bromide (21 ml.) in ether (60 ml.). To this was added a solution of fused zinc chloride (17 g.) in ether (400 ml.). Benzene (350 ml.) was added and the ether removed, the temperature of the distillate rising to 78°. A solution of *o*-phenylbenzoyl chloride (from 20 g. acid) in benzene (100 ml.) was added to the cyclohexylzinc chloride, the mixture refluxed (20 min.), cooled, and poured into ice (100 g.) and concentrated hydrochloric acid (50 ml.). After the usual working up the benzene was evaporated leaving a yellow solid (19 g., m. p. 83°) the infrared spectrum of which contained a strong band at 1710 cm^{-1} . The compound was fluorenone (mixed m. p. and infrared spectrum) (Found: C, 85.9; H, 4.4. Calc. for $\text{C}_{13}\text{H}_8\text{O}$: C, 86.6; H, 4.4%).

1,2,3,4-Tetrahydro-5-methoxy-1-oxo-8-phenyl-naphthalene (V).— β -(2-Methoxy-5-phenyl)-benzoylpropionic acid crystallised from aqueous acetic acid (m. p. 151°, Fieser¹⁵ reports m. p. 155°). A solution of this acid (5 g.) in diethylene glycol (30 ml.) containing potassium hydroxide (4 g.) and hydrazine hydrate (4 ml.) was heated under reflux for 2 hr., the mixture distilled (oil-bath) until the temperature of the liquid reached 180°. The temperature of the oil-bath was kept at 180–190° for 6 hr. The cold solution was then diluted with water (25 ml.) and poured into hydrochloric acid (15 ml.; 6N), and the resulting solid collected. It was dissolved in hot dilute sodium hydroxide solution (15 ml.), dimethyl sulphate (2 ml.) added,⁴² and the mixture shaken well and allowed to cool. The sodium salt separated as pale yellow plates. These were dissolved in hot water and the solution acidified. The acid (IV; Y = OH) crystallised from ethanol–water (2 : 1) (71%; m. p. 113–116°, reported¹⁶ m. p. 109°) (Found: C, 75.1; H, 6.5. Calc. for $\text{C}_{17}\text{H}_{13}\text{O}_3$: C, 75.6; H, 6.7%); λ_{max} . 262 (ϵ 20,300); λ_{min} . 232 (ϵ 4950). A solution of γ -(2-methoxy-5-phenyl)phenylbutyric acid (4 g.) in hydrogen fluoride (60 ml.) was kept at room temperature for 48 hr., the hydrogen fluoride evaporated, and the residue shaken with potassium carbonate solution (50 ml.; 2N) and ether. Starting material (1 g.) was recovered from the alkaline extract. The neutral fraction was crystallised from benzene–petroleum (1 : 1) and then from ethanol; it had m. p. 129–130° (4% yield) (reported¹⁴ m. p. 120°) (Found: C, 80.4; H, 6.2. Calc. for $\text{C}_{17}\text{H}_{18}\text{O}_2$: C, 80.9; H, 6.4%). The infrared spectrum (carbon disulphide) contained the following bands 1699 (C=O), strong bands at 756 and 694 (monosubstituted benzene ring), and a very strong band 819 cm^{-1} (1,2,3,4-tetrasubstituted benzene ring). Starting material was recovered from an attempt to cyclise the acid with tri-fluoroacetic anhydride.⁴³

