Photochemistry of α-Oxo-oximes. Part 5.[1] Photolysis of 3-Ethoxyiminobutan-2-one

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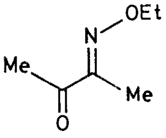
The photolysis of 3-ethoxyiminobutan-2-one (1) with λ 254 nm has been investigated using cyclohexane and acetonitrile as a solvent. Photo-excited (1) undergoes N–O bond homolysis with formation of an α-oxo-iminyl and an ethoxyl radical. The α-oxo-iminyl radical undergoes β-scission with formation of acetonitrile, or recombines with an acetyl radical to yield the *N*-acetyl-α-oxo-imine (17). Mechanisms for the photoformation of a number of the nitrogen containing products from this presumed intermediate (17) are proposed. The ethoxyl radicals yield formaldehyde, acetaldehyde, ethanol, and butane-2,3-dione. A correlation between the amounts of these products, based on the reaction steps proposed for their formation, was found to hold for the initial stages of the photolysis. In acetonitrile as solvent 77% of the ethoxyl radicals disproportionate, 18% react by hydrogen abstraction, and 5% by β-scission.

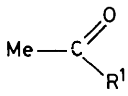
α-OXO-OXIMES and derivatives undergo photoisomerization and photodecomposition. Previously, we reported on the photoisomerization of α-oxo-oximes,[1] their acetates,[1] and ethyl ethers.[2] The photodecomposition of α-oxo-oxime ethers is slow upon irradiation with λ 313 and 366 nm relative to the photoisomerization.[2] However, irradiation with λ 254 nm was found to lead to a fast photodecomposition. In this paper we describe the photolysis of 3-ethoxyiminobutan-2-one (1) with λ 254 nm.



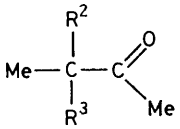
(*E*) - (1)

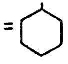
MeCN
(2)

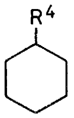
EtOH
(3)

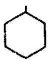


(4) $R^1 = H$
(5) $R^1 = COMe$
(6) $R^1 = NHCOMe$
(7) $R^1 = NH_2$



(8) $R^2 = NHCOMe$, $R^3 = H$
(9) $R^2 = NHCOMe$, $R^3 = COMe$
(10) $R^2 = NHCOMe$, $R^3 =$ 
(11) $R^2 = COMe$, $R^3 = OH$



(12) $R^4 = COMe$
(13) $R^4 =$ 
(14) $R^4 = NHCOMe$

HCHO
(15)

CH_4
(16)

RESULTS

Irradiation of a degassed solution of (*E*)-(1) in cyclohexane (0.09M) with λ 254 nm leads to the formation of acetonitrile (2), ethanol (3), compounds (4)—(6) and (8)—(10), and the cyclohexyl derivatives (12)—(14).† Initially a small amount of the (*Z*)-isomer of (1) is formed as well, but the photodecomposition of both (*E*)- and (*Z*)-(1) is faster than their photo-interconversion.

Irradiation of (*E*)-(1) in acetonitrile (0.35M) with λ 254 nm leads to the formation of (3)—(9), (11), and formaldehyde (15), together with traces of methane (16). The yields of the relatively volatile products for the two solvent systems are in the Table. The major products of higher molecular weight for cyclohexane as solvent are (10), (12), and (13), and for acetonitrile (7)—(9) and (11). For cyclohexane the (8) : (9) : (10) product ratio is 1 : 1 : 20, whereas for acetonitrile the (8) : (9) ratio is 1 : 2.

