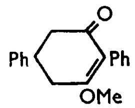
328. *Cyclohexane-1,3-diones. Part V.*[1] *Reaction of 3-Methoxy-2,5-diphenylcyclohex-2-en-1-one with Acetone Cyanohydrin.*

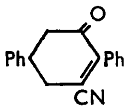
By B. E. BETTS and W. DAVEY.

The reaction of 3-methoxy-2,5-diphenylcyclohex-2-en-1-one with acetone cyanohydrin to give 3-cyano-2,5-diphenylcyclohex-2-en-1-one has been re-investigated and the structure of an additional product, 1,5-dicyano-3,8-diphenyl-6-azabicyclo(3,2,1)octan-7-one has been elucidated. Dehydrogenation of both products to *p*-terphenyl derivatives is described.

NAZAROV, AKHREM, and KAMERNITSKY[2] showed that cyanohydrins can be prepared conveniently by the base-catalysed reaction of the parent ketone with acetone cyanohydrin, and also[3] that β-cyano-ketones are obtained from unsaturated ketones. In Part II[4] it was shown that the product thus obtained from 3-methoxy-2,5-diphenylcyclohex-2-en-1-one (I) was the 3-cyano-compound (II). This reaction and its products have now been investigated further.



(I)



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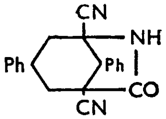

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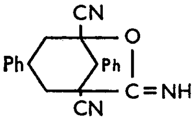

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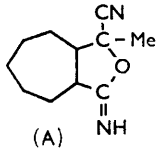

(A)

Conditions for the formation of the cyano-ketone (II) were critical. The optimum conditions, which gave yields of 60—70%, were achieved by slightly basifying a solution of the enol ether (I) in purified acetone cyanohydrin with methanolic potassium hydroxide or triethylamine and storing the mixture overnight. No reaction occurred in non-basic media, and, when excess of potassium hydroxide was used, it was difficult to isolate the cyano-ketone (II). It was desirable to remove free acid from commercial acetone cyanohydrin by distillation. From reaction on a 150-g. scale, triethylamine being used as catalyst, there was obtained a 67% yield of the cyano-ketone (II) together with 4% of a by-product, $C_{21}H_{17}ON_3$. The latter was the sole product (27% yield) of reaction at 80—90°.

To determine whether the cyano-ketone (II) was formed only in acetone cyanohydrin, the enol ether (I) was treated with aqueous-ethanolic potassium cyanide. No reaction occurred, but when acetic acid was added the enol ether (I) was hydrolysed to 2,5-diphenylcyclohexane-1,3-dione. All attempts to convert 3-chloro-2,5-diphenylcyclohex-2-en-1-one into the cyano-ketone (II) by exchange with acetone cyanohydrin or by addition to aqueous ethanolic potassium cyanide gave unchanged material. When 3-chloro-2,5-diphenylcyclohex-2-en-1-one was refluxed with sodium cyanide in dimethylformamide an 80% yield of 2′-hydroxy-*p*-terphenyl was obtained.

The formula $C_{21}H_{17}ON_3$ suggested addition of two molecules of hydrogen cyanide to the initial exchange product (II); but the molecular weight (by Rast's method) was 184 compared with a required value of 327. The same compound was formed from the cyano-ketone (II) and acetone cyanohydrin at 90°, suggesting that the latter was an intermediate in the formation of the new compound. Structure 1,3,3-tricyano-2,5-diphenylcyclohexanol was not supported by the infrared spectrum, which pointed strongly[5a] to the

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[1] Part IV, *J.*, 1958, 1784.

[2] Nazarov, Akhrem, and Kamernitsky, *J. Gen. Chem., U.S.S.R.*, 1954, **25**, 1291 (U.S. translation).

[3] Nazarov and Zavyalov, *J. Gen. Chem. U.S.S.R.*, 1954, **24**, 475 (U.S. translation).