3-Methoxyfluoranthene (VIII).—A mixture of phosphoric acid (10 ml., 85%) and phosphorus pentoxide (15 g.) was heated (oil bath) at 160° for 80 min., γ -(2-methoxy-5-phenyl)phenylbutyric acid (1 g.) added, the mixture stirred for 5 min. and poured on to ice. Next day the sticky solid was washed by decantation with potassium carbonate solution, collected, dried (1 g.; m. p. 110°), and chromatographed (grade H alumina). Elution with petroleum–benzene (1 : 1) gave a pale yellow solid (0.5 g.) which was crystallised from propanol (m. p. 125–145°) (Found: C, 85.3; H, 5.5. Calc. for $\text{C}_{17}\text{H}_{14}\text{O}$: C, 87.2; H, 6.0%). The infrared spectrum (Nujol) showed the absence of a C=O group and an ethanolic solution of the material had a strong fluorescence. This material (200 mg.) was heated to 190° (oil bath) for 30 min. with palladium-charcoal (30 mg.; 30%): the product (VIII) crystallised from propanol in small plates and had m. p. 159–160° (reported¹⁹ m. p. 156–157°) (Found: C, 87.4; H, 5.2. Calc. for $\text{C}_{17}\text{H}_{12}\text{O}$: C, 87.9; H, 5.2%); λ_{max} . 218 (ϵ 29,050), 239 (ϵ 45,700), 283 (ϵ 16,900), 295 (ϵ 35,800), 321 (ϵ 4650), and 361 (ϵ 8830); λ_{min} . 228 (ϵ 23,300), 271 (ϵ 6670), 287 (ϵ 16,900), 312 (ϵ 3800), and 328 (ϵ 4300).

1,2,3,4-Tetrahydro-1-oxo-7-(*p*-methoxyphenyl)naphthalene (III; R = *p*-methoxyphenyl).— β -4-(*p*-Methoxyphenyl)benzoylpropionic acid (m. p. 202°, reported¹⁶ m. p. 200–201°) was reduced (Huang Minlon)⁴² to γ -4-(*p*-methoxyphenyl)phenylbutyric acid (VI), m. p. 150° (reported¹⁶ m. p. 148–149°). This acid (5 g.) was cyclised with polyphosphoric acid (20 ml. of phosphoric acid, 30 g. of phosphorus pentoxide) at 160° for 3 min. The product was worked up in the usual manner. Two crystallisations from ethanol gave the *ketone* (44%), m. p. 121–123° (Found: C, 80.4; H, 6.5. $\text{C}_{17}\text{H}_{16}\text{O}_2$ requires C, 80.9; H, 6.4%); λ_{max} . 209 (ϵ 35,200) 253 (ϵ 34,400), and 320 (ϵ 1550); λ_{min} . 226 (ϵ 10,900) and 308 (ϵ 1390). The infrared spectrum (carbon disulphide) contained the following bands 1684 (C=O), 834 (1,4-disubstituted benzene ring), 813 cm^{-1} (1,2,4-trisubstituted benzene ring). The 2,4-dinitrophenylhydrazone formed

⁴² Gates and Tschudi, *J. Amer. Chem. Soc.*, 1956, **78**, 1380.

⁴³ Hill and Richards, *J. Amer. Chem. Soc.*, 1961, **83**, 4220.

bright red needles, m. p. 231—233° (decomp.) from 2-ethoxyethanol (Found: C, 63.5; H, 4.5; N, 12.5. $C_{23}H_{20}N_4O_5$ requires C, 64.0; H, 4.6; N, 13.0%).

γ -(2-Methoxy-5-phenyl)phenylpropyl Phenyl Ketone (IV; Y = Ph).—Bromobenzene (15.7 g.) in ether (100 ml.) was treated with magnesium (2.4 g.), anhydrous cadmium chloride (11 g.) added, and the mixture heated and stirred for 1 hr.¹¹ Dry benzene (200 ml.) was then added and the ether distilled out of the flask. The solution of diphenylcadmium was then cooled, the acid chloride from γ -(2-methoxy-5-phenyl)phenylbutyric acid (16 g.) in benzene (25 ml.) added slowly, and the mixture boiled for 1 hr. After the usual working up the neutral fraction was steam-distilled and the non-volatile fraction isolated with ether and chromatographed on alumina (Grade H, 450 g.). Elution with benzene yielded the ketone (IV; Y = Ph) (17%). Crystallisation from methanol-benzene (3 : 1) and then from ethanol gave prisms, m. p. 77—79° (Found: C, 83.7; H, 6.9. $C_{23}H_{22}O_2$ requires C, 83.7; H, 6.7%); λ_{\max} . 248 (ϵ 22,000), λ_{\min} . 229 (ϵ 12,400); 1695 cm^{-1} (:CO). The 2,4-dinitrophenylhydrazone crystallised from propanol in crimson needles, m. p. 160—162° (Found: C, 68.0; H, 5.4; N, 10.5. $C_{29}H_{26}N_4O_5$ requires C, 68.2; H, 5.1; N, 11.0%).

