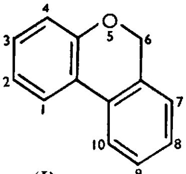
307. *Dibenzo*[b,d]*pyrans and Related Products.*

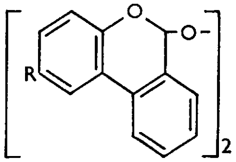
By G. W. K. Cavill, F. M. Dean, J. F. E. Keenan, A. McGookin, Alexander Robertson, and G. B. Smith.

Dibenzo[*b*,*d*]pyrans (cf. I) not substituted in the 6-position have been prepared and shown to produce peroxides (II) by aerial oxidation, and benzocoumarins (V) by permanganate oxidation.

While investigating the structure of citromycetin, Cavill, Robertson, and Whalley[1] examined the action of oxidising agents on various methylene compounds and in 1949 one of us (G. W. K. C.) prepared dibenzo[*b*,*d*]pyran (I), novel in this series because of the absence of 6-substituents. He found that it was oxidisable to a substance which appeared to be a peroxide (II; R = H); dibenzo[*b*,*d*]pyran was subsequently obtained by Inubushi[2] by an alternative method.



(I)



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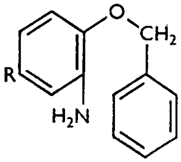

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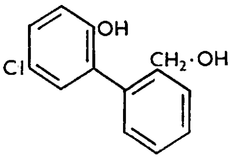
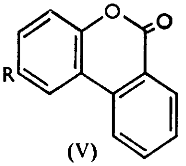


(IV)

Dibenzo[*b*,*d*]pyrans have now been prepared by two routes. In the first, it and its 9-methyl, 2-methyl, and 2-chloro-derivatives resulted from Pschorr ring-closure of the corresponding *o*-aminophenyl benzyl ethers (III). In the second, lithium aluminium hydride reduced 2-chlorobenzo[*c*]coumarin (V; R = Cl) to 5-chloro-2-hydroxy-2′-(hydroxymethyl)diphenyl (IV) which was converted into 2′-bromomethyl-5-chloro-2-hydroxydiphenyl and cyclised to 2-chlorodibenzo[*b*,*d*]pyran. Whilst this work was in progress Inubushi[2] prepared dibenzo[*b*,*d*]pyran by the second process but the method may not be generally applicable because it furnished an impure oil instead of 2-methyldibenzo[*b*,*d*]pyran.



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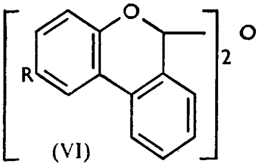

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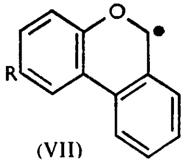

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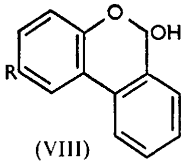

(VIII)

Except for the 2-chloro-derivative, the dibenzopyrans prepared were oils and difficult to purify. For this reason the 2 : 3-dimethoxy- and 3-methoxy-derivatives were not analysed but were oxidised by chromic oxide or potassium permanganate in acetone to the solid benzocoumarins, a method well suited to the characterisation of such dibenzopyrans. For comparison, authentic benzo[*c*]coumarins (dibenzo-2-pyrones) of type (V) were generally prepared by a modification of Cahn's method[3] using anthranilic acid diazonium sulphate and phenols substituted in the *para*-position to avoid the formation of isomerides: the exception was 2 : 3-dimethoxybenzo[*c*]coumarin which was obtained by dehydrogenation of the corresponding *cyclo*hexenocoumarin (cf. Ghosh, Todd, and Wilkinson[4]).

Although small quantities of benzocoumarins (V) are formed by aerial oxidation of the

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[1] Cavill, Robertson, and Whalley, *J.*, 1949, 1567.

[2] Inubushi, *J. Pharm. Soc. Japan*, 1952, **72**, 656; *Chem. Abs.*, 1953, **47**, 2173.

[3] Cahn, *J.*, 1933, 1400.

