

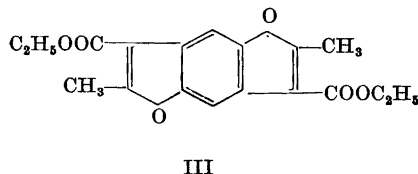
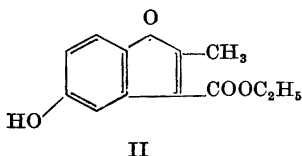
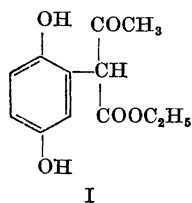
## The Reaction between *p*-Benzoquinone and Ethyl Acetoacetate

ERLING BERNATEK and TORE LEDAAL

*Universitetets Kjemiske Institutt,  
Blindern-Oslo, Norway*

This reaction has since its discovery by v. Pechmann<sup>1</sup> and Ikuta<sup>2</sup> evoked only sporadic interest. Graebe and Levy<sup>3</sup> extended the synthesis to include toluquinone and one of the present authors has in several articles<sup>4-8</sup> treated this and analogous reactions. Recently Grinev and collaborators<sup>9,10</sup> 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).



Quinols of the type I have not been isolated, but indirect evidence for their existence has been furnished<sup>4</sup>. This primary quinol can react in two ways: It can be cyclised to a benzofuran (II) or be oxidised to its corresponding quinone by unreacted benzoquinone. Further this new-formed quinone can add a second molecule of ethyl acetoacetate forming a disubstituted quinol which in turn will be cyclised 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 cyclisation 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. Grinev 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

benzoquinone, the reaction requiring 27 h. We have repeated Grinev's experiments but in no case obtained the yields claimed by him. The amounts of II fell far short of 98 % and appreciable amounts of III were formed. Further it is our experience that alcohols are not ideal as solvents in this reaction as dark substances are formed which contaminate the product.

It is well known that the potentials of reduction-oxidation systems of quinols and quinones are very sensitive to changes in the proton activity. A possible mode of displacing the benzofuran-benzodifuran ratio could therefore be to change the acidity of the reaction mixture. Two reduction-oxidation systems are present: [Quinol-benzoquinone] and [the quinol I — the corresponding quinone]. *A priori* it is impossible to say how changes in the proton activity will alter the potentials of the two systems relative to each other in the very special solvent employed (acetone).

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-hydroxy-benzofuran-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.
2. Ikuta, M. *J. prakt. Chem.* [2] **45** (1892) 65.

3. Graebe, C. and Levy, S. *Ann.* **283** (1894) 245.
4. Bernatek, E. *Acta Chem. Scand.* **7** (1953) 677.
5. Bernatek, E. and Ramstad, S. *Acta Chem. Scand.* **7** (1953) 1351.
6. Bernatek, E. and Thoresen, F. *Acta Chem. Scand.* **9** (1955) 743.
7. Bernatek, E. *Acta Chem. Scand.* **10** (1956) 273.
8. Bernatek, E. and Bø, I. *Acta Chem. Scand.* *In press.*
9. Grinev, A. N., Bon-Khvar, P. and Terent'ev, A. P. *Zhur. Obshchei Khim.* **26** (1956) 2928.
10. Grinev, A. N., Bon-Khvar, P. and Terent'ev, A. P. *Zhur. Obshchei Khim.* **27** (1957) 1087.

Received November 27, 1958.