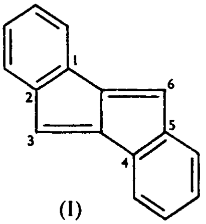
799. *Attempts to prepare New Aromatic Systems. Part VI.** 1 : 2-5 : 6-*Dibenzopentalene and Derivatives.*

By Wilson Baker, J. F. W. McOmie, (Mrs.) S. D. Parfitt, and D. A. M. Watkins.

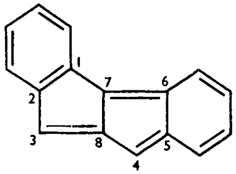
Attempts to synthesise 1 : 2-5 : 6-dibenzopentalene (II) or a substituted derivative have failed although its isomer 1 : 2-4 : 5-dibenzopentalene (I) is known. Kohler's supposed derivative (IV) of 1 : 2-5 : 6-dibenzopentalene has been shown to be the indenone (VIII).

The diketone (X) yields two stereoisomeric diols which do not undergo direct or indirect dehydration, nor does the parent hydrocarbon undergo dehydrogenation. Experiments in the 4-phenyl- and 3 : 4-diphenyl-1 : 2-5 : 6-dibenzopentalene series have shown that here also there is no tendency to generate the fully unsaturated system.

Although attempts to prepare pentalene[1] and benzopentalene (*cyclo*pent[*a*]indene)[2] have failed, 1 : 2-4 : 5-dibenzopentalene[3] (I) and its 3 : 6-dichloro- and 3 : 6-diphenyl derivatives are known. The dye acedianthrone is a complex derivative of 1 : 2-4 : 5-dibenzopentalene.[4] 1 : 2-4 : 5-Dibenzopentalene shows olefinic unsaturation in the five-membered rings, and in addition the failure to prepare benzopentalene suggests that aromatic character cannot be exhibited by pentalene itself. This is probably due to the fact that the eight π-electrons cannot provide two sextets having two electrons in common, as is possible with the ten π-electrons of naphthalene.



(I)



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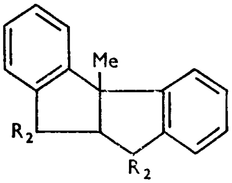

(III)

We have now attempted to synthesise 1 : 2-5 : 6-dibenzopentalene (II) and some of its derivatives. Although it has been stated that the two dibenzopentalenes (I) and (II) should be of almost equal stability, because their resonance energies have been calculated as 120 and 110 kcal./mole respectively,[5] we now record our failure to prepare 1 : 2-5 : 6-dibenzopentalene (II) or any substituted derivative thereof, although we have made many substituted dihydro-derivatives. There appears to be a greater reluctance to form the 1 : 2-5 : 6-dibenzopentalene system than that of its isomer. This difference may be in part due to the fact that (I) but not (II) can be regarded as a 1 : 4-diphenylbutadiene, and also that in (II) one of the benzene rings must be represented as *o*-quinonoid.

To date only two substances are definitely known to contain the carbon skeleton of 1 : 2-5 : 6-dibenzopentalene (II), *viz.*, 3 : 4 : 7 : 8-tetrahydro-7-methyl-1 : 2-5 : 6-dibenzopentalene (III; $R = H$) and its tetramethyl derivative (III; $R = Me$) prepared by

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* Part V, preceding paper.

[1] For references to earlier work and discussions, see Baker, *J.*, 1945, 263; Baker and McOmie, "Non-benzenoid Aromatic Compounds," Chapter 2 of "Progress in Organic Chemistry," Editor J. W. Cook, Volume III, Butterworths Scientific Publications, 1955.

[2] Baker and Leeds, *J.*, 1948, 974; Baker and Jones, *J.*, 1951, 787; Baker, Glockling, and McOmie, *J.*, 1951, 3357; Baker, McOmie, and Ulbricht, preceding paper; Groves and Swan, *J.*, 1951, 863, 867, 871; Dahn, *Helv. Chim. Acta*, 1951, **34**, 1087.

[3] Blood and Linstead, *J.*, 1952, 2263.

[4] B.P. 369,765/1931; 410,552/1932; Clar, *Ber.*, 1939, **72**, 2134.

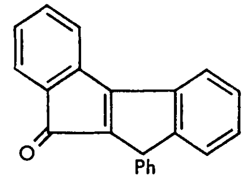
[5] Pullman, Pullman, Bergmann, Bertier, Fischer, Hirschberg, and Pontis, *J. Chim. phys.*, 1952, **49**, 24.

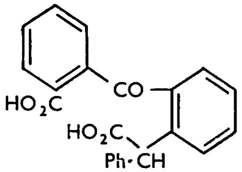
Barnes and Beitchman.[6] The methyl group in position 7 and the *gem*-dimethyl groups make these compounds useless for the present investigation.

Kohler [7] claimed to have prepared 3 : 4-dihydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (IV), m. p. 162°, by the action of phenylmagnesium bromide upon 2-benzylideneindane-1 : 3-dione (V). Oxidation of the supposed (IV) by potassium permanganate gave an acid, m. p. 131—133°, represented by formula (VI), but this acid would be unlikely to survive treatment with potassium permanganate and a re-investigation of this work was undertaken.

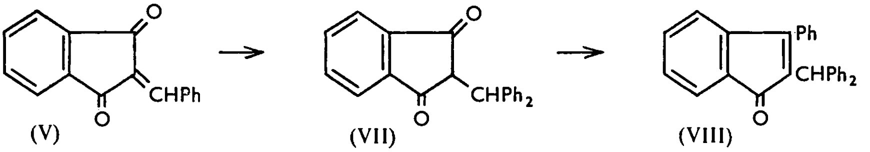
We find that *two* molecules of phenylmagnesium bromide react with 2-benzylideneindane-1 : 3-dione (V) under the conditions given by Kohler, to yield 2-diphenylmethyl-3-phenylinden-1-one (VIII), m. p. 154°, whose structure is established by degradation with chromic acid which gives benzophenone and *o*-benzoylbenzoic acid, m. p. 127°. Kohler's analyses of his product, m. p. 162°, are closer to those required by (VIII) than by (IV), and his analysis of the derived acid is almost as satisfactory for *o*-benzoylbenzoic acid as for (VI). These facts make it almost certain that Kohler's products were really (VIII) and *o*-benzoylbenzoic acid, and we have moreover synthesised an unsaturated ketone which is almost certainly (IV) (see p. 4030) rather than the isomeric ketone (XXII) and find that it has m. p. 272°.

(IV)





(VI)



(V) (VII) (VIII)

The first step in the preparation of the ketone (VIII) is addition of phenylmagnesium bromide to the diketone (V), giving 2-diphenylmethylindane-1 : 3-dione (VII), followed by reaction with a second molecule of Grignard reagent and loss of water. The intermediate 2-diphenylmethylindane-1 : 3-dione (VII) was readily isolated from fairly large-scale experiments. The structure assigned to it is established by oxidation with chromic acid which yields phthalic acid, benzophenone, and a little diphenylacetic acid.

Our first attempts to synthesise 1 : 2-5 : 6-dibenzopentalene (II) started with (diphenylmethyl)malonic acid (IX). The double cyclisation of this acid to 3 : 4 : 7 : 8-tetrahydro-3 : 4-dioxo-1 : 2-5 : 6-dibenzopentalene (X) could not be effected by concentrated sulphuric acid or fluorosulphonic acid,[8] or *via* the acid chloride, but was achieved in 27% yield by reaction with polyphosphoric acid.