The dependence of the yields of the more volatile products on the irradiation time for acetonitrile as solvent is shown in Figure 1. For cyclohexane as solvent the photoconversion of (*E*)-(1) was monitored u.v. spectroscopically at its π–π* absorption band (Figure 2). Its extinction at $\lambda_{max.}$ 234 nm decreases strongly upon irradiation but its maximum remains at the same wavelength. Considering

Product yields after complete photolysis of 3-ethoxyiminobutan-2-one with λ 254 nm

Product	Yield (%) [a]	
	Cyclohexane	Acetonitrile
(2)	49	*b*
(3)	54	46
(4)	26	13
(5)	8	6
(15)	*c*	2

[a] The yields were corrected for differences in the g.l.c. response factors and the molecular weights. [b] The product is identical with the solvent. [c] No analysis was made for this product.

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† In a non-degassed solution the photo-oxidation products cyclohexanol, cyclohexanone, and cyclohexyl acetate are also formed.

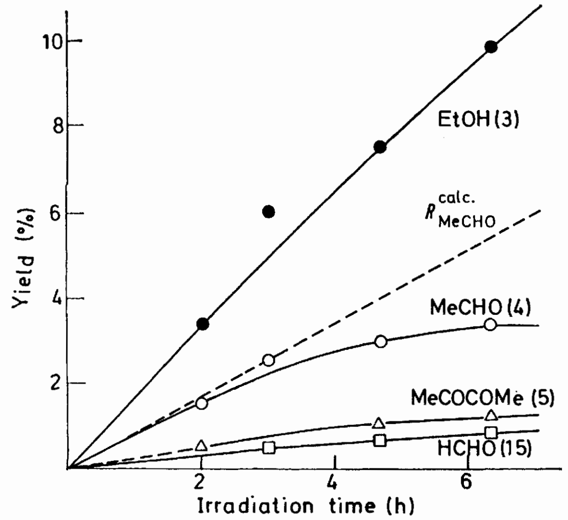
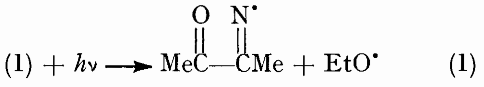


FIGURE 1 The photolysis of 3-ethoxyiminobutan-2-one in acetonitrile with λ 254 nm; product yields *versus* irradiation time

the u.v. data of the π–π^* absorption of (*E*)-(1), $\lambda_{max.}$ 234 nm (ε 10 800) and (*Z*)-(1), $\lambda_{max.}$ 244 nm (ε 3 200),[2b] it follows that after *e.g.* 30 min of irradiation, only 15% of the substrate is left.

DISCUSSION

The products formed in the photolysis of (1) with λ 254 nm can be explained in terms of initial N–O bond homolysis with formation of an α-oxo-iminyl and an ethoxyl radical [step (1)]. A similar N–O bond homo-



$$(1) + h\nu \longrightarrow \mathrm{Me\overset{\overset{\displaystyle O}{\|}}{C}—\overset{\overset{\displaystyle N^{\bullet}}{\|}}{C}Me} + \mathrm{EtO^{\bullet}} \qquad (1)$$

lysis occurs in the photolysis of oxime esters [3] and α-oxo-oxime esters.[4] As was shown previously [2] the photodecomposition of the α-oxo-oxime ethers occurs from the excited singlet state(s).

Reactions of the Ethoxyl Radicals.—The formation of the products (3)—(5), (15), and (16) may be explained

$$2\mathrm{EtO^{\bullet}} \longrightarrow \mathrm{EtOH} + \mathrm{MeCHO} \qquad (2)$$

$$\mathrm{EtO^{\bullet}} \longrightarrow \mathrm{Me^{\bullet}} + \mathrm{CH_2O} \qquad (3a)$$

$$\mathrm{EtO^{\bullet}} \longrightarrow \mathrm{H^{\bullet}} + \mathrm{MeCHO} \qquad (3b)$$

$$\mathrm{EtO^{\bullet}} + \mathrm{Me^{\bullet}} \longrightarrow \mathrm{MeCHO} + \mathrm{MeH} \qquad (4)$$

$$\mathrm{EtO^{\bullet}} + \mathrm{MeCHO} \longrightarrow \mathrm{EtOH} + \mathrm{Me\dot{C}O} \qquad (5)$$

