Tetrahedron Letters No.10, pp. 579-583, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE PHOTOREDUCTION OF BENZOPHENONE BY AN ETHER. EFFECT OF MERCAPTAN[1]

S.G.Cohen and S.Aktipis

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154

(Received 3 December 1964)

Ultraviolet irradiation of benzophenone in 2-propanol[2] leads to the radicals[3,4] $(C_6H_5)_2\dot{C}\text{-}OH$ I and $(CH_3)_2\dot{C}\text{-}OH$ II,

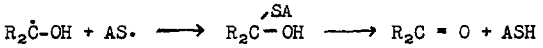
$$(C_6H_5)_2C{=}\overset{*}{O} + (CH_3)_2CHOH \longrightarrow (C_6H_5)_2\dot{C}\text{-}OH + (CH_3)_2\dot{C}OH \tag{1}$$

and then to benzpinacol and acetone. The quantum yield approaches 2 for the disappearance of benzophenone, radical II reacting with benzophenone to form a second radical I[4,5]. The reaction is retarded strongly by low concentration of mercaptan or disulfide, which show equivalent effectiveness and are equilibrated in the process. Rapid new reactions are introduced in which the sulfur compounds reconvert the intermediate radicals I and II to the starting materials[6a,b,c], eq. 2 and 3.

$$(C_6H_5)_2\dot{C}\text{-}OH + AS\cdot\ (ASSA) \longrightarrow (C_6H_5)_2C{=}O + ASH\ (ASH + AS\cdot) \tag{2}$$

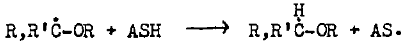
$$(CH_3)_2\dot{C}\text{-}OH + ASH \longrightarrow (CH_3)_2CHOH + AS\cdot \tag{3}$$

The mercaptan and disulfide are regenerated in their alternate oxidation states and function repeatedly, a limit on the period of their effectiveness not having been observed. In this system an effective mechanism for consumption of the sulfur compound is not available, since recombination reactions involving the thiyl radical will regenerate mercaptan.



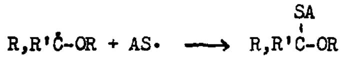
$$R_2\dot{C}\text{-}OH + AS\cdot \longrightarrow R_2\overset{\diagup SA}{C}{-}OH \longrightarrow R_2C = O + ASH \tag{4}$$

We wish to report that in the photoreduction of benzophenone by an ether, mercaptan and disulfide also retard effectively and are equilibrated in the process. Each molecule negates the chemical consequences of many quanta by the competitive reactions, eq. 2 and 3a.



$$R,R'\dot{C}\text{-}OR + ASH \longrightarrow R,R'\overset{H}{C}\text{-}OR + AS\cdot \tag{3a}$$

In this system a reaction is available in which the sulfur compound may be consumed irreversibly, eq. 4a, and a finite inhibition period is observed,



$$R,R'\dot{C}\text{-}OR + AS\cdot \longrightarrow R,R'\overset{SA}{C}\text{-}OR \qquad (4a)$$

Photoreduction of benzophenone in methyl 2-octyl ether proceeds 0.17 as fast as in 2-propanol, indicating a quantum yield of about 0.34. Benzpinacol was obtained in 42% yield, and radical combination products of the ether-derived radical are formed[7a,b]. Photoreduction of 0.2 M benzophenone in optically active methyl 2-octyl ether led to decrease of $[\alpha]_D^{22}$ in the recovered ether, from 9.35° to 8.95°, indicating racemization of 0.24 M ether. Similar reduction of 0.5 M benzophenone led to racemization of 0.58 M recovered ether. The racemization indicates that about half of the initially formed radicals, I and IIa, revert to the starting materials, eq. 1ar, and that the quantum yield for the initial hydrogen abstraction may be about 0.74.

$$(C_6H_5)_2C{=}O^* + R,R'CH\text{-}OR \longrightarrow I + R,R'\dot{C}\text{-}OR \quad \text{IIa} \qquad (1a)$$

$$I + IIa \longrightarrow (C_6H_5)_2C{=}O + R,R'CHOR \qquad (1ar)$$

Photoreduction of 0.5 M benzophenone in methyl 2-octyl ether proceeded with apparent zero order kinetics, at a rate of 0.011 mmole ml.$^{-1}$ hr.$^{-1}$ under our conditions and was complete in 45 hr. In the presence of 0.04 M 2-mercaptomesitylene the rate of photoreduction was decreased markedly, to about 0.0005 mmole ml.$^{-1}$ hr.$^{-1}$, and, after irradiation for 49 hr., benzophenone was recovered in 98% yield. Similar retardation was observed when this concentration of sulfur containing moiety was present initially as 0.02 M 2-mesityl disulfide. The retardation or inhibition broke down after irradiation for 100 hr., and the benzophenone was 80% reduced after 150 hr.