[4] Part II, Ames and Davey, *J.*, 1957, 3480.

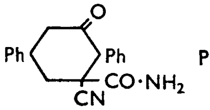
[5] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958, (*a*) pp. 205, 249, and 269, (*b*) p. 220, (*c*) p. 139.

structure (III) as against the possible alternative (IV).* Compound (III) could result from intramolecular rearrangement of an intermediate cyanohydrin as occurs in the formation of 2,2,5,5-tetramethyloxazolid-4-one[7] from acetone and acetone cyanohydrin. The absorption band at 1220 cm.$^{-1}$ would then be due to a C–N or mixed OCN and NH vibration[5b] rather than a C–O vibration.

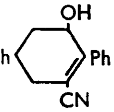
The suspected azabicyclo-octanone (III) was reconverted into the cyano-ketone (II) by hydrochloric–acetic acid or pyridine. 2′-Hydroxy-*p*-terphenyl was formed when the azabicyclo-octanone (III) was heated above its melting point. Since this was the sole product from similarly heating the cyano-ketone (II), the decomposition of the azabicyclo-octanone (III) may have proceeded *via* the cyano-ketone (II). Clearly the carbon skeleton of the cyano-ketone (II) is retained in the compound $C_{21}H_{17}ON_3$. Furthermore, the low value for the molecular weight of the azabicyclo-octanone (III) may be due to this ready thermal decomposition.

Further evidence for the formation of the azabicyclo-octanone (III) was provided by the isolation of the corresponding *N*-acetyl-, *N*-benzoyl-, and *N*-3,5-dinitrobenzoyl-derivatives. Dehydrogenation of the *N*-acetyl derivative afforded a compound $C_{20}H_{12}N_2$ having an ultraviolet spectrum typical of a terphenyl system.[4] Absorption bands corresponding to an aromatic nitrile (2222 cm.$^{-1}$) and a C–H deformation mode of an isolated free hydrogen atom (899 cm.$^{-1}$) were also noted. No band appeared in the frequency range corresponding to two adjacent free hydrogen atoms. This compound is therefore presumably 2′,6′-dicyano-*p*-terphenyl.

No simple carbonyl derivatives of the azabicyclo-octanone (III) could be obtained. Treatment with hydroxylamine hydrochloride, semicarbazide hydrochloride, or phenylhydrazine furnished products believed to be mono-derivatives of 1-cyano-3-oxo-2,5-diphenylcyclohexane-1-carboxyamide (V), formed by hydrolysis of the azabicyclo-octanone (III) and simultaneous loss of hydrogen cyanide. Reaction of the azabicyclo-octanone (III) with sodium sesquicarbonate, as for the preparation of the oxime, yielded a mixture of three compounds, one of which is considered to be the expected amide (V). An attempt to correlate this material with the derived oxime was unsuccessful, for treatment with hydroxylamine yielded only an uncrystallisable oil.



(V)



(VI)

The effect of stronger alkali was next investigated. Treatment of the azabicyclo-octanone (III) with one equiv. of sodium hydroxide gave a high yield of one of the compounds previously obtained by the action of sodium sesquicarbonate. When this experiment was repeated in the presence of excess of methyl iodide the sole product was the cyano-ketone (II). Finally, with excess of sodium hydroxide the azabicyclo-octanone (III) afforded 2′-hydroxy-*p*-terphenyl, as did the cyano-ketone (II), indicating that the decomposition of the azabicyclo-octanone (III) proceeded *via* the cyano-ketone (II).

Dehydrogenation of the cyano-ketone (II) and derived compounds was investigated as a means of determining the orientation of other isomeric cyano-ketones (cf. Part VII). As in Part II,[4] no recognisable product could be isolated after heating the cyano-ketone (II) with sulphur or selenium. Unchanged cyano-ketone (II) was recovered from attempted

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* Ayres and Raphael[6] obtained a compound $C_{11}H_{16}ON_2$ from 1-acetylcyclohept-1-ene and aqueous ethanolic potassium cyanide which they considered to be 8-cyano-10-imino-8-methyl-9-oxabicyclo(5,3,0)decane (A).

