Photochemistry of α-Oxo-oximes. Part 3.[1] Photoisomerization of Some α-Oxo-oxime Ethyl Ethers

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The photoisomerization of four α-oxo-oxime ethyl ethers (1)—(4) has been investigated. The (*E*)-isomers of (1)—(3) exist in the s-*trans* conformation. By spectroscopic analysis and by comparison of the triplet sensitized photoisomerization of (1) and (2) it was established that (*Z*)-(1) has a (possibly slightly twisted) s-*cis* conformation and (*Z*)-(2) a (probably non-planar) s-*trans* conformation. Also with (*Z*)-(3) there are indications for an s-*trans* conformation. Oxime ether (4) with the fixed s-*cis* structure undergoes only (*E*)-(*Z*) isomerization. An energy diagram for the various states of (*E*)- and (*Z*)-(1) has been constructed. Both upon direct and triplet sensitized irradiation (*E*)—(*Z*) isomerization takes place from T_1 (π–π*). Upon direct irradiation also photodecomposition occurs which proceeds from S_1 (*n*–π*). From the quantum yield data it was concluded that all excited molecules of (*Z*)-(1) reach the common triplet state *T*, whereas with (*E*)-(1) only 37% of the excited molecules yield the common triplet state.

THE photochemistry of α-oxo-oximes and their derivatives has received little attention.[2] The isolated oxime group has a π–π* absorption band near 190 nm (ε 8 000), whereas no *n*–π* band is detected.[3] A non-conjugated carbonyl group shows an *n*–π* absorption of low intensity at *ca.* 280 nm (ε *ca.* 20) and a π–π* absorption of relatively high intensity (ε *ca.* 1 000) at *ca.* 190 nm.[4] It was expected therefore that the conjugated O=C–C=N–O moiety could be excited with radiation of λ >300 nm.

The photoreactions of the α-oxo-oximes and their derivatives can be divided into photoisomerization and photodecomposition. Previously we reported on the photoisomerization of 3-ethoxyiminobutan-2-one (1).[5] It was established that the (*E*)-isomer exists in the s-*trans* conformation and the (*Z*)-isomer in the s-*cis* conformation. In order to gain more insight into this change of conformation upon going from (*E*) to (*Z*) the direct sensitized photoisomerization of the non-rigid 2-ethoxyimino-1-phenylpropan-1-one (2) and 4-ethoxyimino-2,6-dimethylheptan-3-one (3), and the rigid 3-ethoxyiminobornan-2-one (4) were investigated.

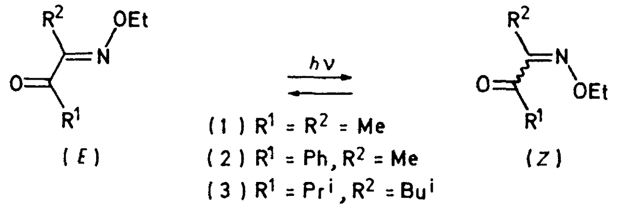


TABLE 1

^{1}H N.m.r. data (δ and a.s.i.s. values) of the (*E*)- and (*Z*)-α-oxo-oxime ethers

