Coumarins and Related Compounds. Part XIX.[1] Synthesis of 3-Phenylbenzo[*h*]coumarin

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3-Phenylbenzo[*h*]coumarin (14) has been synthesised from 1-methoxy-2-naphthaldehyde (12) and an improved synthesis of 1-hydroxy-2-naphthaldehyde (11) is described. Attempts to synthesise 3-phenyl-3,4-dihydrobenzo[*h*]coumarin (15) resulted in the formation of 4-substituted 1-naphthols (3) and (4) when 1-naphthol was condensed with 2-phenylacrylonitrile in the presence of zinc chloride, and of the naphthofuranone (9) when ethyl 2-phenylacrylate and anhydrous aluminium chloride were used.

THE synthesis of 4-benzopyrones was described by Jacobson and Ghosh [2] and re-investigated [3] by Baker and Robinson, who concluded that the 4-benzopyrones described by the previous workers were the isomeric 2-pyrones; the literature was corrected accordingly.[4] However 2-phenyl-4*H*-benzo[*h*]chromen-4-one (17) was subsequently synthesised [5] by Pillon *et al.* and found to have m.p. 154°, identical with that given by Jacobson and Ghosh, whereas the isomeric 4-phenylbenzo[*h*]-coumarin (18) has been found to melt at 126—127°.[6-8] Venkataraman and his co-workers synthesised [9] 3-phenyl-4*H*-benzo[*h*]chromen-4-one (16) by an unambiguous route and obtained a compound having m.p. 187°. We now report the unambiguous synthesis of 3-phenylbenzo[*h*]coumarin (14) with m.p. 214—215°. It appears, therefore, that the compound with m.p. 169—170° described by Ghosh [2b] is neither the benzochromenone (16) as claimed by him nor the benzocoumarin (14) as suggested by Baker.[3]

We first attempted to synthesise coumarin (14) *via* the dihydrocoumarin (15).[10] 1-Naphthol (1) was condensed with 2-phenylacrylonitrile [11] in the presence of zinc chloride at 0° to give two nitrogen-containing products. The first had nitrile and hydroxy absorptions at 2250 and 3333 cm^{-1} in its i.r. spectrum, and the second had carbonyl and hydroxy absorptions at 1660 and 3450 cm^{-1}. Alkaline hydrolysis of both the products gave the same acid (6), and the former product could be converted into the latter by hydrolysis with alkaline hydrogen peroxide.[12] On the basis of spectral and elemental analysis the former product was designated as the nitrile (3) and the latter as the amide (4). The structure of the nitrile (3) was further confirmed by synthesis. 1-Methoxy-4-naphthaldehyde [13] (5) was condensed with phenylacetonitrile [14] to give the unsaturated nitrile (7). Hydrogenation of the nitrile (7) over palladium–charcoal gave the methoxy-nitrile (8). Demethylation of (8) with pyridine hydrochloride afforded the hydroxy-nitrile, identical with product (3) (mixed m.p., i.r., and t.l.c.). Thus, in the reaction of 1-naphthol (1) with 2-phenylacrylonitrile only the *para*-position is attacked. Condensation with aluminium chloride at an elevated temperature failed to give any useful product.

In an attempt to bring about *ortho*-substitution [15] 1-naphthol (1) was condensed with ethyl 2-phenylacrylate [16] in the presence of aluminium chloride and dry hydrogen chloride at 150—170°. The product had

