## **Short Communications**

## The Reaction between Acetylacetone and p-Benzoquinone

IV. Structure of Tetracetyl-p-xyloquinone

ERLING BERNATEK, MARIT JOHNSGARD and TRYGVE STENSRUD

Universitetets Farmasøytiske Institutt, Blindern, Oslo 3, Norway

Under certain conditions p-benzoquinone and acetylacetone react to give  $\omega, \omega, \omega', \omega'$ -tetracetyl-p-xyloquinone. 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 cm<sup>-1</sup> (in KBr) due to the quinone. At 1650 cm<sup>-1</sup> there occurs a shoulder representing the conjugated acetyl carbonyl. A hydroxyl band is found at 3380 cm<sup>-1</sup>, 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 sixmembered 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

enolisation is found here. The aromatic protons occurs at  $\tau=2.95$  and the enol

hydroxyls at  $\tau = -6.8$ .

The reason why (I) prefers the 7-membered chelate ring to the 6-membered one as in (II) may lie in a resonance possibility where a benzenoid (quinol) structure participates, formed by establishing an ordinary O—H bond between the quinone oxygen and the enol proton (IV). Such a structure leads to some degree of charge separation, which makes it less probable, but it may well be of sufficient importance to give structure (I) the edge over a structure with hydrogen bonding only within the side-chains.

Experimental. The NMR-spectra were recorded in approximately 10 % solutions in  $d_6$ -dimethyl sulphoxide on a Varian A 60 spectrometer. Infra-red spectra were recorded on a Beckman IR-5A apparatus. The investigated substances were prepared according to published methods.  $^{1}$ ,  $^{2}$ 

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## Kinetics of the Hydrolytic Cleavage of the Furan Ring ALPO KANKAANPERÄ and

ALPO KANKAANPERÄ and PENTTI SALOMAA

Department of Chemistry, University of Turku, Turku, Finland

In a recent discussion of the acidcatalyzed hydrolysis of vinyl ethers, it was pointed out that the proton transfer mechanism of vinyl ether hydrolysis would be extremely difficult to apply to furans because of their initial aromatic stabilization.

In order to obtain direct experimental information about the hydrolytic cleavage of the furan ring, the kinetics of the acid-catalyzed hydrolysis of 2,5-dimethylfuran in water and the deuterium solvent

isotope effect thereon have been studied. A few comparative experiments were also made with furan itself, although its low reactivity towards water made it less suitable for more extensive studies. The hydrolysis rate coefficients of the former compound in 15 and 25 % ethanol-water mixtures at 25°C, and those of the both compounds in moderately concentrated acids have been previously measured.<sup>2,3</sup>

Furan and 2,5-dimethylfuran were commercial products of Koch-Light Laboratories, Ltd., which were purified by careful fractional distillations in a Todd precision fractionation assembly. The following physical constants were recorded: furan, b.p.  $31.2-31.6^{\circ}\text{C}/746$  torr,  $n_{\rm D}^{20}$  1.4212,  $d_4^{20}$  0.9373; 2,5-dimethylfuran, b.p.  $41-42^{\circ}\text{C}/134$  torr,  $n_{\rm D}^{20}$  1.4122,  $d_4^{20}$  0.8505. The purities of the compounds were also controlled by gas chromatography.

In the kinetic experiments the rate of disappearance of the furan was followed by spectrophotometry. As it was observed that ultraviolet light interfered by bringing about photochemical side reactions, it was necessary to conduct the reactions in the dark, excepting the short periods of time needed for the photometric analysis of the samples withdrawn from the reaction mixtures. Owing to the relatively low solubilities of the investigated furans, the initial concentrations were 0.005 M or less. The optical measurements were made on a Beckman DK 2A Ratio Recording Spectrophotometer at a constant wavelength of approximately 235 mu. The cell housing of the photometer was at the same temperature as the thermostat in which the reactions were carried out. The concentration of the catalyst hydrochloric acid was about 0.2 M in most experiments. First-order kinetics were strictly obeyed in all cases, the standard errors of the rate coefficients being less than 2 %. In a number of additional rate measurements it was confirmed that the directly measured firstorder rate coefficient was proportional to the concentration of the hydrochloric acid up to 0.2 M. The results of the kinetic measurements are shown in Tables 1 and 2.

The value obtained for furan shows that this compound hydrolyzes slower than its aliphatic analog, divinyl ether, by a factor of about 10<sup>4</sup>. This is in agreement with the partial aromatic character of the furan

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