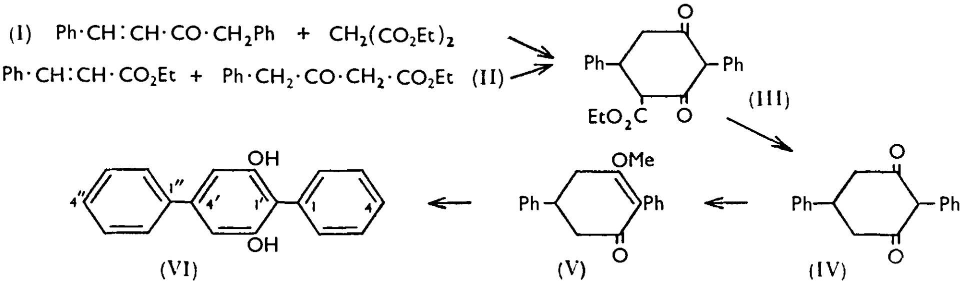
693. cyclo*Hexane*-1 : 3-*diones. Part II.** *A New Synthesis of Substituted* p-*Terphenyls.*

By G. R. Ames and W. Davey.

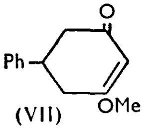
A new synthesis of *p*-terphenyls substituted in the central ring is described. 2 : 5-Diphenyl*cyclo*hexane-1 : 3-dione, which is readily accessible by Michael addition of diethyl malonate to benzyl styryl ketone, is converted into 2'-hydroxy-, 2'-cyano-, 2'-amino-, and 2' : 6'-dihydroxy-*p*-terphenyl and *p*-terphenyl-2'-carboxylic acid.

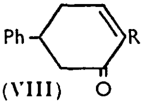
A route to 2' : 6'-dihydroxy-*p*-terphenyl (VI) and other unsymmetrical terphenyls has been developed by an extension of Suter and Smith's synthesis[1] of 3 : 5-dihydroxydiphenyl from benzylideneacetone *via* 5-phenyl*cyclo*hexane-1 : 3-dione.

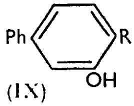


The dione-ester (III) was prepared in 79% yield by the ethoxide-catalysed addition of diethyl malonate to benzyl styryl ketone[2] (I), or, less conveniently, by Michael addition of ethyl γ-phenylacetoacetate (II) to ethyl cinnamate (ethyl γ-phenylacetoacetate was conveniently prepared by Bowman's general method for β-keto-esters[3] from phenylacetyl chloride and diethyl ethoxymagnesiomalonate). Alkaline hydrolysis of the dione-ester (III) yielded the dione (IV), which was converted by diazomethane into the enol ether (V). Dehydrogenation of the latter by sulphur, followed by demethylation, gave the required 2' : 6'-dihydroxy-*p*-terphenyl (VI) in 35% overall yield from the ketone (I).

As a model for the preparation of 2'-hydroxy-*p*-terphenyl (IX; R = Ph), obtained by Fichter and Grether[4] by another route, 5-phenyl*cyclo*hexane-1 : 3-dione was converted by diazomethane into the enol ether (VII), which was reduced by lithium aluminium hydride to the unsaturated ketone (VIII; R = H), dehydrogenation of which by sulphur afforded the


(VII)


(VIII)


(IX)

known 3-hydroxydiphenyl (IX; R = H). The enol ether (V) was then reduced with a slight excess of lithium aluminium hydride and dehydrogenated with sulphur, 2'-hydroxy-*p*-terphenyl (45%) and *p*-terphenyl (23%) being obtained. The *p*-terphenyl presumably arises because in the preparation of the ketone (VIII; R = Ph), some over-reduction occurs, giving an alcohol, which is dehydrated and dehydrogenated when heated with sulphur.

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* Part I, *J.*, 1956, 3001.

[1] Suter and Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 166.

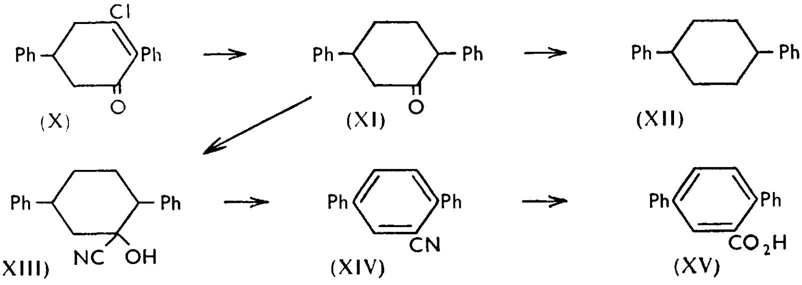
[2] Goldschmiedt *et al.*, *Monatsh.*, 1897, **18**, 437; 1898, **19**, 461; 1901, **22**, 659.

[3] Bowman, *J.*, 1950, 322.

[4] Fichter and Grether, *Ber.*, 1903, **36** 1407.

An attempt to prepare 2 : 5-diphenyl*cyclo*hexanone (XI), by palladium-catalysed hydrogenation of the crude ketone (VIII; R = Ph), failed, the only crystalline product being an isomer of 2 : 5-diphenyl*cyclo*hexanol.

