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Photolysis of Aromatic Oxime Benzoates

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Irradiation of aromatic oxime benzoates, $R^1R^2C{=}N{-}OCOPh$, in benzene solution gives the corresponding azines, $(R^1R^2C{=}N{-})_2$, and ketones, $R^1R^2C{=}O$, along with $PhCO_2NH_4$. $PhCO_2H$ and Ph_2 are also obtained in all cases. The reaction course can be explained by assuming a radical fission of excited $R^1R^2C{=}N{-}OCOPh$ which gives radicals $R^1R^2C{=}N\cdot$ and $\cdot OCOPh$ in the initial step. Sensitization experiment establishes the fact that a triplet state of the oxime benzoate is involved as a chemically reactive species.

Considerable interest has been focused on the photochemical rearrangement of enol esters, in which the acyl group migrates from oxygen to the vinylic carbon atom.[1)] In continuation of our recent investigation on the photochemistry of *N*-acylketimine as an aza-analog of α,β-enone system,[2)] we have studied the photochemical reaction of certain oxime benzoates,[*1,*2] which may be regarded as an aza-analog of enol benzoate and expected to rearrange photochemically in analogous manner. Actually, however, the reaction took place quite differently as described below.

Irradiation of a benzene solution of acetophenone oxime benzoate (Ia) was effected by means of 300 W high pressure mercury arc (Pyrex jacket) under N_2 atmosphere at room temperature. Chromatographic separation on silica gel column afforded acetophenone azine (IIa) (49%), acetophenone (IIIa) (30%), benzoic acid (9%) and diphenyl (11%). Ammonium benzoate (IV) (9%) deposited on the wall during the irradiation.

Irradiation of other oxime benzoates (Ib—d) was effected in the same way. The possible reaction sequences are given in Scheme 1 and the products isolated are summarized in Table 1. Ammonium benzoate (IV) was obtained in the photolysis of *p*-methylacetophenone oxime benzoate (Id) as well, which indicated that this had arisen from the benzoyloxy group of the original oxime benzoates.

Inspection of Table 1 leads to the conclusion that the photochemical primary step is the cleavage of N–O bond and all the products isolated may be ascribed to the imino radical (V) and benzoyloxy radical (VI). Recombination of radicals V yields azine II and abstraction of hydrogen even from benzene[5)] gives the ketimine of the type $R^1R^2C{=}NH$ (VII), which possibly produces the corre-

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[*1] Photochemistry of oximes presents several interesting points. For details, see Ref. 3.

[*2] As the *syn-anti* isomerization of the parent oximes has been reported to occur by the effect of ultraviolet illumination,[4)] the same behavior could be expected in the present system. No attempt has been made to observe this kind of isomerization, as irradiation was conducted up to the complete disappearance of the strating I.

1) a) R. A. Finnegan and A. W. Hagen, *Tetrahedron Letters*, **1963**, 365. b) M. Feldkimel-Gorodetsky and Y. Mazur, *ibid.*, **1963**, 369. c) A. Yogev, M. Gorodetsky and Y. Mazur, *J. Am. Chem. Soc.*, **86**, 5208 (1964). d) M. Gorodetsky and Y. Mazur, *ibid.*, **86**, 5213 (1964). e) M. Gorodetsky and Y. Mazur, *Tetrahedron*, **22**, 3607 (1966). f) V. I. Stenberg, "Advances in Organic Photochemistry," ed. by O. L. Champan, Vol. 1, Marcel-Dekkar, New York (1967), p. 141.

2) T. Okada, M. Kawanisi, H. Nozaki, N. Toshima and H. Hirai, *Tetrahedron Letters*, **1969**, 927.

3) a) T. Oine and T. Mukai, *ibid.*, **1969**, 157. b) G. Just and L. S. Ng, *Can. J. Chem.*, **46**, 3381 (1968). c) H. Izawa, P. de Mayo and T. Tabata, *ibid.*, **47**, 51 (1969).

4) G. Ciamician and P. Silber, *Ber.*, **36**, 4268 (1903).

5) S. S. Hirsch, *J. Org. Chem.*, **32**, 2433 (1967).