4,5,6,6a-Tetrahydro-3-methoxy-6a-phenylfluoranthene (IX; R = Ph).— γ -(2-Methoxy-5-phenyl)phenylpropyl phenyl ketone (1 g.) was added to polyphosphoric acid (10 ml. of phosphoric acid, 15 g. of phosphorus pentoxide), the mixture stirred at 200° for 30 min., and poured on to ice. The neutral fraction was chromatographed on alumina (grade H, 40 g.). Elution with petroleum benzene (3 : 1) yielded solid material; petroleum-benzene (2 : 1) gave orange-coloured gums. The solid was crystallised from acetic acid and then from butanol forming white needles (40 mg.), m. p. 180—182° (Found: C, 88.0; H, 6.5. $C_{23}H_{20}O$ requires C, 88.5; H, 6.4%); λ_{\max} . 282 (ϵ 15,440) and 312 (ϵ 6200), λ_{\min} . 250 (ϵ 3600) and 308 (ϵ 5870).

cis-syn-1,2,3,4,5,8,9,10-Octahydro-1,4-dioxo-5-phenylnaphthalene (XI).—1-Phenylbutadiene (20 g.)²⁶ was dissolved in methanol (180 ml.) and *p*-benzoquinone (18 g.) added. After 4 hr. at room temperature water (18 ml.) was added. Next day the adduct (X) was collected, crystallised from petroleum containing a trace of benzene (m. p. 95—98°; 61% yield). The adduct (X) was reduced immediately to compound (XI), m. p. 136—139°, reported²³ m. p. 139°. The *p*-nitrophenylhydrazone formed yellow needles (from 2-methoxyethanol), m. p. 228—231° (Found: C, 70.0; H, 5.6; N, 11.1. $C_{22}H_{21}N_3O_3$ requires C, 70.4; H, 5.6; N, 11.2%). On one occasion, instead of the simple adduct (X) separating, an orange-coloured solid was obtained. Crystallisation from ethanol gave 5,8-dihydro-5-phenyl-1,4-naphthaquinone (XII) (14 g.), yellow irregular prisms, m. p. 130—132° (Found: C, 80.7; H, 5.2. $C_{16}H_{12}O_2$ requires C, 81.3; H, 5.1%). The infrared spectrum (chloroform) showed a strong band at 1655 cm^{-1} ; and the ultraviolet spectrum had λ_{\max} . 247 (ϵ 16,300), 340 (ϵ 1150). The quinone (XII) (2 g.) was dissolved in glacial acetic acid (70 ml.) containing water (7 ml.) and treated with zinc dust (4 g.). After 10 min. the zinc dust was filtered off and the filtrate diluted with water. Next day the quinol was collected, dried, and crystallised from benzene; it formed white needles (1.5 g.), m. p. 168—169° (Found: C, 80.4; H, 5.7. Calc. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9%) (reported²⁵ m. p. 170°). The compound gave a deep red coloration with concentrated sulphuric acid.

During another attempt to prepare the compound (X) a mixture of tar and solid separated from the methanolic solution. This was triturated with methanol and the insoluble fraction crystallised from ethanol-benzene giving 1,4,5,8,11,12-hexahydro-1,5-diphenylanthraquinone (XIII), m. p. 179.5—180° (reported²⁶ m. p. 185—186°) (Found: C, 84.7; H, 6.1. Calc. for $C_{26}H_{22}O_2$: C, 85.2; H, 6.1%); the infrared spectrum contained a strong band at 1677 cm^{-1} ($\alpha\beta$ -unsaturated ketone), ultraviolet spectrum (chloroform) λ_{\max} . 245 (ϵ 6600), 272 (ϵ 5280), and 367 (ϵ 206).