A more convenient route to the diketone (X) was found *via* 3-phenylindan-1-one (XI) [9] prepared by a much improved process from cinnamic acid and benzene in presence of aluminium chloride. 3-Phenylindan-1-one (XI) was condensed with ethyl carbonate under the conditions given by Brändström,[10] giving ethyl 1-oxo-3-phenylindane-2-carboxylate (XII), and rapid cyclisation of this ester with polyphosphoric acid then gave the

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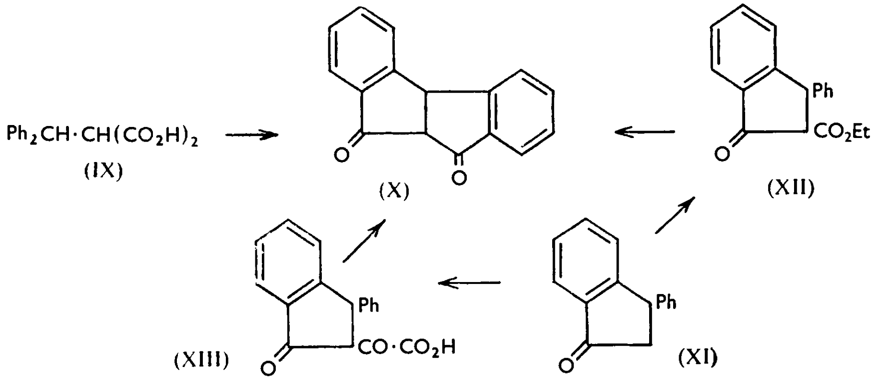
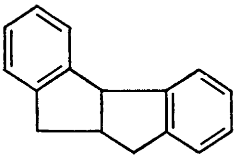
[6] Barnes and Beitchman, *J. Amer. Chem. Soc.*, 1954, **76**, 5430.
[7] Kohler, *Amer. Chem. J.*, 1907, **37**, 371.
[8] Baker, Coates, and Glockling, *J.*, 1951, 1376.
[9] Koelsch, Hockmann, and le Claire, *J. Amer. Chem. Soc.*, 1943, **65**, 59.
[10] Brändström, *Acta Chem. Scand.*, 1950, **4**, 1315.

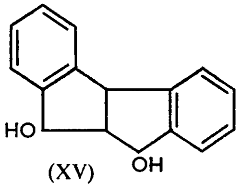
diketone (X). An alternative, but less efficient route from 3-phenylindan-1-one (XI) involved condensation with ethyl oxalate and hydrolysis to give the glyoxylic acid (XIII), and final rapid cyclisation with polyphosphoric acid with loss of carbon monoxide to give the diketone (X).

The compound (X) and the other derivatives of 1 : 2-5 : 6-dibenzopentalene having hydrogen or other substituent in positions 7 and 8 described in this paper probably all have the two five-membered rings fused in the *cis*-positions; the *trans*-configurations would be very highly strained.[11] This diketone shows some tendency to give derivatives of an enolic form (see Experimental section), but it failed to yield an enol acetate. Its ultraviolet absorption spectrum in 0·1N-ethanolic sodium hydroxide was but little different from that in ethanol alone, and this reluctance to enolise is undoubtedly due to increased strain in the enol form.

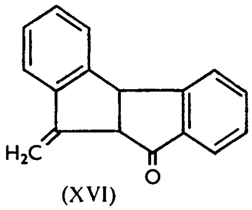


Reduction of the diketone (X) with amalgamated zinc and hydrochloric acid gave 3 : 4 : 7 : 8-tetrahydro-1 : 2-5 : 6-dibenzopentalene (XIV). Many attempts were made to dehydrogenate this hydrocarbon, *e.g.*, by palladium–charcoal in boiling β-methylnaphthalene, or tetrachloro-*o*-benzoquinone in benzene;[12] unchanged material was isolated in high yield. Reaction with chloranil in boiling benzene gave an addition product, which is probably 3(or 7)-(2 : 3 : 5 : 6-tetrachloro-4-hydroxyphenoxy)-1 : 2-5 : 6-dibenzopentalene, and regenerated the hydrocarbon (XIV) when heated. Treatment of the diketone (X) with phosphorus pentachloride gave a mixture of 3 : 3 : 4 : 4 : 7 : 8-hexachloro-3 : 4 : 7 : 8-tetrahydro-1 : 2-5 : 6-dibenzopentalene, and a monochloro-compound which, because it could not be made to lose hydrogen chloride, is probably 8- rather than 7-chloro-3 : 4 : 7 : 8-tetrahydro-3 : 4-dioxo-1 : 2-5 : 6-dibenzopentalene.


(XIV)



(XV)



(XVI)

Reduction of the diketone (X) with lithium aluminium hydride in ether gave two (isomers *A* and *B*) of the three possible stereoisomeric forms of the diol (XV), *cis*-fusion of the two five-membered rings being assumed. Each isomer gives a characteristic diacetyl derivative when boiled with acetyl chloride in pyridine; no dehydration occurred, and the diacetyl derivatives were unchanged when heated with potassium carbonate at 250°.

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[11] See Linstead and co-workers, *J.*, 1934, 935, 946; 1935, 436.

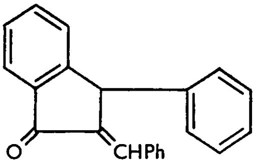
[12] Linstead, Braude, Jackman, and Beames, *Chem. and Ind.*, 1954, 1174; Braude, Jackman, and Linstead, *J.*, 1954, 3564.

Isomer *A* was unchanged when heated with anhydrous copper sulphate in xylene,[13] or with phosphoric anhydride in benzene, and both it and its benzoyl derivative were unchanged by passage through a tube in the vapour state at 500°/0·1 mm.[14] These substances all show a considerable reluctance to generate even one double bond associated with carbon atoms 3, 4, 7, and 8, and this appears to be a characteristic feature of all derivatives of 1 : 2-5 : 6-dibenzopentalenes.

When boiled with an ether or ether–benzene solution of methylmagnesium iodide, the diketone (X) reacted with only one mol. of the Grignard reagent, giving 3 : 4 : 7 : 8-tetrahydro-3-methylene-4-oxo-1 : 2-5 : 6-dibenzopentalene (XVI). The position of the double bond is inferred from the fact that the ultraviolet absorption spectrum is almost identical with that of the original diketone, and very different from that of chalcone[15] which it should resemble if the double bond were endocyclic (see Table).

Work has been carried out in the 3-phenyl-1 : 2-5 : 6-dibenzopentalene series in the hope that the phenyl group might stabilise the pentalene nucleus. 2-Benzylidene-3-phenylindan-1-one (XVII), prepared from 3-phenylindan-1-one (XI) and benzaldehyde,[16] was unaffected by most cyclisation procedures, but yielded the desired 3 : 4 : 7 : 8-tetrahydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (XVIII) when boiled with aluminium chloride in benzene; cyclisation with 50% sulphuric acid–phosphoric acid at 100° was less satisfactory.

