

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

### Part II\*. The Addition of Acetone to *o*-Benzoquinones

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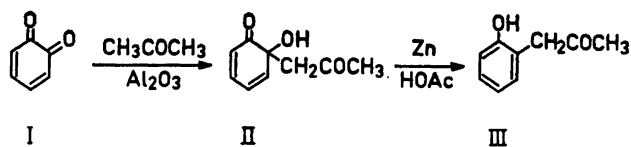
*o*-Benzoquinones react with acetone at room temperature in the presence of aluminium oxide to form 2-acetyl-*o*-benzoquinols by the addition of one mole of acetone at one of the carbonyls by an aldol type condensation. An investigation was made of this reaction with unsubstituted *o*-benzoquinone and various alkyl and alkoxy substituted *o*-benzoquinones. In most cases the *o*-benzoquinol could be isolated in a pure form but in two cases the crude *o*-quinol dimerised too rapidly for it to be purified.

In a preceding communication<sup>1</sup> it was briefly reported that 3,8-dimethoxy-1,2-naphthoquinone and 2,6-dimethoxy-1,4-benzoquinone reacted with acetone in the presence of aluminium oxide; one mole of acetone was added with the formation of an acetyl-quinol. It has now been shown that similar aldol condensations occur with *o*-benzoquinones and the present paper is a report of an investigation of the addition of acetone to a number of *o*-benzoquinones in the presence of aluminium oxide.

The addition of ketones to tetrachloro-*o*-quinone has been investigated by Schenk *et al.*<sup>2</sup> Dry hydrogen chloride was used as a catalyst and the corresponding *o*-quinol was formed.

When an acetone solution of *o*-benzoquinone (I) is shaken with aluminium oxide, pyrocatechol is formed in 11 % yield. The formation of pyrocatechol also occurs spontaneously in an aqueous solution of *o*-benzoquinone and is probably the result of a complicated disproportionation<sup>3</sup>. The expected 2-acetyl-*o*-benzoquinol (II) has not been isolated but its formation has been shown indirectly by the isolation of a small amount of 2-acetyl-phenol (III) after treatment of the acetone solution with zinc and acetic acid.

\* Part I, See Ref. <sup>1</sup>



In the experiments described below the reaction was applied to a number of alkyl and alkoxy substituted *o*-benzoquinones (IV—XIII) which are more stable than *o*-benzoquinone. When a freshly prepared solution of the substituted *o*-benzoquinone in acetone was shaken with neutral aluminium oxide, the colour of the solution turned from red to yellow. Analysis of the reaction products showed that in all cases they were adducts of quinone and acetone in a 1:1 ratio.

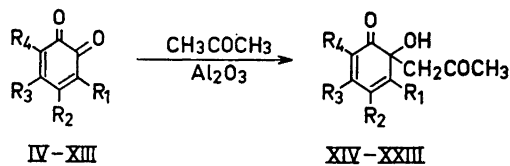
Under these conditions, the aldol condensation between *o*-quinone and acetone was accompanied by competing dimerisation and polymerisation reactions of the *o*-quinones<sup>4-9</sup>. These products however, unlike the acetone adduct, were strongly adsorbed on the aluminium oxide which usually acquired a dark colour. Dimeric *o*-benzoquinone for example was 95 % adsorbed on shaking with aluminium oxide in acetone. Thus the acetone adducts were purified automatically.

Reduction<sup>10</sup> of the *o*-quinone acetone adducts with zinc and acetic acid gave *o*-acetylphenols, supporting the view that the adducts had an *o*-benzoquinol structure.

The addition of acetone to either of the carbonyl groups in the symmetrically substituted *o*-benzoquinone V would give only a single acetyl-quinol, XV, but the unsymmetrically substituted *o*-quinones (IV and VI—XIII) could, formally, give two isomers. However in all cases only one isomer was obtained. To decide which was formed of two possible *o*-acetyl-quinols in the case where one isomer had a free 4-position and the other a free 5-position the following method\* was used. The phenol obtained by reduction of the quinol was treated with potassium nitrosodisulphonate<sup>17</sup>. The formation of a *p*-benzoquinone indicated that the phenol had a free *p*-position and therefore that the 4-position was free in the quinol. The quinones IV, VI, VIII, X, XI and XIII gave quinols which were shown in this way to have a free 4-position and could therefore be ascribed the structures XIV, XVI, XVIII, XX, XXI and XXIII, respectively. The quinone XII gave a quinol, the reduction product of which was slowly oxidised by potassium nitrosodisulphonate to an *o*-quinone with simultaneous loss of a tert-butyl group. The quinol must therefore be substituted in both the 4 and 6 positions, as in structure XXII. The quinones VII and IX gave quinols that were shown by spectrophotometric evidence (see below) to have the structures XVII and XIX.

