673. *Anomalies in the Reduction of* 2 : 2′-*Diacetyldiphenyl.*

By D. MURIEL HALL, JOAN E. LADBURY, MARY S. LESSLIE, and E. E. TURNER.

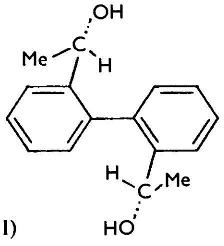
2 : 2′-Diacetyldiphenyl gives 9 : 10-dimethylphenanthrene on Clemmensen reduction. With lithium aluminium hydride it gives two diastereoisomeric 2 : 2′-di-(1-hydroxyethyl)diphenyls. These react normally with hydrobromic acid and, by the action of boiling quinoline on the resulting mixture of isomerides, 2 : 2′-divinyldiphenyl has been prepared. Reduction of 2 : 2′-diacetyldiphenyl under Huang-Minlon conditions gives 2-methyl-3 : 4-5 : 6-dibenzo*cyclo*hepta-1 : 3 : 5-triene.

2 : 2′-Di-(1-hydroxy-1-methylethyl)diphenyl can be dehydrated in three ways, to give (*a*) 2 : 7 : 7-trimethyl-3 : 4-5 : 6-dibenzo*cyclo*hepta-1 : 3 : 5-triene, (*b*) 2 : 2′-di*iso*propenyldiphenyl, or (*c*) 2 : 7-dihydro-2 : 2 : 7 : 7-tetramethyl-3 : 4-5 : 6-dibenzoxepin.

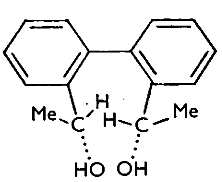
A POSSIBLE route to 2 : 2′-diethyldiphenyl (see Everitt, Hall, and Turner [1]) appeared to be the Clemmensen reduction of 2 : 2′-diacetyldiphenyl. Since the latter is produced by the oxidation of 9 : 10-dihydro-9 : 10-dihydroxy-9 : 10-dimethylphenanthrene, obtained by the action of a Grignard reagent on phenanthraquinone, the method might be applicable to the preparation of a series of 2 : 2′-dialkyldiphenyls.

However, the Clemmensen reduction of 2 : 2′-diacetyldiphenyl gave a high yield of 9 : 10-dimethylphenanthrene. Other sterically hindered ketones have been observed to give anomalous products on Clemmensen reduction (cf. Brewster, Patterson, and Fidler [2]) and acetophenone itself gives predominantly styrene instead of ethylbenzene under certain conditions.[3]

Other methods of reduction were then investigated. With lithium aluminium hydride reduction proceeded normally to give a mixture of two isomeric 2 : 2′-di-(1-hydroxyethyl)-diphenyls. By tedious fractional crystallisation it was possible to isolate the individual diols, *A*, m. p. 147·5—149°, and *B*, m. p. 153—155°. These are presumably the two diastereoisomeric (racemic and *meso*) forms resulting from the presence of two asymmetric carbon atoms. There was no evidence of further stereoisomerism arising from restricted rotation of the diphenyl skeleton, and the evidence of optical instability in related compounds [*e.g.*, 2′-(1-hydroxy-1-methylethyl)diphenyl-2-carboxylic acid [4]] suggests that such stereoisomerism would be of an unstable type. The *meso*-compound is of particular interest in that it can pass through a conformation in which it has a centre of symmetry (I), but not through one in which it has a plane of symmetry (II), since it would be impossible for the two substituent groups to be accommodated on the same side of the diphenyl skeleton whilst the benzene nuclei in the latter were coplanar. Unfortunately the quantities of pure diols were insufficient for investigation of them by optical resolution.



(I)



(II)

The diols were dehydrated separately by heating them with 20% sulphuric acid and gave 2 : 7-dihydro-2 : 7-dimethyl-3 : 4-5 : 6-dibenzoxepin (III). This also appeared to be

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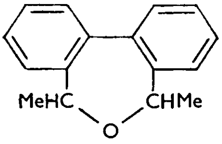
[1] Everitt, Hall, and Turner, *J.*, 1956, 2286.
[2] Brewster, Patterson, and Fidler, *J. Amer. Chem. Soc.*, 1954, **76**, 6368.
[3] Clemmensen, *Ber.*, 1913, **46**, 1837.
[4] Corbellini and Angeletti, *Atti R. Accad. Lincei*, 1932, **15**, 968; Jamison and Turner, *J.*, **1942**, **437**.

a mixture of diastereoisomers but only one form was isolated and was probably not stereochemically pure. This form was the main product from diol *A*. Diol *B* reacted much more slowly and the product was more obviously a mixture, but after several crystallisations the melting point of the oxepin approached that of the oxepin from *A* and was not depressed in the presence of the latter.