		δ					
		$\mathrm{CCl_4}$		$\mathrm{C_6D_6}$		Δ^a (p.p.m.)	
Compound	Proton	(*E*)	(*Z*)	(*E*)	(*Z*)	(*E*)	(*Z*)
(1)	$\mathrm{O{\cdot}C}H_2\mathrm{{\cdot}CH_3}$	4.26	4.06	4.04	3.94	+0.22	+0.12
	$\mathrm{C}H_3\mathrm{{\cdot}C{:}O}$	2.27	2.29	2.18	2.08	+0.09	+0.24
	$\mathrm{C}H_3\mathrm{{\cdot}C{:}N}$	1.85	1.88	1.87	1.72	−0.02	+0.16
	$\mathrm{O{\cdot}CH_2{\cdot}C}H_3$	1.32	1.24	1.08	1.03	+0.24	+0.21
(2)	*o*-H	7.98—7.85	7.85—7.72	8.11—7.98	7.88—7.75	−0.13	−0.03
	(*m* + *p*)-H	7.48—7.21	7.55—7.21	7.24—6.97	*b*	+0.24	
	$\mathrm{O{\cdot}C}H_2\mathrm{{\cdot}CH_3}$	4.25	3.96	3.98	3.86	+0.27	+0.10
	$\mathrm{C}H_3\mathrm{{\cdot}C{:}N}$	2.07	2.03	2.09	1.85	−0.02	+0.18
	$\mathrm{O{\cdot}CH_2{\cdot}C}H_3$	1.32	1.10	1.13	1.02	+0.19	+0.08
(3)	$\mathrm{O{\cdot}C}H_2\mathrm{{\cdot}CH_3}$	4.20	4.02	4.13	3.92	+0.17	+0.10
	$\mathrm{(CH_3)_2{\cdot}C}H\mathrm{{\cdot}C{:}O}$	3.48	2.81	3.65	2.78	−0.17	+0.03
	$\mathrm{(CH_3)_2{\cdot}CH{\cdot}C}H_2\mathrm{{\cdot}C{:}N}$	2.32	2.07	2.60	2.11	−0.28	−0.04
	$\mathrm{(CH_3)_2{\cdot}C}H\mathrm{{\cdot}CH_2{\cdot}C{:}N}$	1.82	1.83	2.05	1.89	−0.23	−0.06
	$\mathrm{O{\cdot}CH_2{\cdot}C}H_3$	1.26	1.18	1.08	0.99	+0.18	+0.19
	$\mathrm{(C}H_3\mathrm{)_2{\cdot}CH{\cdot}C{:}O}$	1.00	1.03	1.12	1.00	−0.12	+0.03
	$\mathrm{(C}H_3\mathrm{)_2{\cdot}CH{\cdot}CH_2{\cdot}C{:}N}$	0.78	0.90	0.89	0.81	−0.11	+0.08
(4)	$\mathrm{O{\cdot}C}H_2\mathrm{{\cdot}CH_3}$	4.19	4.12	4.11	4.14	+0.08	−0.02
	4-H	3.06	2.52	3.02	2.42	+0.04	+0.10
	5- +6-H	2.20—1.50	2.20—1.50 *b*	1.70—1.00	1.70—1.00 *b*	+0.5	+0.5
	$\mathrm{O{\cdot}CH_2{\cdot}C}H_3$	1.27	1.25	1.09	1.13	+0.18	+0.12
	8-$\mathrm{H_3}$	0.90	0.93	0.60	0.64	+0.30	+0.29
	9-$\mathrm{H_3}$	0.90	0.93	0.51	0.50	+0.39	+0.43
	10-$\mathrm{H_3}$	0.82	0.84	0.83	0.78	−0.01	+0.05

[a] $\Delta = \delta(\mathrm{CCl_4}) - \delta(\mathrm{C_6D_6})$. [b] The absorption pattern was too complex to determine the exact shift.

RESULTS

Spectral Properties.—The relevant n.m.r., i.r., and u.v. data of the (*E*)- and (*Z*)-isomers of (1)—(4) are compiled in Tables 1—3. The absorptions of the (*Z*)-isomers were sometimes obtained from the (photolysis) mixture of (*E*) and (*Z*).

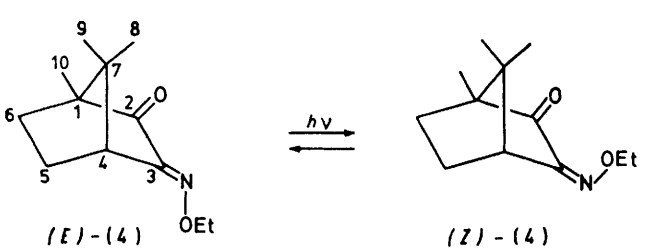
The assignment of the spectral data is easily made. The most striking features are (i) the large difference between the a.s.i.s. (aromatic solvent-induced shift) values for the R^2 protons of the (*E*)- and (*Z*)-isomers of (1)—(3), (ii) the shift to higher frequency for the carbonyl stretching vibration of the non-rigid α-oxo-oxime ethers (1)—(3) on going from (*E*) to (*Z*), and (iii) the large difference between the u.v. absorption of the two geometric isomers of (1), (3), and (4).