cis-syn-1,2,3,4,5,8,9,10-Octahydro-1,4-dioxo-5-phenylnaphthalene 1-Ethylenethiokeal (XV).—The diketone (XI) (15 g., 1 mol.) was dissolved in glacial acetic acid (400 ml.) and ethanedithiol (6 g., 1 mol.) added, followed by boron trifluoride-ether (10 ml.). After 24 hr. the solid which had separated was collected, the mother-liquors poured into water (1 l.) and extracted with ether (3 \times 150 ml.). The extract was washed thoroughly with sodium hydroxide solution (4N) and water, then dried ($MgSO_4$) and the solvent removed. The residue was dissolved in a little methanol and allowed to crystallise. The solids were combined and crystallised from ethyl methyl ketone (15 g.; m. p. 149—156°). A second crystallisation gave magnificent prisms, m. p. 157—160°, unchanged by further crystallisation (Found: C, 67.7, 68.6; H, 6.3, 6.7; S, 19.6. $C_{18}H_{20}OS_2$ requires C, 68.2; H, 6.4; S, 20.2%). The infrared spectrum contained a strong band at 1725 cm^{-1} (:CO). When the diketone (XI) (0.1 g.) was dissolved in acetic acid containing ethanedithiol (0.5 ml.) and boron trifluoride-ether (5 drops) a white solid slowly

separated (0.1 g.). The *bisethylenethioketal* (XIV) formed plates, m. p. 179—180°, from acetic acid (Found: C, 60.9; H, 5.9; S, 31.7. $C_{20}H_{24}S_4$ requires C, 61.2; H, 6.2; S, 32.6%). The diketone (XI) did not give any crystalline material on treatment with toluene- ω -thiol, benzene-thiol, and trimethylenedithiol.

Cis-syn-8-phenyl-1-decalone (XVI).—A solution of the thioketal (XV) (1 g.) in ethanol (100 ml.) was stirred and boiled for 2 hr. with W-2 Raney nickel (10 g.). The nickel was filtered off, the ethanol removed *in vacuo*, the residue taken up in methanol and allowed to crystallise. The product was crystallised from methanol forming needles (0.3 g.) m. p. 119—120.5° (reported³⁴ m. p. 117—118°) (Found: C, 83.6; H, 8.7; S, nil. $C_{16}H_{20}O$ requires C, 84.2; H, 8.8%). The infrared spectrum (carbon tetrachloride) contained a strong band at 1725 cm^{-1} and was identical with a spectrum supplied by Professor House. The n.m.r. spectrum of the compound showed the absence of olefinic protons. The *cis*-ketone (XVI) was isomerised with sodium methoxide; *trans-anti-8-phenyl-1-decalone* formed needles (from hexane), m. p. 141—143° (reported³⁴ m. p. 143—143.5°).

1-(*trans*)-*Hydroxy-cis-syn-1,8-diphenyldecalin* (XVII).—To the ketone (XVI) (2.07 g.) in ether (50 ml.) was added phenyl-lithium (2.4 g.) in ether (15 ml.), the mixture boiled (nitrogen atmosphere) for 5 hr., poured into ice-hydrochloric acid, and worked up in the usual manner. The residue from the ether was crystallised from ethanol, the 1st crop had m. p. 172—177° (1 g.), the 2nd crop (1.5 g.), m. p. 169—174° after a second crystallisation. The two fractions were identical (infrared spectrum). The alcohol formed needles, m. p. 175.5—176.5° (from ethanol) (Found: C, 85.6; H, 8.7. $C_{22}H_{26}O$ requires C, 86.2; H, 8.6%). The compound was free from unchanged ketone (infrared spectrum).

1,8-*Diphenyl-naphthalene* (Id).—The alcohol (XVII) (0.67 g.) was dehydrogenated using palladium-charcoal (0.1 g., 30%) as described above (heated 30 min. at 240°, 30 min. at 300°, 30 min. at 330°). Two crystallisations from hexane gave 1,8-diphenyl-naphthalene as needles (0.16 g.), m. p. 150—151° (Found: C, 94.3; H, 5.8. Calc. for $C_{22}H_{16}$: C, 94.25; H, 5.75%) [ultraviolet spectrum λ_{max} . 214 (ϵ 40,500), 235 (ϵ 57,900) and 299 (ϵ 12,500)]. The *benzotri-furoxan complex* (prepared in acetic acid) formed long yellow plates, m. p. 164—166° (Found: N, 15.9. $C_{28}H_{16}N_6O_6$ requires N, 15.8%). The complex dissociated on attempted recrystallisation.

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