[6] Ayres and Raphael, *J.*, 1958, 1779.

[7] Ultee, *Rec. Trav. chim.*, 1909, **28**, 259; Snyder and Elston, *J. Amer. Chem. Soc.*, 1954, **76**, 3039; see also Pinner, *Ber.*, 1884, **17**, 2009.

dehydrogenation with chloranil and also after treatment with *N*-bromosuccinimide. Dehydrogenation of the corresponding cyano-alcohol (VI) with sulphur had previously[4] been found to give only *p*-terphenyl (7%). 3-Cyano-2,5-diphenylcyclohex-2-en-1-ol (VI) and its acetate were recovered unchanged from treatment with chloranil or palladium-charcoal in boiling *p*-cymene.

The cyano-alcohol (VI) and *N*-bromosuccinimide gave 4-bromo- and 6-bromo-3-cyano-2,5-diphenylcyclohex-2-en-1-one. Both bromo-compounds were dehydrobrominated in pyridine to 2′-cyano-6′-hydroxy-*p*-terphenyl.

EXPERIMENTAL

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

Reaction of 3-*Methoxy*-2,5-*diphenylcyclohex*-2-*en*-1-*one* (I) *with Acetone Cyanohydrin.*—(a) 3-*Cyano*-2,5-*diphenylcyclohex*-2-*en*-1-*one* (II). 3-Methoxy-2,5-diphenylcyclohex-2-en-1-one (1·0 g.) and redistilled acetone cyanohydrin (10 c.c.) containing 13% methanolic potassium hydroxide (0·2 c.c.) were set aside overnight and then poured into water and acidified (Congo Red). The product was crystallised from ethyl acetate–light petroleum, giving 3-cyano-2,5-diphenylcyclohex-2-en-1-one (0·7 g.), m. p. 155° (Found: C, 83·3; H, 5·6; N, 5·2. Calc. for $C_{19}H_{15}NO$: C, 83·5; H, 5·5; N, 5·1%). Ames and Davey[4] gave m. p. 148—149°; a mixture melted at 152—153°.

When heated above its m. p., the cyano-ketone decomposed quantitatively to 2′-hydroxy-*p*-terphenyl, m. p. and mixed m. p. 194°. The cyano-ketone formed an *oxime*, needles, m. p. 225° (from ethanol) (Found: C, 77·2; H, 6·2; N, 9·4. $C_{19}H_{16}N_2O,\frac{1}{2}H_2O$ requires C, 76·7; H, 5·8; N, 9·4%).

(b) 1,5-*Dicyano*-3,8-*diphenyl*-6-*azabicyclo*(3,2,1)*octan*-7-*one* (III). The enol ether (2·0 g.), purified acetone cyanohydrin (20 c.c.), and triethylamine (0·1 c.c.) were heated for 45 min. at 80—90°. The solution was poured into water, and the solid collected and dried. 1,5-*Dicyano*-3,8-*diphenyl*-6-*azabicyclo*(3,2,1)*octan*-7-*one* (0·6 g.) crystallised from ethyl acetate–light petroleum in prisms, m. p. 225° [Found: C, 76·7; H, 5·1; N, 12·9%; *M* (Rast), 184. $C_{21}H_{17}N_3O$ requires C, 77·0; H, 5·2; N, 12·8%; *M*, 327]; $\lambda_{max.}$ *235*, *257*, *263*, and 292 mμ (ε 3200, 1450, 1200, 1300 respectively); infrared spectrum (KBr disc), bands at 3257 (NH, fused ring γ-lactam), 2247 (C⋮N), 1715 (C=O, fused ring γ-lactam), 1600, 1585, 1493, 1449 (aromatic −C=C−), 1220 (C−N?), 766, 740, and 697 cm.$^{-1}$ (phenyl system).