The ketone (XVIII) was not reduced under the normal Clemmensen or Wolff–Kishner conditions, but reduction was effected in 42% yield by Barton's modification of the latter reaction,[17] giving 3 : 4 : 7 : 8-tetrahydro-3-phenyl-1 : 2-5 : 6-dibenzopentalene (XIX; $R = R' = H$), m. p. 112° (cf. below). The same hydrocarbon was prepared from the ketone (XVIII) by reaction with phosphorus pentachloride to give the related 3 : 3-dichloro-compound (XIX; $R = R' = Cl$), followed by reduction with zinc and hydrochloric acid in ether. The dichloro-compound is readily hydrolysed to the parent ketone (XVIII), but attempts to effect dehydrochlorination were unsuccessful; *e.g.*, when heated under reduced pressure or boiled with pyridine it gave in poor yield a trichloro-compound, probably 3 : 3 : 4(or 3 : 3 : 7)-trichloro-3 : 4 : 7 : 8-tetrahydro-4-phenyl-1 : 2-5 : 6-dibenzopentalene. The toluene-*p*-sulphonylhydrazone of (XVIII) when heated with sodium and ethylene glycol or *cyclo*hexanol does not give the expected unsaturated compound (XXI; $R = H$), but 3 : 4 : 7 : 8-tetrahydro-3-(2′-hydroxyethoxy)- and 3-*cyclo*hexyloxy-3 : 4 : 7 : 8-tetrahydro-4-phenyl-1 : 2-5 : 6-dibenzopentalene respectively (XIX; $R = HO{\cdot}CH_2{\cdot}CH_2{\cdot}O$, $R' = H$; and $R = C_6H_{11}O$, $R' = H$) (cf. ref. 18). Two similar examples of the formation of monoethers of ethylene glycol during this type of reaction are recorded by Bamford and Stevens.[18]



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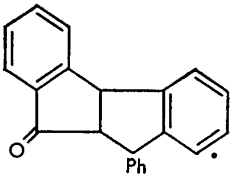
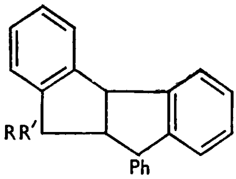


(XVIII)



(XIX)

When the ketone (XVIII) was reduced with lithium aluminium hydride it gave 3 : 4 : 7 : 8-tetrahydro-3-hydroxy-4-phenyl-1 : 2-5 : 6-dibenzopentalene (XX), stereoisomer *A*. A second stereoisomer, *B*, was obtained by reducing the ketone (XVIII) with

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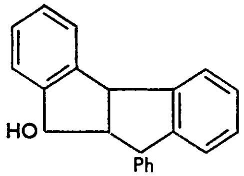
[13] Baker, Glockling, and McOmie, *J.*, 1951, 3357.
[14] Barton, *J.*, 1949, 2174.
[15] Black and Lutz, *J. Amer. Chem. Soc.*, 1953, **75**, 5991.
[16] Pfeiffer and de Waal, *Annalen*, 1935, **520**, 185.
[17] Barton, Ives, and Thomas, *J.*, 1955, 2056.
[18] Bamford and Stevens, *J.*, 1952, 4735.

aluminium *iso*propoxide. Each gives a characteristic acetyl derivative, both of which are unchanged when sublimed or when heated with anhydrous potassium carbonate at 250°.



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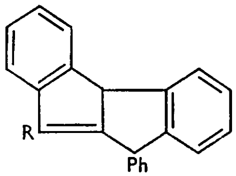
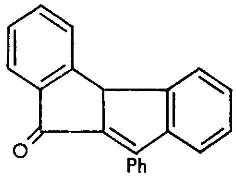


(XXI)



(XXII)

When the hydroxy-compound *A* was heated with anhydrous copper sulphate in xylene for 4 hr., it gave a mixture of a substance, *X*, m. p. 158—159°, whose structure has not been determined, and an anhydro-compound, m. p. 179—180°. After 7 hours' heating relatively little anhydro-compound could be isolated, and after 10 hr. only substance *X* could be isolated. Similar dehydration of hydroxy-compound *B* gave the same anhydro-compound after 1½ hr., but only substance *X* after 3 hr. In all cases the yields were small. The anhydro-compound was also obtained when the ketone (XVIII) was reduced on a larger scale with aluminium *iso*propoxide, presumably *via* the hydroxy-compound *B*. The anhydro-compound is probably 4 : 7-dihydro-4-phenyl-1 : 2-5 : 6-dibenzopentalene (XXI; R = H) unless migration of the double bond has occurred to one of the other two possible positions where it would be more fully conjugated.

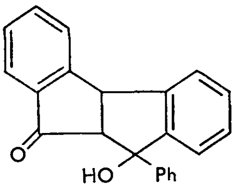
An unexpected result was obtained when either stereoisomer of 3 : 4 : 7 : 8-tetrahydro-3-hydroxy-4-phenyl-1 : 2-5 : 6-dibenzopentalene (XX) was dehydrated with phosphoric anhydride in boiling benzene; the product, instead of being the olefin (XXI; R = H), was a saturated hydrocarbon, $C_{22}H_{18}$, whose infrared spectrum is very similar to that of (XIX; R = R′ = H); both show the absence of double bonds and the presence of a mono-substituted benzene ring, and hence the compound $C_{22}H_{18}$ must be a stereoisomer of (XIX; R = R′ = H), or less likely a structural isomer thereof. The proposed structure is in agreement with the ultraviolet spectrum which is closely similar to that of the saturated compounds (XIX; R = R′ = H), m. p. 112°, and (XX) (isomers *A* and *B*) and different from that of the anhydro-compound, m. p. 179—180°, discussed above. The infrared spectrum disproved the interesting possibility that a hydrocarbon $C_{22}H_{16}$ had arisen *via* (XXI; R = H) followed by cyclisation between carbon atom 3 and an *ortho*-carbon atom of the phenyl group to give a compound with three fused five-membered rings and a three-fold axis of symmetry.

Treatment of the ketone (XVIII) with bromine vapour gave what is probably 3 : 4-dihydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (IV), also made by reaction of phenyl-lithium with the diketone (X). The position of the olefinic bond is inferred from the fact that the ultraviolet absorption curve of this ketone is similar in shape to those of 2-diphenylmethyl-3-phenylinden-1-one (VIII) and of ethyl 1-oxo-3-phenylindene-2-carboxylate,[22] and different from those of 2-benzylidene-3-phenylindan-1-one (XVII) and of chalcone. With phenylmagnesium bromide the diketone (X) gave the tertiary alcohol (XXIII).

2-Benzylidene-3-phenylindan-1-one (XVII) gave the epoxide on reaction with alkaline hydrogen peroxide. When the epoxide was heated with acids in an attempt to convert it into 3 : 7-dihydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (XXII) or the isomeric 3 : 4-dihydro-compound, a phenolic substance, $C_{22}H_{16}O_2$, was obtained instead; this gave no ferric chloride reaction and did not react with 2 : 4-dinitrophenylhydrazine. Its structure as 1 : 3-dihydroxy-2 : 4-diphenylnaphthalene (XXIV) was suggested to us by Dr. J. A. Barltrop. Recently House and Wasson[19] have shown that the epoxides of 2-benzylidenecyclanones are converted into the corresponding 2-phenyl-3-oxohomo-cyclanones by the action of boron trifluoride–ether in benzene. This reaction is analogous

[19] House and Wasson, *J. Amer. Chem. Soc.*, 1956, **78**, 4394.

to the formation of the naphthalene (XXIV), and we find that boron trifluoride also converts the epoxide of (XVII) into (XXIV).