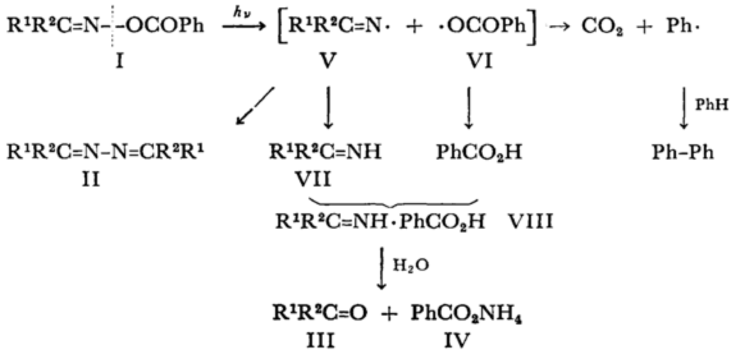

TABLE 1. YIELDS IN MOLE % OF PRODUCTS OF THE PHOTOLYSIS OF OXIME BENZOATES

Oxime benzoate	R^1	R^2	Azine[a)]	Ketone	$PhCO_2NH_4$	$PhCO_2H$	Ph_2
Ia[b)]	Ph	Me[c)]	IIa[d)] 49	IIIa 30	13	9	11
Ib[e)]	Ph	Ph[f)]	IIb[g)] 43	IIIb 33	9	4	21
Ic[h)]	Ph	H	IIc tr[i)]	— —[k)]	12	25	20
Id[l)]	p-Me-C_6H_4	Me	IId[m)] 50	IIId 27	10	14	13
Ia[n)]	Ph	Me	IIa[d)] 49	IIIa 26	15	20	12

a) Authentic samples were prepared by treatment of the corresponding carbonyl compounds with hydrazine sulfate in the presence of equimolar amount of alkali according to the published method.[d,g,j,m)] Photoproducts were identical with the authentic ones with respects to mps, IR spectra and R_f values in TLC.

b) Mp 98—99°C (from ethanol) (lit, 98—100°C; K. von Auwers and H. Müller, *J. prakt. Chem.*, **137,** 81 (1933)).

c) Trace amount of benzonitrile was detected by vpc. Carbon dioxide was detected by aqueous calcium hydroxide.

d) Mp 122—123°C (from ethanol) (lit, 124°C; G. Knopfer, *Monats. Chem.*, **30**, 29 (1909)).

e) Mp 99—100°C (from ethanol) (lit, 98—99°C; A. W. Chapman and C. C. Howis, *J. Chem. Soc.*, **1933,** 806.

f) Benzanilide (18%) was also obtained.

g) Mp 160—161°C (from ethanol) (lit, 162°C; T. Curtius and F. Rauterberg, *J. prakt. Chem.*, (**N**)**44**, 192 (1891)).

h) Mp 99—100°C (from ethanol) (lit, 101—102°C; G. Minnuni and G. Corselli, *Gazz. chim. ital.*, **22**, 164 (1892); *Chem. Zentr.*, **63**, 905 (1892)).

i) A spot of same R_f value (0.80) with the authentic sample[j)] was visualized in TLC.

j) Mp 92—93°C (from ethanal) (lit, 93°C; T. Curtius and R. Ray, *J. prakt. Chem.*, (**N**)**39**, 27 (1889)).

k) Benzoic acid would partly originate from benzaldehyde which is oxidized during the work-up.

l) Mp 88—89°C (from ethanol) (Found: C, 75.8; H, 5.9; N, 5.3. Calcd for $C_{16}H_{15}NO_2$: C, 75.9; H, 6.0; N, 5.5%).

m) Mp 132—133°C (from ethanol) (lit, 136°C; T. Curtius and K. Kopf, *J. prakt. Chem.*, (**N**)**86**, 113 (1912)).

n) Benzophenone-sensitized reaction by means of light of wavelength longer than 350 nm using 10% $CuSO_4$ aq. as a filter solution.

sponding ketone III during chromatography on silica gel column.[6),*3] Radical VI decomposes to carbon dioxide and phenyl radical[8)] which attacks the solvent benzene to give diphenyl.[8)] An alternative reaction of radical VI is the hydrogen abstraction to form benzoic acid.[9)]

Under anhydrous condition an equimolar mixture of benzoic acid and VII ($R^1=R^2=$Ph) is reported to form a salt, *viz.*, diphenylketimine benzoate (VIII).[10)] Ammonium benzoate (IV) is explained by the reaction of benzoic acid with ammonia which is generated by hydrolysis of VII or alternatively by the hydrolysis of VIII during irradiation and subsequent treatment. The assumption is

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6) P. A. S. Smith, "Open-chain Nitrogen Compounds," W. A. Benjamin, Inc., New York (1965), p. 297.

[*3] Silica gel contains 7% free water physically absorbed. See Ref. 7.

7) K. R. Lenge, *Chem. & Ind.* (London), **1968**, 441.

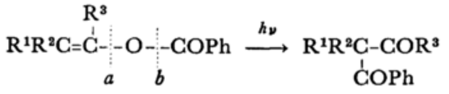
8) W. A. Pryor, "Free Radicals," McGraw-Hill, Inc., New York (1966), p. 253.

9) *Ibid.*, p. 91.

10) D. F. Lynch and J. D. Reid, *J. Am. Chem. Soc.*, **55,** 2515 (1933).

supported by the fact that the intended addition of a small amount of water into an equimolar mixture of benzoic acid and VII ($R^1=R^2=Ph$) in a benzene solution afforded IV and IIIb in a quantitative yield after standing overnight. Photolysis of Ib gave benzanilide in an 18% yield besides the normal products, but the origin is not certain yet.

