578. *The Chemistry of the "Insoluble Red" Woods. Part IV. Some Mixed Benzoins.*

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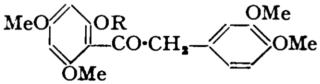
The benzoin structure tentatively suggested in Part III (*J.*, 1949, 1571) for the keto-phenolic oxidation product $C_{14}H_8O_3(OMe)_4$ obtained from *O*-trimethylsantal and from 2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxydeoxybenzoin with potassium permanganate has been confirmed. Similarly, the oxidation products of 2-hydroxy-4 : 6-dimethoxy- and 2-hydroxy-4 : 6 : 4′-trimethoxy-deoxybenzoin are the respective benzoins.

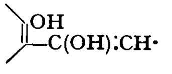
Methylation of 2-hydroxy-4-methoxy-, 4-ethoxy-2-hydroxy-, and 2-hydroxy-4 : 6-dimethoxy-deoxybenzoin with methyl iodide and potassium carbonate in boiling acetone has been shown to give respectively 2 : 4-dimethoxy-, 4-ethoxy-2-methoxy-, and 2 : 4 : 6-trimethoxy-α-methyldeoxybenzoin.

By the oxidation of *O*-trimethylsantal and its hydrolysis product 2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxydeoxybenzoin (I; R = H) with potassium permanganate a phenolic ketone

$C_{14}H_8O_3(OMe)_4$ was obtained which gave a methyl ether identical with the compound formed by the oxidation of 2 : 4 : 6 : 3′ : 4′-pentamethoxydeoxybenzoin (I; R = Me) with the same reagent (Part III, *loc. cit.*). In the course of attempts to define the nature of this unexpected oxidation product it was observed that the closely related 2-hydroxy-4 : 6-dimethoxy-, 2-hydroxy-4 : 6 : 4′-trimethoxy-, and 6 : 3′ : 4′-triethoxy-2-hydroxy-4-methoxy-deoxybenzoin underwent oxidation in a similar manner, and the possibility was envisaged that the products were in all cases the corresponding benzoins (Part III, *loc. cit.*). The production of mixed benzoins in this way does not appear to have been described previously and the present work was undertaken in order to clarify the constitution of the foregoing oxidation products. It also appeared desirable to test further the use of lead tetra-acetate as an agent for the conversion of deoxybenzoins into benzoins (Robertson *et al.*, *J.*, **1949**, 1567), more especially since the methods hitherto available for the preparation of mixed benzoins are somewhat limited in their scope (compare " Organic Reactions," edited by R. Adams, Vol. IV, New York, 1948, p. 269).

As observed with deoxybenzoin (*loc. cit.*), it has been found that on oxidation with lead tetra-acetate 2 : 4-dimethoxy-, 4-ethoxy-2-methoxy-, 2 : 4 : 4′-trimethoxy-, 2 : 4 : 6-trimethoxy-, 2 : 4 : 3′ : 4′-tetramethoxy-, 2 : 4 : 6 : 4′-tetramethoxy-, and 2 : 4 : 6 : 3′ : 4′-pentamethoxydeoxybenzoin, type (I), gave rise to the respective α-*O*-acetylbenzoins of type (IV; R = Me, R′ = Ac) which on hydrolysis furnished the corresponding benzoins of type (IV; R = Me, R′ = H). Thus the phenolic ketone $C_{14}H_8O_3(OMe)_4$ and its methyl ether (Part III, *loc. cit.*) are respectively 2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy- (IV; R and R′ = H) and 2 : 4 : 6 : 3 : 4′-pentamethoxy-benzoin (IV; R = Me, R′ = H). Further, since the methyl ethers of the oxidation products obtained from 2-hydroxy-4 : 6-dimethoxy- and 2-hydroxy-4 : 6 : 4′-trimethoxy-deoxybenzoin with potassium permanganate have been found to be identical with 2 : 4 : 6-trimethoxy- and 2 : 4 : 6 : 4′-tetramethoxy-benzoin, respectively, it is clear that the parent compounds are 2-hydroxy-4 : 6-dimethoxy- and 2-hydroxy-4 : 6 : 4′-trimethoxy-benzoin. By analogy, the oxidation product formed from 6 : 3′ : 4′-triethoxy-2-hydroxy-4-methoxydeoxybenzoin with potassium permanganate (Part III, *loc. cit.*) is the corresponding benzoin. In the conversion of deoxybenzoins of type (I; R = H) into benzoins of type (IV; R and R′ = H) with potassium permanganate the oxidation clearly takes place by the addition of hydroxyl groups to the double bond of the enolic form, type (II), resulting in the intermediate, type (III), which by loss of water yields type (IV; R and R′ = H).


