130. *Condensation Products of Phenols and Ketones. Part VI. The Conversion of an* o-*Quinone into a Derivative of Pyrogallol.*

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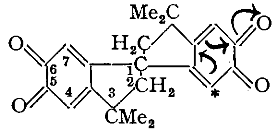
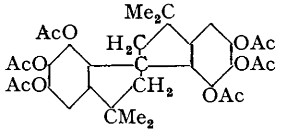
The *o*-quinone (I) is converted by acetic anhydride–sulphuric acid into a mixture of hexa-acetoxy-compounds, from which two pyrogallol derivatives, (II) and an *isomer*, have been isolated. This novel result is discussed.

Catechol and acetone condense in presence of acetic and hydrochloric acids to give a tetrahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene (Baker, J., 1934, 1678; Baker and McGowan, J., 1938, 347), and very strong evidence was brought forward to show that the hydroxyl groups occupied positions 5, 6, 5′, and 6′. Oxidation of this compound with fuming nitric acid in alcohol gives the corresponding red di-*o*-quinone (I) (Baker, *loc. cit.*), and it has now been found that treatment of this quinone with acetic anhydride and a trace of concentrated sulphuric acid gives a mixture of hexa-acetoxy-compounds, one of which is identical with the hexa-acetate (II) of the substance which is obtained by the condensation of pyrogallol with acetone in presence of acetic and hydrochloric acids. The latter substance has already been shown to be a hexahydroxy-3 : 3 : 3′ : 3′-tetramethylbis-1 : 1′-*spiro*hydrindene (Baker and Besly, J., 1939, 196), and the evidence available suggested that the hydroxyl groups were symmetrically arranged and occupied positions 5, 6, 7, 5′, 6′, and 7′.

(I.)



(II.)



That the Thiele acetylation of (I) gives a derivative of pyrogallol rather than of hydroxyquinol is strong evidence that all the reactive cationoid positions para to the oxygen atoms are already substituted, thus confirming the positions previously assigned to the four hydroxyl groups in the catechol–acetone condensation product. It is remarkable, however, that an *o*-quinone should be capable of giving a pyrogallol derivative in this reaction, and it must be assumed that the carbon atoms adjacent to the carbonyl groups may become cationoid owing to the transmission of the electromeric effect through two double bonds of the quinone structure, as shown for one of the reactive positions in (I). Reactions of the Thiele acetylation type have been little investigated with *o*-quinones; β-naphthaquinone yields 1 : 2 : 4-triacetoxynaphthalene (Thiele and Winter, *Annalen*, 1900, **311**, 341).

All four positions 4, 7, 4′, and 7′ in the quinone (I) will probably be almost equally reactive, and as one acetoxyl group is introduced into each aromatic nucleus, three isomeric hexa-acetoxy-compounds should be formed, (II), the 4 : 5 : 6 : 5′ : 6′ : 7′- and the 4 : 5 : 6 : 4′ : 5′ : 6′-isomers, but no evidence is available to show which of the last two structures is to be assigned to the lower-melting, second *isomer* which has been isolated. Owing to molecular asymmetry all the bis-1 : 1′-*spiro*hydrindenes mentioned are racemic forms.

Experimental.

Thiele Acetylation of the Quinone (I).—(a) *Isolation of* 5 : 6 : 7 : 5′ : 6′ : 7′-*hexa-acetoxy*-3 : 3 : 3′ : 3′-*tetramethylbis*-1 : 1′-spiro*hydrindene* (II). The quinone (I) (2 g.) (Baker, *loc. cit.*) was dissolved in boiling acetic anhydride (20 c.c.), cooled rapidly with stirring, and to the fine suspension of crystals was added a solution of concentrated sulphuric acid (4 drops) in acetic anhydride (2 c.c.). After 3 hours a brownish-red solution was obtained, and, after 20 hours water (100 c.c.) was added, the mixture shaken, and the pale amber-coloured precipitate (3·6 g.) collected after the hydrolysis of the acetic anhydride. This amorphous product was dissolved in a little ethyl alcohol and the colourless crystalline deposit which separated overnight was collected, washed with alcohol, and recrystallised from alcohol containing a little acetic acid, and then twice from alcohol, being obtained in almost rectangular plates (0·21 g.), m. p. 245—246° [Found : C, 63·3; H, 5·7; Ac, 41·7. Calc. for $C_{21}H_{18}(OAc)_6$: C, 63·5; H, 5·8; Ac, 41·3%]. The m. p. was unaltered when the substance was mixed with the hexa-acetate of the pyrogallol–acetone condensation product, m. p. 247°, prepared as described by Baker and Besly (*loc. cit.*).

(b) *Isolation of* 4 : 5 : 6 : 4′ : 5′ : 6′ (or 5′ : 6′ : 7′)-*hexa-acetoxy*-3 : 3 : 3′ : 3′-*tetramethylbis*-1 : 1′-spiro*hydrindene*. To the first ethyl-alcoholic mother-liquor from the above crystallisation was added an equal volume of methyl alcohol; after 2 days the colourless crystalline deposit (0·75 g.) was collected, and recrystallised from a mixture of methyl and ethyl alcohols, and then three times from ethyl alcohol, being obtained in bunches of radiating needles (0·22 g.), m. p. 200° after softening from *ca.* 195° [Found : C, 63·4; H, 5·8; Ac, 42·4. $C_{21}H_{18}(OAc)_6$ requires C, 63·5; H, 5·8; Ac, 41·3%]. A mixed m. p. with the isomeric hexa-acetate gave an opaque melt at *ca.* 193°, clearing at about 215°.

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