Analyses were carried out by vapor phase chromatography for concentration of mercaptan and disulfide as a function of time of irradiation. Solutions which were originally either 0.04 M in mercaptan or 0.02 M in disulfide became equivalent during irradiation, containing 70% of the sulfur as mercaptan, 30% as disulfide, redox reactions occurring, as had been found in the benzophenone-2-propanol system[6b,c]. Both shortly after the end of the inhibition period, and after complete reduction of the benzophenone, about 10% of the initial sulfur compound remained as mercaptan, none as disulfide. This low concentration of mercaptan, when present initially, had little inhibiting effect.

That the sulfur compound offered protection by participating in rapid hydrogen transfer reactions is further indicated by the results of photoreductions (a) in optically active methyl 2-octyl ether and (b) in the ether in the presence of t-butyl alcohol-OD. Irradiation of 0.22 M benzophenone in active methyl 2-octyl ether in the presence of 0.04 M 2-mesitylthiyl group led to steady decrease in rotation during 161 hr. of a 187 hr. irradiation period. The recovered ether had $[\alpha]_D^{23}$ 6.75°, down from 8.95°, indicating racemization of 1.4 M ether. The maximum racemization to be expected, assuming quantum yield 0.74 for the hydrogen abstraction, and subsequent return of hydrogen to the ether radical, would be about twice this, a value to be decreased if one takes into account internal masking by the sulfur compounds[6c]. Irradiation of the ether with 0.02 M mercaptan and 0.01 M disulfide without ketone led to little or no racemization. These results are quite consistent with our observations in the inhibited photoreduction of benzophenone in optically active 2-octanol[6b,c].

Ultraviolet irradiation of 0.25 M benzophenone and 0.02 M 2-mercaptomesitylene in 1:1 methyl 2-octyl ether:t-butyl alcohol-OD led to recovery of ether and t-butyl alcohol, both of which contained carbon-bound deuterium, the ether showing 7.1%, 0.40 M deuterated compound. Irradiation of benzophenone alone in the solvent pair led to about 1% deuterated compound in the ether; while irradiation of the solvent pair, alone or in the presence of disulfide without benzophenone, led to essentially no introduction of deuterium. The recovered ether, 0.4 M in deuterated compound, was cleaved to octyl iodide which retained deuterium, and this was converted to 2-octanone which appeared to contain very little deuterium, indicating that the isotope was located largely at the 2-octyl carbon.

These experiments indicate that mercaptan and disulfide provide extended protection by an inhibition period in the non-chain photoreduction of benzophenone in an ether. About twenty-five molecules of benzophenone were protected in the inhibition period by each mercaptan molecule or thiyl group. The sulfur compounds protected by reacting rapidly and repeatedly in the hydrogen transfer reactions which are indicated in equations 2 and 3a. They may have been consumed in reaction 4a.

Triplet[8] benzophenone may abstract the unactivated methyl hydrogen atoms of t-butyl alcohol and this material also may be protected by sulfur compounds.

(1) We are pleased to acknowledge generous support of this work by the U. S. Atomic Energy Commission, Contract AT-(30-1)2499.

(2) G. Ciamician and P. Silber, Ber., 83, 2911 (1900); 34, 1541 (1901).

(3) H. L. J. Backstrom and K. Sandros, Acta. Chem. Scand., 14, 48 (1960).

(4) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, J. Am. Chem. Soc., 81, 1068 (1959).

(5) A. Beckett and G. Porter, Trans. Faraday Soc., 59, 2038 (1963).

(6a) S. G. Cohen, S. Orman and D. Laufer, Proc. Chem. Soc., 301 (1960).
(b) J. Am. Chem. Soc., 84, 1061 (1962);(c)ibid., 84, 3905 (1962).

(7a) E. Bergmann and S. Fujise, Ann., 483, 65 (1930). (b) G. Ciamician and P. Silber, Ber., 44, 1554 (1911).

(8) G. S. Hammond and W. M. Moore, J. Am. Chem. Soc., 81, 6334 (1959).