[4] Ghosh, Todd, and Wilkinson, *J.*, 1940, 1393.

dibenzopyrans, the main products are the corresponding peroxides (II). These compounds are probably produced through free radicals (VII) because this slow oxidation is considerably accelerated by the addition of benzaldehyde which is known to promote similar radical reactions [5] and because dixanthylethanes are known to dissociate into analogous radicals which then react with oxygen giving dixanthyl peroxides.[6]

Our peroxides were stable solids with fairly high melting points, inert to potassium iodide, and resisted hydrogenation. However, reduction with zinc and acetic anhydride was partially successful and gave the chloro- (VI; R = Cl) and the methyl-substituted ether (VI; R = Me) from the corresponding peroxides (II); concentrated sulphuric acid has a similar effect. The view that the intermediate in these reactions is the alcohol (VIII) which, by dehydration of two molecules affords the ether, or by aerial oxidation of one molecule gives the benzocoumarin, is not only supported by the formation of xanthones in the autoxidation of dixanthylethanes and the formation of xanthhydrols when sulphuric acid reacts with dixanthyl peroxides,[6] but also neatly accommodates the formation of 2-chlorobenzo[*c*]coumarin (V; R = Cl) as the sole " reduction " product when lithium aluminium hydride interacts with the peroxide (II; R = Cl). The same chlorocoumarin (V; R = Cl) is obtained by the action of pyridine and acetic anhydride on the peroxide (II; R = Cl) and may then result from decomposition of an acetyl dibenzopyranyl peroxide.

The infrared absorption spectra of the chloro-peroxide (II; R = Cl) and chloro-ether (VI; R = Cl), and of the methyl peroxide (II; R = Me) and methyl ether (VI; R = Me) are almost identical and do not contain peaks that must be attributed to hydroxyl or carbonyl groups. A striking feature of the ethers is the very broad and strong band at 947 cm.$^{-1}$ which is resolved in the spectra of the peroxides into two strong bands at 963 and 945 cm.$^{-1}$. Since the stretching vibration of the peroxide link is weak and not characteristic,[7] it is reasonable to associate these bands (which are absent from spectra of the dibenzopyrans and benzocoumarins) with the acetal groupings of the systems (II) and (VI). The frequencies are somewhat lower than those usually associated with ethers or with the CH vibrations of acetals,[8] but since interactions can be expected in symmetrical systems the data are accepted as supporting evidence for the structures assigned to the peroxides (II) and the ethers (VI).

2-Chloro-6 : 6-diphenyldibenzo[*b*,*d*]pyran was obtained from 2-chlorobenzo[*c*]coumarin by means of phenylmagnesium bromide in excess and, as expected, was stable in air. With a limited quantity of the Grignard reagent, this coumarin supplied an alcohol which could not be isolated but was converted into crystalline 2-chloro-6-phenyldibenzo[*b*,*d*]-pyran-6-yl perchlorate. Attempts to prepare similar salts by reduction of our peroxides in acid media failed.

EXPERIMENTAL

Dibenzo[b,d]*pyran*.—Suspended in 2N-sulphuric acid (400 ml.) at 0°, *o*-aminophenyl benzyl ether hydrochloride (20 g.) was diazotised with a solution of sodium nitrite (6 g.) in water (25 ml.), added during ½ hr. The mixture was then kept for ½ hr., filtered to remove a trace of solid, and, after the addition of copper bronze (4 g.), was rapidly stirred for 4 hr. The product tended to form a sludge with the copper bronze, more of which was added at intervals to ensure complete reaction. Next day the filtered solution was extracted with ether, and the extract washed with water, dried, and evaporated, leaving a brown oil which was chromatographed from light petroleum (b. p. 40—60°) on aluminium oxide. On elution the resulting colourless oil (7·5 g.) was distilled, giving dibenzo[*b*,*d*]pyran, b. p. 138—141°/2·5 mm. (Found: C, 85·1; H, 5·8. Calc. for $C_{13}H_{10}O$: C, 85·7; H, 5·5%).

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[5] Waters, " The Chemistry of Free Radicals," 2nd edn., Oxford Univ. Press.

[6] Conant and Sloan, *J. Amer. Chem. Soc.*, 1925, **47**, 572 and later papers.

[7] Davison, *J.*, 1951, 2456.

