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THE PHOTOCHEMICAL REACTION OF BENZOQUINONE WITH TOLAN[1,2]

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Much of our previous research has concerned itself with the photochemical behavior of carbonyl containing molecules (3). The present paper deals with our observation of a photochemical reaction of benzoquinone with tolan.

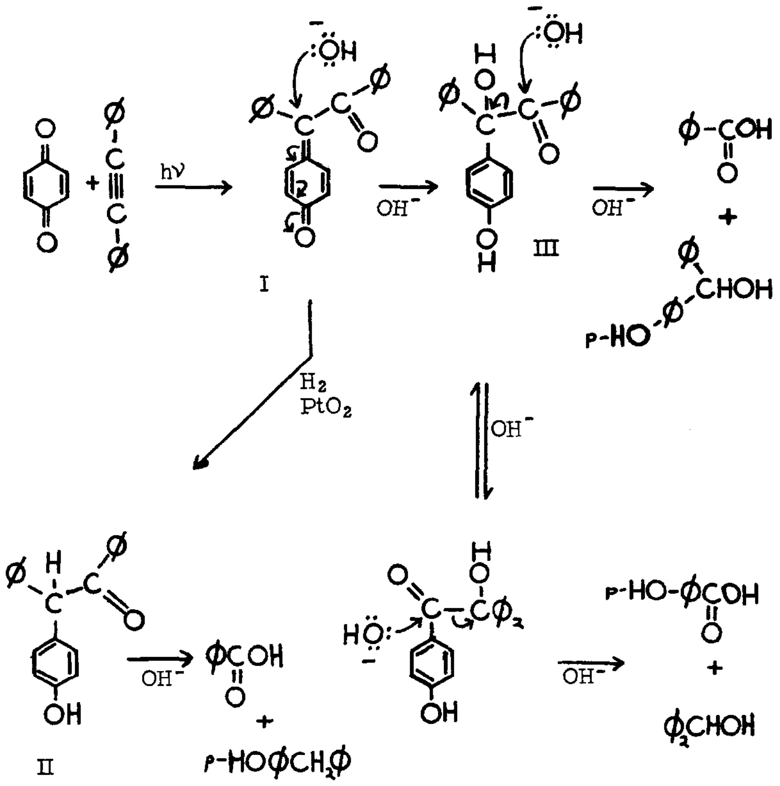
Irradiation of benzoquinone (11.0 g.; 0.10 mole) and tolan (18.0 g.; 0.10 mole) in 750 ml. of acetonitrile under nitrogen, using an AH6 high pressure mercury arc and solution filters excluding light below 310 mμ, led after 12 hr. to a yellow crystalline product, m.p. 105-106°. This product was obtained in 11.8 g. yield after recrystallization from benzene-hexane. The assigned structure I is based on spectral and degradative evidence.

Thus the elemental analysis fit $C_{20}H_{14}O_2$. The UV (EtOH) possessed peaks at 262 mμ (4.32) and 365 (4.45) mμ and the infrared spectrum had carbonyl bands at 6.04 and 6.08 μ, suggesting a highly conjugated system.

Catalytic hydrogenation in ethanol with PtO_2 at atmospheric pressure led to facile uptake of one mole of hydrogen. Chromatography on silica gel followed by recrystallization from benzene-hexane of the material eluted with 1:1:8 ether-benzene-hexane afforded 54% of material melting at 134.5-135.5°. Analysis indicated $C_{20}H_{16}O_2$. The compound proved identical with the known (4) 2-(p-hydroxyphenyl)-2-phenylacetophenone (II) (cf. Chart I); an authentic sample for comparison was prepared from the reaction of benzoin and phenol in 70% sulfuric acid as described by Japp and Wadsworth (4). The infrared spectrum of this compound possessed carbonyl absorption at 6.0 μ and a hydroxyl peak at 3.0 μ. Basic degradation to benzoic acid and p-benzylphenol as reported by Japp and Wadsworth (4) was confirmed. Hydrogenation thus defines the carbon skeleton and the placement of the two oxygen atoms in photoproduct I.

Further evidence for structure I was found in aqueous base treatment. Reaction of 2.03 g. of I in 100 ml. of 1 N sodium hydroxide at reflux for 5 hr. afforded directly 0.31 g. of benzhydrol. Chromatography on silica gel of the phenolic fraction yielded 0.71 g. of p-hydroxybenzhydrol. Similar chromatography of the acidic fraction afforded 0.39 g. of benzoic acid and 0.23 g. of p-hydroxybenzoic acid. These products are reasonably formulated as arising from initial nucleophilic attack of hydroxide to afford III which then undergoes base-catalyzed aryl migration and acyl fission by nucleophilic attack of hydroxide on the carbonyl group; exact analogy is found in the literature (5). The transformations described above are formulated in Chart I.

