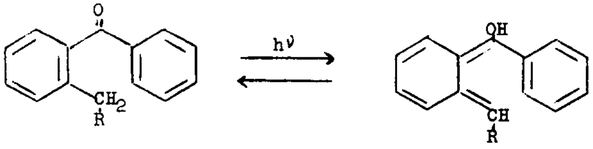
Tetrahedron Letters No.23, pp. 1863-1867, 1965. Pergamon Press Ltd.
Printed in Great Britain.

STRUCTURE OF THE YELLOW SPECIES FORMED ON IRRADIATION OF o-METHYLBENZOPHENONE. A LONG-LIVED ENOL

Edwin F. Ullman and K. R. Huffman
Central Research Division, American Cyanamid Company
Stamford, Connecticut

(Received 1 April 1965; in revised form 20 April 1965)

Yang and his co-workers have recently shown that o-methyl- and o-benzylbenzophenones (Ia and Ib) undergo reversible photo-enolization to give IIa and IIb (1). The occurrence of the reaction was demonstrated by incorporation of deuterium in the recovered ketone during irradiation in deuterio-methanol and by trapping experiments. A transient species (λ max. 405 mμ) having $\sim$10 sec. lifetime was obtained on flash photolysis of Ib in cyclohexane and was assigned the enol structure IIb (2).



I

a R=H
b R=C_6H_5
c R=CH_3

II

Apparently conflicting results have been reported by Beckett and Porter who, on flashing solutions of o-methyl- or o-ethylbenzophenone (Ia or Ic) in isopropyl alcohol, observed the formation of long-lived (> 1 hr.) yellow species (absorption at 340-440 mμ) to which they assigned the enol structures IIa and IIc (3). Although the reported sensitivity of these yellow species toward oxygen appears consistent with the enol formulations, it seemed unlikely to us that II, which could gain considerable aromatic resonance energy by ketonization, could possibly survive in a hydroxylic solvent for this period of time. We have therefore re-examined the mode of formation and chemistry of the yellow species and we report here evidence that the compound derived from Ia in fact has structure III.

Flash irradiation of a degassed 6×10^{-4}M solution of o-methylbenzophenone (*) did indeed produce the reported yellow color, λ max. 383 mμ, which faded only very slowly at room temperature ($t_{1/2} \approx 36$ hrs.). Upon addition of oxygen, this new peak completely disappeared in about 30 minutes although the original $n \rightarrow \pi^*$ absorption of the ketone at 334 mμ remained permanently obscured by generally increased absorption in this region. The presence of a new product in this solution was illustrated by the immediate formation of a characteristic intense yellow color (λ max. 458 mμ) on addition of a drop of 5N sodium hydroxide to the solution. By contrast, upon absorption by a similar degassed solution of Ia (5×10^{-3}M) at 25° of $> 10^4$ times as much light during 6 hours of continuous irradiation (1000 watt General Electric B-H6 lamp) no visually detectable color was produced, although a barely perceptible yellow color appeared on addition of air followed by alkali.

Since within a fraction of one half-life of the colored intermediate so much more light was absorbed in the continuous irradiation experiment than was absorbed during the flash irradiation, competitive thermal fading during continuous irradiation cannot account for the reduced rate of color formation. Rather the data appear to require

---

(*) The sample was contained in a 10 cm. quartz cell (2 cm. diameter) which was positioned as near as possible to one of two simultaneously fired 15.5 cm. long flash tubes spaced 15 cm. apart. Each tube had a 750 joule input and flash duration of ~30 μ sec. We gratefully acknowledge the advice and help of Dr. F. Halverson in the design and execution of this experiment.

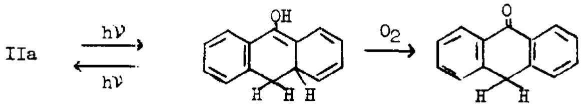
two successive photochemical reactions in which a short-lived transient may be converted in a second photochemical step to the yellow compound. The very slow rate of color formation is then due to a lower steady state concentration of this transient than in the flash experiment.

