Tetrahedron Letters No.34, pp. 3309-3310, 1967. Pergamon Press Ltd. Printed in Great Britain.

PHOTOCHEMICAL REACTION OF HINDERED AROMATIC KETONES[1]

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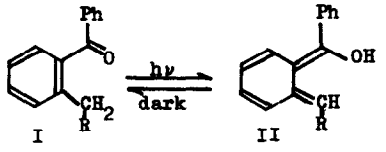
(Received 10 May 1967)

Irradiation of o-alkylbenzophenones (I) results in formation of photoenols (II), which revert to the parent ketones in the dark.[2] 2,5-Dimethylacetophenone also gives a corresponding photoenol, but is slowly converted into presumably a pinacol.[3] It appeared interesting to examine photochemical behaviors of highly hindered aromatic ketones, such as III, which might be difficult to photoenolize because of a steric hindrance.[4] We wish to report the first example of benzocyclobutanol formation from o-methylphenyl ketones and a fragmentation reaction.

In a typical run, irradiation of 2,4,6-trimethylisobutyrophenone[5a] (IIIc, 2.0 g.) in isopropyl alcohol (250 ml.) with a 450 w. high-pressure mercury lamp (Pyrex filter) under bubbling nitrogen for 48 hrs., yielded an isomeric alcohol (IVc, 61%), b.p. $75^{\circ}/10^{-4}$mm., and mesitoic acid (V, 7%), in addition to the recovery (25%) of the starting ketone. The infrared spectrum had a band at 3400 cm^{-1} (OH) but no carbonyl band. Signals were found in the n.m.r. spectrum (60 Mc.) at τ 3.35 (2H, singlet, aromatic proton), 6.75 and 7.20 (2H, AB quartet, J = 14 cps), 7.5-8.2 (1H, obscure septet, J = 6 cps, isopropyl proton), 7.75 and 7.80 (6H, two aromatic Me), and 8.95 and 9.15 (6H, doublets, J = 6 cps, isopropyl Me). On pyrolysis at 200°, the alcohol reverted to the starting ketone (IIIc) almost quantitatively. From the above results, a benzocyclobutanol structure (IVc) was given for the alcohol.

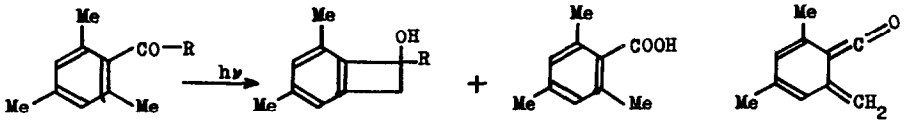
Under similar conditions, 2,4,6-trimethylacetophenone (IIIa)[5b] and 2,4,6-trimethylpropiophenone (IIIb)[5c] yielded corresponding benzocyclobutanols, IVa as crystals, m.p. 58-59°, in 70% yield, and IVb as an oil, b.p. $70^{\circ}/10^{-4}$mm., in 63% yield, respectively. These products rewerted to the starting ketones (III) on pyrolysis and their spectral properties were in agreement with the structures IVa and IVb. On the other hand, irradiation of 2,4,6-trimethylpivalophenone (IIId)[5d] yielded mesitoic acid (V) as the major products (48% in isopropyl alcohol and 46% in benzene), and at least six minor products were detected by thin-layer chromatography.

It can be rationalized that the photolysis of IIIa, IIIb, and IIIc results in cyclobutanol formation[6] rather than photoenolization which is sterically unfavorable. The more hindered a ketone is, the more the yield of mesitoic acid (V) increases. Although the origin of an extra oxygen atom of mesitoic acid formed is unknown at present,[7] it does not appear that the acid is formed *via* a ketene intermediate (VI) which should be led to an ester in isopropyl alcohol. Further mechanistic studies are in progress. Satisfactory analyses were obtained for all new compounds.



I II

IIIa, IVa R = Me
IIIb, IVb R = Et
IIIc, Ivc R = i-Pr
IIId, IVd R = t-Bu



III IV V VI

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(3) G. Wettermark, Photochem. Photobiol., 4, 621 (1965).

(4) In the n.m.r. spectra of the ketones III, the chemical shift of 2- and 6-methyl protons exhibits 0.2-0.3 ppm higher than that of the methyl protons of 2-methylbenzophenone. This indicates that the ketone group is highly hindered. Cf. K. Maruyama, Bull. Chem. Soc. Japan, 39, 2772 (1966).

(5) (a) A. Klages, Ber., 37, 928 (1904); (b) C. R. Noller and R. Adams, J. Am. Chem. Soc., 45, 1889 (1924); (c) A. Klages, Ber., 35, 2255 (1902); (d) H. Suzuki, H. Wada, K. Maruyama, and R. Goto, Bull. Chem. Soc. Japan, 39, 1201 (1966).

(6) The photochemical formation of cyclobutanols from ketones with γ-hydrogen atoms is well Known. See R. B. LaCount and G. E. Griffin, Tetrahedron Letters, 1549 (1965) and references cited therein.

(7) It may be possible that oxygen, which is contained in nitrogen gas, is incorporated into mesitoic acid. Incorporation of water is improbable since the irradiation was carried out under anhydrous conditions.