Use of 3-cyano-2,5-diphenylcyclohex-2-en-1-one in place of the enol ether furnished the same azabicyclo-octanone (35%), m. p. and mixed m. p. 225°. When heated above its m. p. the azabicyclo-octanone decomposed quantitatively to 2′-hydroxy-*p*-terphenyl, m. p. and mixed m. p. 194°.

(c) The enol ether (155 g.) and purified acetone cyanohydrin (400 c.c.) containing triethylamine (3·0 c.c.) were set aside overnight. 3-Cyano-2,5-diphenylcyclohex-2-en-1-one (56 g.), m. p. and mixed m. p. 155°, was filtered off and the mother-liquor was poured into water. The solid material was collected, dried, and recrystallised from ethyl acetate, giving 1,5-dicyano-3,8-diphenyl-6-azabicyclo(3,2,1)octan-7-one (6·0 g.), m. p. and mixed m. p. 225°, followed by more cyano-ketone (46 g.), m. p. and mixed m. p. 155°.

6-*Acetyl*-1,5-*dicyano*-3,8-*diphenyl*-6-*azabicyclo*(3,2,1)*octan*-7-*one*.—The azabicyclo-octanone (0·8 g.) was refluxed for 1 hr. with acetic anhydride (8 c.c.) containing one drop of concentrated sulphuric acid. The mixture was poured into water (200 c.c.) and left overnight. The solid was recrystallised from ethyl acetate, giving the N-*acetyl derivative* (0·6 g.), needles, m. p. 272° (Found: C, 74·8; H, 5·3; N, 11·3. $C_{23}H_{19}N_3O_2$ requires C, 74·8; H, 5·2; N, 11·4%); $\lambda_{max.}$ 246, 251, 257, *263*, *269*, *292* mμ (ε 2900, 2900, 2800, 2350, 1700, 610 respectively); infrared spectrum (KBr disc), bands at 2247, 2237 (C⋮N), 1754, 1698 (CO−N−CO), and 1217 cm.$^{-1}$ (C−N?).

2′,6′-*Dicyano*-p-*terphenyl*.—The *N*-acetyl derivative (2·9 g.) was heated with selenium (3·0 g.) for 1 hr. at 300—350° and the residue was extracted with ethanol. Concentration of this extract afforded 2′,6′-*dicyano*-p-*terphenyl* (0·3 g.), needles, m. p. 236° (from ethyl acetate) (Found: C, 85·2; H, 4·4; N, 10·4. $C_{20}H_{12}N_2$ requires C, 85·7; H, 4·3; N, 10·0%); $\lambda_{max.}$ 210, 232, and 279 mμ (ε 40,700, 31,500, 22,200 respectively); infrared spectrum (KBr disc), bands at 2222 (aromatic C⋮N), 1595, 1575, 1497, 1451 (aromatic –C=C–), and 899 cm.$^{-1}$ (C–H, isolated free hydrogen).

*6-Benzoyl-*1,5-*dicyano*-3,8-*diphenyl*-6-*azabicyclo*(3,2,1)*octan*-7-*one*.—The azabicyclo-octanone (0·5 g.) in dry pyridine (5 c.c.) was refluxed with benzoyl chloride (0·2 g.) for 2 hr. to give the N-*benzoyl derivative* (0·5 g.), prisms, m. p. 227° (from ethyl acetate) [Found: C, 78·0; H, 5·1; N, 9·7%; *M* (Rast), 324. $C_{28}H_{21}N_3O_2$ requires C, 77·9; H, 4·9; N, 9·7%; *M*, 431]; $\lambda_{max.}$ 244, *263*, 270, and 281 mμ (ε 15,350, 4000, 2450, 1650 respectively); infrared spectrum (KBr disc), bands at 2247, 2237 (C⋮N), 1745, 1684 (CO–N–CO), and 1255 cm.$^{-1}$ (C–N?).

