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Photochemistry of α -bis(methoxyimino)alkanes

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Abstract. The photochemistry of the α -bis(methoxyimino)alkanes 1-5 and the, structurally related, conjugated dihydro(methoxyimino)isoxazoles 6 and 7 was studied. Triplet-photosensitized irradiation of 1-7 leads only to stepwise E-Z isomerization. Photostationary-state (pss) ratios for 1, 6 and 7 are reported for the various applied triplet sensitizers. Direct irradiation with 254 nm leads to both E-Z isomerization (which is the dominant reaction) and formation of products resulting from initial N-O homolysis of the excited singlet $\pi\pi^*$ state. Mechanisms for the formation of the various products are proposed and the relative importance of the various steps is indicated and discussed. For the α -bis(methoxyimino)alkanes 1 and 3, only the (E,Z)-isomer undergoes N-O homolysis and not the strained endocyclic bond.

Introduction

The photochemistry of α -diketones^{1,2} and α -oxo oxime ethers^{3,4} has been studied extensively. As an extension of our own studies on these types of compounds^{1,3}, we report studies on the photochemistry of the α -bis(methoxyimino)alkanes 1-5 and the related methoxyimino-substituted di-6 and 7. all containing hydroisoxazoles the O-N=C-C=N-O chromophore. These compounds have, compared to the corresponding x-oxo oxime ethers, an additional mode of E-Z isomerism. For the symmetrical 2,3--bis(methoxyimino)butane (1), this leads, in principle, to six different structures⁵. In view of the dipolar repulsion of the two methoxyimino groups, the s-cis conformers are of relatively high energy. Accordingly, in practice, one has only to deal with the three s-trans (E,E)-, (E,Z)- and (Z,Z)--conformers⁶. Incorporation of one of the alkoxyimino groups in an isoxazoline ring, as with 6 and 7, leads to a fixed orientation of the C=N-O-C group. In fact, (E)- and (Z)-6 may serve as model compounds for the (E,Z)- and (Z,Z)-isomers of acyclic α -bis(methoxyimino)alkanes, respectively and, likewise, (E)- and (Z)-7 as models for the (E,E)- and (Z,E)-isomers.

Recently, a study was made on the structure and UV spectroscopy of a series of aliphatic- and phenyl-substituted α -bis(methoxyimino)alkanes, including 1-5, and the metho-xyimino-substituted dihydroisoxazoles 6 and 7⁵. The compounds all exhibit a strong broad $\pi\pi^*$ -absorption between 215 and 290 nm under which any weak $n\pi^*$ -absorption will be completely hidden.



Results and discussion

Triplet photosensitization of the α -bis(methoxyimino)alkanes 1-5 and the (methoxyimino)isoxazolines 6 and 7 leads to E-Z isomerization only. Direct irradiation of the compounds under study at 254 nm or at "300" nm, which in fact contained some 10% radiation in the 285-300 nm region, leads to both E-Z isomerization and the formation of decomposition products, the former type of process being far more effective than the latter.

Triplet photosensitization

Triplet photosensitization of the (methoxyimino) isoxazolines 6 and 7 in benzene, applying appropriate triplet sensitizers with a triplet energy ranging from 310 (acetophenone) to 197 kJ/mol (7H-benz[de]anthracen-7-one), leads only to

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Entry	Sensitizer	Photostationary states					
	Structure	E _T		<i>E</i> / <i>Z</i>			
	Structure	(kJ/mol)	E,E / E,Z	E,Z / Z,Z	6	7	
1	acetophenone	310	1.02	5.0	1.33	2.85	
2	benzophenone	289	0.58	0.69	1.44		
3	9H-thioxanthen-9-one	272	0.83	0.40	1.44	2.85	
4	phenanthrene	259	0.65	6.1	1.44	2.57	
5	naphthalene	255	0.29	0.08		2.85	
6	4-phenylbenzophenone	251	0.29	0.08	1.70	3.00	
7	1-acetonaphthone	234	0.33	0.07	1.86	3.00	
8	benzil	227				4.26	
9	fluorenone	222	0.94	0.78	3.76	6.69	
10	(E)-stilbene	209			13.3	6.14	
11	pyrene	201			11.5	6.14	
12	7H-benz[de]anthracen-7-one	197			11.5	5.25	

Table I Triplet-photosensitized isomerization of 1, 6 and 7. Dependence of the photostationary state (pss) ratios on the triplet energy of the sensitizer.