(I.)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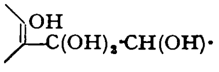
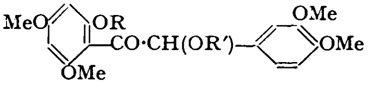

(III.)

When 2-hydroxy-4-methoxydeoxybenzoin was methylated by methyl iodide–potassium carbonate there was obtained in place of the expected 2 : 4-dimethoxydeoxybenzoin a product which we consider to be 2 : 4-dimethoxy-α-methyldeoxybenzoin. Although the analytical values for carbon given by this product and its oxime were consistently slightly lower than those expected for 2 : 4-dimethoxy-α-methyldeoxybenzoin, the oxidation of the compound with aqueous-acidic potassium permanganate to give acetophenone clearly shows the presence of the α-methyl group. In agreement with this structure the compound was resistant to oxidation with potassium permanganate by the method described in Part III (*loc. cit.*) as well as to the action of lead tetra-aceate under vigorous conditions. On account of the well-established tendency of resorcinol and phloroglucinol derivatives to undergo nuclear methylation, we examined the behaviour of the other 2-hydroxydeoxybenzoins employed in this work.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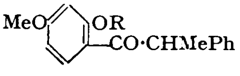
(V.)

By the methyl iodide–potassium carbonate method 2-hydroxy-4 : 4′-dimethoxy-, 2-hydroxy-4 : 3′ : 4′-trimethoxy-, 2-hydroxy-4 : 6 : 4′-trimethoxy-, 2 : 4 : 3′ : 4′-tetramethoxy-, and 4 : 6 : 4′-triethoxy-2-hydroxy-3′-methoxy-deoxybenzoin gave the expected 2-*O*-methyl ethers but, like 2-hydroxy-4-methoxydeoxybenzoin, 4-ethoxy-2-hydroxy- and 2-hydroxy-4 : 6-dimethoxy-deoxybenzoin gave the α-methyl derivatives, type (V), of the 2-*O*-methyl ethers. As in the case of 2 : 4-dimethoxy-α-methyldeoxybenzoin, 4-ethoxy-2-methoxy- and 2 : 4 : 6-trimethoxy-α-methyldeoxybenzoin gave slightly low analytical values for carbon. The structure of the normal methylation products, type (I; R = Me), was confirmed by their preparation according to the method of Friedel and Crafts.

EXPERIMENTAL.

2 : 4-*Dimethoxybenzoin.*—The following method for the preparation of 2 : 4-dihydroxydeoxybenzoin is superior to that of Chapman and Stephen (*J.*, 1923, **123**, 404) who employed the Hoesch reaction. To an agitated solution of resorcinol (24 g.) and phenylacetyl chloride (30 ml.) in nitrobenzene (100 ml.), powdered aluminium chloride (40 g.) was added in 4 portions with occasional cooling during 1½ hours, and 24 hours later the mixture was treated with ice (300 g.) and concentrated hydrochloric acid (40 ml.). After the removal of the nitrobenzene with steam the viscous product was crystallised from aqueous alcohol, giving 2 : 4-dihydroxydeoxybenzoin in colourless plates (31·5 g.), m. p. 115°, which gave a wine-red ferric reaction in alcohol. Methylation of the ketone (5 g.) with methyl iodide (1·5 ml.) and potassium carbonate (6 g.) in boiling acetone (60 ml.) during 3 hours furnished 2-hydroxy-4-methoxydeoxybenzoin, which formed long colourless prisms (4·5 g.), m. p. 88°, from light petroleum (b. p. 80—100°) and had a red-brown ferric reaction (cf. Tambor, *Ber.*, 1910, **43**, 1884, who gives m. p. 90°). Methylation of the 2-hydroxy-4-methoxydeoxybenzoin (0·5 g.) with methyl sulphate (2 ml.) and an excess of potassium carbonate in boiling acetone (50 ml.) during 3 hours gave 2 : 4-dimethoxydeoxybenzoin, m. p. 48°, which had a negative ferric reaction (Tiffeneau *et al.* give m. p. 48°, but Tambor, *loc. cit.*, and Baker and Robinson, *J.*, 1932, 1798, give m. p. 56°). The same compound, m. p. 48°, was prepared from *O*-dimethylresorcinol and phenylacetyl chloride by the method employed for 2 : 4-dihydroxydeoxybenzoin. The oxime, m. p. 121°, was obtained by the pyridine method (Baker and Robinson, *loc. cit.*).

