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PHOTOCHEMICAL DEMETHYLATION OF 2-METHOXYBENZOPHENONES

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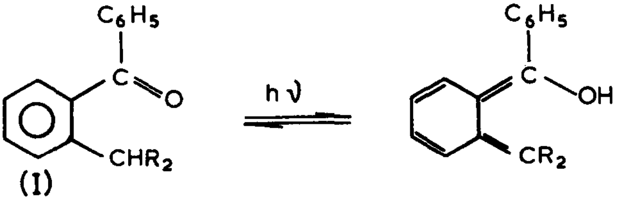
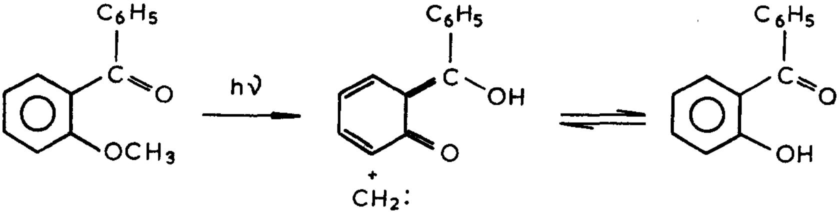
It is well known that 2-hydroxy- and suitable 2-alkyl-benzophenones (I) undergo reversible photoenolization in alcoholic and hydrocarbon solution (1-6). On the other hand, 2-methoxybenzophenone, although it has hydrogen in its 2-substituent, exhibits the normal photochemistry of benzophenones in these solvents, and forms the corresponding pinacol (4). In 2-methoxybenzophenone, tautomerism similar to that shown by the 2-alkyl-benzophenones (I) cannot occur without rupture of the aliphatic O-CH_3 bond (dissociation energy 70 Kcal/mole (7)) and hence, in alcohol for example, pinacol formation via hydrogen abstraction from the solvent is favoured. However, it seems possible that under conditions where hydrogen abstraction by the excited benzophenone molecule from the surrounding medium is impossible, as is the case in the solid state or in carbon tetrachloride solution, demethylation of 2-methoxybenzophenones (II) to 2-hydroxy-benzophenones (III) could occur. This has now been observed



with 2,5-dimethoxybenzophenone and 2,4,6-trimethoxybenzophenone in carbon tetrachloride solution, in benzene solution, and in cellulose acetate films.



(II) (IV) (III)

Under the same conditions 3- or 4- methoxy groups in benzophenones were not cleaved, confirming that the reaction has an intra-molecular mechanism.

The irradiations were carried out using an enclosed 1 Kw. carbon arc and samples were rotated around it at a distance of about 2 ft. Solutions were degassed by alternate freezing and thawing, and sealed in pyrex glass tubes under vacuum. The solid films were covered with pyrex glass sheets and were irradiated in air. Cellulose acetate films were chosen because they were easy to prepare and could be readily dissolved for product analysis.

Irradiation of 2,5-dimethoxybenzophenone (1.33g) in carbon tetrachloride (35 ml) for 400 hours gave a pale brown solution. Thin layer chromatography of this solution using diazotized sulphanilic acid as a detecting agent, indicated the presence of only one phenol, which was probably chelated since it moved well ahead of 2,5-dimethoxybenzophenone. The phenol was isolated by extraction with dilute (2%) aqueous sodium hydroxide and recrystallized from ethanol to give yellow plates of

2-hydroxy-5-methoxybenzophenone (40 mg., 3%), m.p. 81-82° (Lit., 84-85°) (8) (calculated for $C_{14}H_{12}O_3$:C, 73.67; H,5.30. Found: C, 73.47; H, 5.26). A mixed melting point with an authentic sample, prepared by aluminium chloride demethylation of 2,5-dimethoxybenzophenone, showed no depression. The infra-red and n.m.r. spectra of the photoproduct (A, Table I) were also identical with those of the authentic sample. The n.m.r. spectra (60 Mc.) showed peaks at 3.53 ppm. (3H), 6.83 and 7.40 ppm. (8H), and 11.37 ppm. (1H); attributable to one methoxyl group, eight aromatic protons, and a single chelated hydroxyl group. The hydroxyl signal was removed by addition of D_2O. Thin layer chromatography also indicated that some 2-hydroxy-5-methoxybenzophenone was formed when 2,5,-dimethoxybenzophenone was irradiated in cellulose acetate film and in benzene. None was detectable when 2,5-dimethoxybenzophenone was irradiated in ethanol.

TABLE I

Compound	N.M.R. Spectral Data (ppm.)		
2,5-Dimethoxybenzophenone	3.49(3H),3.66(3H) :	6.80,7.32,7.62 (8H) :	
Photoproduct A	3.53(3H)	: 6.83,7.40 (8H)	: 11.37(1H)
2,4,6-Trimethoxybenzophenone	3.63(6H),3.83(3H) :	6.13(2H) :	7.33,7.66(5H)
Photoproduct B	3.45(3H),3.83(3H) :	5.90,6.17(2H) :	7.4(5H)

Similarly, 2,4,6-trimethoxybenzophenone (2 g.) in carbon tetrachloride (35 ml.) gave 2,4-dimethoxy-6-hydroxybenzophenone in low yield (about 3%) (m.p. 97-98°, Lit., 98° (9)) as the only detectable phenolic product of irradiation (500 hr.). In addition to the signals due to the aromatic protons of the unsubstituted benzene ring (7.33 and 7.66 ppm.), the n.m.r. spectrum of 2,4,6-trimethoxybenzophenone showed sharp single peaks at 3.63 ppm. (6H), 3.83 ppm. (3H), and 6.13 ppm. (2H). These single peaks are respectively assignable to the 2- and 6-methoxyl groups, the 4-methoxyl group, and the two equivalent 3- and 5- hydrogen atoms between the methoxyl groups. In the n.m.r. spectrum of the phenolic photo-product (B, Table I), the hydroxyl signal was not discernible, but the methoxyl signals were now at 3.45 and 3.83 ppm. and were of equal intensity (3H each) showing that one of the 2-,6-methoxyl groups had been lost. Furthermore, the singlet which had been at 6.13 ppm. in 2,4,6-trimethoxybenzophenone was now separated into two doublets (2 x 1H; J = 2 cps.) at 5.90 and 6.17 ppm., indicating that the 3- and 5 protons were no longer equivalent. The compound was thus unequivocally 2,4-dimethoxy-6-hydroxybenzophenone.

The fate of the CH_2 fragment (IV) has not been established. When the tubes of carbon tetrachloride were first opened a sharp penetrating odour was noticed. Gas-liquid chromatography showed that there was present a compound more volatile than dichloromethane but less volatile than methane or methyl chloride, but its nature is still unknown.

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