E-Z isomerization. Upon prolonged irradiation in the presence of any of the applied sensitizers, a photostationary state (pss) of the geometric isomers was obtained, the composition of which depended on the triplet energy (E_T) of the sensitizer. The pss isomer ratios are collected in Table I and the variation of the $\{|E|/|Z|\}_{pss}$ with E_T is shown graphically for the isoxazolines 6 and 7 in Figure 1. The constant



Figure 1. Triplet-photosensitized isomerization of the dihydroisoxazole derivatives $6 (\bigcirc --- \bigcirc)$ and 7 (+---+)in benzene.

 $\{|E|/|Z|\}_{pss}$ ratio for high $E_{\rm T}$ is the ratio of decay from the phantom triplet state to the ground state (E) and (Z)-isomer which is apparently 1.48 \pm 0.05 for 6 and 2.80 \pm 0.05 for 7. The triplet energies of the (E)- and (Z)-isomers were obtained from the bell-shaped curves of $\{|E|/|Z|\}_{pss}$ versus $E_{\rm T}$ using the standard interpretation and procedure¹⁰. The

triplet-state energies for E)-6, (Z)-6, (E)-7 and (Z)-7 thus calculated are 224, 209, 226 and Another 220 ± 4 kJ/mol, respectively.

Triplet photosensitization of 2,3-bis(methoxyimino)butane (1) leads to E-Z isomerization, which proceeds in a stepwise fashion, upon starting with the (E,E)-isomer, the initial product is the (E,Z)-isomer, whereas the (Z,Z)-isomer is a secondary product, as is apparent from the induction period for its formation. On the other hand, upon starting from the asymmetrical (E,Z)-isomer, there is no induction for the formation of both the (E,E)- and (E,Z)-isomer. In fact, the behaviour of the E-Z-isomerization upon triplet sensitization of each of the three geometric isomers of 1 is very similar to that observed upon direct irradiation at 254 nm of the α -bis(methoxyimino)alkanes (see later, in particular, Figures 4-6). The triplet-sensitized isomerization of a given geometric isomer of the a-bis(methoxyimino)alkanes proceeds stepwise by E-Z isomerization of one double bond at a time via the various different (phantom) triplet states, which in principle will have different triplet energies. Accordingly, the pss concentration ratios of the various geometric isomers will vary with the triplet energy of the sensitizers, as is in fact observed for 1 (see Table I).

The triplet-sensitized isomerization of the α -bis(methoxyimino)alkanes proceeds differently from the triplet-sensitized isomerization of some trienes¹¹, β -ionone oxime *O*-ethyl ether¹² and 1-methoxyimino-3-phenyl-2-propene (**8a**)¹³ in that the isomerization of an isomer of the former group proceeds stepwise by E-Z isomerization of one double bond at a time, whereas an isomer of the latter group of compounds, in principle, interconverts to any of the other geometric isomers. For the latter type of isomerization, there is a common intermediate on the pathway from the various planar (so-called Franck-Condon) excited triplet states to the various ground-state geometric isomers. With the α -bis(methoxyimino)alkanes, no such common intermediate exists.

This poses the question as to the structure of the intermediate(s) involved in the two different types of tripletsensitized isomerizations. The photoisomerization around a C=N bond proceeds from an excited triplet $\pi\pi^*$ state by a *rotation* mechanism^{14,15} via an excited twisted intermediate (also referred to as phantom triplet), since the alternative *inversion* mechanism¹⁶ has a high activation energy (comparable in size to that for the ground state), which is in fact higher than the barrier to N-O cleavage¹⁷.