TABLE 2

Main i.r. frequencies of the (*E*)- and (*Z*)-α-oxo-oxime ethers [a]

Compound	ν/cm⁻¹ C=O	C=N	C–O–N	other
(*E*)-(1) [b]	1 688 (s)	1 602 (w)	1 041 (s); 927 (w)	1 355 (m); 1 305 (w); 1 120 (m)
(*Z*)-(1) [b]	1 700 (br, s)		1 051 (s); 929 (w)	1 354 (m); 1 282 (w); 1 129 (m)
(*E*)-(2) [b]	1 659 (s)		1 046 (s); 905 (s)	1 597 (m); 1 447 (m); 1 326 (s) 1 194 (s); 712 (s); 662 (m)
(*Z*)-(2) [b]	1 675(s)		1 050 (s); 905 (s)	1 595 (m); 1 450 (m); 1 315 (m) 1 195 (m); 700 (m)
(*E*)-(3) [c]	1 687 (s)	1 598 (vw)	1 042 (s)	1 467 (w); 1 386 (m); 1 089 (m)
(*Z*)-(3) [c,d]	1 702			
(*E*)-(4) [c]	1 743 (s)	1 643 (s)	1 044 (s); 935 (s)	1 452 (m); 1 396 (m); 1 382 (m) 1 023 (m); 1 000 (m); 866 (m)
(*Z*)-(4) [c]	1 740 (s)	1 619 (w)	1 042 (w); 930 (s)	1 453 (m); 1 382 (w); 1 076 (m) 1 015 (m); 976 (w); 832 (w)

[a] The classification s (strong), m (medium), w (weak), and vw (very weak) was assigned on the basis of the following intensities relative to the main band: s 75—100%, m 50—75%, w 25—50%, and vw 0—25%; br = broad. [b] Neat liquid. [c] $CHCl_3$ solution. [d] Assigned from a spectrum of an (*E*)–(Z) mixture.



(*E*)-(4) (*Z*)-(4)

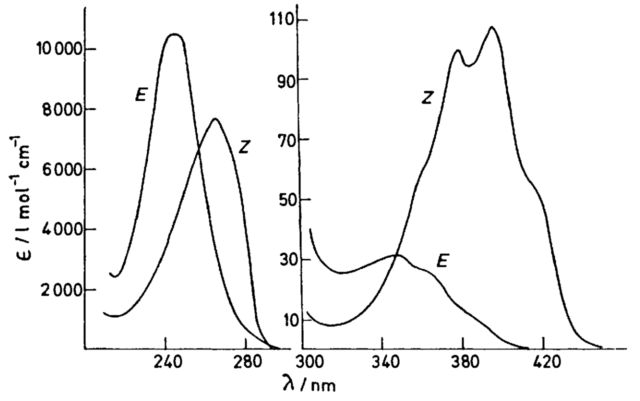


FIGURE 1 U.v. absorption spectrum of (*E*)- and (*Z*)-3-ethoxyiminobornan-2-one (4) in cyclohexane

The u.v. spectra of (*E*)- and (*Z*)-(4) are shown in Figure 1. The (*Z*)-isomer of (4) has a singlet energy of 69 kcal mol⁻¹, as determined from the 0–0 u.v. absorption band.

Irradiation of Compound (2).—The photostationary state (PSS) ratio obtained on direct irradiation of (*E*)-(2) with λ 366 and 254 nm in acetonitrile solution was found to be $([E]:[Z])_{PSS} = 1.3 \pm 0.1$ and 3.2 ± 0.3 respectively. The photoisomerization could not be quenched by cyclohexa-1,3-diene (E_T 52 kcal mol⁻¹ [6a]). Also on triplet sensitization a PSS is obtained. The dependence of the PSS ratio on the triplet energy of the sensitizers [6a] is shown in Figure 2. The triplet energies estimated from Figure 2 are *ca.* 76 for the (*Z*)- and *ca.* 65 kcal mol⁻¹ for the (*E*)-isomer. The shape of the curve in Figure 2 is very similar to one previously obtained for the triplet sensitized irradiation of (1).[5] However, in the latter it gives the relation between $([E]:[Z])_{PSS}$ and E_T and in the former between $([Z]:[E])_{PSS}$ and E_T.