A solution of 2 : 4-dimethoxydeoxybenzoin (0·7 g.) and lead tetra-acetate (1·3 g.) in acetic acid (14 ml.), which had been kept at 100° until a test portion gave a negative reaction for lead tetra-acetate (about 2½ hours), was cooled, diluted with water (70 ml.), and extracted with ether. The combined ethereal extracts were washed with 2N-aqueous sodium hydrogen carbonate, dried, and evaporated, leaving an oily residue which did not solidify. When a solution of this product in alcohol (14 ml.) was mixed with 2N-aqueous sodium hydroxide (7 ml.) and kept for 24 hours 2 : 4-*dimethoxybenzoin* separated and, on crystallisation from alcohol, formed flat yellow prisms (0·17 g.), m. p. 104°, having a negative ferric reaction in alcohol (Found : C, 70·6; H, 6·0. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

2 : 4-*Dimethoxy-α-methyldeoxybenzoin* (V; R = Me).—Methylation of 2-hydroxy-4-methoxydeoxybenzoin (0·5 g.) with an excess of methyl iodide (5 ml.) and potassium carbonate (5 g.) in boiling acetone (50 ml.) during 30 hours gave 2 : 4-*dimethoxy-α-methyldeoxybenzoin* which formed colourless, rhombic tablets (0·36 g.), m. p. 69·5°, from alcohol, insoluble in 2N-aqueous sodium hydroxide and having a negative ferric reaction [Found : C, 75·0; H, 6·5; OMe, 21·0. $C_{15}H_{12}O(OMe)_2$ requires C, 75·5; H, 6·7; OMe, 23·0%]. Prepared by the pyridine method, the *oxime* separated from ethyl alcohol in thin, colourless prisms, m. p. 125° (Found : C, 70·9; H, 6·5; N, 4·9. $C_{17}H_{19}O_3N$ requires C, 71·6; H, 6·7; N, 4·9%).

10% Aqueous potassium permanganate was gradually added to a solution of 2 : 4-dimethoxy-α-methyldeoxybenzoin (1 g.) in a mixture of acetic acid (20 ml.) and concentrated sulphuric acid (1 ml.) until the pink colour of unchanged permanganate persisted. The mixture was diluted with water, clarified with sulphur dioxide, filtered to remove a trace of unchanged deoxybenzoin, and treated with an excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate. 2 Hours later the precipitate was collected, dried, and crystallised from ethyl acetate, giving acetophenone 2 : 4-dinitrophenylhydrazone, m. p. 244°, identical with an authentic specimen.

4-*Ethoxy-2-methoxybenzoin.*—Ethylation of 2 : 4-dihydroxydeoxybenzoin (21·5 g.) with ethyl iodide (7 ml.) and potassium carbonate (25 g.) in boiling acetone (200 ml.) during 3 hours gave 4-*ethoxy-2-hydroxydeoxybenzoin*, which separated from light petroleum or alcohol in colourless, long, slender, rectangular prisms (16·4 g.), m. p. 86°, having a red-brown ferric reaction in alcohol (Found : C, 75·1; H, 6·3. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%). Methylation of this compound (5 g.) with methyl sulphate (10 ml.) and potassium carbonate (20 g.) in boiling acetone (150 ml.) during 3 hours furnished 4-*ethoxy-2-methoxydeoxybenzoin*, which was purified by distillation and then by crystallisation from alcohol, forming feather-like clusters of colourless needles (4·9 g.), b.p. 180°/0·4 mm., m. p. 53·5°, and having a negative ferric reaction (Found : C, 75·7; H, 6·9. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%). The *oxime* of the mixed ether separated in colourless slender prisms, m. p. 126°, from alcohol (Found : N, 5·2. $C_{17}H_{19}O_3N$ requires N, 4·9%).