The N-3,5-*dinitrobenzoyl derivative*, needles, m. p. 262° (from benzene) (Found: C, 64·6; H, 3·4; N, 13·2. $C_{28}H_{19}N_5O_6$ requires C, 64·5; H, 3·7; N, 13·4%), was similarly prepared.

Conversion of the Azabicyclo-octanone into 3-*Cyano*-2,5-*diphenylcyclohex*-2-*en*-1-*one*.—(a) *With pyridine.* The azabicyclo-octanone (1·0 g.) was refluxed in dry pyridine (10 c.c.) for 3 hr., and the solution then poured into dilute hydrochloric acid; the cyano-ketone (0·7 g.), m. p. and mixed m. p. 155°, was obtained.

(b) *In acid solution.* The azabicyclo-octanone (0·7 g.), acetic acid (10 c.c.), concentrated hydrochloric acid (7 c.c.), and water (4 c.c.) were refluxed for 12 hr., then diluted with water to give the cyano-ketone (0·6 g.), m. p. and mixed m. p. 155°.

Treatment of the azabicyclo-octanone (0·7 g.) with methylmagnesium iodide (from 0·1 g. of magnesium and 0·5 g. of methyl iodide) also yielded the cyano-ketone (0·4 g.), presumably owing to hydrolysis during the working up.

Reactions of 1,5-*Dicyano*-3,8-*diphenyl*-6-*azabicyclo*(3,2,1)*octan*-7-*one in Alkali*.—(a) *With sodium sesquicarbonate.* Sodium sesquicarbonate (1·5 g.) in water (30 c.c.) was refluxed with the azabicyclo-octanone (6·4 g.) in ethanol (450 c.c.) for 3 hr. The solvents were evaporated *in vacuo* and the residue was diluted with water. The solid was filtered off, dried, and successively extracted with ethyl acetate, methanol, and dimethylformamide. Evaporation of these extracts afforded, respectively, (i) 1-*cyano*-3-*oxo*-2,5-*diphenylcyclohexane*-1-*carboxyamide* (0·4 g.), needles, m. p. 218° (from ethyl acetate) [Found: C, 75·3; H, 5·5; N, 9·2%; *M* (Rast), 288. $C_{20}H_{18}N_2O_2$ requires C, 75·4; H, 5·7; N, 8·8%; *M*, 318], (ii) *compound A* (0·2 g.), prisms, m. p. 248° (from methanol) [Found: C, 75·4; H, 5·7; N, 8·7. $(C_{10}H_9NO)_n$ requires C, 75·4; H, 5·7; N, 8·8%], and (iii) *compound B* (2·5 g.), prisms, m. p. 334—335° (from dimethylformamide) [Found: C, 72·7; H, 5·5; N, 12·7. $(C_{21}H_{19}N_3O_2)_n$ requires C, 73·0; H, 5·5; N, 12·2%]. The molecular weights of these compounds could not be determined by Rast's method as they were insoluble in camphor. The infrared spectrum of 1-cyano-3-oxo-2,5-diphenylcyclohexane-1-carboxyamide showed bands (KBr disc) at 3370, 3310 (NH), 2247 (C⋮N), 1720 (C=O, cyclohexanone), 1690 (C=O, amide), 752, 700 cm.$^{-1}$ (phenyl system).

(b) *Carbonyl derivatives.* Treatment of the azabicyclo-octanone with hydroxylamine hydrochloride and sodium sesquicarbonate gave 1-*cyano*-3-*oxo*-2,5-*diphenylcyclohexane*-1-*carboxyamide oxime* as an amorphous powder, m. p. 208° (from ethyl acetate) (Found: C, 72·0; H, 6·0; N, 12·4. $C_{20}H_{19}N_3O_2$ requires C, 72·1; H, 5·7; N, 12·6%); infrared spectrum, bands (KBr disc) at 3450 (OH), 3333, 3190 (NH), 2250 (C⋮N), 1678, 1696 cm.$^{-1}$ (C=O, amide I and II).