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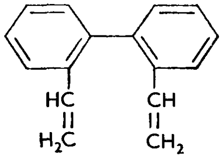
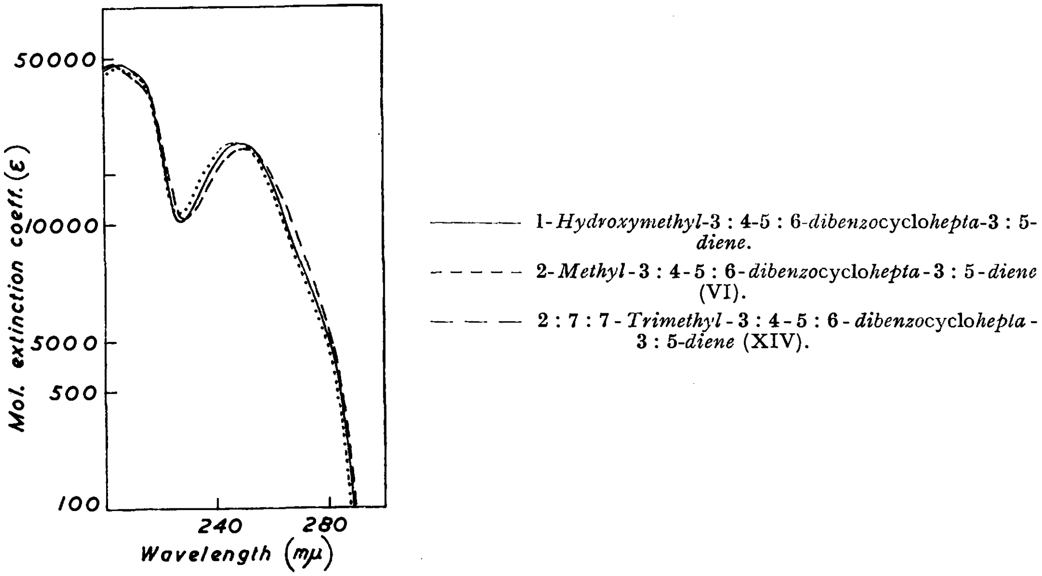


(IV)

The two diols reacted with hot hydrobromic acid to give what was evidently a mixture of diastereoisomeric dibromo-compounds. When heated with quinoline these mixtures gave 2 : 2'-divinyldiphenyl (IV), a crystalline specimen of which, unlike 4 : 4'-divinyldiphenyl,[5] showed no sign of polymerisation. Catalytic hydrogenation of the divinyl derivative (IV) gave 2 : 2'-diethyldiphenyl, and the latter was readily brominated by *N*-bromosuccinimide in presence of benzoyl peroxide, giving the above two dibromo-compounds, again as a diastereoisomeric mixture.



——— 1-*Hydroxymethyl*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-3 : 5-*diene.*

- - - - - 2-*Methyl*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-3 : 5-*diene* (VI).

— — — 2 : 7 : 7-*Trimethyl*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-3 : 5-*diene* (XIV).

Application of Huang-Minlon conditions [6] of reduction to 2 : 2'-diacetyldiphenyl gave an unsaturated hydrocarbon, $C_{16}H_{14}$, m. p. 50°, together with a little 9 : 10-dimethylphenanthrene. Since 2 : 2'-divinyldiphenyl (m. p. 80—81°) is excluded, the only apparent alternative structure is that of 2-methyl-3 : 4-5 : 6-dibenzo*cyclo*hepta-1 : 3 : 5-triene (V). The hydrocarbon contained one olefinic double bond (titration with bromine) and on catalytic hydrogenation gave a non-olefinic hydrocarbon, $C_{16}H_{16}$, with an ultraviolet absorption spectrum very similar to that of 1-hydroxymethyl-3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene [7] (see Table and Figure). The non-olefinic hydrocarbon must therefore be 2-methyl-3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene (VI). Further proof of the structure of the triene (V) comes from its behaviour on oxidation. With selenium dioxide it gave a monoketone (VII), isolated as the 2 : 4-dinitrophenylhydrazone. On oxidation with

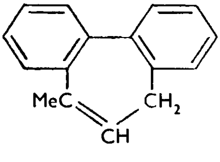
[5] Valyi, Janssen, and Mark, *J. Phys. Chem.*, 1945, **49**, 461.
[6] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.
[7] Beaven, Bird, Hall, Johnson, Ladbury, Lesslie, and Turner, *J.*, 1955, 2708.

Ultraviolet absorption spectra.