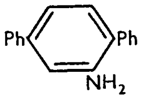
Treatment of the dione (IV) with phosphorus trichloride in boiling chloroform afforded the chloro-ketone (X), which was not isolated but was hydrogenated, at a palladium catalyst, to 2 : 5-diphenyl*cyclo*hexanone (XI), of which only one isomer could be isolated. Wolff–Kishner reduction converted this into 1 : 4-diphenyl*cyclo*hexane (XII). Our product corresponds to the isomer obtained by Nenitzescu and Curcăneanu [5] and by Sidorova, Feiershtein, and Kochetkova [6] as one of the products from the aluminium chloride-catalysed reaction of benzene with 1 : 2-dichloro*cyclo*hexane and 2-phenyl*cyclo*hexanol respectively, and known [5, 6] to give *p*-terphenyl on dehydrogenation with selenium.

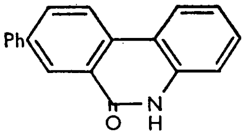


The cyanohydrin (XIII), obtained by the very convenient exchange reaction described by Nazarov, Akhrem, and Kamernitsky,[7] when treated with acetic anhydride and then dehydrogenated with selenium, gave 2′-cyano-*p*-terphenyl (XIV) (43%) and 4% of *p*-terphenyl (presumably some elimination of hydrogen cyanide occurred during dehydrogenation). Hydrolysis of the nitrile (XIV) furnished *p*-terphenyl-2′-carboxylic acid (XV).

Preparation of 2′-amino-*p*-terphenyl (XVI) from the dione (IV) proved difficult. The amine has been synthesised by Basford [8] by nitration of 4-*cyclo*hexyldiphenyl to 4-*cyclo*hexyl-2-nitrodiphenyl, dehydrogenation to 2′-nitro-*p*-terphenyl, and reduction of the latter. Horning and Horning [9] found that substituted anilines could be prepared by palladium-catalysed dehydrogenation of *cyclo*hexenone azines; however, the amine (XVI) was not obtained on attempted dehydrogenation of the azine of the ketone (VIII; R = Ph) or that of (XI). Attempts to dehydrogenate the benzylamine condensation product of the *cyclo*hexenone (VIII; R = Ph) and the phenylhydrazone of the *cyclo*hexanone (XI) by sulphur also failed. No crystalline product was obtained on attempted Wolff aromatisation [10] of the oxime of the ketone (VIII; R = Ph). In the Schmidt reaction the acid (XV) gave an unrecognisable sulphur-containing product, and the amide of the acid (XV) did not undergo the Hofmann reaction (a similar result was reported by Bradsher and Sverlick [11] for

(XVI)





(XVII)

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[5] Nenitzescu and Curcăneanu, *Ber.*, 1937, **70**, 346.

[6] Sidorova, Feiershtein, and Kochetkova, *J. Gen. Chem.* (*U.S.S.R.*), 1956, **26**, 201 (U.S. translation).

[7] Nazarov, Akhrem, and Kamernitsky, *ibid.*, 1955, **25**, 1291 (U.S. translation).

[8] Basford, *J.*, 1937, 1440.

[9] Horning and Horning, *J. Amer. Chem. Soc.*, 1947, **69**, 1907.

[10] Horning, *Chem. Rev.*, 1943, **33**, 89.

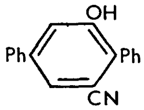
[11] Bradsher and Sverlick, *J. Amer. Chem. Soc.*, 1950, **72**, 4189.

m-terphenyl-4-carboxyamide). Finally, Curtius degradation of *p*-terphenyl-2′-carboxylic acid (XV), in the conditions successfully used for *m*-terphenyl-4-carboxylic acid by Bradsher and Sverlick,[11] gave a 28% yield of 2′-amino-*p*-terphenyl, with a by-product (8%) which was probably 7-phenylphenanthridone (XVII).

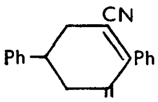
In an attempt to prepare 2′-cyano-6′-hydroxy-*p*-terphenyl (XVIII), the enol ether (V) was subjected to the acetone cyanohydrin exchange reaction. A 93% yield of a compound $C_{19}H_{15}ON$ was obtained, whose infrared spectrum showed bands at 2215, 1691, and 1607 cm.$^{-1}$, which are attributed to conjugated nitrile,[12] αβ-unsaturated ketone,[13] and phenyl [14] systems. This compound is therefore assigned structure (XIX), being formed by displacement of the methoxy- by the cyano-group. It did not give pure compounds when heated with sulphur.

The cyano-ketone (XIX) was reduced by potassium borohydride to 3-cyano-2 : 5-diphenyl*cyclo*hex-2-en-1-ol (XX). Dehydrogenation of the latter gave *p*-terphenyl (7%) as the only crystalline product; presumably some elimination of hydrogen cyanide occurred during dehydrogenation (cf. above).

The dione-ester (III) with diazomethane gave an enol-ether, m. p. 137—138°, in 28% yield. The remainder of the product was an oil, presumably an isomer or a mixture of isomers. Neither the crystals nor the oil could be dehydrogenated to the acid (XXI) or a derivative thereof. The oily enol ether gave a 2% yield of the dione (IV), together with an oil, which, on hydrolysis with hydrochloric acid, gave 2′ : 6′-dihydroxy-*p*-terphenyl (VI) (11%) and 5-oxo-3 : 6-diphenylhexanoic acid (XXII) (4%), which was also obtained by hydrolysis of the dione-ester (III). Dehydrogenation of the crystalline enol ether also gave the dione (IV) (5%), as well as an oil which with dimethyl sulphate yielded a further 3% of the dione (IV) and an 11% yield of 2′ : 6′-dimethoxy-*p*-terphenyl (XXIII) (see below).