The *o*-acetylquinols XVI, XVII, XVIII, XIX, XX, XXI and XXII were crystalline while XIV was an oil and was purified by distillation. The *o*-quinols XV and XXIII were oils and could not be obtained in an analytically pure condition. Most of the *o*-quinols dimerised on keeping at room temperature and in the case of the latter two compounds, dimerisation was so

\* Further details will be given in a following paper<sup>10</sup>.



- IV, XIV  $\text{R}_1 = \text{R}_3 = \text{CH}_3$ ;  $\text{R}_2 = \text{R}_4 = \text{H}$   
 V, XV  $\text{R}_1 = \text{R}_4 = \text{H}$ ;  $\text{R}_2 = \text{R}_3 = \text{CH}_3$   
 VI, XVI  $\text{R}_1 = \text{R}_3 = \text{R}_4 = \text{CH}_3$ ;  $\text{R}_2 = \text{H}$   
 VII, XVII  $\text{R}_1 = \text{OCH}_3$ ;  $\text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$   
 VIII, XVIII  $\text{R}_1 = \text{OCH}_3$ ;  $\text{R}_2 = \text{R}_4 = \text{H}$ ;  $\text{R}_3 = \text{CH}_3$   
 IX, XIX  $\text{R}_1 = \text{OCH}_3$ ;  $\text{R}_2 = \text{R}_4 = \text{H}$ ;  $\text{R}_3 = \text{CH}_2\text{CH}_2\text{CH}_3$   
 X, XX  $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$ ;  $\text{R}_3 = \text{OCH}_3$   
 XI, XXI  $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$ ;  $\text{R}_3 = \text{OCH}_2\text{C}_6\text{H}_5$   
 XII, XXII  $\text{R}_1 = \text{R}_3 = \text{C}(\text{CH}_3)_3$ ;  $\text{R}_2 = \text{R}_4 = \text{H}$   
 XIII, XXIII  $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$ ;  $\text{R}_3 = \text{C}(\text{CH}_3)_3$

fast that it was impossible to purify the monomers. The dimeric products will be dealt with in a following paper <sup>11</sup>.

The infrared spectra of the acetone adducts, some of which are shown in Fig. 1, were in full accord with the postulated *o*-benzoquinol structures. They showed a strong hydroxyl absorption with maxima varying between 3 194 and 3 472  $\text{cm}^{-1}$ . The absorption bands between 1 705 and 1 721  $\text{cm}^{-1}$  confirm the presence of the acetyl groups and the bands between 1 667 and 1 686  $\text{cm}^{-1}$  can be explained by the presence of an  $\alpha, \beta, \gamma, \delta$ -unsaturated carbonyl grouping. The lowest frequency for the conjugated carbonyl band was shown by the substances XVII, XVIII and XIX (1 667, 1 669 and 1 669  $\text{cm}^{-1}$ ) all of which have a 3-methoxyl substituent (see below). All compounds showed two bands in the intervals 1 616—1 647 and 1 538—1 582  $\text{cm}^{-1}$ , which can be ascribed to the two double bonds in the *o*-quinol ring. These absorption bands of the dienone system in the acetone adducts are similar to those reported <sup>12</sup> for the first two *o*-benzoquinols known, 2,3-dimethyl-*o*-benzoquinol and 2,3,5-trimethyl-*o*-benzoquinol.

The ultraviolet spectra of the acetone adducts also confirmed the *o*-benzoquinol structure. This type of conjugated system has been investigated by Derkosch and Kaltenecker <sup>13</sup>, who have determined the ultraviolet spectra of a number of 2-methyl-*o*-benzoquinol acetates and of 2,3,5-trimethyl-*o*-benzoquinol \*. Ethanol solutions of these compounds give a relatively broad K-band with maxima in the region of 298—312  $\text{m}\mu$  and an R-band varying between 349 and 369  $\text{m}\mu$ . The K-band is present in all the spectra shown in Figs. 2 and 3 but the R-band can be seen only in the spectrum of 2-acetyl-4,6-di-tert-butyl-*o*-benzoquinol (XXII). This band is present as an inflection at 373  $\text{m}\mu$  while the main absorption peak for this compound is at 313  $\text{m}\mu$ .

\* In the quoted work the substance was erroneously assumed to be 2,4,6-trimethyl-*o*-benzoquinol (cf. Ref. <sup>14</sup>).