For an isolated double bond in a given molecule, the phantom triplet is a common intermediate on the reaction coordinate of the vertically excited triplet state of both (E)and (Z)-isomers. The different phantom triplets formed by twisting one of the two C=N double bonds of the vertical triplet states, shown in Figure 2, have in principle different energy contents. When the oxime ether moiety is in conjugation with a C=C group, either concomitant twisting of the two unsaturated bonds may occur, or rapid equilibra-



Figure 2. Structures of the various phantom triplets of an α -bis(methoxyimino)alkane.

tion of the various (mono-twisted) triplets may take place. The latter mechanism, which infers that the energy barriers between the various phantom triplets must be relatively low, applies to the triplet-sensitized isomerization of benzylideneacetaldehyde oxime *O*-methyl ether (**8a**)¹³, for which the potential energy surface on rotation around the C=C bond will be fairly flat, as reported for stilbene¹⁸. The triplet energies of the two geometric isomers of **8a** with an (*E*)-configuration of the C=C bond are 201 kJ/mol¹³, a value close to the value for the E_T for (*E*)-stilbene (205 kJ/mol¹⁹). The phantom triplet of stilbene has an energy of 197 kJ/mol^{19,20}. Therefore, it is quite likely that the energies of the two planar *Franck-Condon* triplet states of **8a** are

only 4-8 kJ/mol higher in energy than the phantom triplets formed by rotation around the C=C. Thus, a thermal equilibrium will exist between the relaxed phantom triplets and the Franck-Condon triplet states¹³. The two other geometric isomers of 8a with the (Z)-configuration at the C=C bond have triplet energies of 230 kJ/mol¹³, which is the same as the triplet energies of the (E)- and (Z)-isomers of α,β -unsaturated O-oxime ethers¹², and 8 kJ/mol lower than that of (Z)-stilbene²⁰. The energy of the phantom triplet for the isomerization of the C=N bond in oximes and oxime O-ethers is approximately 193 kJ/mol²¹. The energy gap between the planar and the twisted triplet states is thus about 38 kJ/mol. A MNDO study on formaldoxime²² using the UHF and RHF schemes²³ showed a decrease in energy of 34 and 41 kJ/mol on going from the planar to the twisted excited triplet state, respectively, whereas a recent ab-initio study on the excited states of ethanedial monoxime puts this energy gap at 29-33 kJ/mol¹⁷.

The situation for the excited triplet E-Z isomerization of (E)-[(E)-benzylideneacetaldehyde] oxime O-methyl ether, to be denoted further as (E_{CN}, E_{CC}) -8a, is shown in Figure 3 (solid line curve). Upon population of the planar (E_{CN}, E_{CC}) excited triplet state, relaxation takes place with concomitant twisting to the two T_1 potential minima $(E_{\rm CN}, Tw_{\rm CC})_3$ and $(Tw_{\rm CN}, E_{\rm CC})_3$ of which the latter is in thermal equilibrium with $(Z_{CN}, Tw_{CC})_3$ phantom triplet state. Intersystem crossing of the three phantom triplet states to the corresponding twisted ground states will then occur and the resulting species are partitioned between the $(E_{\rm CN}, E_{\rm CC})$ + $(E_{\rm CN}, Z_{\rm CC})$ -, $(E_{\rm CN}, E_{\rm CC})$ - + $(Z_{\rm CN}, E_{\rm CC})$ -and $(Z_{\rm CN}, E_{\rm CC})$ - + $(Z_{\rm CN}, Z_{\rm CC})$ -isomers, respectively. Thus, triplet-photosensitized isomerization of (E_{CN}, E_{CC}) -8a leads directly to the formation of the other three geometric isomers. Similarly, population of the vertical excited triplet state of any of the other three isomers (Z_{CN}, E_{CC}) , (Z_{CN}, Z_{CC}) and (E_{CN}, Z_{CC}) leads to direct conversion into the other three geometric isomers. The homologue, benzylideneacetone oxime O-methyl ether $(8b)^{24}$, behaves different from that of 8a in that triplet photosensitization of $(E_{\rm CN}, E_{\rm CC})$ - or $(Z_{\rm CN}, E_{\rm CC})$ -8b leads to equilibration of all four geometric isomers by a combination of rapid C=N and



Figure 3. Potential energy curves for the excited triplet state isomerization of (E_{CN}, E_{CC}) -8a (solid line) and a simple (E_{CN}, E_{CN}) - α -bis(methoxyimino)alkane (dotted line).

slower C=C isomerization. This difference in behaviour may be ascribed to steric repulsion between the phenyl and the additional methyl substituent in the (Z_{CN}) -isomers (as observed before²⁵), leading to enhanced energy for their planar, *Franck-Condon*, excited triplet states, thus reducing the rate of thermal equilibration via these states.

