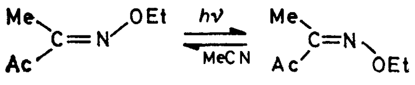
Photochemistry of α-Oxo-oximes. Part 1. Photoisomerization of Biacetyl Mono-oxime Ethyl Ether

By **Peter Baas** and **Hans Cerfontain**,* Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

Upon irradiation at 366 nm (*E*)-3-ethoxyiminobutan-2-one undergoes *EZ*-isomerization. By spectroscopic analysis [i.r., u.v., and n.m.r. (a.s.i.s.)] it was established that the *E*-isomer exists in the s-*trans*- and the *Z*-isomer in the s-*cis*-conformation. The photostationary state (PSS) ratio obtained by direct irradiation of both the (*E*)- and the (*Z*)-oxime ether was found to be 6.0 (±0.3) : 1. The isomerization could also be induced by triplet sensitization. The plot of the PSS ratio against the triplet energy of the sensitizer shows three distinct regions, indicating different routes of energy transfer. It is suggested that the reactive states in the direct photoisomerization and the triplet-sensitized isomerization are the same.

ALTHOUGH photochemical reactions and isomerizations have been observed with several systems possessing a C=N bond,[1] only a few studies have been reported on their α-oxo-derivatives.[2-5] In the present paper we report the direct and sensitized (geometric) photoisomerization of (*E*)- and (*Z*)-3-ethoxyiminobutan-2-one, referred to henceforth as (E) and (Z), respectively.



(E) (Z)

For both configurational isomers there are *a priori* two possible conformations, *viz.* s-*trans* and s-*cis*. Biacetyl mono-oxime in solution exists in the s-*trans*-conformation, as was established by dipole moment measurements.[6] Also pyruvaldehyde 1-oxime in the gas-phase was found to have the s-*trans*-(*E*)-structure by electron diffraction.[7] Furthermore, on the basis of i.r. spectral data, 4-methoxy-3-methylbut-3-en-2-one,† *i.e.* a carbon analogue of (E), was recently reported[8] to exist predominantly in the s-*trans*-conformation.

The conformational and configurational assignments of (*E*)- and (*Z*)-3-ethoxyiminobutan-2-one are based on ^{1}H n.m.r. aromatic solvent-induced shifts [a.s.i.s.;[9] $\Delta = \delta(CCl_4) - \delta(C_6D_6)$], i.r. carbonyl stretching vibrations, and u.v. absorption spectra. The a.s.i.s values are collected in the Table. For (E), the negative value of Δ for the imine methyl group and the positive one for the OCH_2 group are both strong evidence for the s-*trans*-conformation. The ether (Z) has in contrast a positive value of Δ for the imine methyl group, and a slightly smaller positive value of Δ than (E) for the OCH_2; these observations are consistent with an s-*cis*-conformation.

The a.s.i.s. conformational assignments are confirmed by the C=O stretching bands, at 1 682 and 1 700 cm^{-1}, respectively. There is ample evidence for the assignment of the latter band to an s-*cis*- and the former to an s-*trans*-conformation [see *e.g.* i.r. studies on αβ-unsaturated ketones,[10] β-alkoxy-αβ-unsaturated ketones,[8] and (*E*)-3-methylpent-3-en-2-one].[11]

^{1}H N.m.r. data (δ and a.s.i.s. values) of the 3-ethoxyiminobutan-2-ones

	δ					
	CCl$_4$		C$_6$D$_6$		Δ [a] (p.p.m.)	
	(E)	(Z)	(E)	(Z)	(E)	(Z)
O·C*H*$_2$·CH$_3$	4.26	4.06	4.04	3.94	+0.22	+0.12
C*H*$_3$·C:O	2.27	2.29	2.18	2.08	+0.09	+0.24
C*H*$_3$·C:N	1.85	1.88	1.87	1.72	−0.02	+0.16
O·CH$_2$·C*H*$_3$	1.32	1.24	1.08	1.03	+0.24	+0.21

[a] $\delta(CCl_4) - \delta(C_6D_6)$.