A priori photocleavage of enol benzoates (IX) can proceed on both C–O bonds at *a* and *b*, but fission occurs exclusively at *b* to afford X through recombination in a solvent cage.[1] The present system



$$R^1R^2C{=}\overset{R^3}{C}\underset{a}{\vdots}O\underset{b}{\vdots}COPh \xrightarrow{h\nu} R^1R^2\underset{COPh}{C}-COR^3$$

IX X

as an aza-analog of IX is characterized by the absence of participation of benzoyl radical, the fission exclusively occuring at the N–O bond. This is not surprising in view of the bond energies of N–O and C–O bonds calculated as 53 and 85.5 kcal/mol, respectively.[11] The preference of rupture at N–O bond can be considered as prevailing in the photochemical reaction of compounds containing $>$C=N–O– system, such as isoxazoles,[12] benzisoxazoles,[13] oxadiazoles[14] and anthranils.[15]

The benzophenone-sensitized reaction of Ia was induced by the light of wavelength longer than 350 nm*4 to afford the same products in almost same product distributions as in the case of direct photolysis (Table 1). This strongly suggests that a triplet state acts as a chemically reactive species in the photochemical reaction of the oxime benzoates I.

Experimental

All melting points were taken in capillaries and were uncorrected. The TLC was performed on silica gel G using benzene-ethyl acetate (10 : 1) as an eluent and the spots were visualized with iodine vapor. The UV spectra were obtained in ethanol on a Hitachi EPS-2 recording spectrophotometer.

Materials. Oxime benzoates (Ia—d) were prepared by benzoylation of the corresponding oximes by means of benzoyl chloride in the presence of excess pyridine. All the oxime benzoates were recrystallized several times from ethanol and had the same melting points as reported in the literature cited in the footnotes of Table 1.

General Procedure for Irradiation. Unless otherwise stated, experiments were conducted with the solutions of I (10 mmol) in benzene (300 m*l*) by means of immersion-type 300 W high pressure mercury arc (Pyrex jacket for water-cooling) under N_2 atmosphere at room temperature. The progress of the reaction was monitored by TLC analysis of the aliquots. After the starting materials had been completely consumed (*ca.* 50 hr) and the depositing solid was removed by filtration, the filtrate was concentrated *in vacuo* and the residue was chromatographed on silica gel. The products isolated are listed in Table 1.

Irradiation of Ia in the Presence of Benzophenone. A solution of Ia (2.40 g, 10 mmol) in benzene (200 m*l*) containing benzophenone (0.90 g, 5 mmol) was irradiated by light of wavelength longer than 350 nm (10% $CuSO_4$ aq. as a filter solution) under N_2 atmosphere at room temperature for 20 hr. Only benzophenone absorbs the incident light, as Ia has no absorption in this region. The reaction mixture was concentrated *in vacuo* and chromatographed on silica gel column. The products isolated are shown in Table 1. Unchanged benzophenone was recovered quantitatively.

A solution of Ia in benzene was also irradiated in the same manner as a reference. TLC examination of the reaction mixture indicated the complete recovery of Ia.

The Reaction of Benzoic Acid and Diphenylketimine in the Presence of Water. A solution of benzoic acid (1.22 g, 10 mmol) and diphenylketimine[16] (1.81 g, 10 mmol) in benzene (100 m*l*) was added with water (2 m*l*) under vigorous stirring and allowed to stand overnight. Ammonium benzoate IV (1.30 g, 95%) separated as a crystalline mass, which was collected by filtration and the filtrate was dried (Na_2SO_4) and evaporated. The residue was distilled at 120°C/2 mmHg to afford benzophenone.

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[11] J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York (1964), p. 77.

[12] a) E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966). b) D. W. Kurtz and C. H. Schechter, *Chem. Commun.*, **1966**, 689. c) H. Göth, A. R. Gagneux, C. H. Eugster and H. Schmid, *Helv. Chim. Acta*, **19**, 137 (1967).

[13] H. Göth and H. Schmid, *Chimia*, **20**, 148 (1966).

[14] H. Newman, *Tetrahedron Letters*, **1968**, 2417, 2421.

[15] M. Ogata, H. Kano and H. Matsumoto, *Chem. Commun.*, **1968**, 397.

*4 The oxime benzoates had no absorption above 350 nm, but exhibited the following absorptions:

Ia: λ_{max} (EtOH) 254 nm (log ε 4.33) and λ 280 nm (log ε 3.83).

Ib: λ_{max} (EtOH) 263 nm (log ε 4.32) and λ 280 nm (log ε 4.15).

Ic: λ_{max} (EtOH) 261 nm (log ε 4.42) and λ 280 nm (log ε 4.09).

Id: λ_{max} (EtOH) 262 nm (log ε 4.46) and λ 280 nm (log ε 4.21).

[16] P. L. Pickard and T. L. Tobbert, "Organic Syntheses," Vol. 44, p. 51 (1964).