(XVIII)



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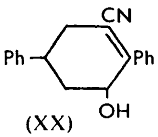
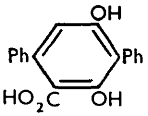
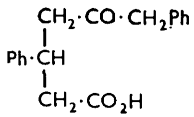


(XX)

A number of new compounds have been prepared from the hydroxyterphenyls (VI) and (IX; R = Ph). The latter was converted by diazomethane into 2′-methoxy-*p*-terphenyl (XXIV; R = H); an attempt to prepare the aldehyde (XXIV; R = CHO) by treatment

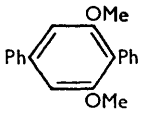


(XXI)

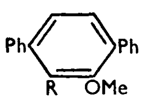


$$\begin{array}{l} CH_2\cdot CO\cdot CH_2Ph \\ | \\ Ph\cdot CH \\ | \\ CH_2\cdot CO_2H \end{array}$$

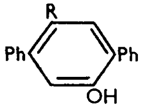
(XXII)



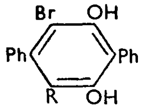
(XXIII)



(XXIV)



(XXV)



(XXVI)

with phosphorus oxychloride–dimethylformamide was unsuccessful. With benzenediazonium chloride it gave an azo-compound, probably (XXV; R = Ph·N:N), which was reduced by zinc in acetic acid–acetic anhydride to the acetamido-compound (XXV; R = NHAc).

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[12] Kitson and Griffith, *Analyt. Chem.*, 1952, **24**, 334.

[13] Cromwell, Miller, Johnson, Frank, and Wallace, *J. Amer. Chem. Soc.*, 1949, **71**, 3337.

[14] Barnes, Gore, Stafford, and Williams, *Analyt. Chem.*, 1948, **20**, 402.

In contrast to 2′-hydroxy-*p*-terphenyl, 2′ : 6′-dihydroxy-*p*-terphenyl (VI) reacts abnormally with diazomethane. The product, m. p. 135—136°, obtained in 64% yield, had the empirical formula $C_{21}H_{21}O_3N$. No titratable groups could be detected on potentiometric titration, and the infrared spectrum contained a band (1704 cm.$^{-1}$) due to a carbonyl group. The compound therefore appears to contain an amide group.

2′ : 6′-Dimethoxy-*p*-terphenyl (XXIII) was obtained quantitatively by means of dimethyl sulphate. Attempts to prepare a terphenyl aldehyde by the Gattermann reaction on 2′ : 6′-dihydroxy-*p*-terphenyl (VI) and by treatment of 2′ : 6′-dimethoxy-*p*-terphenyl (XXIII) with phosphorus oxychloride–dimethyl formamide were unsuccessful. The resorcinol (VI) with bromine gave the monobromo-compound (XXVI; R = H), which was further brominated to the dibromo-compound (XXVI; R = Br).

The ultraviolet absorption spectra of many of the above compounds are recorded in the Table. The spectra of the 2′-substituted terphenyls show a slight hypsochromic shift (6—10 mμ) with respect to *p*-terphenyl; there is also a lowering of the molecular extinction coefficient. Similar results have been recorded for 2-substituted diphenyls.[15] Introduction of a further group in the 6′-position does not cause a further hypsochromic shift. However, when substitution of bromine occurs at the 3′- and 5′-positions of 2′ : 6′-dihydroxy-*p*-terphenyl (VI), there is a marked lowering of the intensity of absorption, presumably because of steric hindrance to coplanarity of the terminal phenyl rings.

Ultraviolet absorption spectra in ethanol (*italicised numerals denote an inflexion*).

Compound	$\lambda_{max.}$ (mμ)	ε	Compound	$\lambda_{max.}$ (mμ)	ε	Compound	$\lambda_{max.}$ (mμ)	ε
(a) *Terphenyls*								
p-Terphenyl[a]	278	32,700	(VI)	*225*	33,100	(XXVI; R = Br)	*228*	26,700
(IX; R = Ph)	271·5	24,700		272	24,600		*252*	13,000
(XXIV; R = H)	270	24,500	(XXIII)	*225*	28,500		296	3,160
(XIV)	*229*	25,500		272	20,600	(XXV; R = Ph–N=N)	237	23,100
	272	24,700	(XXVI; R = H)	258	15,700		*245—520*	23,000
(XV)	*234*	17,700	(XXV; R = NHAc)	*232*	23,900			
	268	24,000		*260*	19,000		287	22,800
				304	7,400		367	19,100
(b) *Other compounds*								
(III)	*230*	11,800	(VIII; R = H)	224	11,000	(XI)	*242*	225
	270	11,500	(VIII; R = Ph)	259	5,700		*247*	300
Enol ether of (III)	273·5	13,500	(XIX)	234	12,600		252	405
(IV)	*230*	10,000		292	5,060		258	489
	268	12,000	(XVII)	260	32,600		264	380
(V)	*224—228*	13,000					*267*	266
							288	94
	271	13,000						

[a] Gillam and Hey (*J.*, 1939, 1170) report $\lambda_{max.}$ 276 mμ (ε 35,000) in hexane and 280 mμ (ε 25,000) in chloroform.