Use of semicarbazide hydrochloride and sodium acetate likewise gave the corresponding *semicarbazone* as an amorphous powder, m. p. 198° (from benzene) (Found: C, 66·9; H, 5·8; N, 19·1. $C_{21}H_{21}N_5O_2$ requires C, 67·2; H, 5·6; N, 18·7%).

The azabicyclo-octanone (0·3 g.) in ethanol (15 c.c.) was refluxed with phenylhydrazine (0·1 g.) for 4 hr. to give the corresponding *phenylhydrazone* (30 mg.), orange prisms, m. p. 238—239° (from ethyl acetate–light petroleum) [Found: C, 76·3; H, 5·9; N, 14·2%; *M* (Rast), 272. $C_{26}H_{24}N_4O$ requires C, 76·4; H, 5·9; N, 13·7%; *M*, 410]; infrared spectrum, bands (KBr disc) at 3407, 3263 (NH), 3311, 3192 (NH, amide), 2242 (C⋮N), 1669, 1695 cm.$^{-1}$ (C=O, amide I and II).

(c) *With excess of sodium hydroxide.* The azabicyclo-octanone (2·5 g.) and ethanol (150 c.c.) containing 20% aqueous sodium hydroxide (5 c.c.) were refluxed for 3 hr. The solvent was evaporated *in vacuo*, and the residue diluted with water. Crystallisation from ethyl acetate gave 2′-hydroxy-*p*-terphenyl (1·7 g.), m. p. and mixed m. p. 194°.

(d) *With sodium hydroxide and methyl iodide.* 6% Aqueous sodium hydroxide (1 mol.) and methyl iodide (1·5 mol.) were successively added to the azabicyclo-octanone (1·0 g., 1 mol.) in ethanol (50 c.c.) and the mixture was refluxed for 3 hr., then worked up as in (c), yielding 3-cyano-2,5-diphenylcyclohex-2-en-1-one (0·5 g.), m. p. and mixed m. p. 155° (from ethyl acetate).

(e) *Use of one equivalent of sodium hydroxide.* When experiment (d) was carried out with omission of methyl iodide the product was compound B (0·3 g.), prisms, m. p. and mixed m. p. 334—335° (from dimethylformamide).

3-*Chloro*-2,5-*diphenylcyclohex*-2-*en*-1-*one*.—2,5-Diphenylcyclohexane-1,3-dione (20·3 g.) in dry chloroform (75 c.c.) was refluxed with phosphorus trichloride (5·7 c.c.) for 2 hr. Crushed ice, ether, and aqueous sodium hydrogen carbonate were successively added and the organic layer was washed with aqueous sodium hydroxide, dried, and evaporated. The residue was recrystallised from ethyl acetate–light petroleum, yielding the *chloro-ketone* (7·0 g.) as needles, m. p. 139—140° (Found: C, 76·9; H, 5·1; Cl, 12·3. $C_{18}H_{15}ClO$ requires C, 76·4; H, 5·3; Cl, 12·5%).

The chloro-ketone (2·0 g.) and sodium cyanide (2·5 g.) in dimethylformamide (50 c.c.) were refluxed for 7 hr. Dilution of the resulting solution with water afforded 2′-hydroxy-*p*-terphenyl (80%), prisms, m. p. and mixed m. p. 194° (from ethyl acetate).

Action of Alkali on 3-*Cyano*-2,5-*diphenylcyclohex*-2-*en*-1-*one* (II).—The cyano-ketone (1·0 g.) in ethanol (50 c.c.) was refluxed with 20% aqueous sodium hydroxide (2 c.c.) for 3 hr. The ethanol was evaporated under reduced pressure, the residue diluted with water, and the product filtered off. 2′-Hydroxy-*p*-terphenyl (0·5 g.) crystallised from ethyl acetate as prisms, m. p. and mixed m. p. 194°.