TABLE 3

U.v. data of the (*E*)- and (*Z*)-α-oxo-oxime ethers [a]

Compound	Solvent [b]	π–π* (*E*)	(*Z*)	n–π* (*E*)	(*Z*)
(1)	A	234 (10 800)	244 (3 200)	318 (27)	328 (62)
	B	238 (12 000)		*c*	
(2)	A	251 (12 400)	246 (11 000)	341 (105)	341 (76)
(3)	A	238 (11 000)	242 (2 100)	328 (32)	322 (46)
(4)	A	246 (10 800)	265 (7700)	347 (31)	379 (99) 396 (106)

[a] $\lambda_{max.}$/nm ($\varepsilon_{max.}$/l mol⁻¹ cm⁻¹). [b] A = cyclohexane, B = ethanol. Shoulder.

Irradiation of Compound (3).—Irradiation of solutions of (*E*)-(3) also led to a PSS ratio of (*E*) and (*Z*) (see Table 4), which was found to be independent of the wavelength of irradiation and the substrate concentration.* However,

TABLE 4

Photostationary state (PSS) ratios for the isomerization of 4-ethoxyimino-2,6-dimethylheptan-3-one (3)

10^2 [(*E*)-(3)]/M	Solvent	Sensitizer	λ/nm	$([E]:[Z])_{PSS}$
5.5	CH_3CN [a]		366	2.2
9.5	CH_3CN [a]		366	2.2
10.1	CH_3CN [a]		313	2.2
10.0	Benzene [a]		313	2.8
11.0	Propan-2-ol [b]		366	4.2
10.1	CH_3CN [a]	Benzophenone [c]	313	0.29
5.5	CH_3CN	Acetophenone [d]	313	0.44
5.5	Acetone	Acetone [e]	313	0.70

[a] Chlorobenzene was used as internal g.l.c. standard. [b] Pentadecane was used as internal g.l.c. standard. [c–e] The respective percentages of the incident light absorbed by the sensitizer were 91, 94, and 97; the triplet energies of these sensitizers are 69, 74, and *ca.* 80 kcal mol⁻¹, respectively.[6a]

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* On direct irradiation with λ 366 nm in various solvents also structural isomerization as a result of a Norrish type II reaction was observed.[1]

the PSS ratio is strongly dependent on the nature of the solvent. The presence of cyclohexa-1,3-diene (E_T 52 kcal mol^{-1} [6a]) had no effect on the photoisomerization, *i.e.* neither on the time required to obtain the PSS, nor on the PSS ratio itself. The (high-energy) triplet sensitizers listed in Table 4 produced a PSS which is substantially richer in (*Z*) than observed in the isomerization upon direct irradiation.

