

482. *Addition Reactions of Quinones. Part II.* The So-called Uncatalysed Addition of Acetyl Chloride to Benzoquinone and Tolu-2 : 5-quinone.*

By H. BURTON and P. F. G. PRAILL.

Acetyl chloride reacts with *p*-benzoquinone in the presence of traces of water or zinc chloride to give a mixture of quinol, chloroquinol, and dichloroquinol diacetates. In the absence of these catalysts the reaction is slow and with tolu-2 : 5-quinone may not occur at all. A mechanism for the reaction is proposed.

In the so-called uncatalysed reaction of acetyl chloride with certain quinones we have observed that at the beginning of the reaction separation of a dark solid, which is undoubtedly a "quinhydrone," usually occurs; this phenomenon is not observed in the Thiele acetylation reaction. Schulz (*Ber.*, 1882, **15**, 652) has investigated the action of acetyl chloride on *p*-benzoquinone and thymoquinone (see also Erdtman, *Proc. Roy. Soc.*, 1933—34, *A*, **143**, 177), and more recently Oliverio (*Gazzetta*, 1948, **78**, 105) has shown that the reaction is not a general one. We have re-investigated the reaction with *p*-benzoquinone and to some extent have confirmed Schulz's findings (*loc. cit.*) that the reaction products are quinol, chloroquinol, and 2 : 5-dichloroquinol diacetates. We have not been able to devise a really satisfactory method of separation of these acetates, either as such or by their conversion (*via* hydrolysis and oxidation) into the corresponding quinones. However, it is apparent from our work that the major product is chloroquinol diacetate. An interesting feature regarding this reaction is that under anhydrous conditions the reaction with *p*-benzoquinone is very slow unless the hydrogen chloride which is evolved is prevented from leaving the sphere of the reaction (cf. Graebe, *Annalen*, 1868, **146**, 13, 23). For example, only 17.5% of converted material is obtained after 4 hours' refluxing, but on passage of dry hydrogen chloride for a short time, or on addition of a small drop of water, a vigorous reaction occurs and this is then complete within 30 minutes. Tolu-2 : 5-quinone, which does not react with acetyl chloride alone on 4 hours' boiling, reacts slowly on addition of a drop of water to give 2 : 5-diacetoxy-4-chlorotoluene and much uncrystallisable material which contains unchanged toluquinone. 1 : 4-Naphthaquinone under similar conditions gives an almost black polymeric material (cf. Knapp and Schultz, *Annalen*, 1881, **210**, 178).

From our work (*J.*, 1951, 726) on the *C*-acetylation of anisole with acetyl chloride in the presence of small amounts of metallic chlorides, we were of the opinion that the observations of earlier workers might be explained if they had used impure acetyl chloride. Experiments with benzoquinone and acetyl chloride containing from 0.025 to 0.1% of zinc chloride (introduced as pure zinc acetate) showed that the reaction followed a similar course to that when a trace of water was used. The reaction was, however, much more vigorous, and separation of the "quinhydrone" did not occur unless external cooling was applied.

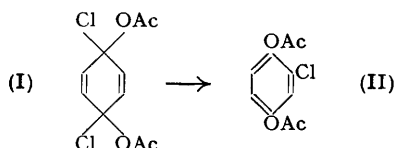
It is apparent from our results that the system acetyl chloride-quinone is not a simple one. The most probable mechanism for the formation of chloroquinol diacetate appears to us to be the addition of hydrogen chloride (see especially Carstanjin, *J. pr. Chem.*, 1881, **23**,

* Part I, *J.*, 1952, 2193.

432; Clark, *Amer. Chem. J.*, 1892, **14**, 574; Schmidlin, *Ber.*, 1911, **44**, 1700), followed by acetylation of the intermediate chloroquinol. Support for this view has been obtained by the isolation of free chloroquinol from experiments with *p*-benzoquinone (1 mol.) and acetyl chloride (4 mols.) containing a trace of zinc salt, when the reaction was allowed to proceed uncontrollably, *i.e.*, so that the excess of acetyl chloride was removed in the volatile products. The formation of chloroquinol occurs in the presence of benzoquinone and consequently the possibility of dehydrogenation is presented. The chloroquinone thus produced could then add hydrogen chloride with formation of the dichloroquinol. The latter would be acetylated together with quinol—which must be formed in the dehydrogenation process. It is pertinent that the chlorine content of the mixed product from benzoquinone corresponds to that calculated for the monochloroquinol diacetate. The ratio of monochloro- to dichloro-compound and quinol must vary according to the rate of loss of hydrogen chloride from the mixture and to the relative rates of acetylation and dehydrogenation. However, the amount of dichloroquinol produced would not be expected to be very large since it is known that a chlorine atom raises the oxidation-reduction potential of the parent quinone; accordingly the oxidation of chloroquinol by benzoquinone should not occur to any appreciable extent.

The mechanism of the reaction catalysed by zinc chloride is not so readily interpreted but a reaction of the Thiele type (*J.*, 1952, 755) would undoubtedly play an important part in initiating the main reaction. It must be noted that, once the reaction has been initiated, evolution of hydrogen chloride is progressive.

We cannot agree with the mechanism for the chlorination-acetylation reaction put forward by Oliverio (*loc. cit.*). It appears highly improbable that an intermediate of type (I)



is produced and that this undergoes rearrangement with elimination of hydrogen chloride to yield chloroquinol diacetate (II).

Our experiments led in all cases to mixed products which were not readily separable by either fractional crystallisation or sublimation in a high vacuum. The melting points of some of the products isolated were often slightly lower than those of the pure compounds; identity was, however, controlled by mixed melting point determinations with samples of known purity.

EXPERIMENTAL

“AnalaR” acetyl chloride was used in all the experiments.