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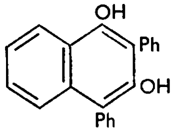
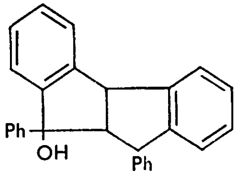


(XXIV)



(XXV)

A few experiments have been carried out in the 3 : 4-diphenyl-1 : 2-5 : 6-dibenzopentalene group. The ketone (XVIII) and phenylmagnesium bromide gave 3 : 4 : 7 : 8-tetrahydro-3-hydroxy-3 : 4-diphenyl-1 : 2-5 : 6-dibenzopentalene (XXV). Dehydration of this with anhydrous copper sulphate in xylene then gave an anhydro-compound, which is either 3 : 7-dihydro-3 : 4-diphenyl-1 : 2-5 : 6-dibenzopentalene (XXI; R = Ph) or the isomeric 3 : 4-dihydro-derivative. Dehydrogenation of this anhydro-compound could not be effected by reaction with chloranil, lead tetra-acetate, *N*-bromosuccinimide, or oxides of nitrogen. The last reagent yielded an addition product of (XXI; R = Ph) with two mols. of nitrogen dioxide.

The ultraviolet absorption spectra of some of the compounds described above are recorded in the Table.

Ultraviolet absorption spectra in ethanol.

1 : 2-5 : 6-*Dibenzopentalene derivatives*	λ (mμ)	$\log_{10} \varepsilon_{\max.}$	λ (mμ)	$\log_{10} \varepsilon_{\max.}$	λ (mμ)	$\log_{10} \varepsilon_{\max.}$
3 : 4 : 7 : 8-Tetrahydro-3 : 4-dioxo-(X) ...	246·5	4·37	285	3·67	—	—
,, ,, ,, (X) *	244	4·17	294	3·51	—	—
,, ,, -3-methylene-4-oxo-, (XVI)	243	4·35	289	3·65	—	—
3 : 4 : 7 : 8-Tetrahydro-4-phenyl-, (XIX; R = R′ = H)	260·5	3·44	267	3·57	274	3·57
3 : 4 : 7 : 8-Tetrahydro-3-hydroxy-4-phenyl-, (XX), Isomer A	260·5	3·23	267	3·33	274	3·29
3 : 4 : 7 : 8-Tetrahydro-3-hydroxy-4-phenyl-, (XX), Isomer B	—	—	266·5	3·34	273·5	3·31
Compound $C_{22}H_{18}$, m. p. 155°	260	3·31	267	3·42	274	3·39
3 : 4-Dihydro-3-oxo-4-phenyl- (IV)	235	3·98	288	3·61	340	3·50
4 : 7-Dihydro-4-phenyl- (XXI; R = H)	235	4·54	264 †	4·06	285 †	3·95
Other compounds						
2-Diphenylmethyl-3-phenylinden-1-one (VIII)	244·5	4·60	284	3·75	410	3·02
Ethyl 1-oxo-3-phenylindene-2-carboxylate	247·5	4·49	305·5	3·87	400	3·21
2-Benzilidene-3-phenylindan-1-one (XVII)	270	4·18	325	4·58	—	—
Chalcone ‡	227·5	3·99	307·5	4·39	—	—

* In 0·1N-ethanolic sodium hydroxide. † Inflection.

‡ Black and Lutz, *J. Amer. Chem. Soc.*, 1953, **75**, 5991.

EXPERIMENTAL

2-*Diphenylmethyl*-3-*phenylinden*-1-*one* (VIII).—A solution of 2-benzylideneindane-1 : 3-dione (V) (12 g., 1·1 mol.) in benzene (50 c.c.) was added to an ethereal solution of phenylmagnesium bromide (1·1 mol.) made from bromobenzene (8·3 g.) and magnesium (1·3 g.), and the mixture boiled for 1 hr. and poured into dilute hydrochloric acid. The product, isolated in the usual way, was purified by passage through a column of alumina and elution with ethanol, giving deep-yellow plates (6·4 g.), m. p. 154°, from ethanol (Found: C, 90·2; H, 5·5. $C_{28}H_{20}O$ requires C, 90·3; H, 5·4%). This 2-*diphenylmethyl*-3-*phenylinden*-1-*one* (VIII) gave a 2 : 4-*dinitrophenylhydrazone* as orange needles, m. p. 249° (from acetic acid) (Found: C, 74·2; H, 4·5;

N, 10·2. $C_{34}H_{24}O_4N_4$ requires C, 74·0; H, 4·35; N, 10·15%), and an *oxime*, m. p. 159—162° (from methanol) (Found: C, 85·9; H, 5·2; N, 4·0. $C_{28}H_{21}ON$ requires C, 86·6; H, 5·4; N, 3·6%); it gives a green solution in concentrated sulphuric acid.

2-*Diphenylmethylindane*-1 : 3-*dione* (VII).—A similar experiment to the above, but on ten times the scale, gave a product which was crystallised directly from light petroleum (b. p. 60—80°), giving first a little starting material and then 2-(diphenylmethyl)indane-1 : 3-dione (VII) as yellow plates (88 g.), m. p. 128—129° (from ethanol) (Found: C, 84·9; H, 5·1. Calc. for $C_{22}H_{16}O_2$: C, 84·6; H, 5·1%). The 2 : 4-dinitrophenylhydrazone, m. p. 248°, formed yellow needles from ethyl acetate. The dione (VII) has been previously prepared in a different manner by Vanags and Zalukajevs,[20] who give the same m. p.

When refluxed with phenylmagnesium bromide (2 mol.) in ether–benzene for 1½ hr., the dione (VII) (2 g.) gave 2-diphenylmethyl-3-phenylinden-1-one (VIII) (1·25 g.) after isolation and purification as described above. It was characterised by m. p. and mixed m. p. determinations.

Oxidation of 2-*Diphenylmethyl*-3-*phenylinden*-1-*one* (VIII).—A solution of chromic anhydride (1·4 g.) in acetic acid (10 c.c.) was added to the indenone (VIII) (2 g.) in acetic acid (10 c.c.), and the mixture was boiled for 1 hr., poured into water, and extracted with chloroform. The chloroform layer after extraction with aqueous sodium hydrogen carbonate yielded benzophenone, m. p. and mixed m. p. 45° (0·7 g., 64%; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 238°). The alkaline extract yielded *o*-benzoylbenzoic acid as needles of the monohydrate (from water), m. p. 94—95°, or as the non-hydrated acid, m. p. and mixed m. p. 127°, from benzene–light petroleum (0·9 g., 75%).

Oxidation of 2-*Diphenylmethylindane*-1 : 3-*dione* (VII).—The oxidation was carried out as in the previous case, and the products were collected into ether which, after shaking with aqueous sodium hydrogen carbonate, yielded benzophenone (0·5 g., 86%), characterised as before. The acidic material was crystallised from water, giving first diphenylacetic acid, m. p. and mixed m. p. 146° (0·05 g., 8%), and then phthalic acid, m. p. and mixed m. p. 202° (decomp.) (0·3 g., 52%).

Cyclisation of (Diphenylmethyl)malonic acid (IX). 3 : 4 : 7 : 8-*Tetrahydro*-3 : 4-*dioxo*-1 : 2-5 : 6-*dibenzopentalene* (X).—Ethyl (diphenylmethyl)malonate was prepared either from diphenylmethyl bromide and ethyl sodiomalonate,[21] or from ethyl benzylidenemalonate by reaction with phenylmagnesium bromide;[7] hydrolysis of the ester with alcoholic potassium hydroxide at 50° for a few minutes (cf. ref. 21) gave (diphenylmethyl)malonic acid (IX), m. p. 186° (decomp.) (from ethanol or light petroleum) in 32% and 16% yield respectively.