The spectra of the dione-ester (III) and dione (IV) are very similar to those of the corresponding enol ethers, which indicates that both compounds are fully enolised.

EXPERIMENTAL

Ultraviolet absorption spectra were determined in 96% ethanol, with a Unicam S.P. 500 Spectrophotometer. " Light petroleum " refers to the fraction, b. p. 60—80°.

Ethyl γ-Phenylacetoacetate (II).—To a benzene solution of diethyl ethoxymagnesiomalonate[3] (from magnesium, 46 g., and diethyl malonate, 320 g.) was added, during 1 hr., phenylacetyl chloride (from the acid, 136 g., and thionyl chloride). The mixture was stirred under reflux for 3 hr., then cooled and poured into ice-cold dilute sulphuric acid. The organic layer was separated, washed thoroughly with water, dried ($MgSO_4$) and evaporated. The crude acylmalonate was refluxed with acetic acid (300 c.c.) containing sulphuric acid (1·3 g.) for 3 hr

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[15] *E.g.*, Braude and Forbes, *J.*, 1955, 3776.

Barium carbonate (6 g.) was then added, and the solution filtered and evaporated. Fractionation *in vacuo* yielded 1-phenylpropan-2-one (40 g., 30%), b. p. 59—62°/1·6 mm., and ethyl γ-phenylacetoacetate (86·1 g., 43%), b. p. 119—121°/1·5 mm. (lit., b. p. 100—101°/14 mm. and 153—155°/9 mm. respectively).

Ethyl 2 : 4-*Dioxo*-3 : 6-*diphenyl*cyclo*hexanecarboxylate* (III).—(a) *From* 1 : 4-*diphenylbut*-1-*en*-3-*one and diethyl malonate.* To sodium (2·65 g.), dissolved in dry ethanol (50 c.c.), was added diethyl malonate (18·2 g.), followed by 1 : 4-diphenylbut-1-en-3-one [2] (25·2 g.) in ethanol (200 c.c.), and the mixture set aside overnight. The solution was concentrated, diluted with water, and filtered. Acidification of the filtrate afforded 30·2 g. (79%) of material, m. p. 157—164°. *Ethyl* 2 : 4-*dioxo*-3 : 6-*diphenyl*cyclo*hexanecarboxylate* formed needles, m. p. 174—175°, from benzene (Found : C, 74·8; H, 5·9. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%).

(b) *From ethyl γ-phenylacetoacetate and ethyl cinnamate.* A series of experiments was conducted to find the optimum conditions. Ethyl γ-phenylacetoacetate and ethyl cinnamate were successively added to sodium ethoxide in ethanol, and the mixture refluxed for 6 hr., then poured into water. Any unchanged reactants were removed by ether; acidification of the aqueous layer afforded the dione-ester. Best results (43% yield) were obtained with ethyl γ-phenylacetoacetate (1 mol.), ethyl cinnamate (4 mols.), and sodium ethoxide (1 mol.).

2 : 5-*Diphenyl*cyclo*hexane*-1 : 3-*dione* (IV).—Ethyl 2 : 4-dioxo-3 : 6-diphenyl*cyclo*hexanecarboxylate (30 g.) was refluxed for 10 hr. with sodium carbonate (decahydrate; 60 g.) in water (180 c.c.). The solution was acidified and then brought to the boil. The *dione* formed square plates, m. p. (inserted at 220°) 247—249°, from 2-methoxyethanol (Found : C, 81·2; H, 6·1. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

3-*Methoxy*-2 : 5-*diphenyl*cyclo*hex*-2-*en*-1-*one* (V).—The preceding compound, in methanol, treated with ethereal diazomethane, gave the *enol ether*, prisms, m. p. 137—138°, from light petroleum (Found : C, 82·0; H, 6·5. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

2′ : 6′-*Dihydroxy*-p-*terphenyl* (VI).—The foregoing enol ether (2·5 g.) was heated at 270° for 2 hr. with sulphur (0·3 g.). The cooled product was taken up in chloroform, and some 2 : 5-diphenyl*cyclo*hexane-1 : 3-dione (0·3 g.) removed by washing with aqueous sodium carbonate. The chloroform was evaporated and the residue refluxed with 58% hydriodic acid (3 c.c.) and acetic acid (8 c.c.) for 15 hr. Water (50 c.c.) was added and the mixture made just acid to Congo-red. 2′ : 6′-*Dihydroxy*-p-*terphenyl* (1·6 g.) crystallised from benzene as prisms, m. p. 206—207° (Found : C, 82·3; H, 5·5. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·4%). The enol ether was recovered unchanged on attempted dehydrogenation by palladised charcoal in refluxing *p*-cymene.

3-*Methoxy*-5-*phenyl*cyclo*hex*-2-*en*-1-*one* (VII).—5-Phenyl*cyclo*hexane-1 : 3-dione [16] (16 g.) in methanol was treated with ethereal diazomethane in the usual way. The *enol ether* (15·3 g.), which had b. p. 146—147°/0·6 mm., n_D^{20} 1·5767, crystallised (m. p. 32—34°) (Found : C, 76·7; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%).