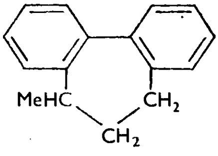
	Short-wave band				Conjugation band		Long-wave features	
	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε	$\lambda_{max.}$	ε	$\lambda_{inf.}$	ε
1-Hydroxymethyl-3 : 4-5 : 6-dibenzo-*cyclo*hepta-3 : 5-diene[7]	206	45,500	227·5	5150	248·5	15,200	(*ca.* 277)	*ca.* 1450
2-Methyl-3 : 4-5 : 6-dibenzo*cyclo*-hepta-3 : 5-diene (VI)	205·5	44,000	227	5830	248	15,300	(*ca.* 276)	*ca.* 1400
2 : 7 : 7-Trimethyl-3 : 4-5 : 6-dibenzo-*cyclo*hepta-3 : 5-diene (XIV)	205	45,000	229	5350	250	14,200	(*ca.* 278)	*ca.* 1500

Solvent, light petroleum (b. p. 80—100°); wavelengths in mμ; values in parentheses denote inflections.

sodium dichromate in acetic acid it gave phenanthraquinone, 2-acetyldiphenyl-2′-carboxylic acid, and 2-acetyl-2′-formyldiphenyl. The behaviour closely resembles that of 3 : 4-5 : 6-dibenzo*cyclo*hepta-1 : 3 : 5-triene [8] and of deaminocolchinol methyl ether [9] on similar oxidation.



(V)



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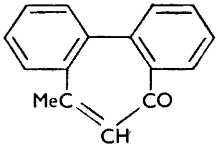
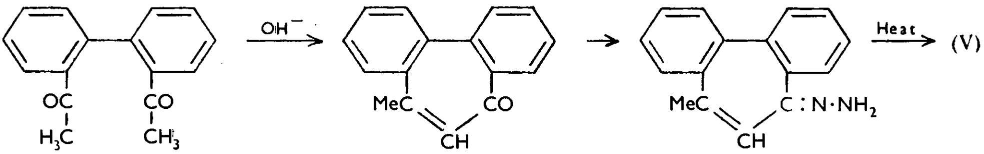


(VII)

Oxidation with sodium dichromate in acetic acid to phenanthraquinone is used by Cook, Loudon, *et al.*[8, 9, 10, 11] as a test for the bridged diphenyl system. However, as a check on the validity of this test, we subjected 2 : 2′-divinyldiphenyl to oxidation under similar conditions and, rather surprisingly, found that this compound, too, gave phenanthraquinone.

A possible route from diacetyldiphenyl to the cyclic triene (V) is an aldol-type condensation (in the presence of the sodium hydroxide) to give the monoketone (VII), followed by hydrazone formation and normal decomposition :



(VII) (VIII)

Attempts were made to prepare the monoketone (VII) from 2 : 2′-diacetyldiphenyl; the latter was practically unaffected by hydrogen chloride in acetic acid solution or by " piperidine–acetate." It underwent reaction in the presence of sodium hydroxide under various conditions but no recognisable compound could be isolated from the product.

Treatment of 2 : 2′-diacetyldiphenyl with warm aqueous-alcoholic hydrazine gave a colourless compound, $C_{16}H_{14}N_2$, m. p. 167—168°, together with some 9 : 10-dimethylphenanthrene. Separation was effected by extracting the unknown compound with warm dilute hydrochloric acid and reprecipitating it with ammonia. On hydrolysis with boiling dilute sulphuric acid the unknown compound gave 2 : 2′-diacetyldiphenyl and when heated with sodium hydroxide in triethylene glycol it gave only 9 : 10-dimethylphenanthrene. It must therefore be 3 : 8-dimethyl-4 : 5-6 : 7-dibenzo-1 : 2-diazocine (IX). The alternative formula (VIII) is precluded by the result of acid hydrolysis, by the failure of the

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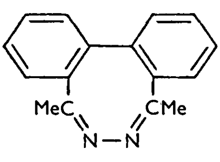
[8] J. W. Cook, Dickson, and Loudon, *J.*, 1947, 746.
[9] Barton, J. W. Cook, and Loudon, *J.*, 1945, 176.
[10] J. W. Cook, Jack, Loudon, Buchanan, and MacMillan, *J.*, 1951, 1397.
[11] J. W. Cook, Loudon, and Razdan, *J.*, 1954, 4234.

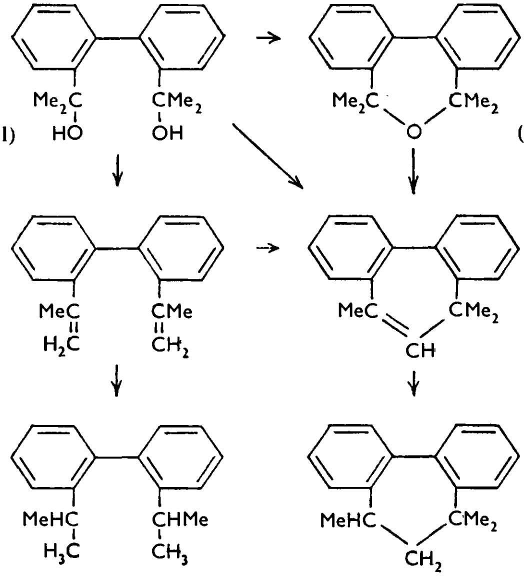
compound to give a salicylidene derivative, and by its failure to decolorise bromine water. The formation of the eight-membered ring azine (IX) and its subsequent decomposition presumably accounts for the 9 : 10-dimethylphenanthrene isolated from the products of the Huang-Minlon reduction. However, the formation of 9 : 10-dimethylphenanthrene during the preparation of the cyclic azine (IX) is less easily accounted for, since the azine itself is stable under the conditions used. It was unaffected by hot aqueous-alcoholic hydrazine or sodium hydroxide or when heated above its melting point, alone or with copper bronze.