The malonic acid (2 g.) was treated with a large excess (*ca.* 20 g.) of polyphosphoric acid (84% P_4O_{10}) at 120° for 1 hr., the dark mixture poured into water, and the brown solid crystallised from benzene (charcoal), giving *tetrahydro*-3 : 4-*dioxo*-1 : 2-5 : 6-*dibenzopentalene* (X) as colourless needles (0·5 g.), m. p. 259° (Found: C, 82·0; H, 4·0. $C_{16}H_{10}O_2$ requires C, 81·9; H, 4·2%). The diketone dissolves in hot but not cold aqueous sodium hydroxide; it gives no colour with alcoholic ferric chloride, but with aqueous alcoholic copper acetate it gives a green copper derivative soluble in chloroform.

The *mono*-2 : 4-*dinitrophenylhydrazone* separates from ethyl acetate in orange needles, m. p. 297° (decomp.) (Found: C, 64·0; H, 3·1; N, 13·5. $C_{22}H_{14}O_5N_4$ requires C, 63·8; H, 3·4; N, 13·5%). The *monotoluene*-p-*sulphonylhydrazone*, prepared in boiling alcoholic solution, separated from ethanol in pale yellow crystals, m. p. 116° (Found: C, 67·9; H, 4·5. $C_{23}H_{18}O_3N_2S$ requires C, 67·6; H, 4·5%); it was unchanged by sodium in hot ethylene glycol which it was hoped would give the olefinic monoketone.[18]

3-*Phenylindan*-1-*one* (XI).—Aluminium chloride was added in small portions to a vigorously stirred suspension of cinnamic acid (85 g.) in dry benzene (375 c.c.), and the solution was boiled under reflux for 14 hr.; evolution of hydrogen chloride had then ceased. The mixture was poured into dilute hydrochloric acid and shaken with ether, and the organic layer washed with aqueous potassium carbonate, dried, and distilled, leaving 3-phenylindan-1-one (XI) which after crystallising from light petroleum had m. p. 78° (95 g.). The 2 : 4-*dinitrophenylhydrazone* formed orange needles, m. p. 209—210°, from acetic acid (Found: C, 65·1; H, 3·9; N, 14·0. $C_{21}H_{16}O_4N_4$ requires C, 65·0; H, 4·1; N, 14·4%). The aqueous alkaline solution yielded

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[20] Vanags and Zalukajevs, *Latvijas PSR Zinātnu Akad. Vēstis*, 1951, 753; *Chem. Abs.*, 1953, **47**, 12,332.

[21] Henderson, *J.*, 1891, 731.

ββ-diphenylpropionic acid, which after crystallisation from benzene had m. p. 153° (yield, 18 g.).

Ethyl 1-*Oxo*-3-*phenylindane*-2-*carboxylate* (XII).—A three-necked flask containing redistilled ethyl carbonate (150 c.c.) was fitted with a dropping funnel, a stirrer, and fractionating column leading to a condenser, then heated to 100°, and sodium (2·3 g.) was added slowly. After the sodium had dissolved a solution of 3-phenylindan-1-one (21 g.) in ethyl carbonate (50 c.c.) was added gradually and the temperature raised to 150°. Ethanol first distilled and, when ethyl carbonate (b. p. 126°) began to be collected, the mixture was cooled and poured into ice-cold dilute acetic acid, and the organic layer and ethereal extracts of the aqueous layer were distilled finally under diminished pressure, leaving the *ester* (XII) which separated from light petroleum (b. p. 60—80°) (charcoal) in colourless needles, m. p. 103—104° (21 g., 74%) (Found: C, 77·6; H, 6·0. $C_{18}H_{16}O_3$ requires C, 77·1: H, 5·7%). The 2 : 4-dinitrophenylhydrazone crystallised from ethanol in orange needles, m. p. 179°.

This ester is probably the *trans*-isomer. Yost and Burger [22] reported preparation of the same substance by catalytic reduction of the related indenone, and obtained a nearly colourless crude ester, m. p. 86—87·5°, which was not analysed and which decomposed when attempts were made to purify it. It is probable that their product was the *cis*-isomer, and that it was becoming converted into the more stable *trans*-form.

Cyclisation of the Ester (XII). 3 : 4 : 7 : 8-*Tetrahydro*-3 : 4-*dioxo*-1 : 2-5 : 6-*dibenzopentalene* (X).—The ester (2 g.) was mixed with a large excess of polyphosphoric acid, heated at 160° for 3 min., then poured into water (cf. ref. 23). The product crystallised from methanol (charcoal), giving the diketone (X) as needles, m. p. and mixed m. p. with the specimen previously described, 259° (0·75 g.).

1-*Oxo*-3-*phenyl*-2-*indanylglyoxylic Acid* (XIII).—A solution of 3-phenylindan-1-one (XI) (10 g.) and ethyl oxalate (9 g.) in ethanol (40 c.c.) was added with stirring to a warm solution of sodium (10 g.) in ethanol (100 c.c.). After being kept overnight at room temperature, the mixture was poured into dilute hydrochloric acid, and the precipitated *glyoxylic acid* (XIII) collected and crystallised from benzene, giving yellow needles, m. p. 213° (9·7 g.) (Found: C, 73·1; H, 4·1. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·3%). It gives a red-brown colour with alcoholic ferric chloride.

Repeated crystallisation of the mother-liquors gave colourless needles, m. p. 185° (Found: C, 90·0; H, 5·6. $C_{30}H_{22}O$ requires C, 90·4; H, 5·5%). This substance is probably 3-*phenyl*-2-(3-*phenyl*-1-*indenylidene*)*indan*-1-*one*.

When the condensation of the indanone (XI) with ethyl oxalate was carried out in methanol, the mixture deposited a sodium salt when cooled to 0°, and acidification then yielded *methyl* 1-*oxo*-3-*phenyl*-1-*indanylglyoxylate* as colourless crystals (from benzene), m. p. 148° (Found: C, 73·6; H, 4·6. $C_{18}H_{14}O_4$ requires C, 73·6; H, 4·8%). The ferric chloride reaction was the same as that of the parent acid.

Cyclisation of the Glyoxylic Acid (XIII). 3 : 4 : 7 : 8-*Tetrahydro*-3 : 4-*dioxo*-1 : 2-5 : 6-*dibenzopentalene* (X).—The acid (XIII) (2 g.) was mixed with polyphosphoric acid and kept at 85° for ½ hr., then poured into water, and the product purified by passage in chloroform through a column of alumina. Final crystallisation from methanol gave 3 : 4 : 7 : 8-tetrahydro-3 : 4-dioxo-1 : 2-5 : 6-dibenzopentalene (X), m. p. and mixed m. p. with the specimens prepared as previously described, 259°.

3 : 4 : 7 : 8-*Tetrahydro*-1 : 2-5 : 6-*dibenzopentalene* (XIV).— A mixture of 3 : 4 : 7 : 8-tetrahydro-3 : 4-dioxo-1 : 2-5 : 6-dibenzopentalene (X) (1·0 g.), amalgamated zinc (6 g.), water (20 c.c.), concentrated hydrochloric acid (50 c.c.), acetic acid (1 c.c.), and toluene (5 c.c.) was boiled under reflux for 40 hr. with the addition of a few c.c. of hydrochloric acid every 10 hr. The product was isolated in the usual way, giving 3 : 4 : 7 : 8-*tetrahydro*-1 : 2-5 : 6-*dibenzopentalene* (XIV) as colourless crystals, m. p. 95° (0·7 g., 80%) (from methanol) (Found: C, 92·9; H, 6·7. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%).