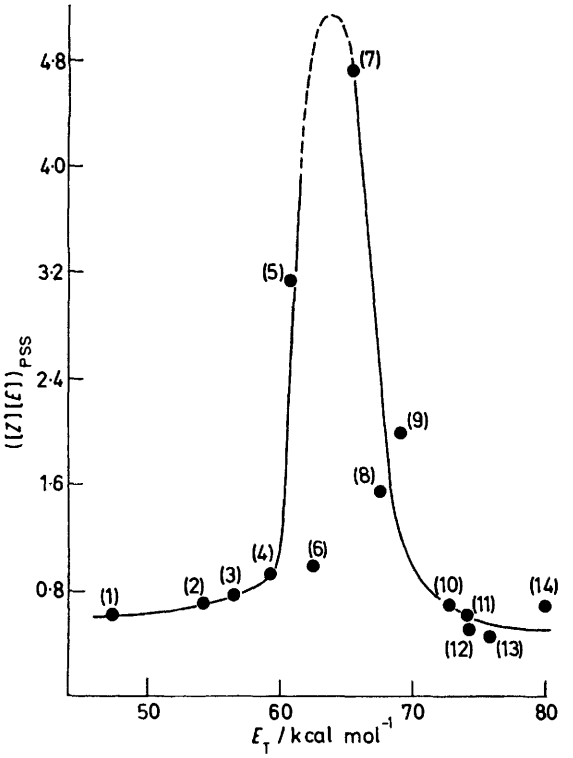

FIGURE 2 Photosensitized isomerization of (*E*)- and (*Z*)-2-ethoxyimino-1-phenylpropan-1-one (2) in acetonitrile solution: (1), acridine; (2), benzil; (3), 1-acetonaphthone; (4), 2-acetonaphthone; (5), *p*-phenylbenzophenone; (6), anthraquinone; (7), xanthenthione; (8), 1,4-diacetylbenzene; (9), benzophenone; (10), 1-tetralone; (11), xanthone; (12), acetophenone; (13), indan-1-one; (14), acetone

Irradiation of Compound (4).—The only initial process upon direct irradiation of (*E*)- or (*Z*)-(4) with λ 366 nm is their interconversion.* The PSS ratio in acetonitrile solution was found to be $([E]:[Z])_{PSS} = 3.05 \pm 0.05$.† Starting with either pure isomer the same PSS ratio was obtained (see Figure 3).

Irradiation with λ 366 nm of a 0.09M-acetonitrile solution of a mixture of (*E*) and (*Z*) (1 : 2) in the presence of xanthone as triplet sensitizer (E_T 74 kcal mol^{-1}; [6a] 98% of the incident radiation was absorbed by the sensitizer) produced an $([E]:[Z])_{PSS} = 2.1$, as determined by two component ^{1}H n.m.r. analysis.

Quantum Yields.—The quantum yields for the (*E*)—(*Z*) photoisomerization of (1) and (3) have been determined, using the Norrish type II photoreaction of valerophenone, leading to acetophenone and propene, as actinometer.[7] From the data in Table 5, it can be seen that the (*E*)—(*Z*) isomerization is a very efficient process, *e.g.* for (3) the total quantum yield is as high as 0.86.‡

TABLE 5

Quantum yields for the direct irradiation with λ 313 nm in acetonitrile solution

	ϕ (±20%)		
Compound	$E \rightarrow Z$	$Z \rightarrow E$	Product
(1)	0.18	0.53	*a*
(3)	0.26	0.60	0.02 *b*

[a] Not determined. [b] Two cyclobutanol derivatives resulting from a Norrish type II process.[5]

DISCUSSION

Conformation of the (*Z*)*-Isomers.*—For (*Z*)-(1) no distinction can be made between a non-planar s-*cis*, a non-planar s-*trans*, and a planar s-*cis* conformation on the basis of a.s.i.s., i.r., and u.v. data. Based on a comparison of the triplet sensitized photoisomerizations of (1) and (2) and by analogy with the slightly non-planar s-*cis* conformation of (*Z*)-3-methylpent-3-en-2-one,[9] we favour for (*Z*)-(1) a slightly non-planar s-*cis* conformation.§

It is unlikely that the (*Z*)-isomers of (2) and (3) exist in the planar s-*cis* conformation, because of steric interactions between R^1 and R^2. The observed C=O stretching vibrations for (2) and (3) at 1 675 and 1 702 cm^{-1}, respectively (*cf.* Table 2), and the low molar extinction coefficient for the π–π* band of (*Z*)-(3) (*cf.* Table 3) argue for a non-planar conformation (either s-*cis* or s-*trans*). The difference in behaviour between (1) and (2) upon triplet sensitization (*cf.* Figure 2 and Figure 2 of ref. 5) can be used to differentiate for (*Z*)-(2) between a