5-*Phenyl*cyclo*hex*-2-*en*-1-*one* (VIII; R = H).—The above enol ether (5 g.) in ether (100 c.c.) was slowly added to lithium aluminium hydride (1·2 g.) in ether (100 c.c.), and the mixture refluxed for 1 hr. Working up in the usual way gave 5-*phenyl*cyclo*hex*-2-*en*-1-*one*, b. p. 115—116°/1 mm., n_D^{19} 1·5693 (Found : C, 84·2; H, 7·4. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%).

3-*Hydroxydiphenyl* (IX; R = H).—5-Phenyl*cyclo*hex-2-en-1-one (2·3 g.) was heated at 260—270° for 1 hr. with sulphur (0·44 g.). Isolation of the acidic fraction yielded an oil, which on extraction with boiling light petroleum, yielded 3-hydroxydiphenyl, blades, m. p. 74—75°. Jacobsen and Loeb [17] record m. p. 75°, and Errara and La Spada [18] 78°.

2 : 5-*Diphenyl*cyclo*hex*-2-*en*-1-*one* (VIII; R = Ph).—3-Methoxy-2 : 5-diphenyl*cyclo*hex-2-en-1-one (5·3 g.) in benzene (100 c.c.) was added to lithium aluminium hydride in ether (75 c.c. of a 1% solution), and the mixture refluxed for 1 hr. Working up in the usual way yielded 2 : 5-*diphenyl*cyclo*hex*-2-*en*-1-*one* (3·8 g.), needles, m. p. 110—111° (from methanol) (Found : C, 87·2; H, 6·4. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%). The *oxime* crystallised from ethanol as needles, m. p. 206—207° (Found : C, 81·9; H, 6·5; N, 5·2. $C_{18}H_{17}ON$ requires C, 82·1; H, 6·5; N, 5·3%).

Dehydrogenation of 2 : 5-*Diphenyl*cyclo*hex*-2-*en*-1-*one*.—The crude ketone (from 5·3 g. of enol ether) was heated with sulphur (0·72 g.) at 240°, the temperature being slowly raised to 300°.

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[16] Vorländer, *Ber.*, 1894, **27**, 2053.

[17] Jacobsen and Loeb, *ibid.*, 1903, **36**, 4082.

[18] Errara and La Spada, *Gazzetta*, 1905, **35**, II, 539.

Recrystallisation from ethyl methyl ketone gave *p*-terphenyl (1 g.), plates, m. p. 213—214° (lit., 213°) (Found: C, 93·8; H, 6·2. Calc. for $C_{18}H_{14}$: C, 93·9; H, 6·1%). Evaporation of the mother-liquors yielded 2′-hydroxy-*p*-terphenyl (IX; R = Ph) (2·1 g.), needles, m. p. 192—193° (from benzene) (Fichter and Grether [4] report m. p. 194°).

2′-Hydroxy-*p*-terphenyl with diazomethane afforded *2′-methoxy-*p*-terphenyl*, prisms, m. p. 97—98°, from methanol (Found: C, 88·0; H, 6·1. $C_{19}H_{16}O$ requires C, 87·7; H, 6·2%).

2 : 5-*Diphenyl*cyclo*hexanol*.—2 : 5-Diphenyl*cyclo*hex-2-en-1-one (crude; 5 g.) in ethanol (100 c.c.) was shaken under hydrogen in the presence of 5% palladised charcoal (1 g.), until absorption ceased. The catalyst was removed and the solution evaporated. The only crystalline solid isolable was 2 : 5-*diphenyl*cyclo*hexanol* (1·4 g.), needles, m. p. 185—186°, from benzene (Found: C, 86·0; H, 7·9. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%). The compound showed no infrared absorption in the carbonyl region.

2 : 5-*Diphenyl*cyclo*hexanone* (XI).—2 : 5-Diphenyl*cyclo*hexane-1 : 3-dione (18·4 g.) in chloroform (50 c.c.) was refluxed with phosphorus trichloride (5·2 c.c.) for 3 hr. Crushed ice, ether, and aqueous sodium hydrogen carbonate were successively added, and the organic layer was separated, washed with aqueous sodium hydroxide, dried ($MgSO_4$), and evaporated. The crude chloro-ketone (10·6 g.) was shaken in ethanol (250 c.c.) under hydrogen with palladous chloride (0·2 g.) and triethylamine (20 c.c.). When the filtered solution was concentrated, there separated 2 : 5-*diphenyl*cyclo*hexanone* (5·8 g.), plates, m. p. 154—155° (from ethanol) (Found: C, 86·1; H, 7·2. $C_{18}H_{18}O$ requires C, 86·4; H, 7·2%). The *oxime* crystallised from ethyl acetate as plates, m. p. 231° (decomp.) (Found: C, 81·1; H, 6·9; N, 5·3. $C_{18}H_{19}ON$ requires C, 81·5; H, 7·2; N, 5·3%).

The *azine*, prepared from the ketone (1 g.) in ethanol (30 c.c.) and 1·7 c.c. of a solution of hydrazine hydrate (78%; 22·9 g.) and concentrated hydrochloric acid (3 drops) in ethanol (made up to 250 c.c.), under reflux for 1 hr., formed needles, m. p. 177—178°, from ethyl acetate (Found: C, 86·9; H, 7·8; N, 5·1. $C_{36}H_{36}N_2$ requires C, 87·1; H, 7·3; N, 5·6%).