3(or 7)-(2 : 3 : 5 : 6-*Tetrachloro*-4-*hydroxyphenoxy*)-1 : 2-5 : 6-*dibenzopentalene*.—The hydrocarbon (XIV) (0·2 g.) and chloranil (0·3 g.) were boiled in benzene (10 c.c.) for 14 hr., then poured into dilute aqueous sodium hydroxide and shaken with ether. The organic layer yielded a product, thought to be 3(or 7)-(2 : 3 : 5 : 6-*tetrachloro*-4-*hydroxyphenoxy*)-1 : 2-5 : 6-*dibenzopentalene*, as colourless needles, m. p. 210° (from ethanol) (Found: C, 58·6; H, 2·7.

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[22] Yost and Burger, *J. Org. Chem.*, 1950, **15**, 1113.

[23] Evans and Smith, *J.*, 1954, 798.

$C_{22}H_{14}O_2Cl_4$ requires C, 58·4; H, 3·0%). When sublimed at 230°/12 mm., it regenerated the hydrocarbon (XIV).

3 : 3 : 4 : 4 : 7 : 8-*Hexachloro*-3 : 4 : 7 : 8-*tetrahydro*-1 : 2-5 : 6-*dibenzopentalene and* 8(or 7)-*Chloro*-3 : 4 : 7 : 8-*tetrahydro*-3 : 4-*dioxo*-1 : 2-5 : 6-*dibenzopentalene*.—3 : 4 : 7 : 8-Tetrahydro-3 : 4-dioxo-1 : 2-5 : 6-dibenzopentalene (X) (0·5 g.) was mixed with phosphorus pentachloride (*ca.* 5 g.) and heated to 100° for 5 min. Crystallisation from ethanol gave a mixture of yellow-brown crystalline aggregates and light yellow needles, which were separated by hand as far as possible, and separately crystallised several times from ethanol (charcoal). The first product formed colourless prisms, m. p. 207° (Found: C, 46·6; H, 1·8; Cl, 51·7. $C_{16}H_8Cl_6$ requires C, 46·6; H, 1·9; Cl, 51·6%), and is 3 : 3 : 4 : 4 : 7 : 8-*hexachloro*-3 : 4 : 7 : 8-*tetrahydro*-1 : 2-5 : 6-*dibenzopentalene*. The second product formed colourless needles, m. p. 172° (Found: C, 71·0; H, 3·4; Cl, 13·2. $C_{16}H_9O_2Cl$ requires C, 71·4; H, 3·4; Cl, 13·2%), and is 8(or 7)-*chloro*-3 : 4 : 7 : 8-*tetrahydro*-3 : 4-*dioxo*-1 : 2-5 : 6-*dibenzopentalene*; it yields an orange 2 : 4-dinitrophenylhydrazone.

3 : 4 : 7 : 8-*Tetrahydro*-3 : 4-*dihydroxy*-1 : 2-5 : 6-*dibenzopentalene* (XV), *Stereoisomers* A and B.—3 : 4 : 7 : 8-Tetrahydro-3 : 4-dioxo-1 : 2-5 : 6-dibenzopentalene (X) (1 g.) in anhydrous ether was slowly added to a suspension of lithium aluminium hydride (0·4 g.) in ether, the mixture was boiled for 1 hr., then cooled, water was cautiously added, and the ether-soluble material crystallised from methanol. 3 : 4 : 7 : 8-*Tetrahydro*-3 : 4-*dihydroxy*-1 : 2-5 : 6-*dibenzopentalene* (XV), *isomer* A (0·75 g., 74%), separated in needles, m. p. 262° (Found: C, 80·6; H, 5·7. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%). From the mother-liquor was obtained (XV) *isomer* B (0·1 g., 8%) as fine needles, m. p. 200° (Found: C, 80·9; H, 5·9%). The diacetyl derivatives were prepared by boiling the dihydroxy-compounds (0·5 g.) for 1 hr. with pyridine (10 c.c.) and acetyl chloride (0·4 c.c.), and then pouring the solutions into water. The *diacetyl derivative* of isomer *A* was purified by passage in benzene over alumina, elution with ether–chloroform, and final crystallisation from methanol, giving needles, m. p. 109—110° (Found: C, 74·8; H, 5·5. $C_{20}H_{18}O_4$ requires C, 74·4; H, 5·6%). The *diacetyl derivative* of isomer *B* crystallised directly from methanol in needles, m. p. 158° (Found: C, 74·7; H, 5·4%). The *monobenzoyl derivative* of isomer *A* was prepared by boiling isomer *A* (0·1 g.) in pyridine (10 c.c.) with benzoyl chloride (0·1 c.c.) for 1 hr., and pouring the whole into water; it separated from methanol in prisms, m. p. 169° (Found: C, 81·0; H, 4·9. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3%).

3 : 4 : 7 : 8-*Tetrahydro*-3-*methylene*-4-*oxo*-1 : 2-5 : 6-*dibenzopentalene* (XVI).—The diketone (X) (1 g.) in ether was boiled under reflux for 2½ hr. with ethereal methylmagnesium iodide prepared from methyl iodide (1·5 c.c.) and magnesium (0·55 g.). The *product* (XVI), isolated as usual, separated from methanol in yellow needles, m. p. 156° (Found: C, 88·9; H, 5·4. $C_{17}H_{12}O$ requires C, 88·8; H, 5·2%). It gives a red solution in concentrated sulphuric acid.

3 : 4 : 7 : 8-*Tetrahydro*-3-*oxo*-4-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (XVIII).—A mixture of 2-benzylidene-3-phenylindan-1-one (XVII) (5 g.), benzene (200 c.c.), and aluminium chloride (50 g.) was boiled under reflux for 6 hr., and then poured into water. The product, isolated in the usual way, crystallised from methanol (charcoal), giving 3 : 4 : 7 : 8-*tetrahydro*-3-*oxo*-4-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (XVIII) as colourless needles (55—75% yield), m. p. 132° (Found: C, 88·9; H, 5·6. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%). The 2 : 4-*dinitrophenylhydrazone* separates from ethyl acetate as orange needles, m. p. 271° (rapid heating) (Found: C, 70·3; H, 4·4; N, 11·0. $C_{28}H_{20}O_4N_4$ requires C, 70·6; H, 4·2; N, 11·7%).

3 : 4 : 7 : 8-*Tetrahydro*-3-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (XIX; $R = R' = H$).—3 : 4 : 7 : 8-Tetrahydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (XVIII) (2·5 g.) was added to a warm solution of sodium (1 g.) in ethylene glycol (50 c.c.). Pure hydrazine (prepared from hydrazine hydrate by refluxing for 3 hr. with an equal weight of potassium hydroxide) was now distilled directly in until the mixture, which was heated, refluxed freely at 180°; the heating was continued for 20 hr. Some hydrazine was then distilled back into the hydrazine generator until the temperature of the solution reached 197°, and the refluxing was then continued for a further 21 hr.; the cooled mixture was poured into water, and the product extracted with ether. 3 : 4 : 7 : 8-*Tetrahydro*-3-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (XIX; $R = R' = H$) crystallised from methanol in needles, m. p. 112° (1 g., 42%) (Found: C, 92·9; H, 6·2. $C_{22}H_{18}$ requires C, 93·6; H, 6·4%).