Confirmation of this hypothesis was obtained by brief (1-2 minutes) continuous irradiation of a degassed isopropyl alcohol solution of Ia at -80° (4) where the life-time of the presumed transient species would be lengthened. Under these conditions a deep yellow color formed, but upon warming the solution to 25°, it rapidly diminished, revealing itself as the expected transient. Moreover, a residual long-lived yellow color remained that was identical to that previously observed (λ max. 383 mµ). Substraction of this residual absorption from the spectrum of the deep yellow solution gave the transient absorption maximum, 400 mµ. The non-radical nature of this transient intermediate was indicated by the disappearance of a weak light-induced e.s.r. signal well in advance of the disappearance of the deep yellow color. Based on these observations, on the fact that Ia undergoes light-induced deuterium exchange, and on analogy with other photo-enolizable ketones (2,5), this transient species is almost certainly the photo-enol IIa.

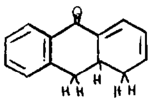
The 383 mµ species was found to arise from the enol IIa in a photochemically reversible process. Thus when the initially formed deep yellow solution at -80° was irradiated with light that was not absorbed by the ketone ($>$ 380 mµ), the deep yellow color partially faded, and, on warming, the solution remained more colored than when the second irradiation was omitted; i.e., the enol was converted to the 383 mµ species. On the other hand, on irradiation of a solution of this long-lived species at room temperature, the reverse reaction appeared to occur; the color faded, and, after addition of oxygen, the characteristic base-induced color formation was substantially reduced.

Efforts to prepare the long-lived yellow species in large amounts by increasing the length of irradiation were frustrated by this photochemical reversibility of the system. Thus even after seven hours of irradiation at -80° followed by warming and exposure to oxygen, > 95% of the starting material was recovered unchanged. However, by careful chromatography on silica it was possible to isolate about 1% of anthrone (IV). The anthrone was found spectroscopically to give the same alkali-induced color change as that of the irradiated and oxidized solutions of Ia. Since this color test indicated that the anthrone could not be formed by addition of oxygen if the 383 mμ species was first destroyed by light, it follows that the anthrone is an oxidation product of the colored species.

We believe that the above described reversible formation of the 383 mμ species from IIa coupled with its spontaneous oxidation to anthrone (IV) and its long wavelength absorption are uniquely accomodated by structure III. The reversible formation of III from the enol IIa has



III IV



V

ample analogy (6), and it is in accord both with the formation of apparently related species from Ib and Ic (3) and with the failure of o-methylacetophenone to give a related long-lived colored species even though it forms a labile colored species (photo-enol) at -80°. The alternative ketonic formulation V for the 383 mμ species does not provide a rationale for its reversible formation from IIa and does not accomodate the formation of an orange color (presumably an enolate) observed immediately upon addition of a drop of 5N sodium hydroxide to its unoxidized solutions. Moreover, structure V is inconsistent with the 383 μ absorption; cf. $C_6H_5CO(CH{=}CH)_2CH_3$ $\lambda^{C_2H_5OH}_{max.}$ 297 mμ (7). By contrast, correction of the longest absorption maximum of $C_6H_5(CH{=}CH)_2CH{=}CH_2$, 325 mμ (8), for the effect of a homocyclic diene, substituents, etc. (Woodward's rules) gives a calculated absorption for III of 379 mμ.

The remarkable stability of this enol in the hydroxylic solvent is probably due principally to the absence of catalytic ionic, acidic or basic contaminants which are generally present in non-photochemical reactions.

References

1. N. C. Yang and C. Rivas, J. Am. Chem. Soc., 83, 2213 (1961).
2. E. F. Zwicker, L. I. Grossweiner and N. C. Yang, ibid., 85, 2671 (1963).
3. A. Beckett and G. Porter, trans. Faraday Soc., 59, 2051 (1963).
4. For the design of the low temperature cell see J. G. Koren, J. S. Brinen and R. C. Hirt, Applied Optics, 3, 1431 (1964).
5. K. R. Huffman, M. Loy and E. F. Ullman, in press.
6. For a review of reversible photo-isomerization of 1,3-cyclohexadienes and 1,3,5-hexatrienes see O. L. Chapman in "Advances in Photochemistry," Vol I, Ed. by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., John Wiley & Sons, Inc. (1963), pp. 381-387.
7. R. Kuhn and H. A. Staab, Angew. Chem., 65, 371 (1953).
8. H. M. Walborsky and J. F. Pendleton, J. Am. Chem. Soc., 82, 1405 (1960).