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# THE REACTION BETWEEN TETRACYCLONE AND SUPEROXIDE RADICAL ANION

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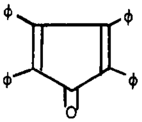
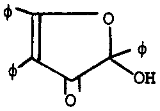
While the generation and subsequent presence of $O_2^-$ in biological systems has provoked a vivid interest in this species,[1] there is yet a dearth of information regarding its net chemical reactions.[2]

We found that tetracyclone (I) reacts very efficiently with superoxide salts to give 2-hydroxy-2,4,5-triphenylfuranone-3 (II).



I



II

$KO_2$-dicyclohexyl-18-crown-6 complex[3] was used as a source of $O_2^-$. We found that this complex is soluble in benzene in concentrations up to 0.05 M. We feel that the use of benzene instead of DMSO as originally suggested[3] avoids potential complications such as formation of anion of DMSO.[4]

Tetracyclone (1 gr, 2.6 mmoles) was added to a mixture of $KO_2$ (0.5 gr, 6.6 mmoles) in 150 ml dry benzene containing dicyclohexyl-18-crown-6 (1 gr, 2.6 mmoles). The mixture was stirred overnight in the dark at room temperature. During this period of time the solution turned from a clear deep red to a cloudy light yellow. The mixture was washed several times with water, dried over $Na_2SO_4$, filtered and evaporated under reduced pressure. The residue was chromatographed on a Kieselgel column (up to 10% acetone in petroleum ether) to yield II (0.7 gr, 2.1 mmoles); mp 190-192°C (lit.[5] 191°C). (Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 79.56; H, 4.95%). The aqueous washings were acidified to pH=1 with 1N HCl, and extracted with $CHCl_3$. After drying over $Na_2SO_4$, the organic layer was evaporated. The residue (0.305 gr, 2.5 mmoles) was found identical to an authentic sample of benzoic acid. When less than one equivalent of the crown ether was used, the reaction rate, as well as the total conversion dropped considerably.

The identity of product II was further established in the following manner. The nmr spectrum ($CDCl_3$, TMS internal standard) was composed of two overlapping multiplets centered at $\delta$=7.48 (15 H) and a broad singlet at $\delta$=4.54 (1H), which disappeared by addition of $D_2O$. The mass spectrum displayed a molecular peak of m/e 328 and prominent fragment-ion peaks at m/e 312, 300, 223, 195, 178. The IR and UV data were consistent with those reported[6] for II. Finally the acetate derivative was prepared as described.[5] Its identity was supported by additional spectroscopic data. Thus the nmr spectrum exhibited two overlapping multiplets at $\delta$=7.48 (15H) and a sharp singlet at $\delta$ =2.24 (3H). Mass spectrum: m/e 370, 328, 311, 265, 223, 178.

Two observations can be made at the present time regarding the mechanism of this reaction. Firstly, in view of the very poor hydrogen donor capabilities of the solvent, benzene, it seems that the crown ether provided the source for the extra hydroxylic hydrogen found in the product. This suggestion is supported by the noticed destruction of the crown ether at the end of the reaction. In this regard we should point out that II was formed independent of the subsequent water treatment required by the work-up of the reaction mixture. Secondly, the reaction does not require atmospheric oxygen; the product II was also formed in a carefully degassed reaction mixture It is noteworthy that this reaction pathway is unique among the other oxidation reactions of I. Neither cis-dibenzoylstilben, nor epoxides, which are the reaction products of I with singlet molecular oxygen[7] and $H_2O_2$ [8] respectively, could be detected in the reaction mixture.

While this reaction provides an obvious synthetic short pathway for II, the more general implications of this process are still obscure. Under similar reaction conditions, related compounds such as fluorenone, tetraphenylethylene, 2,5-diphenylfurane yielded only minute amounts of polar compounds. Furthermore, alkyl-substituted olefins (2,3-dimethyl-2-butene,2-methyl-2-butene, 2-methyl-2-pentene, cyclohexene) and aromatic hydrocarbons (benzene, anthracene, rubrene) were totally unreactive. $KO_2$ does however react with enol ethers such as dihydropyran and these results will be discussed in a future communication.[9]

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