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[15] A. K. Das Gupta, R. M. Chatterje, and M. S. Paul, *J. Chem. Soc.* (*C*), 1971, 3367; A. K. Das Gupta, R. M. Chatterje, and K. R. Das, *ibid.*, 1969, 2618.
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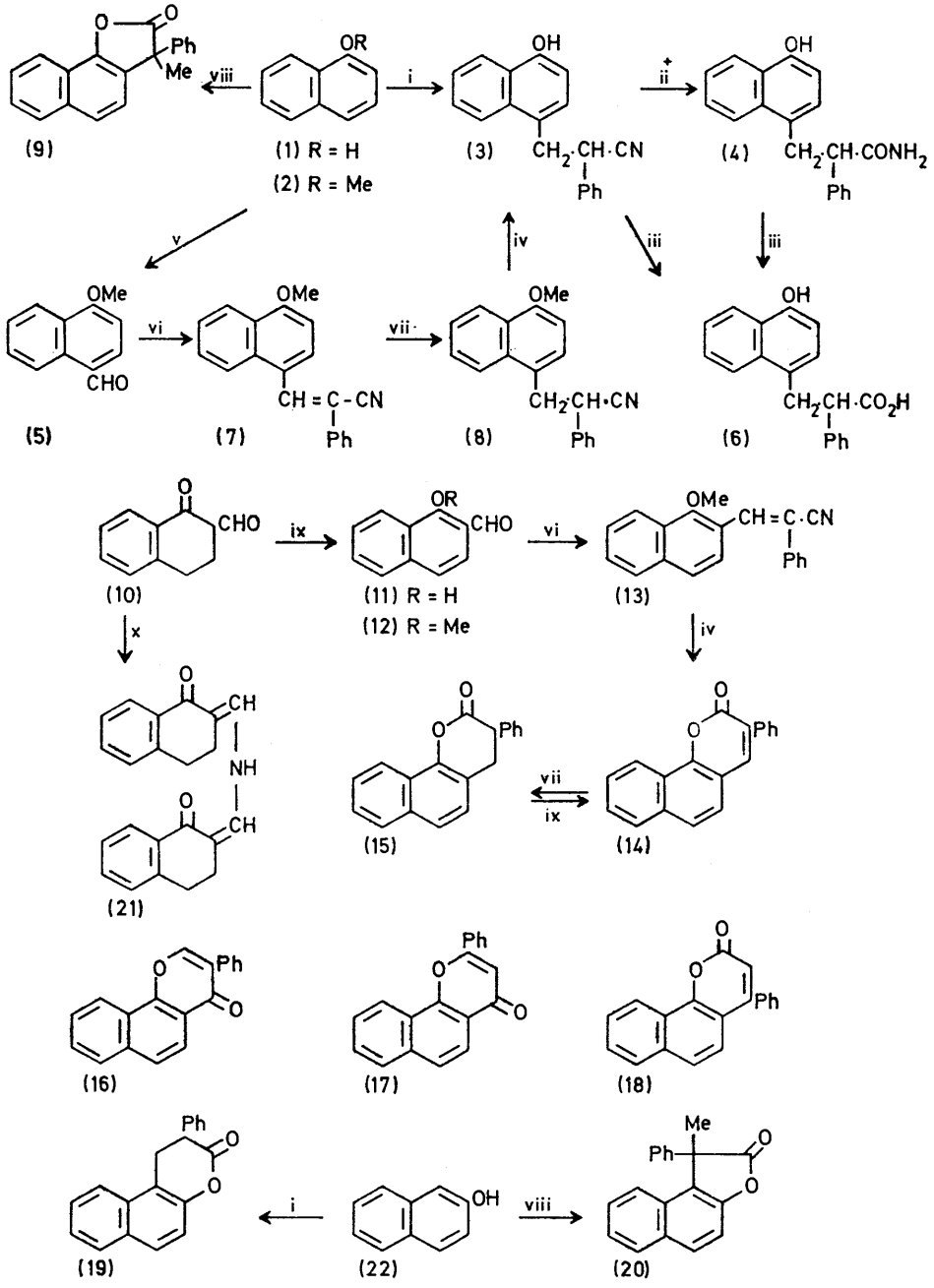
molecular formula $C_{19}H_{14}O_2$ in agreement with the required structure (15) but attempted dehydrogenations with palladium–charcoal, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and iodine under a variety of condensation of 2-naphthol with the corresponding acrylonitrile gave exclusively the dihydrocoumarin (19) [1] and not γ-lactone (20).

As this route to the coumarin (14) failed, we attempted



Reagents. i, CH_2=C(CN)Ph–$ZnCl_2$; ii, H_2O_2–KOH; iii, KOH–EtOH; iv, pyridine, HCl; v, $Zn(CN)_2$–HCl; vi, $PhCH_2$·CN–KOH; vii, H_2/Pd–C; viii, CH_2=C(Ph)CO_2Et–$AlCl_3$; ix, DDQ–dioxan; x, $PhCH_2$·CN–NH_4OAc.

conditions were unsuccessful and the compound was not identical with an authentic specimen of the dihydrocoumarin (15) (see below). The n.m.r. spectrum showed a singlet methyl signal and indicated the γ-lactone structure (9). Similarly, reaction of 2-naphthol (22) with ethyl 2-phenylacrylate gave the naphthofuranone (20) and not the expected dihydrocoumarin (19), whereas the synthesis from 2-formyl-1-tetralone (10).[17] Condensation of (10) with benzyl cyanide [18] in the presence of ethanolic potassium hydroxide, piperidine, or a mixture of piperidine and acetic acid failed. However, with ammonium acetate and acetic acid a product ($C_{22}H_{19}NO_2$)

[17] Ref. 4, 1950, vol. 12B, p. 2658.
[18] G. Jones, *Org. Reactions*, 1967, **15**, 204.

was obtained and assigned structure (21). This compound (21) is obtained by heating the tetralone (10) with ammonium acetate and acetic acid alone.