The situation for the excited triplet E-Z isomerization of a simple aliphatic ((E,E)- α -bis(methoxyimino)alkane is also shown in Figure 3 (dotted line curve). As model compounds for the (E,E)-, (E,Z)-, (Z,Z)- and (Z,E)-isomers, (E)-7, (E)-6, (Z)-6 and (Z)-7, respectively, (see Introduction) were taken, of which the energies of the Franc-Condon triplet states were determined to be 226, 224, 209 and 220 \pm 4 kJ/mol, respectively (see above). Furthermore, the energy contents of the intermediary phantom triplets will be equal to those of oxime O-methyl ethers (193 kJ/mol²¹). The relatively high energy barriers between the phantom triplets now prevent thermal equilibration between the different phantom triplets before intersystem crossing (isc) to the highly excited ground state takes place with subsequent partition to the two contiguous geometric isomers, *e.g.*:

$$|E_{\rm CC}, Tw_{\rm CN}|_3 \xrightarrow{\rm isc} |E_{\rm CC}, Tw_{\rm CN}|_1 \xrightarrow{\rm partition} \\ \alpha (E_{\rm CC}, E_{\rm CN}) + (1-\alpha) (E_{\rm CC}, Z_{\rm CN})$$

The discussion in terms of the occurrence or not of a rapid isomerization of the different phantom triplets, as predicted by the energetics of the potential energy curves shown in Figure 3, satisfactorily explains the difference in the tripletsensitized isomerization of simple α -bis(methoxyimino)alkanes, which proceeds stepwise by $E \cdot Z$ isomerization of one double bond at a time on the one hand. On the other hand, that of, for example, 1-(methoxyimino)-3-phenyl-2--propene (**8a**) proceeds from a given geometric isomer directly to any of the other geometric isomers.

Direct irradiation at λ 254 nm

Direct irradiation of the α -bis(methoxyimino)alkanes 1-4 and the related dihydro(methoxyimino)isoxazoles 6 and 7 at λ 254 nm leads to dissociation, in addition to the more rapid E-Z isomerization. The product distribution obtained upon irradiation of (E,E)-1, (E,E)-3, (E)-6 and (E)-7 are collected in Table II. 1,2-Bis(methoxyimino)indane (5) does not photodissociate, the absence of which may be related to the rigidity of the planar structure of the cross-conjugated molecule⁹.

By analogy with the α -oxo oxime ethers^{26,27}, E-Z isomerization of the α -bis(methoxyimino)alkanes 1-5 and the dihydroisoxazoles 6 and 7 upon direct irradiation is proposed to proceed from the lowest excited triplet state. Since $n\pi^*$

Table II Product distribution upon λ 254 nm irradiation of 0.10M solutions of the α -bis(methoxyimino)alkanes 1, 3, 6 and 7.

Starting	Solvent ^a	Irrad. time (h)	Conver- sion (%)	Reaction mixture composition (%)						Material		
material				(<i>E</i> , <i>E</i>)-1	(<i>E</i> , <i>Z</i>)-1	(Z,Z)-1	СН ₃ ОН	CH ₃ CN				(%) ^b
(<i>E</i> , <i>E</i>)-1	CD ₃ CN ^c	1.0 1.5 3.0 9 20	50 60 85 95 99	50 40 15 5 -	50 56 65 23 17 (<i>E</i> , <i>Z</i>)-3	$ \begin{array}{c} - \\ 3 \\ 13 \\ 47 \\ 31 \end{array} $		- + + (Z)-10	11	12		100 99 93 78-81 57-65
(E,E)- 3	сН	1.0 3.0 20 1.0 7 20	50 80 92 50 70 84	50 20 8 19 15 8	42 35 16 50 30 16	7 23 13 26 23 13	- 2 10 2 5 10	- 2 - 1 2	- 6 - 2 6	1 6 18 3 12 18		100 86 73 100 88 73
				(E) -6	(Z)-6		13	14	15	16	СН₃ОН	
(E)- 6	cH cH ^e CD ₃ CN ^c	3.0 4 11 21 15 1.0 5	50 60 75 87 80 50 60	50 40 25 12.5 20 48 36 50	37 31 17.5 10 14 38 26 27 5		3.5 10 17.5 16 23 1 5	- 1.5 3 4 -	- 1 -		d d d d 9 26 d	91 87 73 56 57 95 81
	Me ₂ CHOH	1.0 6 3.0 8	50 65 50 70	50 35 50 30	37.5 27.5 37.5 22.5		12.5 37.5 12.5 40		2.5	5	d d d	f f f
				(E) -7	(Z)-7		17					
(E)- 7	сН	1.0 5 6	50 60 65	50 40 35	49 40 35		1 5 10					100 85 80