1 : 4-*Diphenyl*cyclo*hexane* (XII).—2 : 5-Diphenyl*cyclo*hexanone (2·8 g.), ethylene glycol (50 c.c.), 78% hydrazine hydrate (5 c.c.), and potassium hydroxide (1·8 g.) in water (4 c.c.) were refluxed together for 6 hr., the internal temperature being allowed to rise to 200° after 1·5 hr. 1 : 4-Diphenyl*cyclo*hexane (1·6 g.), which separated on cooling, was collected: it crystallised from ethanol in plates, m. p. 171—172° (Found: C, 91·4; H, 8·6. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%). Nenitzescu and Curcăneanu [5] record m. p. 172°; Sidorova, Feiershtein, and Kochetkova [6] give m. p. 168°.

p-*Terphenyl*.—1 : 4-Diphenyl*cyclo*hexane (2 g.) was heated for 2 hr. at 350° with selenium (4 g.). The cooled product was dissolved in hot ethanol (400 c.c.), and selenium removed by filtration. The cooled filtrate deposited 1·6 g. of *p*-terphenyl, m. p. 212—213° (lit., 213°) (Found: C, 93·7; H, 6·2. Calc. for $C_{18}H_{14}$: C, 93·9; H, 6·1%).

2 : 5-*Diphenyl*cyclo*hexanone Cyanohydrin* (XIII).—To the ketone (1 g.), dissolved in acetone cyanohydrin (30 c.c.), was added saturated methanolic potassium hydroxide (0·2 c.c.), and the mixture was set aside overnight. Pouring it into water then yielded the *cyanohydrin* (1·05 g.), which crystallised from light petroleum as needles, m. p. 134—135° (Found: C, 82·3; H, 7·0; N, 5·0. $C_{19}H_{19}ON$ requires C, 82·3; H, 6·9; N, 5·1%).

*2′-Cyano-*p*-terphenyl* (XIV).—The foregoing cyanohydrin (2 g.) was refluxed for 1 hr. with acetic anhydride (20 c.c.) containing one drop of sulphuric acid. The mixture was poured into water (500 c.c.) and left overnight. The crude acetyl derivative thus obtained was heated at 350° for 2 hr. with selenium (2 g.). Fractional crystallisation from ethanol gave *p*-terphenyl (0·07 g.), m. p. and mixed m. p. 212—213°, and *2′-cyano-*p*-terphenyl* (0·7 g.), prisms, m. p. 106—107° (Found: C, 89·8; H, 5·1; N, 5·1. $C_{19}H_{13}N$ requires C, 89·4; H, 5·1; N, 5·5%).

p-*Terphenyl-2′-carboxylic Acid* (XV).—(i) A mixture of 2′-cyano-*p*-terphenyl (2·8 g.), ethylene glycol (50 c.c.), and potassium hydroxide (1·8 g.) in water (2 c.c.) was heated to remove the water and then refluxed for 20 hr. The cooled mixture was poured into water (200 c.c.) and ethyl acetate (100 c.c.), and the acidic fraction extracted with 2N-potassium hydroxide. On acidification, the potassium salt of the acid was obtained. The latter was dissolved in boiling 50% aqueous acetic acid (300 c.c.), and dilute sulphuric acid (20 c.c.) added. On cooling, there separated p-*terphenyl-2′-carboxylic acid* (1·3 g.), rods, m. p. 178—179° (from benzene) (Found: C, 83·3; H, 5·2. $C_{19}H_{14}O_2$ requires C, 83·2; H, 5·1%).

The *amide*, prepared *via* the acid chloride, formed needles, m. p. 193—194°, from benzene (Found: C, 84·0; H, 5·6. $C_{19}H_{15}ON$ requires C, 83·5; H, 5·5%).

(ii) 2 : 5-Diphenyl*cyclo*hexanone cyanohydrin (5 g.) was refluxed for 30 min. with pyridine (10 c.c.), phosphorus oxychloride (5 c.c.), and benzene (50 c.c.). The mixture was poured on ice and extracted with ethyl acetate : the organic layer was washed with dilute hydrochloric acid and water, dried ($MgSO_4$), and evaporated. The material thus obtained was heated at 350° for 2 hr. with selenium (5 g.), cooled, and extracted with ethanol (Soxhlet). Concentration of the extracts gave *p*-terphenyl (0·6 g.) and an oil. The latter was hydrolysed by potassium hydroxide in ethylene glycol as described in (i). Isolation of the acidic fraction afforded *p*-terphenyl-2′-carboxylic acid (0·35 g.), identical with that obtained previously.

Curtius Degradation of p-*Terphenyl-2′-carboxylic Acid.*—The acid (0·92 g.) was converted into the methyl ester by diazomethane in the usual way. The ester, in pentyl alcohol (10 c.c.), was refluxed with 100% hydrazine hydrate (5 c.c.) for 24 hr., then poured into water (100 c.c.). After the pentyl alcohol had been removed by steam-distillation, the *hydrazide* (0·82 g.) was collected; it formed needles, m. p. 148—149°, from ethanol (Found : C, 79·0; H, 5·9. $C_{19}H_{16}ON_2$ requires C, 79·1; H, 5·6%).