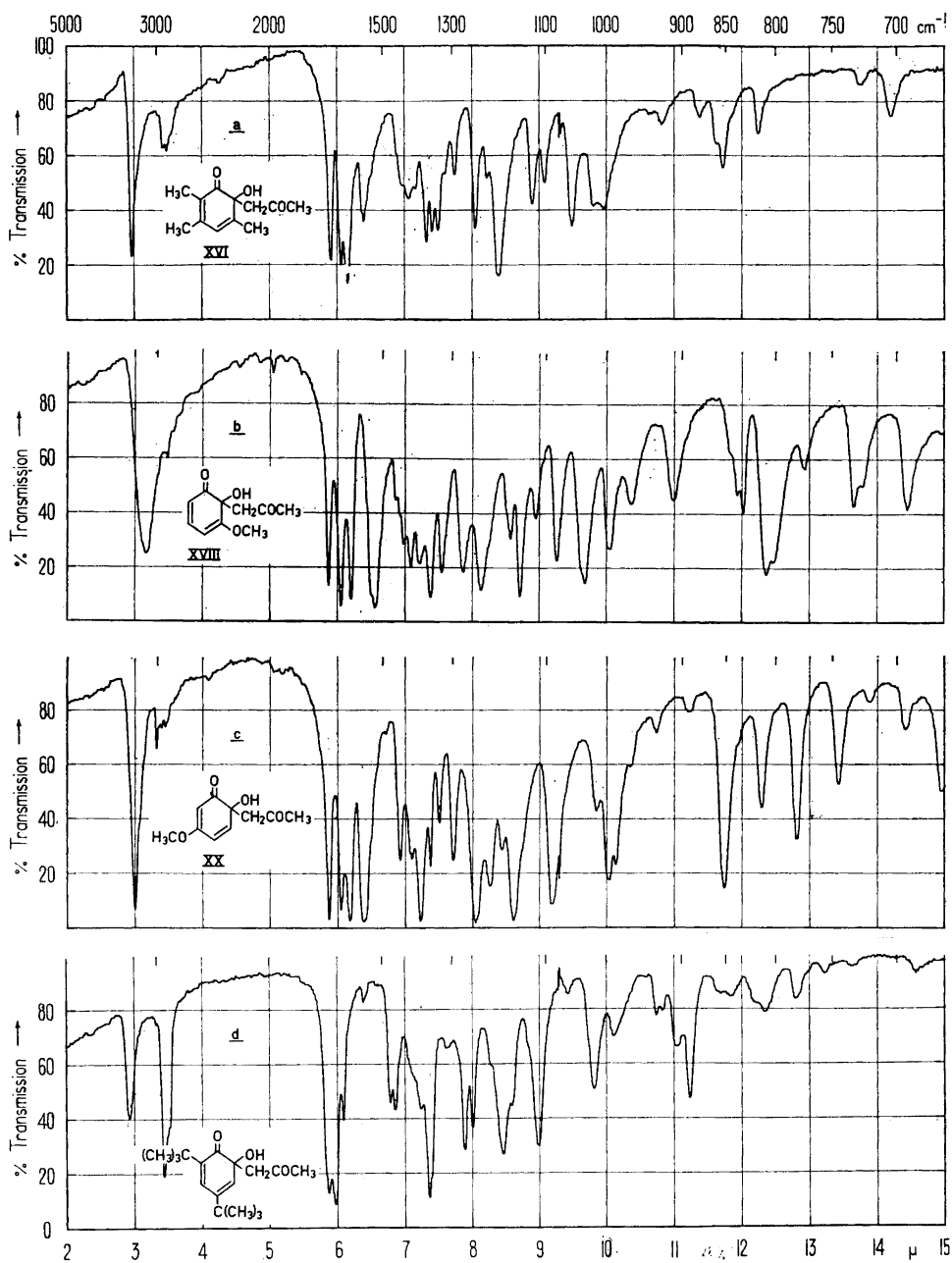


Fig. 1. Infrared absorption spectra (KBr method).

- a. 2-Acetonyl-3,5,6-trimethyl-*o*-benzoquinol (XVI)  
 b. 2-Acetonyl-3-methoxy-*o*-benzoquinol (XVII)  
 c. 2-Acetonyl-5-methoxy-*o*-benzoquinol (XX)  
 d. 2-Acetonyl-4,6-di-*tert*-butyl-*o*-benzoquinol (XXII)