$$\mathrm{Me^{\bullet}} + \mathrm{MeCHO} \longrightarrow \mathrm{MeH} + \mathrm{Me\dot{C}O} \qquad (6)$$

$$2\mathrm{Me\dot{C}O} \longrightarrow \mathrm{MeCOCOMe} \qquad (7)$$

$$\mathrm{EtO^{\bullet}} + \mathrm{RH} \longrightarrow \mathrm{EtOH} + \mathrm{R^{\bullet}} \qquad (8)$$

by the steps (2)—(8). The ethoxyl radicals may disproportionate [steps (2) and (4)], undergo β-scission [steps (3a and 3b)], and abstract hydrogen from acetaldehyde [step (5)] and from other hydrogen donors, RH, present in the system [step (8)].[5] The rate of step (3a) is 5—9 times that of step (3b).[5b] The very small amounts of formaldehyde and methane illustrate that step (3a) is of minor importance. Accordingly, step (3b) can be neglected in this system.

From the rates of formation of (3)—(5) and (15), and steady state treatment for the methyl and acetyl radicals it can be derived for the amounts of products, *R*, that equation (9) holds.[6] The observed amount of

$$R_{\mathrm{MeCHO}} = R_{\mathrm{EtOH}} + R_{\mathrm{CH_2O}} - 4R_{\mathrm{MeCOCOMe}} \qquad (9)$$

formaldehyde in acetonitrile as solvent is in fact equal to that calculated by equation (9) only up to an irradiation time of *ca.* 2 h. Under those conditions, it can be calculated from the yields of (3)—(5) that 76—81 (77)% of the ethoxyl radicals react by disproportionation [steps (2) and (4)], 5% by β-scission [step (3a)], 16—11 (15)% by hydrogen-abstraction from acetaldehyde [step (5)], and 3% by hydrogen abstraction from the other hydrogen donors [step (8)].* For high irradiation times the actual amount of acetaldehyde is substantially less than the calculated one (Figure 1). This is ascribed mainly to the addition of acetaldehyde to photo-excited biacetyl with formation of the secondary product (11).[7]

The ethoxy balance calculated from the yields of (3)—(6) is 96% for cyclohexane as solvent and 74% for acetonitrile. The lower yield of acetaldehyde in acetonitrile compared with cyclohexane (Table) is ascribed to poorer hydrogen donation by the solvent system, and reaction of photo-excited butane-2,3-dione instead with acetaldehyde.

Reactions of the α-Oxo-iminyl Radical.—The formation of acetonitrile in the photolysis of (1) may be explained

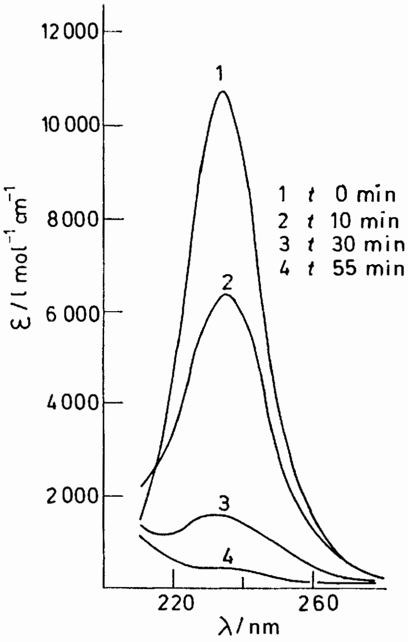


FIGURE 2 Irradiation of 3-ethoxyiminobutan-2-one (0.051M) in cyclohexane with λ 254 nm

