The Reaction between \( p \)-Benzoquinone and Ethyl Acetoacetate

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This reaction has since its discovery by v. Pechmann and Ikuta evoked only sporadic interest. Graebe and Levy extended the synthesis to include tolquione and one of the present authors has in several articles treated this and analogous reactions. Recently Grinov and collaborators have published some results which are the occasion for this article.

The first step in the reaction is believed to be the formation of a quinol (I).

![Chemical Structures]

Quinols of the type I have not been isolated, but indirect evidence for their existence has been furnished. This primary quinol can react in two ways: It can be cyclized to a benzofuran (II) or be oxidized to its corresponding quinone by unreacted benzoquinone. Further this new-formed quinone can add a second molecule of ethyl acetoacetate forming a dissubstituted quinol which in turn will be cyclized to a benzodifuran (III). Normally there is formed a mixture of II and III, the ratio of the amounts being determined by the competition between oxidation and cyclization of I.

In synthetic practice it has for several reasons been an object to obtain a good yield of II and suppress the formation of III. Grinov reports a yield of 98% of II in a procedure where a mixture of anhydrous ethanol and ether is used as solvent and the reaction performed in an extraction apparatus with benzoquinone in the thimble. This technique was adopted in order to ensure a slow addition of ethyl acetoacetate-zinc chloride. Actually it was found that the addition of small amounts of strong bases and acids was very detrimental to the overall yield and in some cases benzodifuran was formed almost exclusively. Acetic acid, however, proved to be a suitable additive, a fair amount of very pure II being obtained while only traces of III were observed. (The effect of acetic acid may also include a kinetic contribution, e.g. catalysis of the ring-closure of I.) On this basis a reliable procedure has been worked out in which acetone has been adopted as solvent as originally proposed by Graebe and Levy. The main advantage of our procedure is that it furnishes II free from III rather than a high overall yield as it is difficult to separate the two compounds without heavy losses.

Experimental. Ethyl 2-methyl-5-hydroxybenzofuran-3-carboxylate, \( p \)-Benzoquinone (27 g) was dissolved in a mixture of ethyl acetoacetate (100 ml) and acetone (100 ml) at...
room temperature. This mixture was added during 10 h to a solution of anhydrous zinc chloride (35 g) in acetone (50 ml) and acetic acid (2.5 ml). The reaction mixture was kept at 75° and stirred mechanically. Afterwards it was kept overnight in an open beaker, cooled well in ice and filtered by suction. The light brownish product was washed with small amounts of ice-cold methanol thus becoming white. M. p. 138°. The substance gave a clean purple colour with hot concentrated sulphuric acid. (The benzodifuran III gives a blue colour with this reagent and even a small contamination of II with III changes the colour to violet.) Yield 33 g (60 %, calculated on the basis of benzoquinone).

1. v. Pechmann, H. Ber. 21 (1888) 3005.

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