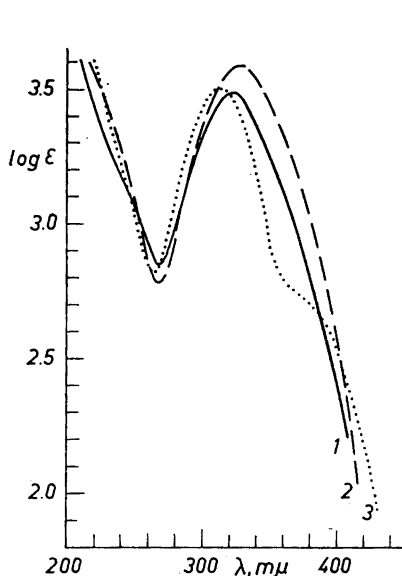


Fig. 2. Absorption spectra.  
 1. 2-Acetyl-3,5-dimethyl-*o*-benzoquinol (XIV)  
 2. 2-Acetyl-3,5,6-trimethyl-*o*-benzoquinol (XVI)  
 3. 2-Acetyl-4,6-di-*tert*-butyl-*o*-benzoquinol (XXII)  
 Solvent: 95 % Ethanol.

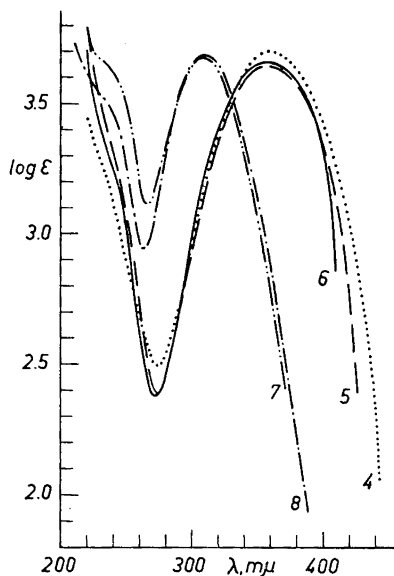
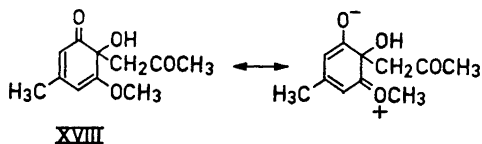


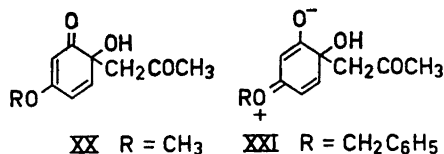
Fig. 3. Absorption spectra.  
 4. 2-Acetyl-3-methoxy-*o*-benzoquinol (XVII)  
 5. 2-Acetyl-3-methoxy-5-methyl-*o*-benzoquinol (XVIII)  
 6. 2-Acetyl-3-methoxy-5-propyl-*o*-benzoquinol (XIX)  
 7. 2-Acetyl-5-methoxy-*o*-benzoquinol (XX)  
 8. 2-Acetyl-5-benzyloxy-*o*-benzoquinol (XXI)  
 Solvent: 95 % Ethanol.

The two other alkyl-substituted quinols, 2-acetyl-3,5-dimethyl- and 2-acetyl-3,5,6-trimethyl-*o*-benzoquinol (XIV and XVI) have maxima at 321 and 327  $m\mu$ , respectively; the K-bands in these two *o*-quinols are thus at a relatively long wavelength and, since they are relatively wide, could possibly cover a smaller R-band.

2-Acetyl-3-methoxy-5-methyl-*o*-benzoquinol (XVIII) has an ultraviolet spectrum (shown in Fig. 3) with an absorption maximum at a significantly longer wavelength, 356  $m\mu$ , than 2-acetyl-3,5-dimethyl-*o*-benzoquinol (XIV), 321  $m\mu$ . This bathochromic shift can be explained by the mesomeric effect of the methoxyl group.

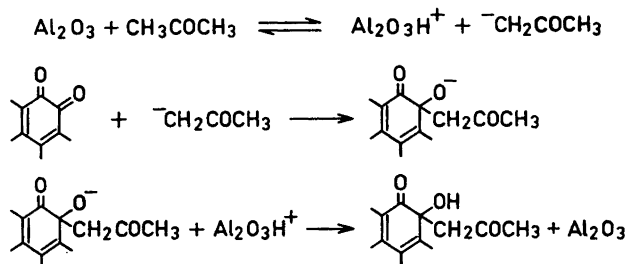


The ultraviolet spectra of XVII, XVIII and XIX are almost identical and since structural investigation<sup>10</sup> has shown that XVIII has a 3-methoxyl group it can be assumed that the same is also true for the other two compounds.