Oxidation of 4-ethoxy-2-methoxydeoxybenzoin (1 g.) with lead tetra-acetate (1·8 g.) in acetic acid (20 ml.) at 100° during 3 hours followed by deacetylation of the product gave 4-ethoxy-2-methoxybenzoin, forming, from alcohol, tiny colourless prisms (0·23 g.), m.p. 91·5°, which retained indefinite amounts of solvent of crystallisation. The solvent-free compound, m. p. 91·5° (unchanged), was obtained by distillation in a vacuum at 140°/0·003 mm. (Found : C, 71·5; H, 6·3. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%). A specimen of this compound was prepared by the following alternative route and found to have the same properties. Oxidation of 4-ethoxy-2-hydroxydeoxybenzoin with potassium permanganate by the method described in Part III (*loc. cit.*) gave 4-*ethoxy-2-hydroxybenzoin*, which separated from alcohol in colourless rhombic prisms, m. p. 82° (Found, in specimen distilled in a high vacuum : C, 70·8; H, 5·9. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%). Methylation of this compound by the methyl sulphate–potassium carbonate method gave 4-ethoxy-2-methoxybenzoin, m. p. and mixed m. p. 91·5°, after purification.

4-*Ethoxy-2-methoxy-α-methyldeoxybenzoin.*—Methylation of 4-ethoxy-2-hydroxydeoxybenzoin with an excess of methyl iodide and potassium carbonate in boiling acetone during 21 hours furnished a product which separated from alcohol in colourless rhombic tablets, m. p. 53°, having a negative ferric reaction and considered to be 4-*ethoxy-2-methoxy-α-methyldeoxybenzoin* [Found : C, 75·4; H, 7·3; OAlkyl, 24·6. $C_{15}H_{12}O(OMe)(OEt)$ requires C, 76·0; H, 7·1; OAlkyl, 26·6%]. Prepared by the pyridine method, the *oxime* separated from ethanol in colourless, flat prisms, m. p. 121° (Found : C, 71·3 ; H, 7·3 ; N, 5·1. $C_{18}H_{21}O_3N$ requires C, 72·0 ; H, 7·0 ; N, 4·7%). Oxidation of the compound (0·5 g.), dissolved in acetic acid (10 ml.) containing concentrated sulphuric acid (0·5 ml.), with 10% aqueous potassium permanganate gave rise to acetophenone, isolated as the 2 : 4-dinitrophenylhydrazone (0·14 g.), m. p. 244°.

2 : 4 : 4′-*Trimethoxybenzoin.*—The interaction of resorcinol (16 g.), *p*-methoxyphenylacetyl chloride (20 g.), and aluminium chloride (27 g.) in nitrobenzene (100 ml.) at room temperature for 24 hours and treatment of the reaction mixture with ice and concentrated hydrochloric acid followed by the removal of the nitrobenzene with steam gave 2 : 4-dihydroxy-4′-methoxydeoxybenzoin, which formed colourless prisms (18·8 g.), m. p. 158°, from alcohol or light petroleum (Found : C, 69·8 ; H, 5·5. Calc. for $C_{15}H_{14}O_4$: C, 69·7 ; H, 5·5%) (compare Baker and Eastwood, *J.*, 1929, 2902). Methylation of this ketone (10 g.) with methyl iodide (3 ml.) and potassium carbonate (15 g.) in boiling acetone (150 ml.) during 3 hours gave 2-hydroxy-4 : 4′-dimethoxydeoxybenzoin (8·7 g.), m. p. 104°, after purification from alcohol (Found : C, 70·4 ; H, 6·0. Calc. for $C_{16}H_{16}O_4$: C, 70·6 ; H, 5·9%), the properties of which were identical with the ether prepared with diazomethane by Wessely and Lechner (*Monatsh.*, 1931, **57**, 395). By the methyl sulphate–potassium carbonate method 2-hydroxy-4 : 4′-dimethoxydeoxybenzoin was converted into 2 : 4 : 4′-trimethoxydeoxybenzoin, m. p. 84° (Baker and Robinson, *J.*, 1932, 1798), characterised by conversion into the *oxime*, colourless prisms, m. p. 104°, from alcohol (Found : N, 4·8. $C_{17}H_{19}O_4N$ requires N, 4·7%). The same trimethyl ether was formed by methylation with excess of methyl iodide and potassium carbonate in boiling acetone for 21 hours, or by condensation of *O*-dimethylresorcinol (3 g.) and *p*-methoxyphenylacetyl chloride (4 g.) with aluminium chloride (3 g.) in nitrobenzene (50 ml.).