[8] Bergman and Pinchas, *Rec. trav. chim.*, 1952, **71**, 161.

A solution of the dibenzopyran (1 g.) in glacial acetic acid (20 ml.) was warmed on a steam-bath for 1 hr. with chromic oxide (1 g.). The ethereal extract of the mixture was washed with dilute alkali and then water, dried, and evaporated, leaving benzo[*c*]coumarin (dibenzo-2-pyrone) [9] which crystallised from benzene–light petroleum (b. p. 60—80°) in prisms (0·4 g.), m. p. 95°. Oxidation of the dibenzopyran (1 g.) with potassium permanganate (1·5 g.) in boiling acetone (100 ml.) gave the same coumarin (0·6 g.), m. p. and mixed m. p. 95°.

2-*Chlorodibenzo*[b,d]*pyran*.—(*a*) 2-Amino-4-chlorophenyl benzyl ether hydrochloride (20 g.) was diazotised and converted into 2-*chlorodibenzo*[b,d]*pyran* by the foregoing procedure. This compound separated from methanol in prisms (8 g.), m. p. 47° (Found: C, 71·6; H, 4·2. $C_{13}H_9OCl$ requires C, 72·1; H, 4·2%). Oxidised by the methods given above, this compound gave 2-*chlorobenzo*[c]*coumarin*, separating from acetic acid in needles, m. p. 181° (Found: C, 67·5; H, 3·2; Cl, 15·4. $C_{13}H_7O_2Cl$ requires C, 67·7; H, 3·0; Cl, 15·4%). An authentic specimen of this coumarin was prepared by gently warming an intimate mixture of anthranilic acid diazonium sulphate (40 g.) and *p*-chlorophenol (40 g.) in a rotating flask. When the initial vigorous reaction had subsided somewhat, *p*-chlorophenol (40 g.) was added and heating was intensified until nitrogen was no longer evolved, whereupon removal of acidic materials by means of aqueous sodium hydroxide left the chlorocoumarin which, on purification from acetic acid, formed needles (10·5 g.), m. p. and mixed m. p. 181°.

(*b*) Suspended in dry ether (1500 ml.), 2-chlorobenzo[*c*]coumarin (6 g.) was added slowly to a well-stirred solution of lithium aluminium hydride (2 g.) in the minimum amount of ether. 1 Hr. later wet ether and then dilute sulphuric acid were added. The organic layer was freed from acid, dried, and evaporated, giving 5-*chloro*-2-*hydroxy*-2′-(*hydroxymethyl*)*diphenyl* which separated from benzene–light petroleum (b. p. 80—100°) in needles (5·7 g.), m. p. 104—106° (Found: C, 66·5; H, 4·9; Cl, 15·1. $C_{13}H_{11}O_2Cl$ requires C, 66·6; H, 4·7; Cl, 15·1%). The *di*-p-*nitrobenzoate* had m. p. 122—123° (Found: C, 60·9; H, 2·9; N, 5·1. $C_{27}H_{17}O_8N_2Cl$ requires C, 60·9; H, 3·2; N, 5·3%).

A solution of this diol (5 g.) in dry benzene (120 ml.) was saturated with anhydrous hydrogen bromide, washed free from acid, dried (Na_2SO_4), and evaporated, leaving the *bromide* (4·75 g.) which was purified from light petroleum (b. p. 40—60°), m. p. 85—87° (Found: C, 52·4; H, 3·3. $C_{13}H_{10}OBrCl$ requires C, 52·4; H, 3·4%), and formed a *phenylurethane*, m. p. 150° (Found: C, 57·8; H, 3·5. $C_{20}H_{15}O_2NBrCl$ requires C, 57·7; H, 3·6%). When this bromide (3·0 g.) in the minimum of methanol was treated with N-methanolic potassium hydroxide (3 ml.), the solution rapidly became warm and deposited potassium chloride. Isolated by means of ether and freed from phenols by aqueous potassium hydroxide, the product was washed with water, dried *in vacuo*, and crystallised from light petroleum (b. p. 40—60°), giving 2-*chlorodibenzo*-[b,d]*pyran* in prisms, m. p. and mixed m. p. 47° (Found: C, 72·2; H, 4·5; Cl, 16·3. $C_{13}H_9OCl$ requires C, 72·1; H, 4·2; Cl, 16·4%).