The successful synthesis of the benzocoumarin (14) started from 1-methoxy-2-naphthaldehyde (12) and used the elegant method of Buu-Hoï.[19] 1-Hydroxy-2-naphthaldehyde (11) was prepared in improved yield[20] by formylating[21] 1-tetralone, and dehydrogenating the formylated product (10) with DDQ[22] in boiling dioxan. Methylation of (11) with alkaline dimethyl sulphate gave 1-methoxy-2-naphthaldehyde (12).[20c] The methoxyaldehyde (12) on condensation with phenyl acetonitrile gave the unsaturated methoxy-nitrile (13), which on demethylation and cyclisation with pyridine hydrochloride afforded the required coumarin (14) showing the expected absorptions in the i.r. and n.m.r. spectra (Experimental section). Hydrogenation of (14) over palladium–charcoal in tetrahydrofuran gave the dihydrocoumarin (15), and dehydrogenation of (15) with DDQ gave back the coumarin (14) in high yield.

EXPERIMENTAL

N.m.r. spectra were measured for solutions in [^{2}H]-chloroform with Varian A-60 and T-60 spectrophotometers (tetramethylsilane as internal standard). Mass spectra were measured with an A.E.I. MS9 machine. Thin layer chromatograms were prepared with silica gel G (Merck) and developed with (A) benzene–dioxan–acetic acid (90 : 25 : 4) and (B) benzene–chloroform (70 : 30) as eluants; spots were visualised by exposure to iodine vapour. Unless otherwise stated, u.v. spectra were determined for solutions in methanol with a Hilger spectrophotometer and i.r. spectra were determined for Nujol mulls. Ethereal extracts were dried over anhydrous sodium sulphate. Petrol refers to light petroleum with b.p. 60—80°.

Attempted Synthesis of 3-Phenyl-3,4-dihydrobenzo[h]*coumarin* (15).—(a) *With 2-phenylacrylonitrile and zinc chloride.* Dry hydrogen chloride was passed into an ice-cooled stirred mixture of 1-naphthol (1) (6 g), freshly distilled 2-phenylacrylonitrile[11] (6 g), and zinc chloride (6 g), in dry ether (50 ml), until the mixture was saturated (2·5 h). The mixture was set aside in a refrigerator for 75 h and then decomposed with dil. hydrochloric acid. After heating on a water-bath (1·5 h) the mixture deposited a semi-solid material on cooling, and this was triturated with chloroform to give a crystalline substance (4·4 g), m.p. 170—185°. Fractional crystallisation from methanol gave 3-(4-*hydroxy*-1-*naphthyl*)-2-*phenylpropionamide* (4) (1·8 g), m.p. 216—217° (Found: C, 78·55; H, 5·8; N, 4·8. $C_{19}H_{17}NO_2$ requires C, 78·35; H, 5·9; N, 4·8%), R_F(A) 0·45, $\nu_{max.}$ 3450, 1660, 1476, 1396, 1290, and 855 cm^{-1}. The mother liquor yielded 3-(4-*hydroxy*-1-*naphthyl*)-2-*phenylpropionitrile* (3) (2·4 g), m.p. 150—151° (from benzene) (Found: C, 83·0; H, 5·8; N, 5·15. $C_{19}H_{15}NO$ requires C, 83·5; H, 5·55; N, 5·15%), R_F(A) 0·72, $\nu_{max.}$ (KBr) 3333, 2232, 1618, 1580, 1447, 1370, 1266, 1148, 1045, and 811 cm^{-1}.