Oxidation of 2 : 4 : 4′-trimethoxydeoxybenzoin (1 g.) with lead tetra-acetate (1·6 g.) in acetic acid (20 ml.) at 100° during 3½ hours and subsequent hydrolysis of the product furnished 2 : 4 : 4′-*trimethoxybenzoin* (0·4 g.), which separated from alcohol in slender, colourless needles (0·4 g.), m. p. 94° (Found : C, 67·4 ; H, 6·1. $C_{17}H_{18}O_5$ requires C, 67·5 ; H, 6·0%).

2 : 4 : 3′ : 4′-*Tetramethoxybenzoin.*—Prepared by the interaction of resorcinol (8·5 g.), 3 : 4-dimethoxyphenylacetyl chloride (10·9 g.), and aluminium chloride (15 g.) in nitrobenzene (60 ml.) in the usual manner, 2 : 4-*dihydroxy*-3′ : 4′-*dimethoxydeoxybenzoin* formed colourless irregular prisms (12·5 g.), m. p. 177·5° from aqueous alcohol, having a wine-red ferric reaction (Found : C, 66·6 ; H, 5·7. $C_{16}H_{16}O_5$ requires C, 66·7 ; H, 5·6%). Treatment of this compound (11 g.) with methyl iodide (4 ml.) and potassium carbonate (15 g.) in boiling acetone (150 ml.) for 3 hours gave rise to 2-*hydroxy*-4 : 3′ : 4′-*trimethoxydeoxybenzoin*, forming slender needles (9·4 g.), m. p. 119°, from light petroleum or alcohol and having a red-brown ferric reaction (Found : C, 67·4 ; H, 6·3. $C_{17}H_{18}O_5$ requires C, 67·5 ; H, 6·0%). Methylation of 2-hydroxy-4 : 3′ : 4′-trimethoxydeoxybenzoin by the methyl sulphate– or the methyl iodide–potassium carbonate method yielded 2 : 4 : 3′ : 4′-*tetramethoxydeoxybenzoin*, which crystallised from alcohol in small colourless needles, m. p. 101°, having a negative ferric reaction (Found : C, 68·3 ; H, 6·3. $C_{18}H_{20}O_5$ requires C, 68·3 ; H, 6·4%). The same compound, m. p. and mixed m. p. 101°, was obtained by condensation of 3 : 4-dimethoxyphenylacetyl chloride and *O*-dimethylresorcinol with aluminium chloride. The *oxime* separated from ethanol in colourless squat prisms, m. p. 135° (Found : N, 4·5. $C_{18}H_{21}O_5N$ requires N, 4·2%).

Oxidation of 2 : 4 : 3′ : 4′-tetramethoxydeoxybenzoin (1 g.) with lead tetra-acetate (1·4 g.) in acetic acid (20 ml.) at 100° during 1 hour and subsequent deacetylation of the product gave 2 : 4 : 3′ : 4′-*tetramethoxybenzoin* (0·4 g.), which separated from alcohol in slender, pale yellow prisms (0·4 g.), m. p. 94°, having a negative ferric reaction (Found : C, 65·0 ; H, 5·8. $C_{18}H_{20}O_6$ requires C, 65·1 ; H, 6·1%).