(IX)

Meerwein–Ponndorf–Verley reduction of 2 : 2′-diacetyldiphenyl was also attempted but the product appeared to be a mixture and no pure compounds could be isolated.

2 : 2′-Di*iso*propenyldiphenyl (X) was required for comparison of its absorption spectrum with that of 2 : 2′-divinyldiphenyl. Accordingly 2 : 2′-di-(1-hydroxy-1-methylethyl)diphenyl (XI) was prepared,[12] and dehydrated at 140° with naphthalene-2-sulphonic acid, giving a hydrocarbon, $C_{18}H_{18}$, m. p. 100—101° (Cook and Turner [12] give m. p. 97—98°). On hydrogenation over Adams's platinum oxide catalyst this absorbed only one molecular proportion of hydrogen, giving a compound, m. p. 69—71°, whose absorption spectrum was that of a 2 : 2′-bridged diphenyl. Dehydration of diol (XI) with boiling 4N-sulphuric acid gave 2 : 7-dihydro-2 : 2 : 7 : 7-tetramethyl-3 : 4-5 : 6-dibenzoxepin (XII), m. p. 92—93°. This compound was first recognised as an oxepin from its ultraviolet absorption spectrum. Authentic 2 : 2′-di*iso*propenyldiphenyl (X) was obtained by dehydration of the boiling diol (XI) in presence of activated alumina and copper bronze; this hydrocarbon absorbed two molecular proportions of hydrogen in the presence of Adams catalyst, giving 2 : 2′-di*iso*propyldiphenyl,[1] m. p. 67—68°. Cook and Turner's isomeric hydrocarbon must therefore be 2 : 7 : 7-trimethyl-3 : 4-5 : 6-dibenzo*cyclo*hepta-1 : 3 : 5-triene (XIII), and its hydrogenation product 2 : 2 : 7-trimethyl-3 : 4-5 : 6-dibenzo*cyclo*hepta-3 : 5-diene (XIV). The absorption spectrum of the latter is very similar to that of its monomethyl analogue (VI) (see Table and Figure) and quite different from that of a non-bridged diphenyl with two *ortho*-substituents.



(XI) (XII) (X) (XIII) (XIV)

The triene (XIII) was also formed by the action of boiling hydrobromic acid on the diol (XI) or the oxepin (XII), or by treatment of the isomeric hydrocarbon (X) with boiling 50% sulphuric or hydrobromic acid. In the absence of acids the diol was remarkably stable and could be distilled unchanged at atmospheric pressure (b. p. 320°).

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[12] D. E. Cook and Turner, *J.*, 1937, 117.

In contrast to 2 : 2'-di*iso*propenyldiphenyl (X), 2 : 2'-divinyldiphenyl (IV) reacted normally with hydrobromic acid, undergoing addition to give 2 : 2'-di-(1-bromoethyl)diphenyl, the compound from which it had originally been obtained.

Oxidation of the triene (XIII) with sodium dichromate in acetic acid gave 2-acetyl-2'-formyldiphenyl, a little phenanthraquinone, and unidentified acids.

EXPERIMENTAL

9 : 10-*Dihydro*-9 : 10-*dihydroxy*-9 : 10-*dimethylphenanthrene*.—The following method was a considerable improvement on that of Zincke and Tropp.[13] Finely ground phenanthraquinone (84 g., 1 mol.) was added in approx. 2 g. lots to a Grignard reagent made from magnesium (39 g., 4 atom-equiv.), about 500 c.c. of ether and enough methyl iodide to cause complete dissolution of the magnesium. After addition of 500 c.c. of benzene, the mixture was heated under reflux on a water-bath for 2 hr., the ether being allowed to distil off gradually through a selective condenser. The cooled mixture was added carefully to ice and water, kept well stirred. Dilute sulphuric acid was added until, on continued stirring, no further colour change occurred. The two layers were separated, ether being added to dissolve any solid that separated. The aqueous layer was extracted twice with ether. The combined ethereal extract was washed twice with brine and then several times with concentrated aqueous sodium hydrogen sulphite solution, until the latter, treated with alkali, gave no phenanthraquinone. (The combined bisulphite extracts, on such treatment, gave 6·5 g. of phenanthraquinone, once crystallised from glacial acetic acid.)

The ether–benzene solution was washed with brine and then distilled, without being dried, until the volume was about 300 c.c. On cooling, the diol crystallised and more was obtained from the mother-liquor. Recrystallisation from benzene gave 75 g. of pure diol, m. p. 163—164°. After allowance for the recovered phenanthraquinone, the yield was 88%.

The use of 6 mol. of Grignard reagent did not improve the yield and greatly extended the time of operating.