(b) *With ethyl 2-phenylacrylate and aluminium chloride.* Anhydrous aluminium chloride (8·3 g) was added in portions to a cooled stirred solution of ethyl 2-phenylacrylate (10·4 g) and 1-naphthol (1) (9 g) in dry ether (30 ml). Dry hydrogen chloride was passed into the mixture for 2·5 h at ~10° and for another 2·5 h at 145—155°, and then the temperature was further raised to 180° for 0·5 h. The solid mass was decomposed with dil. hydrochloric acid, heated on a water-bath (3·5 h), and extracted with chloroform. Evaporation of the solvent gave an oil, which was distilled at 240—250° and 0·7 mmHg to give 3-*methyl*-3-*phenylnaphtho*[1,2-b]*furan*-2(3H)-*one* (9) (10 g), m.p. 115—116° (from methanol) (Found: C, 82·95; H, 5·0. $C_{19}H_{14}O_2$ requires: C, 83·2; H, 5·15%), *m/e* 274, R_F(B) 0·67, $\lambda_{max.}$ (EtOH) 230, 288, 309, and 345 nm (log ε 4·67, 3·78, 3·36, and 3·36), $\nu_{max.}$ ($CHCl_3$) 1800, 1595, 1490, 1435, 1375, 1020, and 994 cm^{-1}, δ 7·20—8·18 (11H, m, aromatic) and 1·98 p.p.m (3H, s, CH_3).

Hydrolysis of Nitrile (3).—(a) *With alcoholic hydrogen peroxide.* A solution of hydrogen peroxide (6%; 10 ml) was added slowly with shaking to a solution of the nitrile (3) (0·27 g) in 2N-potassium hydroxide (5 ml) at 45°. Initial external heating was required, and oxygen was liberated with foaming during the addition. After 0·5 h, the mixture was chilled in ice and the pH was adjusted to 5·5—6 with cold dilute hydrochloric acid. The separated solid yielded the amide (4) (0·26 g), m.p. 215—216° (from methanol). This compound showed no depression in m.p. when mixed with the amide obtained previously.

(b) *With alcoholic potassium hydroxide.* The nitrile (3) (0·8 g) and ethanolic 2N-potassium hydroxide (20 ml) were heated under reflux, until the liberation of ammonia ceased (20 h). Most of the ethanol was removed under reduced pressure and the residue was treated with cold dilute hydrochloric acid. The mixture was extracted with chloroform and washed with sodium carbonate, and the carbonate layer on acidification gave a tarry solid which was purified by distillation (200—220° at 0·8 mmHg) to give 3-(4-*hydroxy*-1-*naphthyl*)-2-*phenylpropionic acid* (6) (0·1 g) as a glass, m.p. 154° (from toluene) (Found: C, 77·8; H, 5·4. $C_{19}H_{16}O_3$ requires C, 78·05; H, 5·5%), R_F(A) 0·61, $\nu_{max.}$ 3340, 1704, 1590, 1460, 1383, 1257, 1160, 1022, and 855 cm^{-1}.

Hydrolysis of the Amide (4).—The amide (4) (1 g) was hydrolysed with alcoholic potassium hydroxide as for the nitrile (3) to give the acid (6) (0·1 g), m.p. 153—154° (from toluene), identical (mixed m.p. and i.r. spectrum) with the sample obtained earlier.

3-(4-*Methoxy*-1-*naphthyl*)-2-*phenylpropionitrile* (8).—Aqueous 10% potassium hydroxide (a few drops) was added with shaking to a solution of 4-methoxy-1-naphthaldehyde (5) (2·2 g) and phenylacetonitrile (1·5 g) in ethanol (15 ml). The mixture was refluxed on a water-bath for 15 min (crystals separated out) and then stirred at room temperature for 1 h. The crystals yielded 3-(4-*methoxy*-1-*naphthyl*)-2-*phenylacrylonitrile* (7) (1·5 g), m.p. 129—130° (from ethanol) (Found: C, 83·85; H, 5·55; N, 4·8. $C_{20}H_{15}NO$ requires C, 84·2; H, 5·3; N, 4·9%), R_F(B) 0·62, $\nu_{max.}$ 2227, 1613, 1565, 1445, 1361, 1250, 1093, and 826 cm^{-1}. The nitrile (7) (1·2 g) in tetrahydrofuran (50 ml) was hydrogenated at room temperature over 10% palladium–charcoal (0·2 g) for 4 h to give an oil which was distilled at 140—150° and 0·8 mmHg to yield a glass. Crystallisation from ethanol gave the

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nitrile (8) (0·85 g) as needles, m.p. 77—78° (Found: C, 83·3; H, 5·95; N, 4·8. $C_{20}H_{17}NO$ requires C, 83·6; H, 5·95; N, 4·9%), R_F(B) 0·56, $\nu_{max.}$ 2210, 1605, 1540, 1470, 1300, 1260, 1180, 1120, and 815 cm^{-1}.