Finally, there is a striking difference in the u.v. absorption of the two isomers (Figure 1). A similar difference in π–π* bands of s-*trans*- and s-*cis*-conformations (in both wavelength and extinction coefficient) was observed with the 2-acetylcyclohexenes: 2-acetylcyclohexene with an s-*trans*-conformation has $\lambda_{max.}$ 235 nm (ε 12 500), whereas 2-acetyl-1-methylcyclohexene with a (possibly non-planar) s-*cis*-conformation has $\lambda_{max.}$ 244 nm (ε 6 500).[12]

Upon direct irradiation of (E) or (Z) at 366 nm the only initial process is their interconversion. This photoisomerization may be explained as in the Scheme. The equilibrium of the *E*-conformers lies far to the left-hand side. At −55 °C there is no sign of the s-*cis*-(*E*)-isomer in the ^{1}H n.m.r. spectrum. In the i.r. spectrum of (E) there is, surprisingly, no carbonyl band assignable to the s-*cis*-conformer, in contrast to the findings of Dabrowski[8] for the related α-oxo-enol ethers. Furthermore, there is

---

† It only proved possible to synthesize the thermodynamically more stable *E*-isomer.[8]

[1] A. Padwa and F. Albrecht, *J. Amer. Chem. Soc.*, 1974, **96**, 4849, and references cited therein.

[2] A. Mustafa, A. K. Mansour, and H. A. A. Zaher, *J. Org. Chem.*, 1960, **25**, 949.

[3] A. Stojiljković and R. Tasovac, *Tetrahedron Letters*, 1970, 1405.

[4] J. C. Danilewicz, *J. Chem. Soc.* (*C*), 1970, 1049.

[5] G. A. Delzenne and U. K. Laridon, *European Polymer J.*, 1970, **6**, 933.

[6] C. Pigenet, J. Armand, and H. Lumbroso, *Bull. Soc. chim. France*, 1970, 2124.

[7] P. Alderliesten, A. Almenningen, and T. G. Strand, *Acta Chem. Scand.*, 1975, **29**, 811.

[8] J. Dabrowski and M. Tencer, *Bull. Chem. Soc. Japan*, 1975, **48**, 1310.

[9] J. Ronayne and D. H. Williams, *Ann. Rev. NMR Spectroscopy*, 1969, **2**, 83.

[10] W. P. Hayes and C. J. Timmons, *Spectrochim. Acta*, 1968, **A24**, 323.

[11] R. Mecke and K. Noack, *Chem. Ber.*, 1960, **93**, 210.

[12] H. H. Jaffé and M. Orchin, ' Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, p. 421.

no i.r. evidence for restricted rotation around the N–O bond.

For the (*Z*)-isomer there is again an equilibrium of two conformers, but this is far to the side of the s-*cis*-conformer.* Also (Z) shows no sign of the presence of the

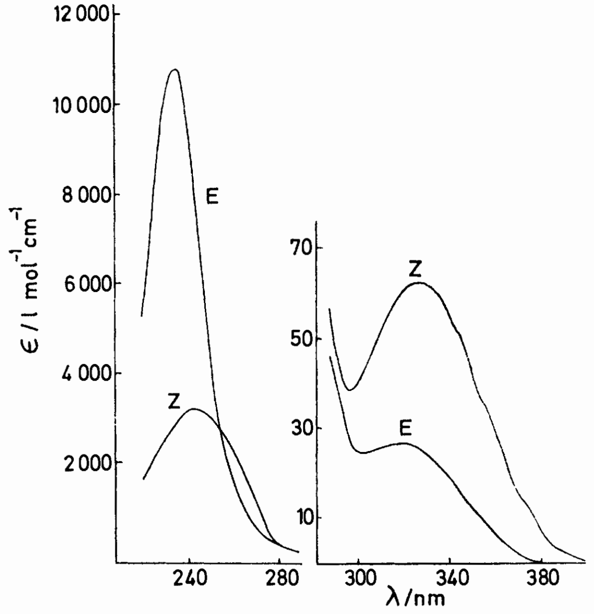
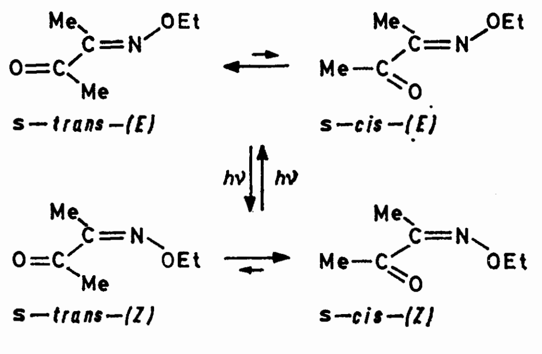


FIGURE 1 U.v. absorption spectra of (*E*)- and (*Z*)-3-ethoxyiminobutan-2-one

s-*trans*-conformer, neither at −55 °C in the ^{1}H n.m.r. spectrum, nor at room temperature by i.r.