3 : 3-*Dichloro*-3 : 4 : 7 : 8-*tetrahydro*-4-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (XIX; $R = R' = Cl$).—The ketone (XVIII) (10 g.) and phosphorus pentachloride (10 g.) were boiled in benzene

(100 c.c.) for 10 hr. and then distilled to dryness under reduced pressure. The residue crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 151° (9·5 g., 80%) (Found: C, 75·2; H, 4·7; Cl, 20·7. $C_{22}H_{16}Cl_2$ requires C, 75·1; H, 4·6; Cl, 20·2%). This 3 : *3-dichloro-*3 : 4 : 7 : *8-tetrahydro-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* (XIX; R = R′ = Cl) readily gives the ketone (XVIII) on exposure to damp air or when hydrolysed with alcoholic potassium hydroxide or boiled with silver acetate in dry benzene. When reduced in ether with zinc and a trace of hydrochloric acid, it gives the hydrocarbon (XIX; R = R′ = H), m. p. and mixed m. p. 112°.

When the dichloro-compound (XIX; R = R′ = Cl) was either melted under reduced pressure or boiled in pyridine for 45 min., it was converted into a product which separated from light petroleum (b. p. 40—60°) as a crystalline powder, m. p. 214° (decomp.), which is probably 3 : 3 : 4(or 3 : 3 : 7)*-trichloro-*3 : 4 : 7 : *8-tetrahydro-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* (Found: C, 69·2; H, 4·1; Cl, 27·6. $C_{22}H_{15}Cl_3$ requires C, 68·4; H, 3·9; Cl, 27·0%).

3 : 4 : 7 : 8*-Tetrahydro-3-2′-hydroxyethoxy-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* (XIX; R = $HO{\cdot}CH_2{\cdot}CH_2{\cdot}O$, R′ = H) *and* 3-cyclo*Hexyloxy-*3 : 4 : 7 : *8-tetrahydro-4-phenyl-*1 : 2-5 : 6-*dibenzopentalene* (XIX; R = $C_6H_{11}O$, R′ = H).—The foregoing ketone (XVIII) was converted in the usual way [18] into the toluene-*p*-sulphonylhydrazone, m. p. 204°, which was then added (1 g.) to a solution of sodium (0·7 g.) in ethylene glycol (30 c.c.), and the mixture boiled for 1½ hr. Water was then added. The *2′-hydroxyethyl ether*, collected and crystallised from methanol, had m. p. 147° (Found: C, 84·4; H, 6·5. $C_{24}H_{22}O_2$ requires C, 84·3; H, 6·4%). A similar experiment using *cyclo*hexanol as solvent, subsequently removed under reduced pressure, gave 3-cyclo*hexyloxy-*3 : 4 : 7 : *8-tetrahydro-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* as needles, m. p. 133° (Found: C, 88·5; H, 7·3. $C_{28}H_{28}O$ requires C, 88·4; H, 7·4%).

3 : 4 : 7 : *8-Tetrahydro-3-hydroxy-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* (XX) (*Isomer* A).—3 : 4 : 7 : 8-Tetrahydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (XVIII) (3 g.) in dry ether (40 c.c.) was added slowly to a suspension of lithium aluminium hydride (0·5 g.) in ether (30 c.c.), and the mixture boiled for 1 hr. Next day water was added and the ethereal layer yielded 3 : 4 : 7 : *8-tetrahydro-3-hydroxy-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* (XX) (*isomer* A) as needles (from methanol) (2·5 g., 83%), m. p. 176—178° (Found: C, 88·1; H, 6·0. $C_{22}H_{18}O$ requires C, 88·6; H, 6·1%). The *acetyl derivative*, prepared by boiling isomer *A* (0·5 g.) with pyridine (10 c.c.) and acetyl chloride (0·2 g.) for 1 hr., crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 151° (Found: C, 84·8; H, 5·95. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%); it sublimes unchanged at 190°/12 mm., and is unaffected by anhydrous potassium carbonate at 250° for 3½ hr.

3 : 4 : 7 : *8-Tetrahydro-3-hydroxy-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* (XX) (*Isomer* B).—A solution of aluminium *iso*propoxide was prepared in the usual way from aluminium (0·3 g.), *iso*propyl alcohol (10 c.c.), and a trace of mercuric oxide, and a solution of 3 : 4 : 7 : 8-tetrahydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (XVIII) (2·0 g.) in toluene was added. The mixture was slowly distilled for 4 hr. with the addition of more toluene as necessary, then added to dilute sulphuric acid, and the toluene and ether extract distilled under reduced pressure. The residue separated from light petroleum (b. p. 60—80°) as fine crystals (2·0 g.), m. p. 148°, of 3 : 4 : 7 : *8-tetrahydro-3-hydroxy-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* (XX) (*isomer* B) (Found: C, 87·9; H, 5·9. $C_{22}H_{18}O$ requires C, 88·6; H, 6·1%). The *acetyl derivative*, prepared and crystallised as in the case of the isomer (above), formed needles, m. p. 145° (mixed m. p. with starting material 128°) (Found: C, 84·7; H, 5·8. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%). It is unchanged when heated alone or with potassium carbonate at 250°.

When the reduction was carried out on five times the scale and for 6 hr., the product was the anhydro-derivative of (XX) (isomer *B*) (6·5 g.), m. p. and mixed m. p. with the specimen of the anhydro-derivative described below, m. p. 179—180°.

Dehydration of Isomers A *and* B *of* 3 : 4 : 7 : *8-Tetrahydro-3-hydroxy-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* (XX) *with Copper Sulphate.*—The hydroxy-compound (XX), isomer *A* (1 g.), was boiled in xylene (30 c.c.) with anhydrous copper sulphate (1 g.) for 4 hr. The solution was filtered and the solids were washed with ether. The filtrate and washings were evaporated under reduced pressure, and the residue crystallised from petroleum (b. p. 60—80°), then from ethanol, yielding 4 : 7(?)*-dihydro-4-phenyl-*1 : 2-5 : *6-dibenzopentalene* (XXI; R = H) as needles (20 mg.), m. p. 178—180° (Found: C, 94·6; H, 5·9. $C_{22}H_{16}$ requires C, 94·3; H, 5·7%), and compound *X* (20 mg.), m. p. 158—159° (Found: C, 92·7, 92·5; H, 6·7, 6·6%).

The isomer *A* (1 g.), after being heated as above for 7 hr., gave the anhydro-compound

(10 mg.) and compound *X* (75 mg.). After 10 hours' heating, compound *X* (90 mg.) only was obtained.

The hydroxy-compound (XX), isomer *B* (0·5 g.), was boiled in xylene (10 c.c.) with anhydrous copper sulphate (1 g.), and the product worked up as above. After 1·5 hours' boiling, the anhydro-compound (10 mg.) was obtained; after 3 hours the product was compound *X* (20 mg.).

Action of Phosphoric Anhydride on 3 : 4 : 7 : 8-*Tetrahydro*-3-*hydroxy*-4-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (XX) (*Isomers* A *and* B).—The hydroxy-compound (isomer *A* or *B*) (0·5 g.) was boiled in benzene (20 c.c.) with a large excess of phosphoric anhydride for 2—4 hr. After addition of water, the benzene layer yielded a residue which crystallised from light petroleum (b. p. 60—80°) in colourless needles which melted about 60°, solidified about 80°, and then had m. p. 154° (0·3 g.) (Found: C, 93·5; H, 6·2. $C_{22}H_{18}$ requires C, 93·6; H, 6·4%. $C_{22}H_{16}$ requires C, 94·3; H, 5·8%). The 3 : 4 : 7 : 8-*tetrahydro*-4-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (XIX; R = R′ = H) gave no tests for the presence of an olefinic group.