^a cH stands for cyclohexane. ^b The material balance refers to the sum of the geometric isomers and the products resulting from the initially produced iminyl radical. ^c The quantitative product analysis was made by ¹H NMR. ^d Not determined. ^e The solution contained 0.10M 1-dodecanethiol. ^f No internal standard was used in the GLC analysis.

absorption is hidden under the $\pi\pi^*$ absorption⁹, the excited singlet $n\pi^*$ and $\pi\pi^*$ states will be close in energy content. Due to the relatively larger singlet-triplet energy gap between the states of $\pi\pi^*$ as compared with those of $n\pi^*$ character²⁸, the lowest triplet state of 1-7 will be undoubtedly of $\pi\pi^*$ character.

Upon direct irradiation of a given geometric isomer of any of the compounds 1 and 3-5, E-Z isomerization was found to proceed in a step-wise fashion. In Figure 4, the photoisomerization of (E,E)-1 is shown as a typical example. The formation of (Z,Z)-1 shows an induction period. This isomer is apparently not directly formed from (E,E)-1, but from (E,Z)-1, which is the primary photoproduct upon starting from (E,E)-1.

The photoisomerization of (E,E)-1 to (E,Z)-1 and of (E,Z)-1 to (Z,Z)-1 are both quenched by 30% upon performing irradiation at 254 nm under an atmosphere of oxygen instead of argon (see Figure 4). No such quenching ef-



Figure 4. E-Z isomerization of (E,E)-1 (0.10M) in cyclohexane as solvent upon direct irradiation at λ 254 nm, and the effect of oxygen.

fect was observed with the α -oxo oxime ethers, for which the intersystem crossing is close to unity²⁹. Triplet-photosensitized E-Z isomerization of the three isomers of 1 are not quenched by oxygen. Accordingly, the excited singlet states of the geometric isomers of 1 are those which are quenched by oxygen. The difference in the behaviour of the two classes of compounds may be rationalized in terms of the difference in the life-times of the excited singlet states of the α -bis(methoxyimino)alkanes and the α -oxo oxime ethers. For these will be substantially greater for the former than the latter type of compounds, in view of the larger singlet-triplet energy gap³⁰ of the former, the values being 210–290 and 40–100 kJ/mol, respectively²⁷.

The photodecomposition products (λ 254 nm) of (*E*,*E*)-2,3--bis(methoxyimino)butane [(*E*,*E*)-1] in cyclohexane are acetonitrile and methanol, and those of the phenyl analogue (*E*,*E*)-2 are acetonitrile, benzonitrile and methanol³¹. The cyclic compound 3 was studied in more detail. Irradiation of



Figure 5. Irradiation of (E,E)-3 and (E,Z)-3, both 0.10M, in cyclohexane at 254 nm.

(*E*,*E*)-3 and of (*E*,*Z*)-3 in cyclohexane at λ 254 nm leads predominantly to *E*-*Z* isomerization, the former yielding as primary product (*E*,*Z*)-3 and the latter both (*E*,*E*)-3 and (*Z*,*Z*)-3 (Figure 5). The photodecomposition of 3 is slow relative to the *E*-*Z* isomerization and the ratio between the concentrations of the three geometric isomers becomes constant after 5 h of irradiation with {|*E*,*E*|/|*E*,*Z*|}_{pss} = 0.51 ± 0.02 and {|*E*,*Z*|/|*Z*,*Z*|}_{pss} = 1.28 ± 0.05³¹. The major photodecomposition products of 3 are (*E*)-5-(methoxyimino)-2,2,4,4-tetramethylcyclopentanone [(*E*)-10], 2,2,4,4-tetramethylpentanedinitrile (11) and 2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrole-5-carbonitrile (12)³².