1-*Acetoxy*-3-*cyano*-2,5-*diphenylcyclohex*-2-*ene*.—Potassium borohydride (1·5 g.) in water (15 c.c.) was added to 3-cyano-2,5-diphenylcyclohex-2-en-1-one (2·5 g.) in methanol (75 c.c.); the mixture was set aside for 5 hr., then poured into water, and the cyano-alcohol (2·3 g.) was filtered off, dried, and refluxed in acetic anhydride (10 c.c.) containing one drop of concentrated sulphuric acid for 1 hr. Dilution of this solution with water furnished the corresponding *acetate*, needles, m. p. 133° (from ethyl acetate–light petroleum) (Found: C, 79·3; H, 6·4; N, 4·5. $C_{21}H_{19}NO_2$ requires C, 79·5; H, 6·0; N, 4·4%).

Reaction of 3-*Cyano*-2,5-*diphenylcyclohex*-2-*en*-1-*ol with* N-*Bromosuccinimide*.—*N*-Bromosuccinimide (7·0 g.) and benzoyl peroxide (0·05 g.) were added to 3-cyano-2,5-diphenylcyclohex-2-en-1-ol (10·0 g.) in dry carbon tetrachloride (500 c.c.) and the mixture was refluxed for 2 hr. The precipitated succinimide was removed, and the filtrate was concentrated to an oil which solidified on trituration with benzene. Crystallisation from ethyl acetate gave 6-*bromo*-3-*cyano*-2,5-*diphenylcyclohex*-2-*en*-1-*one* (4·4 g.), plates, m. p. 183° (Found: C, 64·7; H, 4·2; N, 4·1; Br, 21·3. $C_{19}H_{14}BrNO$ requires C, 64·8; H, 4·0; N, 4·0; Br, 22·7%); $\lambda_{max.}$ *215*, *225*, and 302 mμ (ε 15,300, 12,600, 3800 respectively); infrared spectrum (KBr disc), bands at 2217 ($C{\vdots}N$), 1695 (α′-bromo-αβ-unsaturated C=O), and 565 cm.$^{-1}$ (C–Br). After several days, 4-*bromo*-3-*cyano*-2,5-*diphenylcyclohex*-2-*en*-1-*one* (2·2 g.) crystallised from the benzene mother-liquor as yellow needles, m. p. 162° (Found: C, 64·4; H, 4·1; N, 4·0; Br, 22·8%); $\lambda_{max.}$ *214·5*, *228*, and 303 mμ (ε 15,700, 13,200, 4000 respectively); infrared spectrum (KBr disc), bands at 2208 ($C{\vdots}N$), 1686 (αβ-unsaturated C=O), 534, and 522 cm.$^{-1}$ (C–Br).

2′-*Cyano*-6′-*hydroxy*-p-*terphenyl*.—4-Bromo-3-cyano-2,5-diphenylcyclohex-2-en-1-one (0·8 g.) in dry pyridine (5 c.c.) was refluxed for 3 hr. and then poured into dilute hydrochloric acid (200 c.c.). The solid (0·6 g.) was dried, and recrystallised from ethyl acetate, giving 2′-*cyano*-6′-*hydroxy*-p-*terphenyl* as needles, m. p. 193° (Found: C, 83·8; H, 5·2; N, 5·3. $C_{19}H_{13}NO$ requires C, 84·1; H, 4·8; N, 5·2%); $\lambda_{max.}$ 234, 267, and 321 mμ (ε 36,900, 15,500, 9600 respectively). The same product was obtained when 6-bromo-3-cyano-2,5-diphenylcyclohex-2-en-1-one was used in place of the 4-bromo-isomer.

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