The photostationary state (PSS) ratio obtained on direct irradiation in acetonitrile solution at 366 nm was found to be 6.0 (±0.3) : 1 in favour of (E). The isomerization was not quenched by (*Z*)-penta-1,3-diene, not even in high concentration (up to 1.5M). This indicates



that the reaction proceeds from an excited singlet or from a very short-lived excited triplet state. Also on triplet sensitization a PSS is obtained. The results for a variety of sensitizers with known triplet energies[14] are shown in Figure 2. Clearly there are two groups of sensitizers, one group (compounds 1—12; solid circles) producing a plot analogous to that observed with acetophenone oxime methyl ether,[1] and the other (compounds 13—18; open circles) consisting of fully aromatic hydrocarbons, the points of which are scattered around the solid line.† The curve of Figure 2 consists of three distinct regions, *viz.* (i) the high-energy region for which the PSS ratio is constant [1.1 (±0.1) : 1] and for which the energy transfer to both the *E*- and *Z*-isomer is diffusion controlled, (ii) the region from 69 to 57 kcal mol^{-1} for which the energy transfer to the *E*-isomer becomes non-vertical (as first proposed by Saltiel and Hammond),[17] and (iii) the region from 57 to 50 kcal mol^{-1} in which the rates of energy transfer to both isomers become less than the decay rate of the sensitizer. The triplet energies

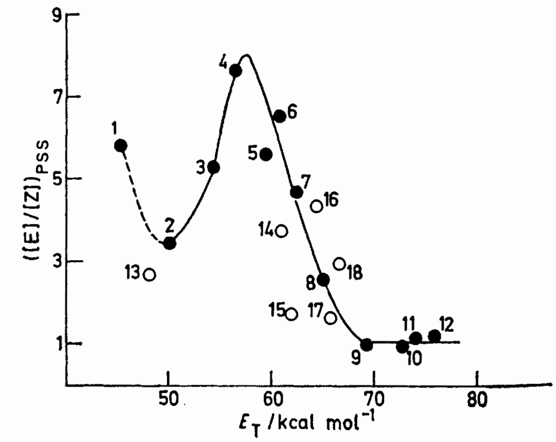


FIGURE 2 Photosensitized isomerization of 3-ethoxyiminobutan-2-one: 1, acridine; 2, (*E*)-stilbene; 3, benzil; 4, 1-acetonaphthone; 5, 2-acetonaphthone; 6, *p*-phenylbenzophenone; 7, anthraquinone; 8, xanthenthione; 9, benzophenone; 10, 1-tetralone; 11, acetophenone; 12, indan-1-one; 13, pyrene; 14, naphthalene; 15, phenanthrene; 16, *m*-terphenyl; 17, biphenyl; 18, triphenylene

estimated from Figure 2 are 69 for the *E*- ‡ and 57 kcal mol^{-1} for the *Z*-isomer.§

The photosensitized isomerization of (E) and (Z) may be explained by the steps (1)—(8),[15] in which S stands for the sensitizer, the superscripts 1 and 3 indicate the multiplicity of the excited state, and T represents a common triplet state of (E) and (Z). Steps (2) and (4)

---

* Such a shift in conformational equilibrium was also observed in the photoisomerization of some β-phenyl-αβ-unsaturated ketones.[13] Similarly, (*E*)-3-methylpent-3-en-2-one is reported to exist as a mixture of s-*trans*- and s-*cis*-conformers, whereas the *Z*-isomer exists only in the s-*cis*-conformation.

† The open circles, together with the solid circles, form a curve resembling that reported by Hammond and his co-workers[15] for the photoisomerization of the stilbenes. Among possible reasons for abnormal behaviour with the sensitizers 13—18 are singlet sensitization and excimer formation.[16]

‡ The *E*-isomer has a singlet energy of 78 kcal mol^{-1}, as determined from the *O–O* u.v. absorption band.

§ Padwa observed a difference of 13 kcal mol^{-1} between the triplet energies of (*E*)- and (*Z*)-acetophenone oxime methyl ether.[1]

[13] P. Baas and H. Cerfontain, *Tetrahedron*, in the press.

[14] S. L. Murov, ' Handbook of Photochemistry,' Dekker, New York, 1973, pp. 3—35.

[15] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

[16] P. S. Engel and B. M. Monroe, *Adv. Photochem.*, 1971, **8**, 245.