The mechanisms for the formation of the various photodecomposition products upon irradiation of the α -bis(methoxyimino)alkanes 1-3 are shown in Scheme 1, and those for

the irradiation of the 4,5-dihydro-4-(hydroxyimino)isoxazole 6 in Scheme 2. The initial step in the photodissociation of 1-3, 6 and 7 is presumed to be N-O cleavage of one of the iminoxy groups (step 1) by analogy with the photodecomposition of the related α -oxo oxime ethers^{17,27,33}. This may also be deduced from the formation of methanol from all the α -bis(methoxyimino)alkanes studied, the formation of (E)- and (Z)-10 from 3 via the unstable imines (E)- and (Z)-9, of the imine 13 and its cyclohexyl derivative 14 from 6, and of trans-3-acetyl-4,5-diethyl-4,5-dihydroisoxazole (17) upon irradiation of (E)-7. The excited state exhibiting the N-O homolysis is the S¹ state (steps 1a and 1b, Scheme 1), since triplet photosensitization of the compounds under study does not lead to photodecomposition, but only to E-Z isomerization (see above). Studies on the dependence of product composition on the irradiation time made for (E,E)-1 (Figure 6) and (E,E)- and (E,Z)-3 (Figure 5) illustrate that (E,Z)-1 and (E,Z)-3 are the geometric isomers undergoing photodissociation and that the (E,E)--isomers are not, in view of the induction time for the formation of the photodecomposition products on starting with the latter type of isomers (cf., Figures 5A and 6). The results further indicate that the (Z,Z)-isomers might undergo some photodissociation, but this is thought to be unlikely in view of their relatively low molar extinction coefficients at λ 254 nm⁹. Moreover, if N-O cleavage would only occur from the (Z,Z)-isomer, then one would expect (Z)-10 to be the isomer formed initially upon irradiation of (E,E)-3. In fact, the primary product is (E)-10, which subsequently photoisomerizes to (Z)-10 (see Table II). It appears that the (E,Z)-isomer is that undergoing photodissociation and that it is the methoxyimino group having the (Z)-configuration which exhibits N-O cleavage. This behaviour deviates from that of the α -oxo oxime ethers of which only the (E)-isomers undergo N-O bond dissociation^{17,27}.



Scheme 1. Routes of product formation upon irradiation of the α -bis(methoxyimino)alkanes 1–3 in cyclohexane at λ 254 nm.



Scheme 2. Routes of product formation upon irradiation of the 4,5-dihydro-4-(methoxyimino)isoxazole 6 in cyclohexane at λ 254 nm.

The step subsequent to initial N–O homolysis in product formation from the α -bis(methoxyimino)alkanes 1–3 may be either loss of the other methoxy group (Scheme 1, steps 2a and 2b), followed by α cleavage (steps 3–5), or α cleavage followed by loss of a methoxy radical, of which the former order of events is considered more likely³⁴.

The mono-iminyl radical formed from 1-3 may either lose the other methoxy group as a radical, followed by homolysis of the inter-iminyl C-C bond of the bis(iminyl) diradical with formation of acetonitrile and benzonitrile (as in the case of 1 and 2, step 3) or of 2,2,4,4,-tetramethylpentanedinitrile (11) (as in the case of 3, step 4). Alternatively, the mono-iminyl radical may initially undergo homolysis of the



Figure 6. Dependence of product composition on the irradiation (λ 254 nm) time for (E,E)-1 (0.10M) in acetonitrile-d₃.

