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ON THE FATE OF INITIALLY FORMED RADICALS IN PHOTOCHEMICAL HYDROGEN ABSTRACTION REACTIONS

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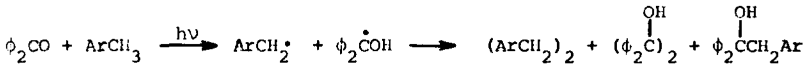
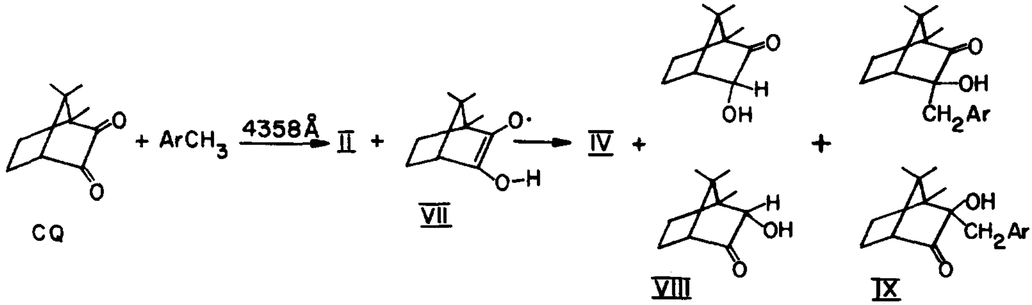
We wish to report evidence on the behaviour of initially formed radicals in photochemical reactions of benzophenone (I) and camphorquinone (CQ). Both of these compounds abstract hydrogen[1] from a variety of hydrogen donors via their n,π* triplet states. For example, irradiation of I in toluene and substituted toluenes[2,3,4,5] results in formation of p-methylbenzyl (II) and benzophenone ketyl (III) radicals which couple to give di-p-tolylethane (IV), benzpinacol (V) and diphenylbenzylcarbinol (VI) with quantum efficiencies



$$\phi_2CO + ArCH_3 \xrightarrow{h\nu} ArCH_2^{\bullet} + \phi_2\dot{C}OH \longrightarrow (ArCH_2)_2 + (\phi_2\overset{OH}{\overset{|}{C}})_2 + \phi_2\overset{OH}{\overset{|}{C}}CH_2Ar$$

I II III IV V VI

of about 50% for disappearance of I. Similarly, irradiation[6,7,8] of CQ in p-xylene at 4358Å (ϕ_{CQ} 0.07) affords II and hydroxybornanone radicals VII which proceed to IV, hydroxybornanones (VIII) and isomeric adducts IX.



The adducts VI and IX could be formed either by: (A) immediate coupling of the initially formed, geminate pair of radicals, or (B) by separation of these radicals and coupling during subsequent encounters. Results of sensitization experiments indicate that alternative (A) is the major pathway in the reaction of CQ while (B) is the major, if not exclusive, route for the reaction of I.[2] The Table summarizes the results of a series of irradiations at 3660Å of degassed p-xylene solutions, 0.055 M in I (>99% of light absorbed by I), and containing varying concentrations of CQ.

TABLE

Photoreactions[a] of Benzophenone, Camphorquinone, p-Xylene Mixtures

CQ (M)	Benzophenone (M)	λ (Å)	ϕ_{CQ}	Product Ratio[b] IV	VIII	IX[c]
0.05	0.055	3660	0.07	1.7	1	3.5
0.025	"	"	0.10	1.2	1	2.1
0.01	"	"	0.17	1.1	1	1.2
0.005	"	"	0.23	1	1	0.6
0.01-0.05	0	4358	0.07	1	1	6-7

a. Degassed solutions. Light intensity 2.7 x 10^{-7} Einstein/min. b. Determined by GLC analysis on 10' x 1/8" XE-60, column temp 160°, nitrogen flow 20 ml/min. Under these conditions, benzpinacol undergoes appreciable reversal to benzophenone. c. The isomeric adducts were formed in 2:1 ratio in all cases.

At higher concentrations of CQ, both the quantum yield and product composition were not greatly different from those obtaining in direct irradiation of CQ, suggesting that benzophenone functions as a typical triplet sensitizer. If triplet energy transfer were the only mechanism operating, the quantum yield for reaction of CQ should decrease with decreasing concentration of CQ. In fact, this quantum yield *increased* with *decreasing* CQ concentration and the product composition changed dramatically, as can be seen from the Table. Furthermore, it should be noted that VI was not detected in any of the reaction products unless irradiation was continued until after all the CQ had been consumed.

A somewhat similar situation has recently been reported by Monroe and Weiner[7] in the benzophenone sensitized photoreduction of CQ in 2-propanol, It was suggested that hydrogen atom transfer from III to CQ becomes important at low CQ concentration ("chemical

$$\mathrm{CQ} + \phi_2\dot{\mathrm{C}}\mathrm{OH} \longrightarrow \mathrm{VII} + \phi_2\mathrm{CO}$$

sensitization"); other workers[9] have also suggested that such a process occurs with III. Such a mechanism provides a rational explanation for the results obtained in the present work.

If the adduct VI were formed by coupling of the initially formed radicals II and III within the solvent cage in which they are generated, VI (stable to 3660Å light) should have been observed at least in solutions of low CQ concentration. Since this was not the case, it must be concluded that II and III separate and, in the absence of a hydrogen acceptor such as CQ, subsequently couple in a statistically controlled manner* to give IV, V and VI as had been suggested[2] earlier.

On the other hand, when radicals II and VII are generated in proximity by reaction of photoexcited CQ, the major product is the adduct mixture IX. When II and VII are generated separately, II by reaction of triplet benzophenone with p-xylene and VII by hydrogen transfer from III to CQ, the adducts IX are no longer the preponderant products. Instead, the product composition approaches that to be expected from purely statistical encounters between the radical intermediates. Thus, the radicals II and VII formed in proximity appear in the main to couple before separating.

Reasons for this difference in behaviour between benzophenone and CQ have not been established. A possible factor may be the fact that hydrogen abstraction involving

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*Since dimerization of either radical specie necessarily requires dimerization (or some other reaction involving two radicals) of the second radical, the statistically determined ratio of each radical dimer to cross-coupling product is 2:1.

the triplet state of one specie generates a pair of radicals having parallel spins of their unpaired electrons. In order for such geminate radicals to couple, spin inversion must occur.

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