Synthesis of the Nitrile (3).—A mixture of fresh pyridine hydrochloride (2·7 g) and the nitrile (8) (0·7 g) was refluxed for 20 min in anhydrous conditions. The mixture was cooled, treated with water (25 ml) and a few drops of hydrochloric acid, and then heated on a water-bath for 45 min. Filtration gave the nitrile (3) (0·5 g), m.p. 150—151° (from benzene–hexane), identical (mixed m.p., i.r. spectrum, and t.l.c.) with the sample obtained earlier. It gave a brown colouration with ferric chloride.

Attempted Synthesis of 3-(1-*Hydroxy*-3,4-*dihydro*-2-*naphthyl*)-2-*phenylacrylonitrile*.—A mixture of 2-formyl-1-tetralone (10) (7·6 g), phenylacetonitrile (5·4 g), acetic acid (4·5 ml), and benzene (50 ml) was heated under reflux for 2 h while ammonium acetate (3 g) was added in portions. The mixture was washed with water, dried, and evaporated *in vacuo* to leave a dark residue which solidified on trituration with ether. Recrystallisation from ethyl acetate gave *bis*-(1-*oxo*-1,2,3,4-*tetrahydro*-2-*naphthylidenemethyl*)*amine* (21) (4·4 g) as orange-red needles, m.p. 181—182° (Found: C, 80·7; H, 6·05; N, 4·55. $C_{22}H_{19}NO_2$ requires C, 80·2; H, 5·8; N, 4·25%), *m/e* 329, $\lambda_{max.}$ 220, 270, and 435 nm (log ε 4·15, 4·23, and 4·67), R_F(A) 0·75, $\nu_{max.}$ 1670, 1660, 1601, 1525—1575br cm^{-1}. Repetition of the experiment without using phenylacetonitrile also yielded compound (21), m.p. 180—182°, identified by mixed m.p. and t.l.c.

1-*Methoxy*-2-*naphthaldehyde* (12).—To a warm solution of DDQ (5 g) and toluene-*p*-sulphonic acid (0·25 g) in dry dioxan (100 ml) was added in one batch with shaking a solution of freshly distilled 2-formyl-1-tetralone (10) (3·2 g) in dry dioxan (15 ml). Immediate precipitation occurred, and the mixture was refluxed for 30 min.* Evaporation of the filtered mixture gave a residue which was chromatographed over alumina and distilled at 110—120° and 2·5 mmHg to yield 1-hydroxy-2-naphthaldehyde (11) (0·77 g), as yellow needles, m.p. 57° (lit.,[20] † 57°) (Found: C, 76·65; H, 5·0. Calc. for $C_{11}H_8O_2$: C, 76·75; H, 4·7%), R_F(B) 0·58, $\lambda_{max.}$ 218, 254, 262, 285, 296, 307, and 380 nm (log ε 4·43, 4·59, 4·58, 3·91, 3·95, 3·71, and 3·82), $\nu_{max.}$ (KBr) 2915, 1630, 1449, 1369, 1212, 1028, and 813 cm^{-1}. Methylation of (11) (0·6 g) with dimethyl sulphate (0·9 g) and anhydrous potassium carbonate (1·8 g) in dry acetone (50 ml) gave the methoxy-compound (12) (0·55 g), m.p. 62—63° (from hexane) (lit.,[20c] 47°) (Found: C, 77·2; H, 5·5. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4%), R_F(B) 0·43, $\nu_{max.}$ (KBr) 1675, 1449, 1235, 1083, and 827 cm^{-1}.