The infrared spectrum examined in *cyclo*hexane showed strong bands at 745 and 702 cm.$^{-1}$, the former being the more intense. *ortho*-Substituted benzenes do not have a strong band near 702, whereas monosubstituted benzenes do. The 745 cm.$^{-1}$ band would be due to the second band present in monosubstituted benzenes plus a considerable contribution from the *ortho*-substituted rings, as the frequency 745 cm.$^{-1}$ lies very near to the typical band for *ortho*-compounds.

3 : 4-*Dihydro*-3-*oxo*-4-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (IV).—A slow stream of dry air was drawn through a solution of bromine (0·1 c.c.) in chloroform (50 c.c.) and then through a solution of 3 : 4 : 7 : 8-tetrahydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (XVIII) (1 g.) in chloroform (50 c.c.) until no bromine remained in the first chloroform solution (7 hr.). The second solution was evaporated and the residue passed through a column of alumina and eluted with ether. The first fraction was crystallised from methanol and consisted of unchanged starting material (XVIII) (0·6 g.), m. p. 132°; the second fraction gave yellow crystals, m. p. 266—269° (decomp.), of 3 : 4-*dihydro*-3-*oxo*-4-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (IV) (Found: C, 90·0; H, 4·9. $C_{22}H_{14}O$ requires C, 89·8; H, 4·8%).

Reaction of Phenylmagnesium Bromide with 3 : 4 : 7 : 8-*Tetrahydro*-3 : 4-*dioxo*-1 : 2-5 : 6-*dibenzopentalene* (X). 3 : 4 : 7 : 8-*Tetrahydro*-3-*hydroxy*-4-*oxo*-3-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (XXIII) *and* 3 : 4-*Dihydro*-3-*oxo*-4-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (IV).—The diketone (X) and ethereal phenylmagnesium bromide (2 mol.) were boiled under reflux for 1 hr. The product, obtained in poor yield and isolated in the usual way, crystallised from aqueous methanol in colourless needles, m. p. 120°, of 3 : 4 : 7 : 8-*tetrahydro*-3-*hydroxy*-4-*oxo*-3-*phenyl*-1 : 2-5 : 6-*dibenzopentalene* (XXIII) (Found: C, 84·1; H, 5·1. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%). When the experiment was repeated using more of the Grignard reagent, or better phenyl-lithium, the product (poor yield) was 3 : 4-dihydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (IV) which separated from light petroleum (b. p. 40—60°) as yellow crystals, m. p. 269—270° (decomp.) alone or mixed with the previously made compound (Found: C, 89·2; H, 4·8%).

Epoxide of 2-*Benzylidene*-3-*phenylindan*-1-*one* (XVII).—Hydrogen peroxide (3·5 c.c.; 30%) and 6N-sodium hydroxide (1·6 c.c.) were added to a suspension of 2-benzylidene-3-phenylindan-1-one (2 g.) in ethanol. After 48 hours' stirring at room temperature, water (100 c.c.) was added and the solid collected and recrystallised from methanol, giving the *epoxide* as needles (1·8 g., 86%), m. p. 164° (Found: C, 84·3; H, 5·2. $C_{22}H_{16}O_2$ requires C, 84·7; H, 5·1%).

1 : 3-*Dihydroxy*-2 : 4-*diphenylnaphthalene* (XXIV).—The epoxide of 2-benzylidene-3-phenylindan-1-one was (*a*) added rapidly to a large excess of polyphosphoric acid at 160° with stirring and then kept at 192° for 2 min., (*b*) heated with an excess of concentrated aqueous hydrochloric acid on the water-bath for 3 hr., and then poured into water, or (*c*) kept (0·7 g.) in benzene (20 c.c.) with boron trifluoride in ether (3·7 c.c.; 45% solution) for 5 min., then diluted with ether (25 c.c.). After having been washed with water, the ethereal layer yielded a solid. Crystallisation from methanol then gave in each case colourless needles, m. p. 163—165° (mixed m. p. with the epoxide, 140°) (Found: C, 84·2; H, 5·3. $C_{22}H_{16}O_2$ requires C, 84·7; H, 5·1%). This 1 : 3-*dihydroxy*-2 : 4-*diphenylnaphthalene* (XXIV) gives no colour with alcoholic ferric chloride, but dissolves in dilute aqueous sodium hydroxide, and is recovered on acidification.

3 : 4 : 7 : 8-*Tetrahydro*-3-*hydroxy*-3 : 4-*diphenyl*-1 : 2-5 : 6-*dibenzopentalene* (XXV).—A solution of 3 : 4 : 7 : 8-tetrahydro-3-oxo-4-phenyl-1 : 2-5 : 6-dibenzopentalene (8 g.) in ether was added to a solution of phenylmagnesium bromide, prepared from bromobenzene (8 c.c.), magnesium (2 g.),

and ether (100 c.c.), and the mixture boiled for 5 hr. The product, isolated in the usual way, crystallised from light petroleum (b. p. 40—60°), giving 3 : 4 : 7 : 8-*tetrahydro*-3-*hydroxy*-3 : 4-*diphenyl*-1 : 2-5 : 6-*dibenzopentalene* (XXV) as needles, m. p. 160° (8·2 g., 80%) (Found: C, 89·4; H, 5·8. $C_{28}H_{22}O$ requires C, 89·8; H, 5·9%).

4 : 7-*Dihydro*-3 : 4-*diphenyl*-1 : 2-5 : 6-*dibenzopentalene* (XXI; R = Ph).—The above hydroxy-compound (XXV) (8·2 g.) and anhydrous copper sulphate (8 g.) were boiled in xylene for 4 hr., then added to water and shaken with ether. The organic layer was distilled under reduced pressure and the residue crystallised from light petroleum (b. p. 60—80°), giving 4 : 7-*dihydro*-3 : 4-*diphenyl*-1 : 2-5 : 6-*dibenzopentalene* (XXI; R = Ph) as colourless needles, m. p. 202—204° (decomp.) (6·7 g., 86%) (Found: C, 94·1; H, 5·7. $C_{28}H_{20}$ requires C, 94·4; H, 5·6%).

Dinitrogen Tetroxide Addition Product of 4 : 7-*Dihydro*-3 : 4-*diphenyl*-1 : 2-5 : 6-*dibenzopentalene*.—4 : 7-Dihydro-3 : 4-diphenyl-1 : 2-5 : 6-dibenzopentalene (XXI; R = Ph) (0·3 g.), dissolved in carbon tetrachloride (10 c.c.), was treated with liquid oxides of nitrogen (0·4 c.c.; b. p. 25—35°) prepared by distilling fuming nitric acid (8·3 c.c.) with concentrated sulphuric acid (3·3 c.c.) and arsenious oxide (10 g.). The mixture was stirred at room temperature for 1 hr. and then evaporated to dryness under reduced pressure. The residue was crystallised from benzene, giving the crystalline *addition product*, m. p. 242° (Found: C, 75·4; H, 4·8; N, 6·7. $C_{28}H_{20}O_4N_2$ requires C, 75·2; H, 4·5; N, 6·3%).

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