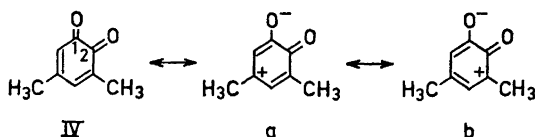


In 2-acetyl-5-methoxy-*o*-benzoquinol (XX) the methoxyl group makes possible a cross-conjugated resonance structure. This does not however give rise to any bathochromic displacement of the K-band. The spectra of this 5-methoxy-substituted quinol and of 2-acetyl-5-*tert*-butyl-*o*-benzoquinol (XXIII) show absorption maxima at the same wavelength (305 m $\mu$ ) and 2-acetyl-5-benzyloxy-*o*-benzoquinol (XXI) with a maximum at 310 m $\mu$  shows only a very slight shift.

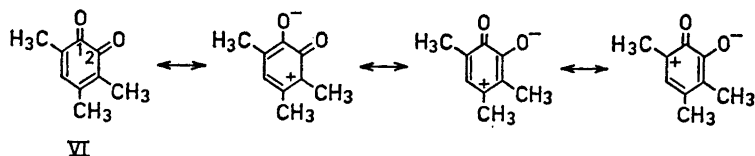
The aluminium oxide-catalysed addition of acetone to *o*-benzoquinones is of an aldol condensation type and therefore should be catalysed by alkali as well. Because of the instability of *o*-benzoquinones, alkali cannot be used as a catalyst in this case. The aluminium oxide may be assumed to act as a Lewis base, and the mechanism of the addition reaction may be presented as follows.



The acetyl anion, when attacking the *o*-benzoquinone, would be expected to prefer the more positive of the two carbonyl carbon atoms. Which of carbon atoms 1 and 2 of the *o*-quinone ring will be the more strongly positive will depend on the inductive and mesomeric effects of the substituents in the ring. Thus the methyl groups in 3,5-dimethyl-*o*-benzoquinone (IV) by electron

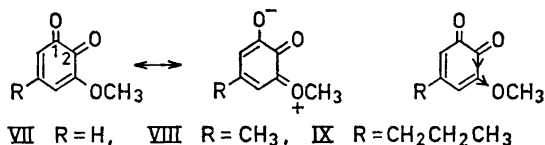


release should favour the resonance structures a and b. This will weaken the carbonyl character of the carbonyl group in position 1 and as a result carbon atom 2 will be comparatively more positive. Addition can therefore be expected to occur at 2, which is in agreement with the experimental result. Analogously favoured resonance structures can similarly be postulated for 3,5,6-trimethyl-*o*-benzoquinone (VI). In this case one of the methyl groups (that in the three

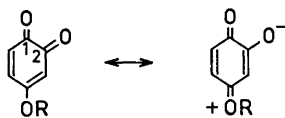


position) will favour reaction at carbonyl group 2 while the two others (in positions 4 and 6) will favour reaction at carbonyl group 1. The product of the reaction of 3,4,6-trimethyl-*o*-benzoquinone was 2-acetyl-3,5,6-trimethyl-*o*-benzoquinone (XVI) which shows that the two methyl groups acting together exerted the dominant effect.

In 3-methoxy-*o*-benzoquinone (VII), 3-methoxy-5-methyl-*o*-benzoquinone (VIII) and 3-methoxy-5-propyl-*o*-benzoquinone (IX), the methoxyl group



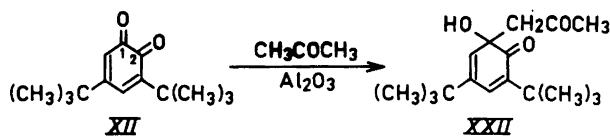
weakens the carbonyl character of carbonyl group 1 by a resonance effect and the acetyl anion will therefore be accepted by carbon atom 2. Electron attraction by the methoxyl group may also contribute to make carbon atom 2 more positive than carbon atom 1. In VIII and IX, the alkyl group will co-operate with the methoxyl group to make carbonyl group 1 less reactive towards acetone than carbonyl group 2.



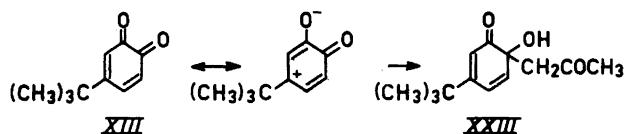
X R = CH<sub>3</sub>, XI R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>

For both 4-methoxy-*o*-benzoquinone (X) and for 4-benzyloxy-*o*-benzoquinone (XI) *p*-quinonoid resonance structures are possible and as a result carbonyl group 2 will be less receptive to attack than carbonyl group 1.