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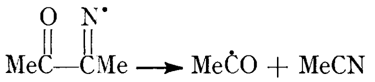
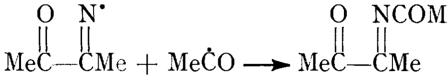
* The data in parentheses were calculated by presuming that the ratio of disproportionation to hydrogen abstraction for the methyl radical by the steps (4) and (6) respectively is the same as that for the ethoxyl radical by the steps [(2) + (4)] and (5), respectively.

in terms of β-scission of the α-oxo-iminyl radical [step (10)]. The secondary amides (8)—(10) are thought to



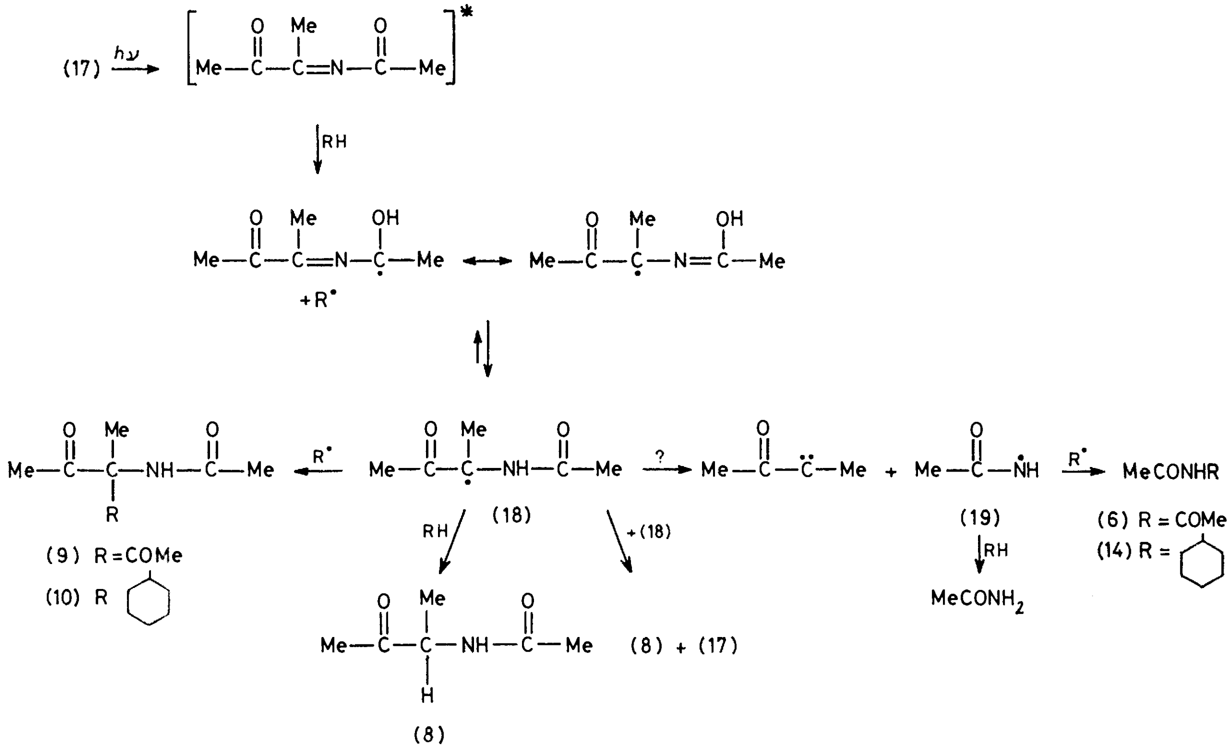
$$\mathrm{Me}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\displaystyle \mathrm{N}^{\bullet}}{\|}}{\mathrm{C}}\mathrm{Me} \longrightarrow \mathrm{Me}\dot{\mathrm{C}}\mathrm{O} + \mathrm{MeCN} \qquad (10)$$



$$\mathrm{Me}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\displaystyle \mathrm{N}^{\bullet}}{\|}}{\mathrm{C}}\mathrm{Me} + \mathrm{Me}\dot{\mathrm{C}}\mathrm{O} \longrightarrow \mathrm{Me}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\overset{\overset{\displaystyle \mathrm{NCOMe}}{\|}}{\mathrm{C}}\mathrm{Me} \qquad (11)$$