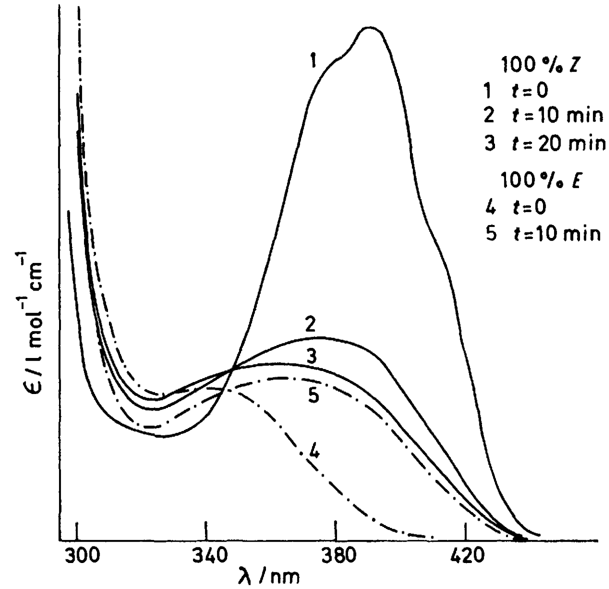

FIGURE 3 Photoisomerization of 0.010M-(*E*)- and -(*Z*)-3-ethoxyiminobornan-2-one (4) with λ 366 nm in acetonitrile

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* Upon irradiation with λ 254 nm a very fast photodecomposition was observed. More details on the product formation in this photodecomposition will be reported later.

† Determined u.v. spectroscopically from the extinctions of the irradiated mixture at 380 and 410 nm using the known molar extinction coefficients of pure (*E*) and (*Z*).

‡ For acetophenone oxime methyl ether upon direct irradiation with λ 254 nm in pentane solution, Padwa reported a total quantum yield of 0.66 with $\phi_{Z \rightarrow E}$ 0.29 and $\phi_{E \rightarrow Z}$ 0.37.[8]

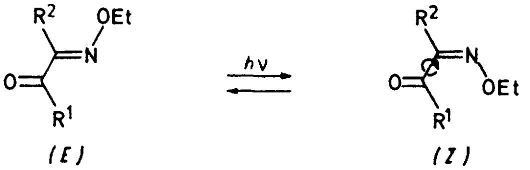
§ The conformation proposed now differs somewhat from that previously suggested.[5]

non-planar s-*cis and* a non-planar s-*trans* conformation. The triplet energies of (*Z*)-(1) and -(2) are 57 [5] and 76 kcal mol^{-1}, respectively, and those of (*E*)-(1) and -(2) 69 [5] and 65 kcal mol^{-1}, respectively. The small difference between (*E*)-(1) and -(2) can be explained by the presence of the fully conjugated PhC=O system of (2). The large difference between (*Z*)-(1) and -(2) may be rationalized as follows. For acrolein the electronically excited states of the s-*cis* conformer are stabilized with respect to those of the s-*trans* one: [10] thus it is to be expected (and is in fact observed) that E_T is higher for (*E*)-(1) (which has the s-*trans* conformation) than for (*Z*)-(1) (which has the s-*cis* conformation). Further, for an olefin the triplet energy is often higher for the (*Z*)- than for the (*E*)-isomer.[11] For (2), of which the two isomers both exist in the s-*trans* conformation, it may therefore be expected that E_T is higher for (*Z*) than for (*E*) (as is in fact observed), and thus that E_T is higher for (*Z*)-(2) than -(1). On the basis of the large difference of 19 kcal mol^{-1} between E_T of (*Z*)-(1) and -(2) and the high $\phi_{Z\longrightarrow E}$ of (1) (*cf.* Table 5), it is concluded (i) that the ground state of (*Z*)-(1) has a (possibly slightly twisted) s-*cis* conformation, and (ii) that the ground state of (*Z*)-(2) has a (probably non-planar) s-*trans* conformation.

The three sensitizers used with (3) (*cf.* Table 4) produce the same variation in $([E] : [Z])_{PSS}$ as a function of E_T, as observed with (2). This may indicate also a higher E_T for (*Z*)-(3) than (*E*)-(3), and then infers a (non-planar) s-*trans* conformation for (*Z*)-(3). The photoisomerization of (2) and (3) may therefore be visualized as in Scheme 1.