2 : 2'-*Diacetyldiphenyl*.—Using the calculated amount of chromic anhydride as recommended by Zincke and Tropp [14] the oxidation was incomplete and the product was difficult to purify. The following procedure was found satisfactory :

To a solution of the preceding diol (38 g., 1 mol.) in glacial acetic acid (380 c.c.), at about 70°, was added, during 10 min., chromic anhydride (16 g., 1·5 mol.) in water (160 c.c.). After a further 10 min. at about 70°, excess of water was gradually added, and the crystalline diacetyldiphenyl filtered off and washed with water. The well-pressed solid, crystallised from ethanol and then from *cyclo*hexane, had m. p. 93—94° (yield 89%) (Zincke and Tropp [14] gave m. p. 84°, Cook and Turner [12] 94—95°).

2 : 2'-Di-(1-hydroxy-1-methylethyl)diphenyl [12] (XI) was obtained in 80% yield from diacetyldiphenyl and 4 mols. of methylmagnesium iodide in ether. Crystallised from ethanol, it had m. p. 139—140°, b. p. 320°/760 mm.

Clemmensen Reduction of 2 : 2'-*Diacetyldiphenyl*.—A mixture of diacetyldiphenyl (28 g.) and hydrochloric acid was boiled under reflux for 6 hr. in presence of amalgamated zinc. The solution was then decanted and extracted with ether. The residue was also repeatedly extracted with boiling ether to dissolve the solid coating the unchanged zinc. Removal of ether from the combined extracts gave a residue (24·5 g.) which, after crystallisation from ethanol, had m. p. 144° (Found : C, 92·8; H, 7·0. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%) and gave a picrate, m. p. 192—193°. 9 : 10-Dimethylphenanthrene [13] has m. p. 144° and its picrate [15] m. p. 192°.

2 : 2'-*Di*-(1-*hydroxyethyl*)*diphenyl*.—Finely ground 2 : 2'-diacetyldiphenyl (11·9 g., 1 mol.) was washed with ether (300 c.c.) into lithium aluminium hydride (2·9 g., 1·5 mols.) in ether (100 c.c.). The mixture was heated for 1 hr. and then decomposed with ethyl acetate, water, and N-sulphuric acid. The solid obtained after removal of the ether was subjected to repeated fractional crystallisations from benzene; the nearly pure diols were finally crystallised from ethanol. *Diol A* was obtained as prisms, m. p. 147·5—149° (Found : C, 79·2; H, 7·6. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·5%). *Diol B* (which was more soluble than *A* in benzene) was obtained as long prisms, m. p. 153—155° (Found : C, 79·5; H, 7·6%).

2 : 7-*Dihydro*-2 : 7-*dimethyl*-3 : 4-5 : 6-*dibenzoxepin*.—(i) *From diol A*. The diol (1·0 g.) was heated with 20% sulphuric acid (15 c.c.) on a steam-bath for 2½ hr. with occasional shaking.

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[13] Zincke and Tropp, *Annalen*, 1908, **362**, 242.

[14] *Idem, ibid.*, **363**, 302.

[15] Rimmer, Christiansen, Brown, and Sandin, *J. Amer. Chem. Soc.*, **1950**, **72**, 2298.

The oil solidified on cooling. After one crystallisation from ethanol it had m. p. 74—76°, with previous softening. Two further crystallisations from methanol raised the m. p. to 77—80°, with softening from 74° (Found: C, 85·9; H, 7·3. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%).

(ii) *From diol B*. The diol was treated as above but it was necessary to heat it for 7 hr. to complete the reaction (indicated by the absence of solid in the oil floating on the hot acid). After one crystallisation from methanol the *oxepin* had m. p. 68—73°, with previous softening. Further crystallisation raised the m. p. to 74—78° (mixed m. p. with oxepin from *A*, 75—78°).

2 : 2′-*Di*-(1-*bromoethyl*)*diphenyl*.—The above diol (either *A* or *B* or a mixture of both) was heated for about 15 min. with a large excess of hydrobromic acid (*d* 1·49). The oil solidified on cooling; it was washed with water, dried *in vacuo* over sodium hydroxide, and crystallised several times from light petroleum (b. p. 40—60°) or *n*-hexane. The *dibromide* (*ca.* 20% from either diol) then had m. p. 88—92°, with previous softening (85°) (Found: C, 52·0; H, 4·6; Br, 43·3. $C_{16}H_{16}Br_2$ requires C, 52·2; H, 4·4; Br, 43·4%). Second crops were obtained with lower m. p.s (*e.g.*, 71—79°); these also gave the diene when heated with quinoline and presumably contained more of the second isomer.

2 : 2′-*Divinyldiphenyl* (*with Miss* P. M. EVERITT).—A solution of the above dibromide in quinoline was boiled for 5 min. The cooled solution was poured into dilute hydrochloric acid, and the solid separated and crystallised from *n*-hexane and then from methanol. 2 : 2′-*Divinyldiphenyl* had m. p. 80—81° (Found: C, 93·2; H, 6·6. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). The m. p. was unchanged after several months. Hydrogenation in ethanolic solution at Adams's platinum oxide catalyst gave 2 : 2′-diethyldiphenyl,[1] b. p. 139—140°/13·5 mm., n_D^{25} 1·5626.