(17)

result from photoreactions of the intermediate (17) which is formed by combination of the α-oxo-iminyl and an acetyl radical formed by (5), (6), and (10) [step (11)]. The intermediate (17) is an *N*-acetyl-α-oxo-imine. This type of compound is not described in the literature. However, the photochemistry of *N*-acylimines was studied by the groups of Hirai[8] and Padwa.[9] In hydrogen-donating solvents like propan-2-ol the *N*-acylimines are photoreduced, whereas in olefinic solvents containing allylic hydrogens addition products are formed. Padwa concluded that hydrogen abstraction occurred rather by the carbonyl oxygen than by the iminyl nitrogen.[9] On this basis it is proposed for the present system (Scheme) that hydrogen abstraction of excited (17) from a suitable donor present in the reaction system occurs by the oxygen atom of the *N*-acetyl group. The eventually resulting relatively stable (*cf.* ref. 10) radical (18) can (i) disproportionate to yield (8) and (17), (ii) abstract hydrogen to form (8), and (iii) recombine with acetyl and cyclohexyl radicals to yield (9) and (10), respectively.



SCHEME

The formation of the minor products (6), (7), and (14) may indicate the presence of the acetylaminyl radical (19)[11] in the system. A possible way of formation is from radical (18) (see Scheme). The fate of the then concomitantly formed carbene remains however obscure. Moreover it is to be expected that the yield of acetamide (7) would be greater with cyclohexane than acetonitrile as solvent, since the former is the better hydrogen donor. In fact, in cyclohexane the amount of acetamide is below the limits of detection.

EXPERIMENTAL

Materials.—The synthesis of α-oxo-oxime ether (1) has been described.[2a] The solvents were purified by distillation and dried before use.

Irradiations.—The irradiations were performed in a Rayonet photochemical reactor (RPR 208) equipped with 254 nm lamps.

Analyses.—The i.r. spectra (cm^{-1}) were recorded on an Unicam SP 200 or a Perkin-Elmer 125 spectrometer. The ^{1}H n.m.r. spectra (δ) were obtained on Varian A-60D, HA-100, or XL-100 instruments, using tetramethylsilane as an internal standard. The u.v. spectra were recorded on a Cary 14 spectrophotometer. Mass spectra were obtained on an A.E.I. MS-902 spectrometer with an all-glass heated inlet system; mass peaks with relative intensities below 5% have not been listed in the mass tables.

Methane (16) was identified on comparison of its g.l.c. (2 m × 1/4 in; Porapak Q + S; 60—80 mesh; 60°) retention times with that of an authentic sample. Acetonitrile (2), ethanol (3), acetaldehyde (4), butane-2,3-dione

(5), and formaldehyde (15) were identified on a 2 m × 1/4 in, Porapak Q + S, 60—80 mesh, copper column (150°; 2° min^{-1} up to 175°). *N*-Acetylacetamide (6), acetamide (7), and bicyclohexyl (13) were identified by comparison of their spectral data with those in the Sadtler spectra collection.

The following compounds were assigned directly on the basis of their spectral data.

3-*Acetamidobutan*-2-*one* (8).—The i.r. and ^{1}H n.m.r. spectra were identical with those of a sample synthesized independently by the Dakin–West reaction,[12] δ ($CDCl_3$) *ca*. 6.4br (1 H, NH), 4.62 (1 H, quintet, *J* 7 Hz, CH), 2.25 (3 H, s, CH_3COC), 2.04 (3 H, s, CH_3CON), and 1.40 (3 H, d, *J* 7 Hz, CH_3CH); *m*/*e* (15 eV) 127 [12, $(M - 2H)^{+\cdot}$], 111 (6), 92 (6), 87 [18, $(M - CH_2{=}C{=}O)^{+\cdot}$], 86 [100, $(M - CH_3CO)^+$ or $(M - H - CH_2{=}C{=}O)^+$], 85 (24), 60 (5), 59 (9), 44 [62, $(86 - CH_2{=}C{=}O)^+$], 43 [12, $(M - C_4H_8NO)^+$], and 42 (8); the i.r. spectrum was identical with the Sadtler spectrum 19626.

