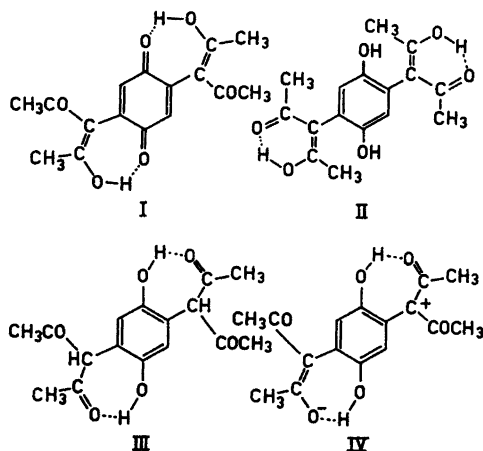


## Short Communications

The Reaction between Acetylacetone and *p*-BenzoquinoneIV. Structure of Tetracetyl-*p*-xyloquinoneERLING BERNATEK, MARIT JOHNSGARD  
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Under certain conditions *p*-benzoquinone and acetylacetone react to give  $\omega,\omega,\omega',\omega'$ -tetracetyl-*p*-xyloquinone.<sup>1,2</sup> NMR-spectroscopy indicates that this substance in solution (DMSO) occurs almost exclusively in a doubly enolised form, probably with hydrogen bonding to the quinone carbonyls (I).



The NMR-spectrum revealed two methyl peaks at  $\tau = 8.30$  (vinyl methyl) and  $\tau = 7.60$  (acetyl methyl) of equal area, corre-

sponding to six protons each. Further there were two peaks at  $\tau = 3.45$  and 2.41 representing two ring protons and two hydroxyl protons, respectively. The occurrence of an enolic hydroxyl proton, participating in a hydrogen bond, at the relatively high field of  $\tau = 2.41$  is unusual (in pure acetylacetone at  $\tau = -5.5$ ) and probably connected with the size of the chelate ring (seven-membered). In a molecule where only a five-membered chelate ring is possible, a similar phenomenon is observable; e.g. in 3,6-dichloro-2,5-dihydroxyquinone the hydroxyl proton occurs at  $\tau = 1.75$ .

The infrared spectrum of (I) shows carbonyl absorption at  $1635\text{ cm}^{-1}$  (in KBr) due to the quinone. At  $1650\text{ cm}^{-1}$  there occurs a shoulder representing the conjugated acetyl carbonyl. A hydroxyl band is found at  $3380\text{ cm}^{-1}$ , its relative sharpness indicating intramolecular hydrogen bonding.

On hydrogenation of the quinoid system, the enol hydroxyl moves downfield to  $\tau = -6.7$ . At  $\tau = 8.12$  the only conspicuous methyl peak occurs. This is caused by a different hydrogen bonding tendency where we have a structure as in (II). The six-membered rings in the side-chains will give a similar hydroxyl frequency as in acetylacetone, and the resonance in such a ring will make the two methyl groups equivalent (also as in acetylacetone). The enolisation in this compound is probably not more than 85–90% complete (10% DMSO solution), as a lesser methyl peak appears at  $\tau = 7.74$  originating from a ketonic form as (III). Consequently a small CH peak is found at  $\tau = 4.76$  and the enolic hydroxyl signal is correspondingly lower in intensity than those of the aromatic protons (at  $\tau = 3.40$ ) and phenol hydroxyls (at  $\tau = 1.30$ ).

Acetylation of the phenol groups gives a compound with two methyl peaks at  $\tau = 8.04$  (from the side-chain rings) and  $\tau = 7.80$  (from the acetoxy groups) with areas in the ratio 2:1. No indication of incomplete