CHART I

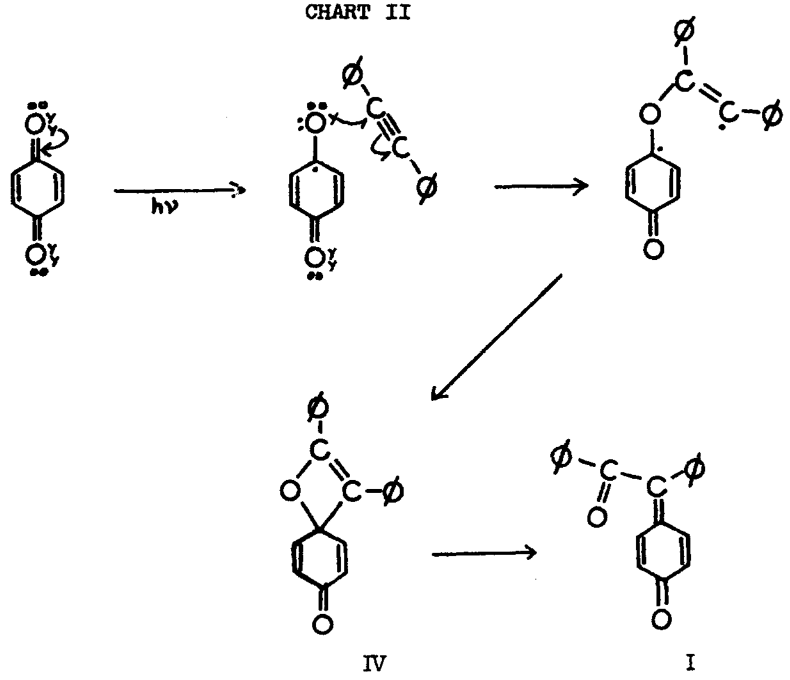


The reaction of benzoquinone with tolan to form the quinomethide I is reminiscent of the reaction of dibutylacetylene with acetophenone and also with benzaldehyde described by Büchi and coworkers (6) as giving unsaturated ketones. It is known that the lowest singlet excited state of benzoquinone is n-Pi* (7) and it is reasonable but not unequivocal that the lowest triplet is similarly n-Pi*. One characteristic of n-Pi* excited states which we have noted in earlier papers (8) is the aggressive behavior of the odd electron containing p_y orbital towards hydrogen abstraction and attack on Pi systems, a behavior reminiscent of alkoxyl free radicals which also have a localized odd electron containing orbital.[+]

[+] This assumption of non-interaction of the p_y non-bonding orbital is, of course, an approximation. As SCF MO calculations on formaldehyde indicate (refs. 9a, 9b) even in the ground state there is interaction of the coplanar sigma bonds with the p_y orbital. In the case of the excited state one may picture interaction as arising from delocalization of the positive "hole" left on n-Pi* promotion, with the hole weakly distributed in the sigma system. Such overlap can be considered to be involved in the Norrish Type I process as has been pointed out (ref. 10). However, thus far the evidence seems to indicate sigma delocalization to be less effective than Pi electron delocalization. Thus, the n-Pi* state more closely parallels alkoxyl radical than aryloxyl radical behavior, and the greater reactivity of the former may be ascribed to less efficient sigma than Pi electron delocalization.

In the present instance quinone oxygen attack on the tolane triple bond leads, perhaps partially concertedly, to an oxetene intermediate (here IV) as postulated by Büchi (6) for simple ketone reactions. Ring opening of IV accounts[+] for the observed photochemical product I (cf. Chart II).

CHART II



[+] Mixtures of benzoquinone and tolan in acetonitrile at reaction concentrations showed absorption to be the sum of the two individual contributions, arguing against a charge transfer complex as the light absorbing and reacting species.

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2. Support of this research by the U. S. Army Research Office (Durham) grant DA-ORD-36 and by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

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11. We are pleased to cooperate in simultaneous publication with Professor D. Bryce-Smith. In our laboratory infrared and ultraviolet spectral comparisons of Professor Bryce-Smith's photoproduct with ours shows these to be the same compound.