9-*Methyldibenzo*[b,d]*pyran*.—A mixture of *o*-nitrophenol (30 g.), *p*-xylyl chloride (27 g.), potassium iodide (10 g.), and anhydrous potassium carbonate (60 g.) was heated in acetone (200 ml.) for 12 hr. When the oily product was triturated with light petroleum (b. p. 60—80°) it solidified and the resulting o-*nitrophenyl* p-*xylyl ether* crystallised from chloroform–light petroleum (b. p. 60—80°), forming pale yellow needles (22 g.), m. p. 68° (Found: C, 68·8; H, 5·5; N, 5·5. $C_{14}H_{13}O_3N$ requires C, 69·1; H, 5·4; N, 5·8%). o-*Aminophenyl* p-*xylyl ether* resulted in 71% yield from reduction of the nitro-compound with sodium polysulphide and formed needles, m. p. 82°, when purified from light petroleum (b. p. 60—80°) (Found: C, 78·3; H, 6·8; N, 6·6. $C_{14}H_{15}ON$ requires C, 78·8; H, 7·1; N, 6·6%). With gaseous hydrogen chloride this amine in ether gave the hydrochloride (10 g.), the diazonium salt from which decomposed to a pale yellow oil that distilled at 98—101°/0·01 mm., giving 9-*methyldibenzo*[b,d]*pyran* (2·4 g.) (Found: C, 85·4; H, 6·4. $C_{14}H_{12}O$ requires C, 85·7; H, 6·2%). The oxidation of this with permanganate or chromic acid furnished 9-*methylbenzo*[b]*coumarin* which crystallised from alcohol in prisms (55% yield), m. p. 164° (Found: C, 79·5; H, 4·9. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%).

2-*Methyldibenzo*[b,d]*pyran*.—A mixture of *o*-nitrobenzyl *p*-tolyl ether [10] (22 g.) in alcohol (300 ml.), sodium sulphide (48 g.), and sulphur (8 g.) was heated under reflux for 6—7 hr. and after the usual purification an ethereal solution of the amine was saturated with hydrogen chloride and the precipitated salt crystallised from glacial acetic acid, furnishing o-*aminobenzyl*

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[9] Rule and Bretscher, *J.*, 1927, 925.

[10] Frische, *Annalen*, 1884, **224**, 142.

p-*tolyl ether hydrochloride* in plates (19 g.), m. p. 202° (Found: C, 67·0; H, 6·3. $C_{14}H_{16}ONCl$ requires C, 67·3; H, 6·4%). This hydrochloride (15 g.) was diazotised and treated with copper bronze, giving 2-*methyldibenzo*[b,d]*pyran* (5 g.), b. p. 122—124°/1 mm. (Found: C, 85·4; H, 6·2. $C_{14}H_{12}O$ requires C, 85·7; H, 6·2%). Oxidation of this with permanganate or chromic acid gave 2-*methylbenzo*[c]*coumarin* which formed needles, m. p. 133°, from methanol (Found: C, 80·0; H, 5·0. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%). The same coumarin resulted from the addition of small portions of anthranilic acid diazonium sulphate (18 g.) to *p*-cresol in a gently warmed and constantly rotating flask and, when isolated from the cooled mixture by means of ether and freed from phenols by means of aqueous sodium hydroxide, separated from methanol in needles (17·1 g.), m. p. and mixed m. p. 134°.

2-*Chloro*-6 : 6-*diphenyldibenzo*[b,d]*pyran*.—To phenylmagnesium bromide (from 4·5 g. of bromobenzene) was added 2-chlorobenzo[*c*]coumarin (1·0 g.) in benzene (50 ml.). After filtration and evaporation of the solvent the mixture gave 2-*chloro*-6 : 6-*diphenyldibenzo*[b,d]*pyran* which on purification from alcohol formed prisms (1·1 g.), m. p. 197°, insoluble in alkali (Found: C, 81·3; H, 4·8; Cl, 9·6. $C_{25}H_{17}OCl$ requires C, 81·4; H, 4·6; Cl, 9·6%).