[17] J. Saltiel and G. S. Hammond, *J. Amer. Chem. Soc.*, 1963, **85**, 2516.

comprise both the radiative and the non-radiative processes; steps (5) and (6) include both the classical and the non-classical energy transfer. From a steady

$$\mathrm{S} + h\nu \longrightarrow \mathrm{S}^1 \tag{1}$$

$$\mathrm{S}^1 \longrightarrow \mathrm{S} \tag{2}$$

$$\mathrm{S}^1 \longrightarrow \mathrm{S}^3 \tag{3}$$

$$\mathrm{S}^3 \longrightarrow \mathrm{S} \tag{4}$$

$$\mathrm{S}^3 + (\mathrm{E}) \longrightarrow \mathrm{S} + \mathrm{T} \tag{5}$$

$$\mathrm{S}^3 + (\mathrm{Z}) \longrightarrow \mathrm{S} + \mathrm{T} \tag{6}$$

$$\mathrm{T} \longrightarrow (\mathrm{E}) \tag{7}$$

$$\mathrm{T} \longrightarrow (\mathrm{Z}) \tag{8}$$

state treatment, equation (9) follows, in which k_6/k_5 and

$$([\mathrm{E}][\mathrm{Z}])_{\mathrm{PSS}} = (k_6/k_5)(k_7/k_8) \tag{9}$$

k_7/k_8 are called the ' excitation ratio ' and the ' decay ratio,' respectively.

The PSS ratio for the direct irradiation is given by equation (10), provided that this photoisomerization proceeds from the same excited state as the photosensitized one and that the quantum yield for intersystem crossing of (E) and (Z) leading to that state is the same. The PSS ratio was calculated to be 3.9 (±0.9) : 1

$$([\mathrm{E}]/[\mathrm{Z}])_{\mathrm{PSS}} = (\varepsilon_{\mathrm{Z}}/\varepsilon_{\mathrm{E}})(k_7/k_8) \tag{10}$$

by using $\varepsilon_{\mathrm{Z}}/\varepsilon_{\mathrm{E}} = 3.5 \pm 0.5$ * and $k_7/k_8 = 1.1 \pm 0.1$.† This value (of 3.9 ± 0.9) is in fair agreement with that (6.0 ± 0.3) observed for the direct irradiation. Accordingly, and further considering that the photoisomerization of the oxime ethers cannot be quenched by (*Z*)-penta-1,3-diene, the isomerization of the α-oxo-oxime ether upon direct irradiation probably proceeds also from the triplet excited state, but at a rate exceeding that of diffusional control.

Prolonged irradiation of (E) at 366 nm eventually led to decomposition. With irradiation at 254 nm, the decomposition is much faster and a variety of products have been observed,‡ presumably formed from the excited singlet state.§ More details on the photodecomposition will be reported shortly.

EXPERIMENTAL

Materials.—(*E*)-3-Ethoxyiminobutan-2-one was synthesized by nitrosation of butanone with methyl nitrite in hydrochloric acid, followed by reaction with diethyl sulphate in basic solution.[18] The *Z*-isomer was prepared by irradiation of (E) in acetonitrile at 254 nm, and separation of the resulting mixture by g.l.c. on a copper column [4 m × 1/4 in; 12% OV-225 on Chromosorb W (AW) (60—80 mesh); He as carrier gas with flow rate 60 $\mathrm{cm^3\ min^{-1}}$]. Acetonitrile was obtained from Merck (zur Rückstand quality). The sensitizers were from a Photosensitizer and Quencher kit (Baker).

Irradiations.—Rayonet photochemical reactors were used, equipped with 366, 313, or 254 nm lamps, as required. The concentration of oxime ether was within the range 0.05—0.25M (1 ml of solution); the concentration of sensitizer was adjusted so as to absorb more than 95% of the incident radiation.

Spectral Identifications.—I.r. spectra were recorded for the pure components with a Perkin-Elmer 177 grating spectrophotometer. U.v. spectra were recorded with a Cary 14 spectrophotometer. ^{1}H N.m.r. spectra were recorded with a Varian A60 spectrometer (tetramethylsilane as internal standard).

[6/2194 *Received*, 29*th November*, 1976]

---

* The full spectral output of the Rayonet 366 nm lamps was used; from its spectral distribution this value of $\varepsilon_{\mathrm{Z}}/\varepsilon_{\mathrm{E}}$ was estimated.

† In the high-energy region energy transfer to both isomers will be diffusion-controlled; thus $k_5 = k_6$. Then [*cf.* (9)] the PSS ratio becomes equal to the decay ratio, which is known from Figure 2 to be 1.1 (±0.1) : 1.

‡ Ethanal, ethanol, biacetyl, acetamide, 3-acetamidobutan-2-one, and 3-acetamido-3-methylpentane-2,4-dione have been identified.

§ After 68 h of irradiation of (E) at 313 nm there remained a PSS mixture of (Z) and (E) (30%). In contrast, the benzophenone-sensitized irradiation (313 nm; 68 h) of (E) did not lead to photodecomposition of the oxime ether.

[18] A. F. Ferris, *J. Org. Chem.*, 1959, **24**, 1726.