2 : 4 : 6-*Trimethoxybenzoin.*—Trihydroxydeoxybenzoin was prepared by the following modification of the method described by Chapman and Stephen (*loc. cit.*). The brown oil, which separated during 24 hours from a mixture of phloroglucinol (20 g.), benzyl cyanide (20 g.), zinc chloride (8 g.), and ether (200 ml.), saturated with hydrogen chloride, was washed with ether and heated with water (200 ml.) at 100° for 2 hours. On cooling the hydrolysate deposited 2 : 4 : 6-trihydroxydeoxybenzoin hydrate (17·3 g.), m. p. 162°, after loss of water at 90°. Methylation of this ketone (8·6 g.) with methyl sulphate (6·4 g.) and potassium carbonate (20 g.) in boiling acetone (75 ml.) during 1 hour gave 2-hydroxy-4 : 6-dimethoxydeoxybenzoin (6·6 g.), m. p. 117°, after purification (Part III, *loc. cit.*). Treatment of this dimethyl ether with an excess of the same methylating agents for 3 hours gave 2 : 4 : 6-*trimethoxydeoxybenzoin*, which formed slender, colourless prisms, m. p. 72° (from alcohol), having a negative ferric reaction (Found : C, 71·3 ; H, 6·3. $C_{17}H_{18}O_4$ requires C, 71·3 ; H, 6·3%).

Oxidation of 2 : 4 : 6-trimethoxydeoxybenzoin (2 g.) by the lead tetra-acetate method at 70° gave rise to a very small yield of 2 : 4 : 6-*trimethoxybenzoin*, forming colourless prisms, m. p. 135·5°, from alcohol (Found : C, 66·1 ; H, 6·0. $C_{17}H_{18}O_5$ requires C, 66·3 ; H, 6·0%). The same benzoin, m. p. and mixed m. p. 135·5°, was formed on methylation of 2-hydroxy-4 : 6-dimethoxybenzoin (Part III, *loc. cit.*) by the methyl sulphate–potassium carbonate method.

2 : 4 : 6-*Trimethoxy-α-methyldeoxybenzoin.*—When 2-hydroxy-4 : 6-dimethoxydeoxybenzoin (1 g.) was methylated with methyl iodide (5 ml.) and potassium carbonate (5 g.) in boiling acetone (50 ml.) the product was 2 : 4 : 6-*trimethoxy-α-methyldeoxybenzoin*, which separated from alcohol in colourless plates (0·5 g.), m. p. 101°, insoluble in 2N-aqueous sodium hydroxide and having a negative ferric reaction (Found : C, 71·4 ; H, 6·2. $C_{18}H_{20}O_4$ requires C, 72·0 ; H, 6·7%). Oxidation of this compound (0·5 g.), dissolved in acetic acid (10 ml.), with a slight excess of 10% aqueous potassium permanganate gave acetophenone, isolated as the 2 : 4-dinitrophenylhydrazone, m. p. 244°.

2 : 4 : 6 : 4′-*Tetramethoxybenzoin.*—Prepared by the interaction of phloroglucinol (20 g.), *p*-methoxybenzyl cyanide (20 g.), and zinc chloride (8 g.) in ether (200 ml.), saturated with hydrogen chloride, during 24 hours and hydrolysis of the resulting oily ketimine hydrochloride with water (200 ml.) on the steam-bath, 2 : 4 : 6-*trihydroxy-4′-methoxydeoxybenzoin* crystallised from aqueous alcohol or ethyl acetate–light petroleum as a *hydrate* in slender, colourless prisms (25 g.), m. p. 195°, having a red-brown

ferric reaction (Found : C, 61·6 ; H, 5·5. $C_{15}H_{14}O_5,H_2O$ requires C, 61·6 ; H, 5·5%. Found, in a specimen dried in a high vacuum at 100° : C, 65·7 ; H, 5·4. $C_{15}H_{14}O_5$ requires C, 65·7 ; H, 5·1%). Heated under reflux with methyl sulphate (18 ml.) and potassium carbonate (60 g.) in acetone (50 ml.) for 3 hours, this compound (24 g.) gave 2-hydroxy-4 : 6 : 4′-trimethoxydeoxybenzoin (17 g.), m. p. 89°, identical with an authentic specimen (Part III, *loc. cit.*). With an excess of the same methylating agents or by the methyl iodide–potassium carbonate method this ether was converted into 2 : 4 : 6 : *4′-tetramethoxydeoxybenzoin*, a pale yellow oil, b. p. 204°/0·8 mm., having a negative ferric reaction (Found : C, 68·5 ; H, 6·3. $C_{18}H_{20}O_5$ requires C, 68·3 ; H, 6·4%). The 2 : 4-*dinitrophenylhydrazone* separated from alcohol in tiny, slender, orange prisms, m. p. 178° (Found : C, 58·1 ; H, 4·5 ; N, 11·8. $C_{24}H_{24}O_8N_4$ requires C, 58·1 ; H, 4·9 ; N, 11·3%). The *oxime* crystallised from ethanol in colourless, squat prisms, m. p. 120° (Found : N, 4·7. $C_{18}H_{21}O_5N$ requires N, 4·2%). The same deoxybenzoin was prepared by condensation of *O*-trimethylphloroglucinol (3 g.) and *p*-methoxyphenylacetyl chloride (3·5 g.) with aluminium chloride (3 g.) in nitrobenzene (10 ml.) at 0° during 24 hours and gave the 2 : 4-dinitrophenylhydrazone, m. p. 178°.