A solution of the hydrazide (0·68 g.) in acetic acid (6 c.c.) was cooled to 0°, and sodium nitrite (0·10 g.) in water (1 c.c.) added. After 2·5 hr. at room temperature, water (25 c.c.) was added and the crude azide collected. The latter was refluxed for 2 hr. with concentrated hydrochloric acid (6 c.c.) and acetic acid (6 c.c.). Dilution with water gave a solid, which on recrystallisation from methanol afforded, probably, 7-*phenylphenanthridone* (XVII) (0·05 g.), needles, m. p. 222° (Found : C, 84·3; H, 5·3; N, 5·0. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·8; N, 5·2%). The infrared spectrum (in Nujol) showed bands at 3424 (NH) and 1685 cm.$^{-1}$ (CO·NH).

The mother-liquors were diluted with water, basified, and extracted with ethyl acetate, and the extracts dried and evaporated. The residue was taken up in dry ether and a stream of hydrogen chloride passed in. The material which separated was collected and boiled for 30 min. with methanol (25 c.c.) and 10% aqueous sodium hydroxide (5 c.c.). Dilution with water gave 2′-amino-*p*-terphenyl (0·18 g.), prisms, m. p. 171—172°, from ethanol (Found : C, 87·5; H, 5·7; N, 5·6. Calc. for $C_{18}H_{15}N$: C, 88·1; H, 6·2; N, 5·7%); Basford[8] reports m. p. 169°. The benzoate crystallised from ethanol as needles, m. p. 148° (Found : N, 4·0. Calc. for $C_{25}H_{19}ON$: N, 4·0%); Basford [8] gives m. p. 144°.

3-*Cyano*-2 : 5-*diphenyl*cyclo*hex*-2-*en*-1-*one* (XIX).—A solution of 3-methoxy-2 : 5-diphenyl*cyclo*hex-2-en-1-one (1 g.) in acetone cyanohydrin (10 c.c.), containing 0·2 c.c. of saturated methanolic potassium hydroxide, was set aside overnight and then poured into water (100 c.c.). 3-*Cyano*-2 : 5-*diphenyl*cyclo*hex*-2-*en*-1-*one* (0·93 g.) crystallised from benzene–light petroleum as prisms, m. p. 148—149° (Found, after drying at 110°/0·1 mm. : C, 83·0; H, 5·4; N, 5·6. $C_{19}H_{15}ON$ requires C, 83·5; H, 5·5; N, 5·1%).

3-*Cyano*-2 : 5-*diphenyl*cyclo*hex*-2-*en*-1-*ol* (XX).—To the cyano-ketone (1·6 g.) in methanol (50 c.c.) was added potassium borohydride (1 g., 3 mol.) in water (10 c.c.). After 5 hr., the solution was poured into water and the precipitated solid (1·2 g.) collected. 3-*Cyano*-2 : 5-*diphenyl*cyclo*hex*-2-*en*-1-*ol* formed prisms, m. p. 157—158°, from benzene–light petroleum (Found : C, 82·6; H, 6·4; N, 4·8. $C_{19}H_{17}ON$ requires C, 82·9; H, 6·2; N, 5·1%).

Action of Diazomethane on Ethyl 2 : 4-*Dioxo*-3 : 6-*diphenyl*cyclo*hexanecarboxylate.*—The dione ester (5 g.), treated with ethereal diazomethane in the usual way, furnished an *enol ether* (1·4 g.), blades, m. p. 137—138° (from benzene–light petroleum) (Found : C, 74·9; H, 6·2. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·3%). Evaporation of the mother-liquors gave an oil (3·2 g.).

The oil (3·2 g.) was dehydrogenated by sulphur (0·3 g.) at 260°, and the oily product dissolved in ethyl acetate. Extraction with sodium carbonate solution yielded 2 : 5-diphenyl*cyclo*hexane-1 : 3-dione (0·05 g.). The uncrystallisable material remaining in the organic layer was hydrolysed with concentrated hydrochloric acid and the product taken up in ether. Extraction with aqueous sodium carbonate and sodium hydroxide gave 5-oxo-3 : 6-diphenylhexanoic acid (0·1 g.) and 2′ : 6′-dihydroxy-*p*-terphenyl (0·18 g.) respectively.

The crystalline enol ether (2·4 g.) was dehydrogenated by sulphur, and, after removal of 2 : 5-diphenyl*cyclo*hexane-1 : 3-dione (0·09 g.) as before, the product was treated with dimethyl sulphate in refluxing sodium hydroxide solution. Filtration gave a semisolid material, which on trituration with benzene, afforded 2′ : 6′-dimethoxy-*p*-terphenyl (0·18 g.). Acidification of the filtrate gave more 2 : 5-diphenyl*cyclo*hexane-1 : 3-dione (0·05 g.).

5-*Oxo*-3 : 6-*diphenylhexanoic Acid* (XXII).—Ethyl 2 : 4-dioxo-3 : 6-diphenyl*cyclo*hexanecarboxylate (2 g.) was refluxed with concentrated hydrochloric acid (50 c.c.) and acetic acid

(50 c.c.) for 10 hr. Evaporation yielded the *hexanoic acid* (1·4 g.), prisms, m. p. 107—108° (from benzene–light petroleum) (Found : C, 76·5; H, 6·5. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%).