An exception to the rule that acetone addition will take place at the carbonyl group that can be regarded as having the more strongly positive C-atom was found in the addition of acetone to 3,5-di-*tert*-butyl-*o*-benzoquinone (XII). This gave 2-acetyl-4,6-di-*tert*-butyl-*o*-benzoquinone (XXII), probably



because carbonyl group 2 which should have the more strongly positive C-atom was hindered by the bulky butyl group in the 3-position. A tert-butyl group not present in a sterically hindering position directs the addition in the same way as methyl groups. 4-tert-Butyl-*o*-benzoquinone (XIII) gave 2-acetyl-5-tert-butyl-*o*-benzoquinol (XXIII) which is in harmony with the expected electron displacement shown in the formula below.



#### EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer model 21 spectrophotometer using KBr discs in the case of solid substances and films between salt plates in the case of oils. Ultraviolet spectra were measured with a Beckman DU spectrophotometer. Microanalyses were done by Alfred Bernhardt, Mülheim (Ruhr).

**Materials.** *o*-Benzoquinone and 3-methoxy-*o*-benzoquinone were prepared by dehydrogenation of pyrocatechol and pyrogallol-1-methyl ether, respectively, with tetrachloro-*o*-quinone\* according to Horner and Dürkheimer<sup>15</sup>. 3,5-Di-tert-butyl-*o*-benzoquinone was prepared according to Flaig *et al.*<sup>16</sup> and the other quinones with the exception of 4-tert-butyl-*o*-benzoquinone (see below) were prepared according to Teuber and Staiger<sup>17</sup>. Neutral aluminium oxide "Woelm" of activity 1 and acetone purum or p.a. were used. No differences were observed between the two grades.

**4-tert-Butyl-*o*-benzoquinone (XIII).** This *o*-quinone was prepared by dehydrogenation of the corresponding pyrocatechol by periodate according to the procedure described by Adler and Magnusson<sup>18</sup>. A solution of 1,2-dihydroxy-4-tert-butylbenzene (7.0 g) in water (1 l) was mixed with sodium metaperiodate (10 g) dissolved in water (150 ml). The red reaction mixture was extracted immediately with methylene chloride. The extract was dried with sodium sulphate and evaporated. The residue was recrystallised from a mixture of ether and light petroleum, giving red needles of 4-tert-butyl-*o*-benzoquinone, m.p. 66–67° (3.8 g, 54 %).

#### Addition of acetone to *o*-benzoquinones

**General procedure.** A solution of the *o*-benzoquinone in acetone was shaken with aluminium oxide at room temperature. The end of the reaction was indicated by a colour change from red or red-brown to yellow. The quantities of reactants used and the time of shaking are given below. The solution was decanted and the aluminium oxide, which usually was strongly discoloured, was washed several times with acetone. The combined solutions were centrifuged to remove traces of alumina. The acetone solution was then evaporated in a rotary vacuum evaporator and the reaction product obtained purified as described below.

\* *o*-Benzoquinone as well as 3-methoxy-*o*-benzoquinone when prepared in this way on keeping sometimes suddenly decomposed. However if the crude substance was recrystallised immediately from ether it was usually stable.



*o*-Benzoquinone (I) a) *o*-Benzoquinone (0.82 g) in acetone (15 ml) was shaken with aluminium oxide (12.5 g) for 30 min. The reaction solution on evaporation (see above) gave a partially crystalline residue. It was extracted with boiling hexane. On cooling, the extract gave *pyrocatechol* (89 mg, 11 %), identified by m.p. and mixed m.p.

b) *o*-Benzoquinone (8.0 g) in acetone (300 ml) was shaken with aluminium oxide (200 g) for 30 min. The solution was decanted and shaken with zinc dust (20 g) and acetic acid (20 ml) until colourless. The aluminium oxide was washed with acetone and the washings were treated in the same way. The combined solutions were filtered and neutralised with sodium bicarbonate solution. The acetone was distilled off under reduced pressure and the aqueous solution remaining was extracted with ether. The ether solution, which contained 2.0 g of product, was extracted with 20 % aqueous sodium bisulphite (10 × 50 ml). The bisulphite solution was neutralised with sodium bicarbonate and extracted with ether. The ether solution was dried and evaporated giving an oil (0.55 g) which crystallised after a day. Recrystallisation from hexane gave colourless plates of *2-acetylphenol* (III), m.p. 62–64° (0.20 g, 2 %). After sublimation (0.05 mm Hg, bath temperature 70°) and further recrystallisation from hexane it had m.p. 63–64°. (Found: C 71.99; H 6.82. Calc. for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>: C 71.98; H 6.71). Infrared bands (cm<sup>-1</sup>): 3408 (OH), 1712 (C=O), 1616, 1597 and 1504–1513 (benzene ring); ultraviolet maximum at 276 mμ, log ε, 3.12. The substance could be converted into 3-methylcoumarone by boiling with ethanolic hydrochloric acid.