Bis(*dibenzo*[b,d]*pyran*-6-*yl*) *Peroxide*.—Dibenzo[*b*,*d*]pyran (1 g.) in chloroform (50 ml.) was ozonised for ½ hr. Removal of the solvent left a brown oil which crystallised from acetic acid, affording the *peroxide* (0·08 g.), m. p. 186° (Found: C, 78·8; H, 4·8. $C_{26}H_{18}O_4$ requires C, 79·2; H, 4·6%). The same product was obtained when the dibenzopyran (1 g.) in glacial acetic acid was exposed to the air; the peroxide, m. p. 186°, separated during 6 days.

Di-(2-*chlorodibenzo*[b,d]*pyran*-6-*yl*) *Peroxide*.—2-Chlorodibenzo[*b*,*d*]pyran (1·5 g.) in glacial acetic acid (70 ml.) was kept in air for 8 days. The precipitate which slowly separated was crystallised from ethyl acetate, giving the *peroxide* (1·05 g.) in needles, m. p. 196° (decomp.) (Found: C, 67·2; H, 3·7; Cl, 15·3. $C_{26}H_{16}O_4Cl_2$ requires C, 67·4; H, 3·5; Cl, 15·3%). The residual acetic acid solution was diluted with water and the solid product isolated with ether, washed with aqueous sodium hydroxide, and crystallised from methanol, giving 2-chlorodibenzo[*c*]coumarin (0·15 g.), m. p. and mixed m. p. 181°. The addition of benzaldehyde (3 ml.) during the oxidation almost doubled its rate, but the addition of *tert*.-butyl hydroperoxide or cobalt naphthenate had but little effect.

Oxidation of the dibenzopyran with hydrogen peroxide in acetic acid gave an 18% yield of 2-chlorobenzo[*c*]coumarin, the remaining material being resinous. On being kept in nitrogen for 28 days 2-chlorodibenzo[*b*,*d*]pyran, dissolved in glacial acetic acid, was recovered unchanged but when it (0·5 g.) was heated with benzaldehyde in acetic acid (30 ml.) at 120° for 50 hr. an orange solution was formed which contained a neutral water-insoluble material and was purified by chromatography on aluminium oxide from benzene, giving 2-chlorobenzo[*c*]coumarin (0·3 g.), m. p. and mixed m. p. 181°. The same coumarin, m. p. and mixed m. p. 181°, resulted when: (*a*) the peroxide (0·5 g.) in diethylene glycol diethyl ether was added to lithium aluminium hydride (0·1 g.) in the same solvent (25 ml.) and kept at 120° for 6 hr.; careful dilution with water, followed by dissolution of the metallic hydroxides in dilute sulphuric acid, left a crystalline residue of the coumarin (0·18 g.); and (*b*) the peroxide (0·1 g.) and pyridine (25 ml.) were heated for 5 min. under reflux in an excess of acetic anhydride and the product was isolated in the conventional fashion and purified from benzene on a column of aluminium oxide.

Di-(2-*chlorodibenzo*[b,d]*pyran*-6-*yl*) *Ether*.—(*a*) A solution of the peroxide (0·5 g.) in boiling acetic acid (80 ml.) was gradually treated during 4 hr. with zinc dust (0·5 g.) and a large excess of acetic anhydride. An ethereal solution of the product was washed, dried, and evaporated and the residue triturated with benzene–light petroleum (b. p. 60—80°) and then purified from ethyl acetate, giving *di*-(2-*chlorodibenzo*[b,d]*pyran*-6-*yl*) *ether* in plates (0·05 g.), m. p. 231°. (*b*) The green solution of the peroxide (0·5 g.) in sulphuric acid (20 ml.) rapidly became brown and when poured on ice gave a precipitate which, in ether, was freed from acid. The product was dried by distillation of a solution in benzene and, after desiccation *in vacuo*, was chromatographed from benzene on a column of aluminium oxide. Thus obtained di-(2-chlorodibenzo-[*b*,*d*]pyran-6-yl) ether (0·2 g.), m. p. 232°, was identical with a specimen prepared as in (*a*) (Found: C, 70·0; H, 3·9; Cl, 16·1. $C_{26}H_{16}O_3Cl_2$ requires C, 69·8; H, 3·6; Cl, 15·9%).