Nature of the Excited State.—The u.v. absorption spectra of α-oxo-oxime ethers are similar to those of αβ-unsaturated ketones for which the *n*–π* and π–π* triplet states may lie very close together.[12]

The (*E*)—(*Z*) isomerization of α-oxo-oxime ethers takes place both upon direct and triplet-sensitized irradiation. On direct irradiation substrate decomposition is also observed. On triplet-sensitized irradiation the (*E*)—(*Z*) isomerization is the *only* observed process. The energy diagram of (*E*)- and (*Z*)-(1), is shown in Scheme 2. The triplet energies used were those estimated previously.*[,5]

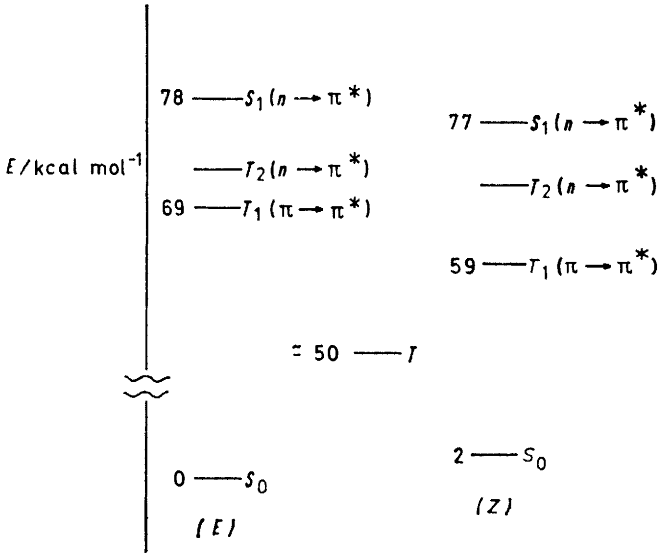


SCHEME 1

For (2) (*cf.* Figure 2) and probably (3) the (*Z*)-isomer has a higher E_T than the (*E*)-isomer [for comparison of (2) and (3), see later].

For the ground state of acrolein it was calculated that the s-*cis* conformation is 1.4 kcal mol^{-1} less stable than the s-*trans* one,[10] while this energy gap was estimated experimentally to be 2 kcal mol^{-1}.[13] Therefore, the energy difference between the ground states of (*E*)- and (*Z*)-(1) was set as 2 kcal mol^{-1}. For (*E*)-(1) the singlet energy of 78 kcal mol^{-1} was determined from the 0–0 u.v. absorption band; for (*Z*)-(1) this energy will be *ca.* 3 kcal mol^{-1} lower, as can be seen from the difference in $\lambda_{max.}$ (*cf.* Table 3).

For α-oxo-oxime ethers the lowest excited triplet state will have predominantly π–π* character, as it exhibits (*E*)-(*Z*) isomerization. Further evidence for this assignment can be found in the observation that upon irradiation of α-oxo-oxime ethers (and esters) in propan-2-ol no products were found originating from intermolecular hydrogen abstraction by the ketone function, which process is known to occur in ketones of which the first excited triplet state is an *n*–π* state. The energy difference between T_2 (*n*–π*) and T_1 (π–π*) of (1) is not known; for 4-methyltestosterone acetate it is 7.7 kcal mol^{-1}.[12a] The energy of the common triplet *T* has been estimated to be *ca.* 50 kcal mol^{-1}, since the time required to reach the PSS on triplet sensitization is a factor of *ca.* 3 larger for acridine (E_T 45 kcal mol^{-1}) [6a] than for benzil (E_T 54 kcal mol^{-1}),[6a] and that for (*E*)-stilbene (E_T 50 kcal mol^{-1}) [6a] lies in between these two.



