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RESEARCH NOTES

PHOTOCHEMICAL ENOLIZATION IN *ORTHO* ALKYL SUBSTITUTED PHENYL-ALKYL-KETONES

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THE PHOTOCHEMICAL enolization of *ortho* alkyl substituted benzophenones has been described by Yang and Rivas.⁽³⁾ Zwicker *et al.*⁽⁴⁾ demonstrated furthermore that the photochemical formation of the enol of *o*-benzylbenzophenone proceeds with the triplet as intermediate. Evidence is presented here for keto-enol tautomerization in other aromatic compounds besides benzophenone derivatives.

2,4-Dimethylacetophenone (I) in CH₃OD, 99 per cent isotopic purity (Volk Radiochemical Company), yields an NMR spectrum recorded on a Varian A-60 with resonances due to 'aromatic hydrogens' in the interval δ (ppm)=7.0-7.7 and three well separated methyl proton resonances, one narrow at δ (ppm)=2.47, and two broader at δ (ppm)=2.42 and 2.27, all with reference to TMS. The two broader peaks, at δ (ppm)=2.42 and 2.27, are attributed to the methyl groups substituted on the phenyl ring. Initially the ratio between the integrated intensities of these three methyl peaks was 1.0:1.0:1.0 and no change took place when the solution was left standing in the dark. Irradiation of I in CH₃OD with u.v. light from a high pressure mercury lamp produced a decrease in the δ (ppm)=2.42 peak. When the compound was separated from the reaction mixture by preparative gas chromatography* and redissolved in CH₃OD, the spectrum appeared identical to the one observed for the unirradiated solution, except for this band at δ (ppm)=2.42, which was broadened and showed a decrease in intensity. For the sample given the highest dose of ultraviolet light, integrated intensities for the three peaks at δ (ppm)=2.47, 2.42 and 2.27, now yielded the ratio 1.0:0.6:1.0. The infrared spectrum of the isolated, irradiated compound recorded in the form of an oil between KBr plates showed on a Beckman IR 9 spectrophotometer a new band at 2190 cm⁻¹. (Unirradiated compound in CH₃OD showed no changes in NMR and IR spectra).

2,5-Dimethylacetophenone (II) showed similar changes after irradiation in CH₃OD and isolation. In this case the unirradiated compound gave a narrow aliphatic methyl proton resonance at δ (ppm)=2.47 and two broader bands showing triplet splitting for the methyl groups attached to the benzene nucleus at δ (ppm)=2.36 and 2.28. The ratio of the

* Aerograph Autoprep A700, Wilkens Instrument and Research, Inc., Walnut Creek, California. Column: 30% Carbowax 20 M, length 10ft., diam. $\frac{3}{16}$ in., temp. 230°C, Carrier: Helium, Flow rate. 20 ml. min⁻¹.

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integrated intensities of these bands, which for an unirradiated sample was 1.0:1.0:1.0 became 1.0:0.7:1.0 for an irradiated sample. Also irradiation produced a new band in the infrared spectrum at 2200 cm^{-1} .

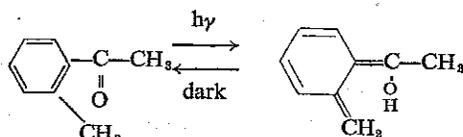
The new infrared bands at around 2200 cm^{-1} are attributed to C-D stretching frequencies. This assignment coupled with the decreased intensities of the NMR band indicates that the irradiation produces hydrogen-deuterium exchange in one of the methyl groups attached to the benzene ring.

The gas chromatographic separation shows that irradiation with ultraviolet light also causes partial consumption of the samples to form photoproducts, presumably due to pinacol-type reactions.^(1,2)

2-Methylbenzaldehyde (III) was also investigated for hydrogen-deuterium exchange but in this case the photodecomposition consumed most of the compound at doses of ultraviolet light comparable to those given to the acetophenone derivatives and it was not possible to recover enough compound for analysis by the above techniques.

Ethanol solutions of 2,4-dimethylacetophenone (I), 2,5-dimethylacetophenone (II), 2-methylbenzaldehyde (III), acetophenone (IV), and benzaldehyde (V) were investigated at near liquid nitrogen temperature. In the case of I, II and III, u.v. irradiation caused the solutions to turn deeply yellow. The color reversibly disappeared upon melting the glass. No yellow species was formed from IV and V.

The results suggest that I and II isomerize as follows:



The yellow species observed at near liquid nitrogen temperature appears to be the enol-form, and the enolization gives rise to hydrogen-deuterium exchange in the *ortho* methyl group of the keto-form when irradiated in a solvent with 'exchangeable' deuterium. In the case of III, which possesses a hydrogen in place of the methyl group adjacent to the carbonyl group, the yellow species is probably also an enol isomer but at room temperature, at least, irreversible photochemical reactions seem to predominate. It appears that photoactivated carbonyl groups can abstract hydrogen in an intramolecular reaction when the compound has a "donatable" hydrogen in the immediate proximity of the carbonyl group. In the case of the compounds I, II and III such a configuration arises from the *ortho* alkyl group, which may allow transfer *via* a six membered ring.

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