

Fig. 2. Ring system numbering of rosin acids. Stereochemical configuration at carbon atoms 1, 11, and 12 indicated.

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## Reactions between Quinones and Carbonyl Compounds Catalysed by Aluminium Oxide

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In the course of studies on the oxidation of 2,6-dimethoxyphenol with sodium periodate<sup>1</sup>, an attempt was made to separate, by chromatography on a column of aluminium oxide, a benzene solution of the previously unknown 3,8-dimethoxy-1,2-naphthoquinone (I) and 2,6-dimethoxy-*p*-benzoquinone (III). By irrigation with benzene, compound III was eluted while a red compound, assumed to be the naphthoquinone I, remained strongly adsorbed on the upper part of the column. This

latter material was eluted with acetone and from the eluate two crystalline products were obtained. One of those was the expected naphthoquinone I; the other was a yellow substance. This indicated that an unexpected transformation of I had taken place either during the adsorption or during the elution step. To clarify this question, the following investigations were carried out.

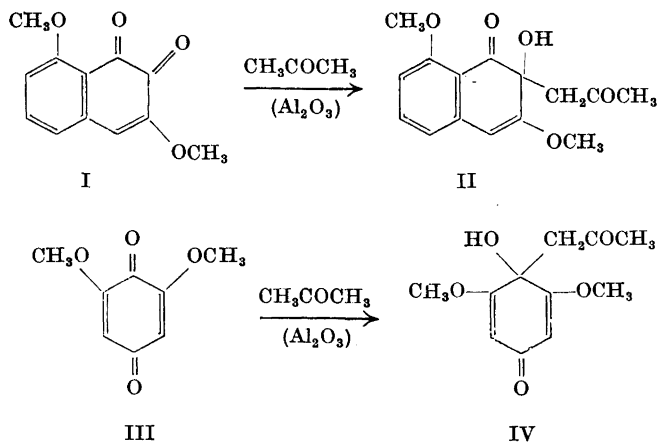
When an acetone solution of the pure naphthoquinone I (m. p. 196°) was boiled for a few minutes in the presence of aluminium oxide the red solution became yellow, and from it yellow crystals (m. p. 142°) were obtained in a yield of 90%. (In the absence of aluminium oxide a reaction did not occur and acetone was then a very suitable recrystallization solvent for I.) Analysis of the substance indicated that it might be an addition product formed from equimolar amounts of acetone and compound I. Ultra-violet and infra-red absorption data, and the fact that on reduction the substance was converted into a compound having the properties of an  $\alpha$ -naphthol with a free *p*-position, all suggested that the addition product might be the *o*-naphthoquinol of structure II.

2,6-Dimethoxy-*p*-benzoquinone (III) when heated in acetone solution in the presence of aluminium oxide also yielded an apparently similar type of addition product having m. p. 154°. Spectrographic examination of this compound, and its reduction to a phenol, to which the structure of 3,5-dimethoxy-4-acetylphenol could be ascribed, indicated that the acetone addition compound of III was a *p*-quinol of structure IV.

Since the formation of the quinols II and IV involves a reaction of the aldol condensation type, it appeared possible that it might have been catalysed by traces of alkali present in the commercial aluminium oxide. This is improbable, however, as the catalytic effect of the aluminium oxide preparation was retained even after its thorough treatment with dilute hydrochloric acid (followed by washing with water). Thus, neutral aluminium oxide would appear to act as a catalyst of the reactions described.

Other ketones, for example methyl ethyl ketone, were also found to add to the quinones I and II in the presence of aluminium oxide.

Addition of acetone and of other ketones to tetrachloro-*o*-quinone has been reported by Schenck *et al.*<sup>2</sup> to be catalysed by dry



hydrogen chloride and probably resulted in the formation of the corresponding *o*-quinols. No other observations on the addition of ketones to quinones appear to have been published.

The quinols II and IV are stable in ethanol and in other neutral solvents. However, if an ethanolic solution of IV is heated in the presence of aluminium oxide, the quinone III is regenerated. It is possible, therefore, to reverse the reaction under those modified conditions.

This work is being continued and a detailed report will be published later.

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