Bromination of 2 : 2′-*Diethyldiphenyl* (*with Miss* P. M. EVERITT).—2 : 2′-Diethyldiphenyl (21 g., 1 mol.), *N*-bromosuccinimide (35·6 g., 2 mol.), and benzoyl peroxide (0·1 g.) in dry carbon tetrachloride (80 c.c.) were heated under reflux for 3 hr. More carbon tetrachloride (80 c.c.) was added and the hot solution filtered. The solvent was distilled off from the filtrate and the residue was crystallised from light petroleum (b. p. 40—60°), giving 2 : 2′-di-(1-bromoethyl)diphenyl (25·5 g., 70%), m. p. 75—79°, with previous softening. After five crystallisations it had m. p. and mixed m. p. (with a specimen prepared from the diol) 87—90°, with previous softening (Found: C, 52·4; H, 4·6; Br, 44·0. Calc. for $C_{16}H_{16}Br_2$: C, 52·2; H, 4·4; Br, 43·4%).

Huang-Minlon Reduction of 2 : 2′-*Diacetyldiphenyl*.—2 : 2′-Diacetyldiphenyl (20 g.), powdered sodium hydroxide (34 g.), 85% aqueous hydrazine hydrate (34 c.c.), and triethylene glycol (500 c.c.) were heated together under reflux for 2 hr. Water and excess of hydrazine hydrate were removed by distillation until the temperature reached 195°. Heating under reflux was then resumed for 4 hr. The mixture was poured into water and extracted with ether, and the ethereal solution washed and dried (K_2CO_3). The ether was removed and the residual oil distilled under reduced pressure, giving fraction 1, b. p. 140—150°/1 mm. (15·8 g.), and fraction 2, b. p. 160—168°/1 mm. (2·9 g.). Both fractions solidified and were crystallised separately from methanol, giving the main product (12·3 g.), 9 : 10-dimethylphenanthrene (0·2 g., from fraction 2), and a residual oil. Recrystallisation of the main product from methanol gave pure 2-*methyl*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-1 : 3 : 5-*triene*, m. p. 49·5—50·5° (10 g., 40%) (Found: C, 93·1; H, 7·0. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%) (0·4052 g. of hydrocarbon required 33·3 c.c. of 0·1123N-bromine, equiv. to 0·95 double bond). The residue in the distillation flask was extracted with benzene, and the solution concentrated and treated with a solution of picric acid in benzene. 9 : 10-Dimethylphenanthrene picrate (0·5 g.) separated.

2-*Methyl*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-3 : 5-*diene*.—The above triene (7·5 g.) in glacial acetic acid (35 c.c.) was shaken with hydrogen in the presence of palladium (1·0 g.). The product was isolated in the usual manner and distilled twice under reduced pressure. The *diene* was obtained as an oil, b. p. 120°/1 mm., n_D^{25} 1·6102 (Found: C, 92·3; H, 8·0. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%).

Oxidation of 2-*Methyl*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-1 : 3 : 5-*triene*.—(a) *With selenium dioxide.* The triene (0·513 g.) in xylene (2·5 c.c.) was heated under reflux with selenium dioxide (0·304 g.) for 5½ hr. The solution was filtered and the xylene distilled off. The residue was dissolved in ether and benzene and washed with water and alkali. The solvents were removed; on further heating the residue began to decompose and could not be distilled. It was extracted with alcohol and treated with 2 : 4-dinitrophenylhydrazine reagent. 2-*Methyl*-7-*oxo*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-1 : 3 : 5-*triene* 2 : 4-*dinitrophenylhydrazone* crystallised from benzene–light petroleum and had m. p. 252° (decomp.) (Found: C, 66·3; H, 4·4; N, 14·0. $C_{22}H_{16}O_4N_4$ requires C, 66·0; H, 4·0; N, 14·0%).

(b) *With sodium dichromate in acetic acid.* The triene (1·6 g., 1 mol.) in acetic acid (7·5 c.c.), and sodium dichromate (7·0 g., 3 mol.) in acetic acid (20 c.c.), were heated together on a steam-bath for 1¾ hr. The solution was poured into water and extracted with chloroform. The chloroform solution was shaken with aqueous sodium carbonate, washed with water, and dried (Na_2SO_4), and the solvent distilled off. The residue was treated with a little benzene, and a yellow solid filtered off. It had m. p. and mixed m. p. with phenanthraquinone 208—209° and with *o*-phenylenediamine gave the quinoxaline, m. p. 222—223°, mixed m. p. 223—224°. The benzene solution, after removal of the phenanthraquinone, was diluted with benzene and light petroleum and passed through alumina. The column was eluted with the same solvent and finally with benzene. Concentration of the eluate gave a gum which later became crystalline. After several crystallisations from *cyclo*hexane it had m. p. 80—83°, not depressed on admixture with 2-acetyl-2′-formyldiphenyl (see below). The sodium carbonate washings (of the original chloroform solution) were acidified and gave a gum which later solidified. After several crystallisations (from aqueous alcohol and *cyclo*hexane) it had m. p. 120—121° (Found: C, 74·8; H, 5·0. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·0%). Lucien and Taurins [16] give m. p. 121—122 for 2′-acetyldiphenyl-2-carboxylic acid.