Di-(2-*methyldibenzo*[b,d]*pyran*-6-*yl*) *Peroxide*.—(*a*) Ozonised in chloroform (20 ml.) for ½ hr., 2-methyldibenzo[*b*,*d*]pyran (1 g.) furnished the *peroxide* in prisms (0·05 g.), m. p. 185° (decomp.), from benzene. The m. p. of this was depressed on admixture with bis(dibenzo[*b*,*d*]pyran-6-yl) peroxide, m. p. 186°. (*b*) Exposed to air for 5 days 2-methyldibenzo[*b*,*d*]pyran (1·25 g.) in acetic acid (100 ml.) afforded the peroxide (0·87 g.), m. p. 185° (Found: C, 79·4; H, 5·2. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·3%), accompanied by 2-methylbenzo[*c*]coumarin (0·07 g.), m. p. 134—135°.

Di-(2-methyldibenzo[b,d]*pyran-6-yl) Ether.*—As in the previous example, the peroxide (0·5 g.) with sulphuric acid (20 ml.) afforded the *ether* (0·17 g.), m. p. 200°, after purification from ethyl acetate (Found: C, 83·1; H, 5·6. $C_{28}H_{22}O_3$ requires C, 82·7; H, 5·5%).

4-*Methoxy*-2-*methylbenzo*[b]*coumarin* was obtained by a modification of Cahn's method, with use of creosol, and separated from alcohol in needles (yield 23%), m. p. 207—208° (Found: C, 74·9; H, 5·3; OMe, 12·8. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0; OMe, 12·9%).

8-*Bromo*-2-*methylbenzo*[c]*coumarin* was formed by the interaction of 5-bromoanthranilic acid diazonium sulphate (31 g.) with *p*-cresol and formed needles (10·4 g.), m. p. 172°, from alcohol (Found: C, 58·2; H, 2·9; Br, 27·7. $C_{14}H_9O_2Br$ requires C, 58·1; H, 3·1; Br, 27·7%).

8 : 10-*Dibromo*-2-*methylbenzo*[c]*coumarin* was obtained by decomposition of 3 : 5-dibromoanthranilic acid diazonium sulphate (27·6 g.) in *p*-cresol (12 g.) and separated from alcohol in needles (5·5 g.), m. p. 184° (Found: Br, 42·1. $C_{14}H_8O_2Br_2$ requires Br, 43·4%. Because of its somewhat unusual elementary composition, this compound did not give satisfactory analytical values for C and H).

7 : 8 : 9 : 10-*Tetrahydro*-2 : 3-*dimethoxybenzo*[c]*coumarin*.—Condensation of 4-hydroxyveratrole (1 g.) and ethyl 2-oxo*cyclo*hexanecarboxylate (1·1 g.) was induced by gradual addition of concentrated sulphuric acid (2 ml.) in the cold (cf. Ghosh, Todd, and Wilkinson [4]). After 24 hr. the mixture was poured on ice, and the solid product crystallised from alcohol, giving the *product* (0·6 g.) in needles, m. p. 182° (Found: C, 68·8; H, 6·2; OMe, 23·8. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2; OMe, 23·8%).

2 : 3-*Dimethoxybenzo*[c]*coumarin*.—(*a*) The diazonium salt from 2-aminobenzyl 3 : 4-dimethoxyphenyl ether (4·7 g.) was decomposed, giving the oily 2 : 3-dimethoxydibenzo[*b,d*]pyran which was directly oxidised with potassium permanganate to the coumarin, m. p. 177°. (*b*) When 7 : 8 : 9 : 10-tetrahydro-2 : 3-dimethoxybenzo[*c*]coumarin (0·2 g.) was dehydrogenated with palladium–charcoal in nitrogen at 320°, the benzocoumarin sublimed on to a cold finger and then formed needles (0·1 g.), m. p. 177°, from methanol (Found: C, 70·0; H, 4·6; OMe, 24·2. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7; OMe, 24·2%).