Reactions with p-Benzoquinone.—(a) The quinone (0.05 g.-mol.) and acetyl chloride (0.2 g.-mol.) began to deposit a dark green solid almost immediately after mixing. On warming, the solid redissolved with evolution of hydrogen chloride; the reaction was vigorous when a drop of water was added to the dry mixture, or when no precautions were taken to exclude moisture. After 30 minutes' refluxing on a steam-bath the excess of acetyl chloride was distilled from the clear solution. The residue (11.3 g.) solidified on cooling (Found: Cl, 15.0. Calc. for $C_{10}H_6O_4Cl$: Cl, 15.5%). When the crude material was allowed to crystallise slowly from methanol a mass of crystals (4 g.) was obtained which consisted of: (A) large colourless prisms (at least 2.3 g.), m. p. (after crystallisation from ether) 70–71°, which did not depress the m. p. of chloroquinol diacetate; and (B) fine needles, m. p. 114°, which did not depress the m. p. of 2:5-dichloroquinol diacetate. Evaporation of the mother-liquors gave an oil which could not be induced to crystallise.

A better separation of the dichloro-compound was obtained by allowing the original mixture to cool before removing the acetyl chloride. The material which crystallised (1 g.) contained a considerable amount of 2:5-dichloroquinol diacetate, m. p. 135°. A little material, m. p. 114–115°, was obtained from the acetyl chloride soluble portion, which did not depress the m. p. of quinol diacetate.

(b) A similar experiment carried out with carefully dried materials and under anhydrous conditions for the same time gave slightly impure *p*-benzoquinone (0.028 g.-mol.), m. p. 112°.

(c) In another experiment the mixture was refluxed in an oil-bath (*ca.* 80°) (to avoid extraneous moisture) for 2 hours. After removal of the excess of acetyl chloride the residue was suspended in water and treated with sulphur dioxide to remove unchanged quinone. The insoluble residue (2 g., 17.5%) crystallised from alcohol in colourless needles, which softened over a wide range and gave a clear melt at 104°.

(d) In a further experiment the reagents were mixed as before under rigorously dry conditions and dry hydrogen chloride was passed into the boiling mixture for about 10 minutes. Shortly afterwards the mixture became lighter in colour, a mild exothermic reaction occurred and the "quinhydrone" dissolved with evolution of hydrogen chloride. After a total time of 20—25 minutes the mixture was allowed to cool and set aside overnight. The crystalline material (C) (3.9 g.) was filtered off and the solution was evaporated, to yield solid (D) (7.7 g.).

On fractional crystallisation from ether, (C) yielded needles (1 g.), m. p. 133—136°, raised to 140° by recrystallisation from 96% alcohol (Found: Cl, 27.2. Calc. for $C_{10}H_8O_4Cl_2$: Cl, 27.0%).

Similarly (D) gave a mixture of chloroquinol diacetate as colourless prisms, m. p. 70—71°, and needles (1.5 g.), which on recrystallisation from methanol gave colourless flakes, m. p. 119—120°, which did not depress the m. p. of quinol diacetate.

(e) Acetyl chloride (0.2 g.-mol.) containing zinc acetate (41 mg.) was refluxed under anhydrous conditions for 2—2½ hours to remove any dissolved hydrogen chloride. The quinone (0.05 g.-mol.) was added to the cold mixture and within approx. 30 seconds a vigorous reaction occurred with evolution of hydrogen chloride. After refluxing for ½ hour, volatile products were removed in a vacuum; the residue solidified when kept. Crystallisation from alcohol gave a fraction (3.8 g.) which yielded 2 : 5-dichloroquinol diacetate (0.8 g.), m. p. and mixed m. p. 138—139°, and quinol diacetate (0.3 g.), m. p. and mixed m. p. 120—121°; the remaining solid was mainly chloroquinol diacetate (m. p. and mixed m. p.). Complete removal of the solvent from the mother-liquors gave a water-soluble solid (5.2 g.), from which chloroquinol (1.2 g.), m. p. 100°, was obtained by fractional crystallisation from benzene. This was characterised by conversion into the diacetate (m. p. and mixed m. p.).

(f) When the previous experiment was repeated with 8 mg. of zinc acetate and control of the reaction by external cooling (ice-bath), some "quinhydrone" formation occurred. By using a very efficient condensing system, loss of acetyl chloride was restricted and the only products isolated were quinol, chloroquinol, and 2 : 5-dichloroquinol diacetates.

Reactions with Tolu-2 : 5-quinone.—(a) When a solution of the quinone (0.025 g.-mol.) in acetyl chloride (0.1 g.-mol.) was boiled for 4 hours the solution became slightly lighter in colour but otherwise little change was observed. Removal of the acetyl chloride by evaporation left a residue of essentially unchanged quinone.

(b) When a drop of water was added to the above mixture some deepening of the colour was observed but no solid separated. After refluxing for 30 minutes or for 4 hours the excess of acetyl chloride was evaporated; the residue solidified on cooling. Recrystallisation from alcohol and then from methanol gave long colourless prisms of 2 : 5-diacetoxy-4-chlorotoluene (1.3 g.), m. p. and mixed m. p. 112—113°.

Vacuum-distillation of the syrup obtained by evaporation of the mother-liquors, gave some unchanged quinone.

(c) When small amounts of zinc acetate were used under the same conditions as for *p*-benzoquinone, a vigorous reaction occurred. The product was, however, so intractable that it was not possible to separate more than small amounts of 2 : 5-diacetoxy-4-chlorotoluene and (?) 2 : 5-diacetoxy-3 : 4-dichlorotoluene. No 2 : 5-diacetoxy-3-chlorotoluene was isolated (*cf. J.*, 1952, 757).

We thank Imperial Chemical Industries Limited for a grant towards the cost of this investigation.