Oxidation of 2 : 4 : 6 : 4′-tetramethoxydeoxybenzoin with lead tetra-acetate gave a poor yield of a product from which 2 : 4 : 6 : *4′-tetramethoxybenzoin* was obtained by hydrolysis. This compound formed small, squat, irregular, yellow prisms, m. p. 137°, from alcohol (Found : C, 64·9 ; H, 5·7. $C_{18}H_{20}O_6$ requires C, 65·1 ; H, 6·1%) and was identical with a specimen prepared by methylation of 2-hydroxy-4 : 6 : 4′-trimethoxybenzoin (Part III, *loc. cit.*) with methyl sulphate and potassium carbonate in boiling acetone.

2 : 4 : 6 : 3′ : *4′-Pentamethoxybenzoin* (IV; R = Me, R′ = H).—Prepared by the Hoesch reaction from phloroglucinol (18 g.) and 3 : 4-dimethoxybenzyl cyanide (18·5 g.), 2 : 4 : 6-*trihydroxy*-3′ : 4′-*dimethoxydeoxybenzoin* separated from dilute alcohol as a *hydrate* (21·5 g.) in small colourless needles, m. p. 181° (Found : C, 59·6; H. 5·6. $C_{16}H_{16}O_6,H_2O$ requires C, 59·6; H, 5·6%. Found, in dried specimen : C, 62·8 ; H, 5·4. $C_{16}H_{16}O_6$ requires C, 63·2 ; H, 5·3%). Methylation of this ketone (20 g.) with methyl sulphate (17 ml.) and potassium carbonate (20 g.) in boiling acetone (20 ml.) during 3 hours gave 2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxydeoxybenzoin, m. p. 117° (Part III, *loc. cit.*). A solution of this compound (6 g.) in acetone (120 ml.) containing methyl iodide (12 ml.) and potassium carbonate (12 g.) was boiled for 12 hours. On isolation and purification the resulting 2 : 4 : 6 : 3′ : 4′-pentamethoxydeoxybenzoin had m. p. 110°, and was identical with an authentic specimen (Part III, *loc. cit.*). The same compound (3·5 g.), m. p. and mixed m. p. 110°, was obtained by condensation of *O*-trimethylphloroglucinol (3 g.) and 3 : 4-dimethoxyphenylacetyl chloride (3·8 g.) with aluminium chloride (3 g.) in nitrobenzene (10 ml.) at 0° during 24 hours.

Oxidation of the foregoing pentamethyl ether (1 g.) with lead tetra-acetate (1·3 g.) in acetic acid (20 ml.) at 100° for 45 minutes and deacetylation of the product gave rise to 2 : 4 : 6 : 3′ : 4′-pentamethoxybenzoin (0·5 g.), m. p. 174°, after purification, identical with the methyl ether of the oxidation product from *O*-trimethylsantal (Part III, *loc. cit.*).

4 : 6 : *4′-Triethoxy*-2 : *3′-dimethoxydeoxybenzoin*.—On methylation by the methyl iodide–potassium carbonate method, 2-hydroxy-3-methoxy-4 : 6 : 4′-triethoxydeoxybenzoin (Part III, *loc. cit.*) gave 4 : 6 : *4′-triethoxy*-2 : *3′-dimethoxydeoxybenzoin*, which separated from alcohol in slender, colourless needles, m. p. 117°, having a negative ferric reaction in alcohol (Found: C, 68·1 ; H, 7·2. $C_{22}H_{28}O_6$ requires C, 68·0 ; H, 7·3%).

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[*Received, June 2nd,* 1950.]