Tetrahedron Letters No. 42, pp 3707 - 3710, 1974. Pergamon Press. Printed in Great Britain.

THE PHOTOCHEMICAL FORMATION OF KETIMINES FROM AROMATIC KETOXIMES

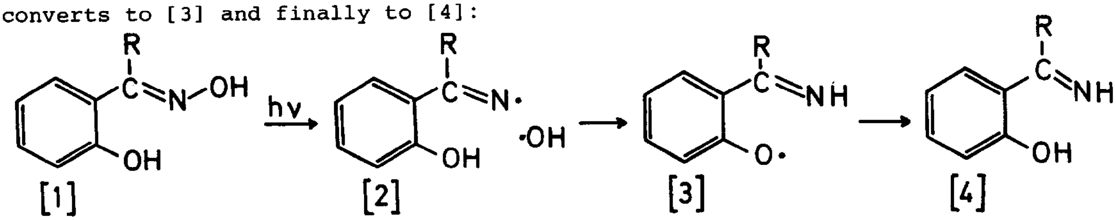
K.H. Grellmann and E. Tauer*
Max-Planck-Institut für Biophysikalische Chemie
Abt. Spektroskopie, D 34 Göttingen, Germany

(Received in UK 19 August 1974; accepted for publication 4 September 1974)

We have been investigating the photochemical reactions of o-hydroxyacetophenone oxime [1a] and some related compounds. Formation of 3-methyl benzisoxazole, 2-methyl benzoxazole, and o-hydroxyacetophenone from [1a], and of benzisoxazole, benzoxazole, salicylonitrile, and salicylaldehyde from [1d] has been observed by us (1) and in other laboratories (2). A more detailed study of the mechanism of these reactions will be published elsewhere. In this paper we wish to report still another photoreaction, namely the formation of o-hydroxyacetophenone imine [4a] which has not yet been described in the literature.

The reaction does not depend on light intensity and solute concentration, and only slightly on solvent polarity. It was observed in degassed and undegassed methylcyclohexane (MCH), benzene, diethylether, propanol-2, ethanol, methanol, water and acetonitrile. Some chemical yields and quantum yields are listed in Table 1. In carbon tetrachloride and chloroform the chemical yield is very small, in dichloromethane it is practically zero. In water and water-containing solvents the ketimines hydrolyse to ketones and ammonia. The halflife is 40 min in water at room temperature in the case of [4a].

The first photoproduct after excitation is presumably the radical [2] which converts to [3] and finally to [4]:



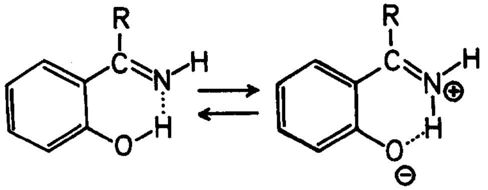
R: a = $-CH_3$; b = $-C_6H_5$; c = $-(o\text{-}OH)C_6H_4$; d = $-H$;

The dimerization of [2] to the corresponding azine does not occur. Okada et al. (3) observed it in the case of acetophenone oxime ester, which does not contain the o-hydroxygroup. The occurence of an •OH radical during illumination of a solution of [1a] has been shown by means of e.s.r. spectroscopy. Reaction [1a] → [4a] takes also place in the solid state if one illuminates crystals of [1a] between two glass plates.

From o-hydroxybenzophenone oxime [1b] the stable syn- and anti forms are known (4) (syn and anti with respect to the hydroxyphenyl group). By means of uv spectroscopy one can show that only the anti form yields the ketimine [4b]. In the case of o-hydroxyacetophenone oxime only one isomer is stable, which is according to I.Murase (5) the anti form [1a]. Since its conversion to [4a] is independent of light intensity photochemical isomerization to a thermally instable syn form cannot be a prerequisite for the reaction.

It is easy to detect the ketimines [4] in the reaction mixture after illumination of a solution of [1] because of the strong solvent dependence of the absorption spectra of these compounds. In nonpolar solvents the long wavelength peaks of [4] are located around 320 nm, in polar solvents they are shifted to about 400 nm, a wavelength region where neither [1] nor all the other photoproducts mentioned above absorb. The shift is due to the zwitterionic from [6] which is more stable in a polar medium. Thus, formation of [4] in a nonpolar solvent can easily be detected by diluting the reaction mixture with propanol-2 after illumination.