*2′-Hydroxy-5′(?)-phenylazo-*p*-terphenyl* (XXV; $R = Ph{\cdot}N{:}N$).—A solution of 2′-hydroxy-*p*-terphenyl (2 g.) in ethanol (200 c.c.) was mixed with sodium acetate (8 g.) in water (10 c.c.), cooled to 0°, and treated with aqueous benzenediazonium chloride (from 0·74 g. of aniline). On dilution with water (100 c.c.) there separated dark brown material which was removed by filtration. Further dilution then gave *2′-hydroxy-5′(?)-phenylazo-*p*-terphenyl*, orange blades, m. p. 159° (from benzene–light petroleum) (Found, after drying at 78°/0·1 mm. : C, 80·7; H, 5·2; N, 7·7. $C_{24}H_{18}ON_2,\frac{1}{2}H_2O$ requires C, 80·2; H, 5·3; N, 7·8. Found, after drying at 110°/0·1 mm.; C, 81·9; H, 5·1. $C_{24}H_{18}ON_2$ requires C, 82·1; H, 5·2%).

*5′(?)-Acetamido-2′-hydroxy-*p*-terphenyl* (XXV; R = NHAc).—The foregoing azo-compound (0·9 g.) was added during 30 min. to a vigorously shaken mixture of zinc (2 g.), acetic acid (5 c.c.), and acetic anhydride (4 c.c.) at 0°. After 30 minutes' shaking, the solid was removed and the filtrate evaporated. *5′(?)-Acetamido-2′-hydroxy-*p*-terphenyl* (0·4 g.) crystallised from benzene as plates, m. p. 209—210° (Found : C, 78·6; H, 5·4; N, 4·9. $C_{20}H_{17}O_2N$ requires C, 79·2; H, 5·6; N, 4·6%). The infrared spectrum, measured in tetrahydrofuran, showed maxima at 3490 (OH), 3314 (NH), 1689, and 1530 $cm.^{-1}$ (NAc).

No crystalline compounds were obtained from the acetamido-compound by hydrochloric acid.

*Reaction of 2 : 6′-Dihydroxy-*p*-terphenyl with Diazomethane.*—The compound (1·1 g.) in methanol (20 c.c.) at 0° was treated with excess of ethereal diazomethane overnight. The solution was then washed with aqueous sodium hydroxide and water, dried ($MgSO_4$), and evaporated. The *product* (0·9 g.) formed needles, m. p. 135—136°, from benzene–light petroleum (Found : C, 75·2; H, 6·1; N, 4·2; OMe, 15·1. $C_{21}H_{21}O_3N$ requires C, 75·2; H, 6·3; N, 4·2; 2OMe, 18·5%), $\lambda_{max.}$ 263·5 mμ (ε 21,400), $\nu_{max.}$ 3324 (m), 2722 (w), 2342 (w), 1704 (s), 1614 (m), 1523 (m), 1397 (w), 1335 (w), 1304 (w), 1253 (m), 1232 (m), 1206 (w), 1164 (w), 1126 (s), 1071 (s), 928 (m), 875 (w), 852 (m), 760 (s), 755 (s), 721 (m), 697 (s) (s = strong, m = medium, w = weak).

*2′ : 6′-Dimethoxy-*p*-terphenyl* (XXIII).—2′ : 6′-Dihydroxy-*p*-terphenyl (1·1 g.) was refluxed with 2N-aqueous sodium hydroxide (11 c.c.) and dimethyl sulphate (2·1 c.c.) for 2 hr., more of the reagents (11 c.c. and 2·1 c.c. respectively) being added after 1 hr. The excess of dimethyl sulphate was destroyed by boiling sodium hydroxide solution, and the product (1·2 g.) collected. *2′ : 6′-Dimethoxy-*p*-terphenyl* crystallised from light petroleum as plates, m. p. 168—169° (Found : C, 82·9; H, 6·5. $C_{20}H_{18}O_2$ requires C, 82·8; H, 6·2%). This compound was also obtained by methylation of the crude dehydrogenation product of 3-methoxy-2 : 5-diphenyl-*cyclo*hex-2-en-1-one.

*3′-Bromo-2′ : 6′-dihydroxy-*p*-terphenyl* (XXVI; R = H).—Bromine (0·1 g., 1 mol.) in carbon tetrachloride (1 c.c.) was added to 2′ : 6′-dihydroxy-*p*-terphenyl (0·5 g.) in carbon tetrachloride (50 c.c.). Evaporation furnished the *bromo-compound*, needles, m. p. 124—125° (from light petroleum) (Found : Br, 23·4. $C_{18}H_{13}O_2Br$ requires Br, 23·5%).

*3′ : 5′-Dibromo-2′ : 6′-dihydroxy-*p*-terphenyl* (XXVI; R = Br).—To the preceding compound (0·21 g.) in carbon tetrachloride (20 c.c.) was added bromine (0·1 g., 1 mol.) in carbon tetrachloride (1 c.c.), and the mixture refluxed for 15 min. Evaporation yielded the *dibromo-compound*, plates, m. p. 137° (from light petroleum) (Found : C, 51·2; H, 2·9. $C_{18}H_{12}O_2Br_2$ requires C, 51·5; H, 2·9%).

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