2-*Methoxybenzo*[c]*coumarin* was prepared by Cahn's method and separated from methanol, m. p. 166—168° (Found: C, 74·2; H, 4·5; OMe, 13·7. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·5; OMe, 13·7%), in 13·5% yield.

3-*Methoxybenzo*[c]*coumarin*.—4-Nitroresorcinol 1-methyl ether (20 g.) was etherified with benzyl bromide (8 ml.) and potassium carbonate in boiling acetone, giving *benzyl* 5-*methoxy*-2-*nitrophenyl ether* as yellowish needles (21 g.), m. p. 73°, from light petroleum (b. p. 60—80°) (Found: C, 64·8; H, 5·1; N, 5·4. $C_{14}H_{13}O_4N$ requires C, 64·9; H, 5·1; N, 5·4%). Reduced with sodium polysulphide this ether gave 2-amino-5-methoxyphenyl benzyl ether isolated as the *hydrochloride* (3·3 g.), m. p. 220° (Found: C, 62·8; H, 5·8; N, 5·2. $C_{14}H_{16}O_2NCl$ requires C, 63·3; H, 6·0; N, 5·3%). On diazotisation, this hydrochloride (3 g.) afforded 3-methoxydibenzo[*b,d*]pyran as an oil which was directly oxidised by potassium permanganate to 3-methoxybenzo[*c*]coumarin (1·4 g.), m. p. and mixed m. p. 143° (cf. Hurtley [11]).

8-iso*Propylbenzo*[c]*coumarin* was prepared by the decomposition of anthranilic acid diazonium sulphate (18 g.) in *p*-*iso*propylphenol (40 g.) and formed needles (5·4 g.), m. p. 128—129°, from methanol (Found: C, 80·5; H, 6·1. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%).

2-*Chloro*-6-*phenyldibenzo*[b,d]*pyran*-6-*yl Perchlorate*.—To a stirred ethereal solution of phenylmagnesium bromide from bromobenzene (1·55 g.), 2-chlorobenzo[*c*]coumarin (1·0 g.) in dry ether was added slowly and ½ hr. later the mixture was poured on ice and dilute hydrochloric acid. The orange layer was washed free from acid and dried, the solvent was distilled, and the solution of the oily residue in anhydrous ether was saturated with hydrogen chloride, whereupon an orange precipitate was formed at 0° but redissolved at room temperature. Addition of 60% perchloric acid gave the *perchlorate* (1·1 g.) which on purification from glacial acetic acid had m. p. 250° (Found: Cl, 18·2. $C_{19}H_{12}O_5Cl_2$ requires C, 18·2%). This perchlorate exploded above its m. p.

3 : 4-*Dimethoxyphenyl* 2-*nitrobenzyl ether* was prepared from 4-hydroxyveratrole (10 g.) with 2-nitrobenzyl chloride in the usual manner and crystallised from benzene, forming pale yellow needles (9 g.), m. p. 109° (Found: C, 61·8; H, 5·1; N, 4·9; OMe, 21·9. $C_{15}H_{15}O_5N$ requires C, 62·3; H, 5·2; N, 4·8; OMe, 21·5%). Produced by reduction of this nitro-compound (11·6 g.)

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[11] Hurtley, *J.*, 1929, 1870.

with sodium polysulphide, 2-*aminobenzyl* 3 : 4-*dimethoxyphenyl ether* formed needles (2·5 g.), m. p. 71°, from benzene–light petroleum (60—80°) (Found: C, 69·7; H, 6·5; N, 5·2. $C_{15}H_{17}O_3N$ requires C, 69·5; H, 6·6; N, 5·4%).