3-*Phenylbenzo*[h]*coumarin* (14).—To a mixture of 1-methoxy-2-naphthaldehyde (12) (1·45 g) and phenylacetonitrile (0·94 g) in ethanol (12 ml), a few drops of aqueous potassium hydroxide (10%) were added, and the mixture was warmed at 60—70° for 10 min. The solid which separated out gave 3-(1-*methoxy*-2-*naphthyl*)-2-*phenylacrylonitrile* (13) (1·9 g) as hexagons (from ethanol), m.p. 140—141° (Found: C, 84·2; H, 5·2; N, 5·15. $C_{20}H_{15}NO$ requires C, 84·2; H, 5·3; N, 4·9%), R_F(B) 0·66, $\nu_{max.}$ 2217, 1613, 1456, 1364, 1250, 1087, and 827 cm^{-1}. A mixture of (13) (1·4 g) and freshly redistilled pyridine hydrochloride (5·4 g) was heated under reflux for 15 min, treated with water and a few drops of acetic acid, and warmed on a water-bath for 30 min. On cooling, the coumarin (14) (1·1 g) separated, m.p. 202—204°, and gave *needles* (from acetic acid), m.p. 214—215° [m.p. 212—213° (from THF) and 208—209° (from ethanol)] (Found: C, 83·6; H, 4·4. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·45%), R_F(B) 0·49, $\lambda_{max.}$ (EtOH) 242, 279, 338, and 375 nm (log ε 4·36, 4·38, 4·22, and 4·08), $\nu_{max.}$ 1720, 1470, 1240, 865, 822, and 780 cm^{-1}, δ ($CDCl_3$) 8·57 (1H, m, 4-H) and 7·33—7·88 p.p.m. (11H, m, aromatic).

3-*Phenyl*-3,4-*dihydrobenzo*[h]*coumarin* (15).—The coumarin (14) (1 g) was hydrogenated over palladium–charcoal (10%; 200 mg) in tetrahydrofuran (150 ml) at room temperature. Uptake of hydrogen was slow and a drop of perchloric acid was added to promote the reaction, which was complete after *ca.* 10 h (t.l.c.). Work-up in the usual way gave a bluish-green oil which was distilled and chromatographed over silica gel [elution with benzene–petrol (1 : 1)] to afford the *dihydrocoumarin* (15) (500 mg), m.p. 148—149° (from benzene–hexane) (Found: C, 83·7; H, 4·85. $C_{19}H_{14}O_2$ requires C, 83·2; H, 5·15%), R_F(B) 0·52, $\lambda_{max.}$ 231, 278sh, 288, and 323 nm (log ε 4·5, 3·5, 3·5, and 3·0), $\nu_{max.}$ 1765, 1620, 1470, 1240, 1140, 840, and 770 cm^{-1}. The dihydrocoumarin (15) was unstable, giving a ring-opened hydroxy-acid.

Dehydrogenation of Dihydrocoumarin (15).—To a warm solution of DDQ (0·06 g) in dry dioxan (6 ml), the dihydrocoumarin (15) (0·06 g) and a crystal of toluene-*p*-sulphonic acid were added and the mixture was heated under reflux for 14 h. A solid separated out. The dioxan was removed under reduced pressure, and the residue was purified over alumina with chloroform as eluant to give the coumarin (14), m.p. and mixed m.p. 212—213°.

1-*Methyl*-1-*phenylnaphtho*[2,1-b]*furan*-2(1H)-*one* (20).—Anhydrous aluminium chloride (4·2 g) was added in portions to a cold stirred mixture of 2-naphthol (4·5 g) and ethyl 2-phenylacrylate (5·2 g) in dry ether (50 ml), and dry hydrogen chloride was passed into the mixture for 1·5 h in the cold and for 2 h at 150—160°. After 16 h at room temperature, the mixture was decomposed with dilute hydrochloric acid. Working up in the usual way gave a gum which on distillation at 210—230° and 0·7 mmHg gave the lactone (20) (4 g), m.p. 120—121° (from ethanol) (lit.,[23] 119°) (Found: C, 83·4; H, 5·4. Calc. for $C_{19}H_{14}O_2$: C, 83·7; H, 5·15%), R_F(B) 0·62, $\lambda_{max.}$ 231, 269, 280, 291, 314, and 328 nm (log ε 4·67, 2·58, 2·69, 2·64, 2·21, and 2·34), $\nu_{max.}$ 1800, 1600, 1480, 1400, 1265, 1020, and 985 cm^{-1}, δ (CCl_4) 7·20—7·85 (11H, m, aromatic) and 2·05 p.p.m. (3H, s, CH_3).

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* On longer heating (3—4 h) a yellow fluffy material, m.p. 250—255° was also obtained during chromatography, but this could not be identified.

† Different m.p.s have been reported: (*a*) 53·2—54·2°, (*b*) 55°, (*c*) 59°, (*d*) 59—60°, (*e*) 57°.

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