Oxidation of 2 : 2′-*Divinyldiphenyl.*—The hydrocarbon (1·0 g., 1 mol.) in acetic acid (5 c.c.), and sodium dichromate (4·4 g., 3 mol.) in acetic acid (13 c.c.), were heated together on a steam-bath for 1¾ hr. Evolution of a gas (presumably carbon dioxide) began after a few min. The cooled solution was poured into water and extracted with chloroform. The extract was washed with aqueous sodium carbonate and water, dried and evaporated. The semi-solid residue was treated with a little benzene and filtered. The solid was crystallised from benzene and then had m. p. and mixed m. p. with phenanthraquinone 209°. The quinoxaline had m. p. and mixed m. p. 224—225°.

3 : 8-*Dimethyl*-4 : 5-6 : 7-*dibenzo*-1 : 2-*diazocine* (IX).—A solution of 2 : 2′-diacetyldiphenyl (5 g.) and 85% aqueous hydrazine hydrate (2·5 c.c.) in ethanol (20 c.c.) was kept at *ca.* 60—40° overnight. On cooling, the solution deposited prisms and, after the addition of water, a mixture of needles and prisms. A sticky third crop was obtained on addition of more water. The crops were combined and warmed with dilute hydrochloric acid and filtered. The insoluble needles were 9 : 10-dimethylphenanthrene (m. p. and mixed m. p. 144—145° after crystallisation) (*ca.* 0·2 g.). Addition of aqueous ammonia to the filtrate precipitated the *azine* (IX); it crystallised from aqueous ethanol in pointed prisms, m. p. 167—168° (2·6 g., 53%) (Found: C, 82·0; H, 6·2; N, 11·8. $C_{16}H_{14}N_2$ requires C, 82·0; H, 6·0; N, 12·0%). In other preparations the solution was boiled under reflux for several hours; rather more dimethylphenanthrene and less azine were then obtained.

Reactions of the Azine (IX).—(*a*) Dilute sulphuric acid (15 c.c.) and the azine (0·3 g.) were boiled under reflux for 1 hr. Oily drops were present and solidified on cooling. The solid was extracted with alcohol (a little did not dissolve); the solution deposited 2 : 2′-diacetyldiphenyl, m. p. and mixed m. p. 91—93°. (*b*) The azine (0·6 g.), powdered sodium hydroxide (0·7 g.), and triethylene glycol (11 c.c.) were heated together at 195° for 3½ hr. Water and hydrochloric acid were added to the cooled mixture. A solid (0·5 g.) was collected (m. p. *ca.* 125—135°). After crystallisation from ethanol it had m. p. 143—145° (mixed m. p. with 9 : 10-dimethylphenanthrene, 143—145°).

2 : 7-*Dihydro*-2 : 2 : 7 : 7-*tetramethyl*-3 : 4-5 : 6-*dibenzoxepin* (XII).—A suspension of the diol (XI) (2 g.) in 4N-sulphuric acid (60 c.c.) was boiled under reflux for 1 hr. Some oxepin collected in the condenser. The contents of condenser and flask were extracted with ether, and the ethereal solution dried (K_2CO_3) and evaporated. The *oxepin* was crystallised once from ethanol and then twice from methanol, forming flat prisms, m. p. 92—93° (slight softening at 87°) (Found: C, 85·5; H, 8·1. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%). The oxepin is formed as a by-product in the preparation of the tetramethyl-diol if all traces of acid are not removed before distillation of the ether.

2 : 7 : 7-*Trimethyl*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-1 : 3 : 5-*triene* (XIII).—(*a*) A mixture of 2 : 2′-di-(1-hydroxy-1-methylethyl)diphenyl (10 g.) and naphthalene-2-sulphonic acid (0·1 g.) was heated at 140° for ½ hr. The mixture was treated with hot water. On cooling, the cyclic *hydrocarbon* solidified and, after crystallisation successively from ethanol, light petroleum (b. p. 40—60°), and ethanol, had m. p. 100—101° (Found: C, 92·4; H, 7·7. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%) (Cook and Turner found m. p. 97—98° for what must have been the same hydrocarbon, although they regarded it as 2 : 2′-di*iso*propenyldiphenyl).

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[16] Lucien and Taurins, *Canad. J. Chem.*, 1952, **30**, 208.

(*b*) A suspension of the diol (XI) or of the oxepin in hydrobromic acid (*d* 1·49) was boiled under reflux for 1 hr. On cooling, the hydrocarbon became a crystalline cake, which after recrystallisation from ethanol, had m. p. 100—101°.