inter-iminyl C-C bond, followed by loss of the methoxy radical leading to the same products. Upon starting with 3, the main product is the cyclic carbonitrile 12, resulting from the bis(iminyl) diradical by β cleavage³⁵ of one of NC-CMe₂ bonds and subsequent ring closure (steps 5 and 6). The ratio of 11/12 is 0.33. Accordingly, the rate of cleavage of the inter-iminyl C-C bond is a factor of 0.66 times that of one of the adjacent C-C bonds. The monoiminyl radical may also abstract hydrogen from, for example, the solvent, as appears to occur from the formation of the imine 13 upon irradiation of the isoxazole 6. The high stability of the imine 13 should be noted, even under GLC conditions, since imines in general are highly unstable and hydrolyze rapidly to the corresponding ketones^{27,41}. This is apparent in the present study from the formation of (E)-and (Z)-5-(methoxyimino)-2,2,4,4-tetramethylcyclopentanone [(E)- and (Z)-10] upon irradiation of (E,E)-3 and of trans-3-acetyl-4,5-diethyl-4,5-dihydroisoxazole (17) upon irradiation of (E)-7, as well as from the rapid and complete conversion of the imine 13 into the corresponding ketone 15 upon addition of aqueous 10% hydrochloric acid, or dilute acetic acid to the irradiated solution of (E,E)-6. In the presence of a good hydrogen-atom donor, such as 2-propanol or 1-dodecanethiol⁴², a complete photoconversion of (E)-6 into the imine 13 takes place³². In acetonitrile as solvent, the photoreaction proceeds cleanly, yielding in addition to isomer (Z)-6, mainly methanol, the stable imine 13 and the dimer 16³⁶

Another fate of the primarily formed mono-iminyl radicals is recombination either with a similar radical, as exemplified by the formation of the dimer 16 upon irradiation of (E)-6 (Scheme 2, step 2), or with a solvent-derived radical, as exemplified by the formation of (E)- and (Z)-14, which are formed in a 10:1 ratio upon irradiation of (E)-6 in cyclohexane as solvent (Scheme 2, step 3).

The irradiation of (E)-4,5-dihydro-4-(methoxyimino)-3,5,5--trimethylisoxazole [(E)-6] at λ 254 nm leads selectively to homolysis of the exocyclic N-O bond. This observation renders the conclusion of *Kumagai* et al.⁴³ that the "bond dissociation of 184 kJ/mol of the N-O bond and the rigidity of the five-membered ring along with the loose and active character of the N-O stretching mode in the excited state easily account for the facile scission of the N-O bond of isoxazolines" somewhat doubtful.

Experimental

The syntheses and the spectral data of the photoreactants and their geometric isomers have been reported previously⁵.

¹H NMR spectra were recorded on Varian A-60D (using TMS as internal standard), Bruker AC-200 or Bruker WM-250 spectrometers. For ¹³C NMR, the latter two spectrometers were used. IR spectra were obtained using Perkin–Elmer 254, 298 or 1310 spectrophotometers. The UV absorption data were recorded on a Cary 14 or Hewlett–Packard 8451-A diode array spectrophotometer. The mass spectra and the accurate mass data were obtained using a Varian MAT-711 spectrometer at 70 eV.

Irradiation procedures, analysis and product separation

All solutions were purged with argon or nitrogen for 10 min prior to irradiation. For direct irradiation at 254 nm, quartz vessels and quartz NMR tubes were employed. Triplet-sensitized experiments were performed in degassed solutions in benzene at λ 300 or 350 nm. Care was taken to ensure that the photosensitizer absorbed more than 98% of the incident radiation. The triplet sensitizers came from a Baker photosensitizer and quencher kit. Irradiation was performed in a Rayonet RPR 208 photoreactor equipped with eight RUL-3000-Å, eight RUL-3500-Å or four RUL-2537-Å light sources. The irradiated samples were analyzed by ¹H NMR or GLC. For the latter, a Varian 3700 aerograph with TC detector using various columns, coupled to a Varian CDS-111C or Shimadzu C-R3A integrator, was used to analyse the samples. For product separation, either flash chromatography⁴⁴ (Merck silica gel, 230-400 mesh and various eluents) or preparative GLC were used. For semi-preparative GLC separation, a Varian 2700 aerograph was employed using the following columns: a $2 \text{ m} \times 1/4'$ copper column, 15% OV-225 on chromosorb W-AW (80-100 mesh), He flow 60 ml/min; a $5 \text{ m} \times 1/4''$ copper column, 15%SE-30 on chromosorb W-AW (45-60 mesh), He flow 60 ml/min, $170\,^\circ\text{C};\,2.5\ m\times1/4''$ copper column, 10% OV-225 on chromosorb W-AW (45-60 mesh), He flow 60 ml/min; a $2 \text{ m} \times 1/4^{"}$ stainlesssteel column, 15% OV-225 on chromosorb W-AW (45-60 mesh), He flow 60 ml/min; and a $1.5 \text{ m} \times 3/8''$, 10% FFAP on Supelcoport (80-100 mesh), He flow 60 ml/min.