3-*Acetamido*-3-*methylpentane*-2,4-*dione* (9).—This had $\nu_{max.}$ ($CHCl_3$) 3 390m (NH), 2 990w, 1 700s (C=O, ketone), 1 660s (amide I), 1 480s (amide II), 1 430w, 1 364m, 1 352m, and 1 170w cm^{-1}; δ ($CDCl_3$) *ca*. 7.3br (1 H, NH), 2.09 (6 H, s, CH_3COC), 2.05 (3 H, s, CH_3CON), and 1.68 (3 H, s, CH_3C); *m*/*e* (70 eV) 129 [13, $(M - CH_2{=}C{=}O)^{+\cdot}$], 128 [8, $(M - CH_3CO)^+$], 112 (5), 111 (47), 110 (5), 87 [48, $(129 - CH_2{=}C{=}O)^{+\cdot}$; $m^*_{obs.}$ 58.70, $m^*_{calc.}$ 58.67], 86 [93, $(128 - CH_2{=}C{=}O)^+$], 70 [8, $(87 - NH_3)^{+\cdot}$; $m^*_{obs.}$ 56.38, $m^*_{calc.}$ 56.32], 69 (5), 68 (9), 60 (8), 58 (5), 55 (14), 45 [8, $(87 - CH_2{=}C{=}O)^{+\cdot}$], 44 [62, $(86 - CH_2{=}C{=}O)^+$; $m^*_{obs.}$ 22.58, $m^*_{calc.}$ 22.51], 43 [100, $(M - C_6H_{10}NO_2)^+$], 42 (30), 41 (11), and 40 (5).

3-*Acetamido*-3-*cyclohexylbutan*-2-*one* (10).—This had $\nu_{max.}$ ($CHCl_3$) 3 440w (NH), 3 380vw (NH), 2 990m, 2 930s, 2 850m, 1 705s (C=O, ketone), 1 660s (amide I), and 1 490s (amide II) cm^{-1}; δ ($CDCl_3$): 6.31br (1 H, NH), 2.14 (3 H, s, CH_3COC), 1.98 (3 H, s, CH_3CON), 1.92—0.96 (11 H, m, cyclohexyl), and 1.46 (3 H, s, CH_3C).

3-*Hydroxy*-3-*methylpentane*-2,4-*dione* (11).—This had $\nu_{max.}$ ($CHCl_3$) 3 500w (OH), 3 060w, 1 710s (C=O), 1 420m, 1 360s, 1 145s, 1 100w, and 970s cm^{-1}; δ (CCl_4) 2.17 (6 H, s, CH_3CO), 2.08br (1 H, OH), 1.47 (3 H, s, CH_3C); δ 2.05 an impurity was present (18%).

Cyclohexyl Methyl Ketone (12).—The i.r. and ^{1}H n.m.r. spectra were identical with those of a commercial sample.

N-*Cyclohexylacetamide* (14).—The i.r. and ^{1}H n.m.r. spectra were identical with those of a sample synthesized from cyclohexylamine and acetic anhydride, $\nu_{max.}$ ($CHCl_3$) 3 480w (NH), 3 370w (NH), 3 040m, 2 960s, 2 870m, 1 660s (amide I), 1 520s (amide II), and 1 450m cm^{-1}; δ (CCl_4) 7.13br (1 H, NH), 3.63br (1 H, CH–N), 1.86 (3 H, s, CH_3CO), and 2.08—0.95 (10 H, m, cyclohexyl).

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