2 : 2 : 7-*Trimethyl*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-3 : 5-*diene* (XIV).—A solution of 2 : 7 : 7-trimethyl-3 : 4-5 : 6-dibenzo*cyclo*hepta-1 : 3 : 5-triene (10 g.) in a mixture of glacial acetic acid and ethyl acetate was shaken in hydrogen under pressure in presence of Adams's platinum oxide for several hours. After removal of the catalyst the ethyl acetate was distilled off and water was added to the acetic acid solution. The solid which separated (9·5 g.) was crystallised twice from ethanol; it formed stout rectangular prisms, m. p. 69—71° (Found: C, 91·5; H, 8·5. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%).

2 : 2′-*Di*iso*propenyldiphenyl* (X).—The diol (XI) (5 g.) was boiled (320°) in a large test-tube, and a little copper bronze and activated alumina were added. Vigorous dehydration occurred and the b. p. dropped within 10 min. to 295°. The cooled mixture was extracted with ether, the ether evaporated, and the residue distilled. 2 : 2′-*Di*iso*propenyldiphenyl* (3 g.) had b. p. 136°/5 mm., n_D^{21} 1·5890 (Found: C, 92·1; H, 7·8. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). A little of the oxepin was also isolated.

Hydrogenation of 2 : 2′-*Di*iso*propenyldiphenyl.*—A glacial acetic acid solution of the diene was shaken in hydrogen in presence of Adams's platinum oxide for 1 hr. The catalyst was removed and water added to the solution. The solid which separated, after being crystallised from ethanol, had m. p. 67—68° alone or when mixed with 2 : 2′-di*iso*propyldiphenyl.[1]

Action of Hydrobromic Acid on 2 : 2′-*Di*iso*propenyldiphenyl.*—A mixture of the diene (1·3 g.) with hydrobromic acid (20 c.c.; *d* 1·49) was boiled for 1½ hr., then cooled and extracted with ether. Evaporation of the ether gave a solid which after being crystallised twice from ethanol had m. p. 100—101° alone or when mixed with the cyclic triene (XIII).

Action of 50% *Sulphuric Acid on* 2 : 2′-*Di*iso*propenyldiphenyl.*—A mixture of the diene (1·0 g.) with 50% (w/w) sulphuric acid (18 c.c.) was boiled for 5 hr., then cooled and extracted with ether. Evaporation of the ether followed by crystallisation from ethanol gave the cyclic triene (0·5 g.), m. p. 100—101°.

Action of Hydrobromic Acid on 2 : 2′-*Divinyldiphenyl.*—A mixture of the hydrocarbon (0·5 g.) and hydrobromic acid (10 c.c.; *d* 1·49) was boiled for 1½ hr., then cooled, and the oil was washed with water and aqueous sodium carbonate. It solidified and after 3 crystallisations from methanol had m. p. 85—89°. The mixed m. p. with 2 : 2′-di-(1-bromoethyl)diphenyl was 85—90°.

Oxidation of 2 : 7 : 7-*Trimethyl*-3 : 4-5 : 6-*dibenzo*cyclo*hepta*-1 : 3 : 5-*triene* (XIII).—The triene (1·1 g., 1 mol.) in acetic acid (5 c.c.) and sodium dichromate (5·6 g., 4 mols.) in acetic acid (17 c.c.) were heated together on a steam-bath for 1¾ hr. The solution was poured into water and extracted with chloroform. The chloroform solution was shaken with aqueous sodium carbonate, washed with water, dried (Na_2SO_4), and evaporated. The residue was extracted with light petroleum (b. p. 40—60°). The small insoluble orange residue was dissolved in ethanol and treated with an ethanolic solution of *o*-phenylenediamine. The precipitated quinoxaline, after crystallisation from benzene, had m. p. 222—223°, not depressed on admixture with the quinoxaline from phenanthraquinone. The light petroleum extract deposited a gum which, after treatment with *cyclo*hexane, followed by recrystallisation, yielded 2-*acetyl*-2′-*formyldiphenyl*, m. p. 84° (Found: C, 80·1; H, 5·5. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·4%). Cook *et al.*[10] obtained this aldehyde as a gum by the oxidation of 9-methylphenanthrene. Dinitrophenylhydrazone formation was accompanied by cyclisation; 7-oxo-3 : 4-5 : 6-dibenzo*cyclo*hepta-1 : 3 : 5-triene 2 : 4-dinitrophenylhydrazone, m. p. *ca.* 208° (decomp.), was isolated (Found: C, 65·2; H, 3·5; N, 13·8. Calc. for $C_{21}H_{14}O_4N_4$: C, 65·3; H, 3·65; N, 14·5%) (Cook *et al.*[8] give m. p. 231—232°). The sodium carbonate washings (of the original chloroform solution) were acidified and gave a gum from which two impure crystalline acids were eventually isolated. Quantities were too small for further investigation.

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