Since this experiment was carried out, the preparation of the compound in another way has been reported<sup>20</sup>.

*3,5-Dimethyl-o-benzoquinone* (IV) (2.30 g) in acetone (125 ml) was shaken (15 min) with aluminium oxide (50 g). The reaction mixture when worked up gave a yellow oil (1.26 g). Distillation at 10<sup>-3</sup> mm Hg (bath temp. 110°) gave *2-acetyl-3,5-dimethyl-o-benzoquinol* (XIV) as a yellow viscous oil. (Found: C 68.45; H 7.66. Calc. for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>: C 68.02; H 7.26). Infrared bands (cm<sup>-1</sup>): 3 401 (OH), 1 715 (C=O), 1 671 (conj. C=O), 1 645 (C=C) and 1 580 (C=C); ultraviolet spectrum, see Fig. 2. The yield was low since a part of the substance decomposed on distillation giving a black tarry residue. The substance dimerises<sup>11</sup> at room temperature but can be stored at -20° for some weeks without change.

*4,5-Dimethyl-o-benzoquinone* (V) (3.80 g) in acetone (150 ml) was shaken with aluminium oxide (100 g) for 5 min and the mixture was then cooled to -80°. It was worked up rapidly at low temperature (ca. 0°) giving *2-acetyl-4,5-dimethyl-o-benzoquinol* (XV) as a yellow viscous oil (1.45 g). Infrared bands (cm<sup>-1</sup>): 3 448 (OH), 1 712 (C=O), 1 686 (conj. C=O) and 1 647 (C=C). On warming to room temperature the product dimerised rapidly and after 30 min the dimer was crystalline. Recrystallisation twice from acetone gave colourless prisms (0.91 g) of *2-acetyl-4,5-dimethyl-o-benzoquinol dimer* which turned dark at 186° and decomposed at 205° [Found: C 67.89; H 7.16; MW 388 (cryoscopic in acetic acid). Calc. for C<sub>22</sub>H<sub>28</sub>O<sub>6</sub>: C 68.02; H 7.26; MW 388.44].

*3,4,6-Trimethyl-o-benzoquinone* (VI) (1.58 g) in acetone (50 ml) was shaken with aluminium oxide (30 g) for 30 min. The reaction solution on evaporation gave a yellow oil (1.22 g) which was distilled at 10<sup>-3</sup> mm Hg (bath temperature 90°) and after one day crystallised. The product was recrystallised from ethanol giving *2-acetyl-3,5,6-trimethyl-o-benzoquinol* (XVI), yellow prisms, m.p. 57–59° (0.28 g) (Found: C 68.91; H 7.64. Calc. for C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>: C 69.20; H 7.55). Infrared spectrum, see Fig. 1; ultraviolet spectrum, see Fig. 2. In another experiment the crude undistilled *o*-quinol was seeded with crystalline material. The solid obtained was recrystallised giving 53 % of XVI. The substance is stable at room temperature.

*3-Methoxy-o-benzoquinone* (VII) (6.58 g) in acetone (400 ml) was shaken with aluminium oxide (200 g) for 15 min. The reaction mixture when worked up gave a yellow oil (2.61 g) which crystallised on standing for some days. The product was dissolved in ethanol at room temperature and cooled to -20° giving *2-acetyl-3-methoxy-o-benzoquinol* (XVII) as a yellow crystalline conglomerate, m.p. 68–69° (2.10 g, 23 %) (Found: C 61.37; H 6.30; OCH<sub>3</sub> 16.04. Calc. for C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>: C 61.21; H 6.18; OCH<sub>3</sub> 15.81). Infrared spectrum, see Fig. 1; ultraviolet spectrum, see Fig. 3. The substance is stable at room temperature.

*3-Methoxy-5-methyl-o-benzoquinone* (VIII) (1.78 g) in acetone (100 ml) was shaken (1 h) with aluminium oxide (50 g). The reaction solution when evaporated gave a yellow oil (1.04 g) which crystallised after some hours. The product was recrystallised from

ethanol giving *2-acetyl-3-methoxy-5-methyl-o-benzoquinol* (XVIII) as a yellow crystalline conglomerate, m.p. 109° (0.64 g, 26 %) (Found: C 62.72; H 7.01; OCH<sub>3</sub> 14.74. Calc. for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub>: C 62.84; H 6.71; OCH<sub>3</sub> 14.76). Infrared bands (cm<sup>-1</sup>) 3 344 (OH), 1 718 (C=O), 1 669 (conj. C=O), 1 629 (C=C), 1 558 (C=C); ultraviolet spectrum, see Fig. 3. The substance is stable at room temperature.