3 : 4-*Dimethoxybenzyl* 2-*Nitrophenyl Ether*.—*o*-Nitrophenol (25 g.) and veratroyl chloride (30 g.) interacted, forming 3 : 4-*dimethoxybenzyl* o-*nitrophenyl ether* which separated from benzene –light petroleum (b. p. 60—80°) in pale yellow needles (32 g.), m. p. 85° (Found: C, 62·1; H, 5·5; N, 5·5. $C_{15}H_{15}O_5N$ requires C, 62·3; H, 5·2; N, 4·8%). This ether (20 g.) was reduced with sodium polysulphide, to yield 2-*aminophenyl* 3 : 4-*dimethoxybenzyl ether*, needles (14 g.), m. p. 81° (from benzene) (Found: C, 69·2; H, 6·6; N, 5·5. $C_{15}H_{17}O_3N$ requires C, 69·5; H, 6·6; N, 5·4%). The *acetyl derivative* had m. p. 103° (Found: N, 4·6. $C_{17}H_{19}O_4N$ requires N, 4·7%).

Benzyl 4 : 5-*Dimethoxy*-2-*nitrophenyl Ether*.—By the standard method, 4-hydroxy-5-nitroveratrole (13·5 g.) gave the *ether* (16 g.) which separated from ethyl acetate in needles, m. p. 143° (Found: C, 62·0; H, 5·1; N, 4·9. $C_{15}H_{15}O_5N$ requires C, 62·3; H, 5·2; N, 4·8%), and when reduced by sodium polysulphide supplied 2-*amino*-4 : 5-*dimethoxyphenyl benzyl ether* (45% yield), crystallising from chloroform–light petroleum (b. p. 60—80°) in needles, m. p. 78°, which became pink in air (Found: N, 5·1. $C_{15}H_{17}O_3N$ requires N, 5·4%).

4-*Methoxybenzyl* 2-*Nitrophenyl Ether*.—Interaction of *o*-nitrophenol (20 g.) and 4-methoxybenzyl chloride (20 g.) gave the *ether* (13 g.) which crystallised from light petroleum (b. p. 60—80°) in pale yellow plates, m. p. 96° (Found: C, 65·2; H, 5·2; N, 5·4; OMe, 10·2. $C_{14}H_{13}O_4N$ requires C, 64·9; H, 5·1; N, 5·4; OMe, 12·0%). Reduced by sodium polysulphide, this nitro-compound (10 g.) furnished 2-*aminophenyl* 4-*methoxybenzyl ether* (6·5 g.) which on purification from chloroform–light petroleum (b. p. 60—80°) had m. p. 103° (Found: C, 73·6; H, 6·6; N, 6·2; OMe, 13·0. $C_{14}H_{15}O_2N$ requires C, 73·3; H, 6·6; N, 6·1; OMe, 13·5%). The *acetyl derivative* had m. p. 126° (Found: C, 70·7; H, 6·0; N, 5·2; OMe, 9·3. $C_{16}H_{17}O_3N$ requires C, 70·8; H, 6·3; N, 5·2; OMe, 11·4%).

3′ : 4′ : 5′ : 6′-*Tetrahydro*-2-*hydroxy*-2′-*hydroxymethyl*-4-*methoxydiphenyl*.—7 : 8 : 9 : 10-Tetrahydro-3-methoxybenzo[*c*]coumarin (11·5 g.) in dry ether (300 ml.) was added to lithium aluminium hydride (4 g.) in stirred ether, and the resulting *diol* (8·5 g.) crystallised from light petroleum (b. p. 60—80°)–methanol, forming needles, m. p. 81°, soluble in aqueous sodium hydroxide and having a violet ferric reaction (Found: C, 72·4; H, 7·6. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%). The *di*-p-*nitrobenzoate* formed pale yellow plates, m. p. 126° (Found: C, 62·6; H, 4·0; N, 5·5. $C_{28}H_{24}O_9N_2$ requires C, 63·2; H, 4·5; N, 5·3%).

2-*Hydroxy*-2′-*hydroxymethyl*-5-*methyldiphenyl* was prepared by the reduction of 2-methylbenzo[*c*]coumarin (6 g.) with lithium aluminium hydride in the usual manner and formed rods (5·5 g.), m. p. 94—95°, from benzene (Found: C, 78·4; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%). The *di*-p-*nitrobenzoate* had m. p. 137—138° (Found: C, 65·6; H, 4·1; N, 5·5. $C_{28}H_{20}O_8N_2$ requires C, 65·6; H, 3·9; N, 5·5%).

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[*Received, July* 23*rd*, 1957.]