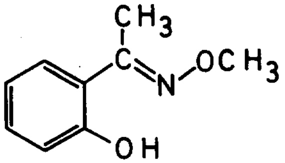
λ_{max} (MCH)
4 a = 323 nm
4 b = 327 nm
4 c = 324 nm



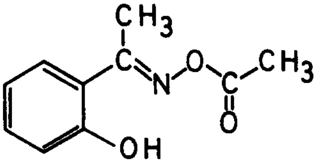
[5] [6]

λ_{max} (propanol-2)
4 a = 395 nm
4 b = 412 nm
4 c = 406 nm

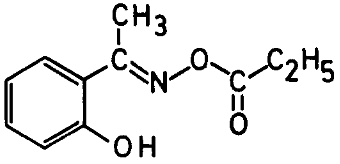
The oxime ether [7] and the esters [8] and [9] also yield ketimine [4a]. In the latter two cases a very interesting additional reaction occurs, in which carbon dioxide is evolved during irradiation and the alkyl part of the ester group is substituted into the phenyl ring:



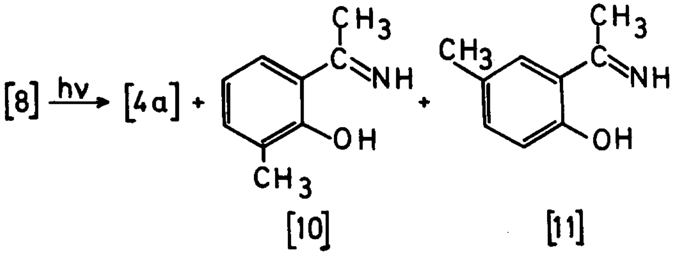
[7]

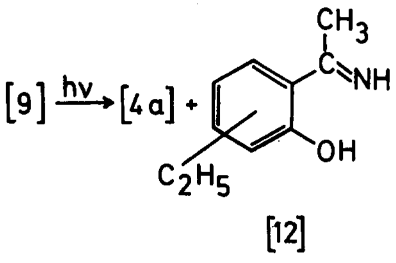


[8]



[9]





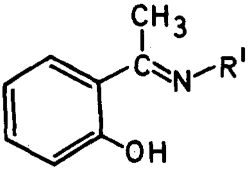
Compounds [4a], [4b], [4c], [10], and [11] have been identified by comparison with authentic samples, [12] by uv and mass spectrometry. In the last case the position of the ethyl group has not yet been determined. In addition the mixture of [4a], [10], and [11] was hydrolysed and the gas chromatograms of the resulting ketones compared with authentic samples. The ketimines were prepared by saturating a solution of 10 g ketone in 100 ml absolute methanol at -20° with dry gaseous ammonia. After standing over night at room temperature yellow crystals precipitated which were recrystallized from MCH. All substances gave the correct elemental analysis and the exact mass spectrometrically determined molecular weight. Melting points: [4a] = 139; [4b] = 100; [4c] = 225 - 230 (dec.) ; [10] = 147; [11] = 168 - 171 °C. We did not succeed in synthesizing salicyl aldimine [4d] thermally. Under the above mentioned conditions a white, insoluble substance with high molecular weight is formed. The photoproduct of salicylaldoxime [1d] was therefore only identified by the characteristic solvent dependence of its absorption spectrum.

Table 1

Solvent	o-hydroxyacetophenone oxime		o-hydroxyacetophenoneacetyl oxime*		p-hydroxyacetophenone-O-methyl oxime	
	chem. yield	quantum yield	chem. yield	quantum yield	chem. yield	quantum yield
propanol-2	46	2	48	8	64	12 %
MCH	82	5	57	10	58	13 %

*overall yield for the mixture of [4a], [10], and [11].

Derivatives containing a -N-N- bond instead of a -N-O- bond, such as the hydrazones [14 a-c], the semicarbazone [14d] and the aminoguanidine [14e]



[14]

R': a = $-NH_3$ b = $-N(CH_3)_2$

c = -NHPh   d = $-NH\underset{\underset{O}{\|}}{C}NH_2$

e = $-NH-\underset{\underset{NH}{\|}}{C}-NH_2$

do not yield the ketimine [4a].

REFERENCES

(1a) K.H. Grellmann and E. Tauer, Tetrahedron Lett., 1967, 1909

(1b) E. Tauer, Ph. d. Thesis, Erlangen 1969

(2) J.P. Ferris and F.R. Antonucci, J.Amer.Chem.Soc.,96,2010 (1974)

(3) T. Okada, M.Kawanisi and H. Nozaki, Bull.Chem.Soc.Jap.,42,2981(1969)

(4) J. Meisenheimer and O. Dorner, Ann., 502,156 (1933)

(5) I. Murase, Mem.Fac.Sci.Kyushu Univ. Ser. C4,183 (1961)