

The Photochromic Property of *ortho*-Alkyl Aromatic Imines

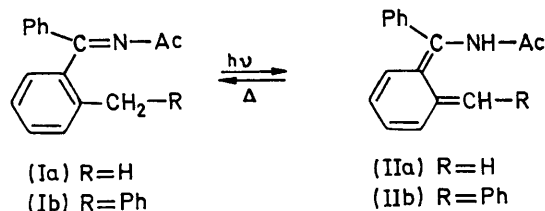
By NAOKI TOSHIMA, MASARU SAEKI, and HIDEFUMI HIRAI*

(Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo 113, Japan)

Summary *N*-Acetyl-*o*-(methyl or benzyl)methaneimine was found to be a new type of photochromic compound, which isomerises photochemically to enamide by an intramolecular hydrogen transfer.

THE photochemical isomerisation of *o*-alkylbenzophenones has been extensively studied,^{1,2} but the corresponding imino-compounds have received little attention. *N*-Acetyldiphenylmethaneimine is readily reduced photochemically, in the presence of a hydrogen-donating alcohol or ether, to give *N*-acetyldiphenylmethylamine by an intramolecular hydrogen transfer,³ and in the presence of alkene or alkyl benzene to give the adduct of alkene⁴ or alkyl benzene⁵ to C=N.

We expected that *o*-alkyl aromatic imino-derivatives would isomerise by an intramolecular hydrogen transfer. Here we report that *o*-alkyl aromatic imines photochemically isomerise to enamide derivatives by a hydrogen transfer; they are a new type of photochromic compound.



SCHEME

On irradiation of a solution of (Ia)† at room temperature, no change was observed. At 77 K, in a dry propan-2-ol-methanol (1:1) glass, there was a change in the electronic absorption spectrum owing to the formation of (IIa) (Scheme). After a few minutes irradiation (through a glass filter) new absorption bands appeared in the visible

region, as shown in the Figure, which were stable at this temperature, but not at room temperature. The resulting spectrum was identical to that of (Ia). When methyl-

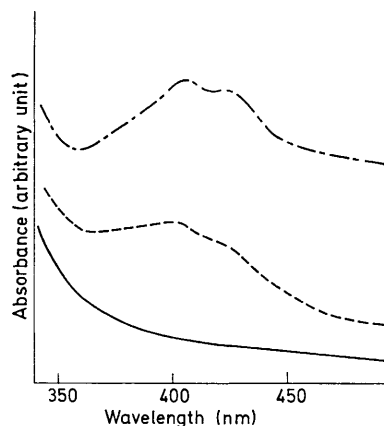


FIGURE. The electronic spectrum of *N*-acetyl-*o*-methyl-diphenylmethaneimine (Ia) in propan-2-ol-methanol (1:1) (ca. 0.1 M) at 77 K. — before irradiation; - - - after irradiation for 5 min.; - · - · after irradiation for 60 min.

cyclohexane-toluene (1:1) was used similar spectra were obtained (λ_{\max} , 405 and 430 nm).

The spectrum of (IIb) either in propan-2-ol-methanol (1:1) or in methylcyclohexane-toluene (1:1) showed a red shift in comparison with that of (IIa) (λ_{\max} , 430 and 480 nm). The λ_{\max} values of these photochemical isomers are comparable with those reported for *o*-alkylbenzophenones.³

This light-induced imine-enamine isomerisation was further confirmed by irradiating a solution of (Ib) in CH₃OD for 8 h, when the recovered (Ib) was found by n.m.r. and mass spectroscopy to contain 0.4 atom of deuterium per molecule. N.m.r. analysis also showed that the deuterium was located at the benzylic position.

† *o*-Alkyl aromatic imines were prepared from the corresponding nitriles and Grignard reagents. *N*-Acetylation was carried out in the usual manner with acetic anhydride. Satisfactory analyses and spectral data were obtained for all compounds.

Exposure of colourless solutions of (I) to visible light at dark at this temperature. Further mechanistic investigations are in progress. *ca.* -120°C caused rapid formation of yellow to red coloured species. The colour faded in a few seconds in the

(Received, September 1st, 1971; Com. 1525.)

¹ N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213; E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *ibid.*, 1963, **85**, 2671.

² K. R. Huffman, M. Loy, and E. F. Ullman, *J. Amer. Chem. Soc.*, 1965, **87**, 5417.

³ T. Okada, M. Kawanisi, H. Nozaki, N. Toshima, and H. Hirai, *Tetrahedron Letters*, 1969, 927; A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, 1969, **91**, 2653; B. Fraser-Reid, A. McLean, and E. W. Usherwood, *Canad. J. Chem.*, 1969, **47**, 4511.

⁴ N. Toshima, S. Asao, K. Takada, and H. Hirai, *Tetrahedron Letters*, 1969, 5123.

⁵ N. Toshima, S. Asao, and H. Hirai, unpublished results.