*3-Methoxy-5-propyl-o-benzoquinone*<sup>19</sup> (IX) (1.67 g) in acetone (30 ml) was shaken with aluminium oxide (25 g) for 1 h. On evaporation the reaction solution gave a yellow oil (0.90 g) which crystallised after several days. The product was recrystallised from ethanol giving *2-acetyl-3-methoxy-5-propyl-o-benzoquinol* (XIX) as a yellow crystalline conglomerate, m.p. 56° (0.65 g, 30 %) (Found: C 65.08; H 7.36; OCH<sub>3</sub> 13.17. Calc. for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>: C 65.43; H 7.61; OCH<sub>3</sub> 13.02). Infrared bands (cm<sup>-1</sup>): 3 425 (OH), 1 718 (C=O), 1 669 (conj. C=O), 1 629 (C=C), 1 553 (C=C); ultraviolet spectrum, see Fig. 3. The substance is stable at room temperature.

*4-Methoxy-o-benzoquinone* (X) (3.0 g) in acetone (200 ml) was shaken with aluminium oxide (90 g) for 20 min and the mixture was then cooled rapidly (ca. 0°) and worked up fairly quickly (30 min). The product was an orange-coloured oil (1.06 g) which was kept at -80° and crystallised after some days. It was dissolved in ether at room temperature and cooled to -20° giving *2-acetyl-5-methoxy-o-benzoquinol* (XX) as pale yellow needles, m.p. 66-67° (0.48 g, 11 %) (Found: C 61.52; H 6.12; OCH<sub>3</sub> 15.93. Calc. for C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>: C 61.21; H 6.17; OCH<sub>3</sub> 15.82). Infrared spectrum, see Fig. 1; ultraviolet spectrum, see Fig. 3. The substance can be kept at -20° without changing but dimerises at room temperature.

*4-Benzoyloxy-o-benzoquinone* (XI) (4.40 g) in acetone (220 ml) was shaken with aluminium oxide (110 g) for 20 min. On evaporation the reaction solution gave a yellow oil (1.05 g) which crystallised after several hours. After treatment with charcoal and recrystallisation from ethanol it gave *2-acetyl-5-benzoyloxy-o-benzoquinol* (XXI) as almost colourless needles, m.p. 108° (0.77 g, 14 %) (Found: C 70.65; H 6.01. Calc. for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>: C 70.57; H 5.92). Infrared bands (cm<sup>-1</sup>): 3 356 (OH), 1 721 (C=O), 1 670 (conj. C=O), 1 634 (C=C), 1 577 (broad, C=C and phenyl ring) and 1 504 (phenyl ring); ultraviolet spectrum, see Fig. 3. This compound could be kept at room temperature for several days. Changes occurring after that have not been investigated.

*3,5-Di-tert-butyl-o-benzoquinone* (XII) (20.0 g) in acetone (600 ml) was shaken with aluminium oxide (400 g) for 1 h. The product obtained on working up was a brown oil which crystallised from light petroleum giving *2-acetyl-4,6-di-tert-butyl-o-benzoquinol* (XXII) as yellow needles, m.p. 64-65° (11.8 g, 47 %) (Found: C 73.53; H 9.26. Calc. for C<sub>17</sub>H<sub>26</sub>O<sub>3</sub>: C 73.34; H 9.42). Infrared spectrum, see Fig. 1; ultraviolet spectrum, see Fig. 2. The substance has been kept for several months at room temperature without change.

*4-tert-Butyl-o-benzoquinone* (XIII) (3.14 g) in acetone (100 ml) was shaken with aluminium oxide (50 g) for 30 min and the mixture was then cooled to -80°. It was worked up rapidly at low temperature (ca. 0°) and gave *2-acetyl-5-tert-butyl-o-benzoquinol* (XXIII) as a viscous yellow oil (2.22 g); infrared bands at 3 449 (OH), 1 712 (C=O), 1 670 (conj. C=O), 1 645 (C=C) and 1 577 (C=C) cm<sup>-1</sup>; ultraviolet maximum at 305 mμ (log ε, 3.50). On warming to room temperature the substance dimerised rapidly and after 30 min the dimer began to crystallise. Recrystallisation from ethanol gave colourless prisms, m.p. 173-175° (Found: C 70.60; H 8.02; MW 472 (cryoscopic in acetic acid). Calc. for C<sub>26</sub>H<sub>36</sub>O<sub>6</sub>: C 70.24; H 8.10; MW 444.52).

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