SCHEME 2 Energy diagram of 3-ethoxyiminobutan-2-one (1)

On triplet sensitization only (*E*)—(*Z*) isomerization is observed, and no photodecomposition. Therefore, photodecomposition originates neither from T_1 (π–π*) nor from T_2 (*n*–π*). On direct irradiation with λ 366 or 313 nm both (*E*)-(*Z*) isomerization and decomposition take place. The (*E*)—(*Z*) isomerization proceeds from T_1(π–π*) at a rate exceeding that of diffusional control (in view of the absence of quenching by cyclohexadiene). The T_1 (π–π*) state is populated by intersystem crossing from S_1(*n*–π*), probably *via* T_2(*n*–π*). Very likely, the

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* The singlet energy of (*Z*)-(4), which is fixed in the s-*cis* structure, is 69 kcal mol^{-1}. The energy difference between S_1 and T_1 of (*E*)-(1) is 9 kcal mol^{-1}. Accordingly, for (*Z*)-(1), which also has the s-*cis* conformation, E_T will be 60 (= 69 − 9) kcal mol^{-1}, in agreement with the observed value of 57 kcal mol^{-1}.

decomposition originates from $S_1(n\text{-}\pi^*)$. Upon irradiation with λ 254 nm probably in addition decomposition occurs from $S_2(\pi\text{-}\pi^*)$, as the photodecomposition is faster with λ 254 nm than with λ 366 nm.

Common Triplet State T.—For (1) the triplet decay ratio from the common triplet state T (k_7/k_8, see ref. 5) was determined from the triplet sensitized irradiation to be 1.1 ± 0.1.[5] If the photoisomerization proceeds only *via* T, then $\phi_{E\rightarrow Z}$ would be equal to $k_8/(k_7 + k_8) = 0.48$ and $\phi_{Z\rightarrow E}$ to $k_7/(k_7 + k_8) = 0.52$. The calculated value of $\phi_{Z\rightarrow E}$ is in excellent agreement with the observed one of 0.53 (see Table 5). Therefore, it is concluded that all excited molecules of (Z)-(1) yield the common triplet state T. The observed value for $\phi_{E\rightarrow Z}$ (= 0.18) is substantially smaller than the calculated one. This is taken to indicate that only (0.18/0.48) 100% = 37% of the excited molecules of (E)-(1) yield the common triplet state T, and that accordingly 63% of the excited molecules of (E)-(1) are deactivated by other routes.

EXPERIMENTAL

Materials.—The α-oxo-oxime ethyl ethers were prepared from the corresponding oximes either with diethyl sulphate,[14] as for (1), b.p. 45—47.5° at 18 mmHg (lit.,[14] 42—42.5° at 13 mmHg), (2), b.p. 58° at 4 mmHg, and (4), b.p. 110—122° at 0.2 mmHg, or with ethyl iodide [8] as for (2), b.p. 117—119° at 0.9 mmHg. The corresponding α-oxo-oximes were synthesized according to the method of Ferris,[14] except for 3-hydroxyiminobornan-2-one which was prepared using bornan-2-one and isopentyl nitrite in basic solution.[15] The (Z)-isomers of the α-oxo-oxime ethers were prepared by irradiation of the corresponding (E)-isomers with λ 254 or 366 nm in acetonitrile solution, and separation of the resulting mixture by g.l.c. on a 12% OV-225 [on Chromosorb W (AW) (60—80 mesh)] copper column (4 m × ¼ in), using helium as carrier gas. The photosensitizers were from a Photosensitizer and Quencher kit (Baker).

Irradiations.—Rayonet photochemical reactors (RPR 208) were used, equipped with 366, 313, or 254 nm lamps, as required. In the sensitization experiments solutions (1 ml) containing the α-oxo-oxime ether (0.05—0.25M) and the sensitizer (in a concentration, adjusted so as to absorb >95% of the incident radiation) were irradiated with the appropriate wavelength.

Actinometry.—Valerophenone [7] actinometry was used for the quantum yield determination. An aqueous solution containing potassium chromate (0.27 g l^{-1}) and sodium carbonate (1 g l^{-1}) [6b] with a pathlength of 1 cm was used to isolate the 313 nm line of the Rayonet 313 nm lamps. All samples were degassed three times on a vacuum line. The irradiation of the samples was carried out in the RPR 208 photochemical reactor using a merry-go-round attachment (MGR-100). The substrate conversions were ⩽10%. The acetophenone analyses were performed by g.l.c. on a 12% OV-225 [on Chromosorb W (AW) (60—80 mesh)] copper column (1.5 m × ¼ in). The error in the single run determination is ⩽20%.

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