Product assignments

The assignments of the products methanol⁴⁴, acetonitrile⁴⁴, benzonitrile⁴⁴, 10^{26} and 15^{39} were based on comparison with available spectral data. Those of the other products were made directly on the basis of their spectral data:

2.2.4.4-Tetramethylpentanedinitrile (11). ¹H NMR (CDCl₃, δ)³⁹: 1.520 (s, 12H), 1.819 (s, 2H). IR (CHCl₃, cm⁻¹)³⁹: 2980, 2940, 2870, 2220, 1470, 1450, 1395, 1370, 1230, 910. FI-MS (*m*/*z*): 151 (M + 1)[‡]. MS (70 eV, *m*/*z*): (150 M[‡]), 69 (base); accurate mass obsd.: 150.1160; calcd. for C₉H₁₄N₂: 150.1157.

3.4-Dihydro-2.2.4.4-tetramethyl-2H-pyrrole-5-carbonitrile (12). ¹H NMR (CDCl₃, δ): 1.281 (s, 6H), 1.308 (s, 6H), 1.760 (s, 2H). ¹³C NMR (CDCl₃, δ): 27.1 (4-Me₂), 30.3 (2-Me₂), 50.2 (3-C), 52.9 (4-C), 75.3 (2-C), 113.3 (C=N), 156.4 (C=N). IR (CHCl₃, cm⁻¹): 2960, 2920, 2860, 1615, 1470, 1450, 1370, 1160, 905. MS (70 eV, *m/z*): 150 (M[±]), 135 (base).

4.5-Dihydro-4-imino-3.5.5-trimethylisoxazole (13). ¹H NMR (CDCl₃, δ): 1.375 (s, 6H), 2.104 (s, 3H). IR (CHCl₃, cm⁻¹): 3250, 2980, 2930, 2860, 1650, 1582, 1455, 1435, 1390, 1380, 1360, 1150, 1080, 1015, 980, 915, 870. Accurate mass obsd.: 126.0798, calcd. for C₆H₁₀N₂O: 126.0793. UV [λ_{max} (nm), (ϵ) (1 · mol⁻¹ · cm⁻¹)]: acetonitrile, 257 (5770); cyclohexane, 259 (6380).

4-(Cyclohexylimino)-4,5-dihydro-3,5,5-trimethylisoxazole (14). (E)-14: ¹H NMR (CDCl₃, δ): 1.491 (s, 6H), 1.2–1.9 (m, 10H), 2.006 (s, 3H), 3.626 (septet, J 4.7 Hz, 1H). MS (70 eV, m/z): 208 (M⁺), 83 base).

(Z)-14: ¹H NMR (CDCl₃, δ): 1.311 (s, 6H), 1.2–1.9 (m, 10H), 2.308 (s, 3H), 3.849 (septet, J 4.7 Hz, 1H).

4,4'-Hydrazinediylidenebis(4.5-dihydro-3,5,5-trimethylisoxazole) (16). ¹H NMR (CDCl₃, δ): 1.608 (s, 12H), 2.134 (s, 6H). IR (CHCl₃, cm⁻¹): 2985, 2940, 2860, 1635, 1570, 1455, 1430, 1375, 1360, 1145, 1010, 920, 900, 850. MS (70 eV, m/z): 250 (M⁺), 43 (base), Accurate mass obsd.: 250.1428; calcd. for C₁₂H₁₈N₄O₂: 250.1430. trans-3-Acetyl-4,5-diethyl-4,5-dihydroisoxazole (17). ¹H NMR (CDCl₃, δ): 0.860 (t, J 7.4 Hz, 3H), 0.940 (t, J 7.4 Hz, 3H), 1.44–1.77 (m, 2 × 2H), 2.462 (s, 3H), 3.03–3.10 (m, 1H), 4.36–4.43 (m, 1H). ¹³C NMR (APT, CDCl₃, δ): 8.9 + 10.6 (2 × ethyl-Me), 23.8 (4-CH₂), 26.8 (acetyl-Me), 27.9 (5-CH₂), 50.7 (4-C), 90.3 (5-C), 159.9 (C=N), 193.3 (C=O). IR (CHCl₃, cm⁻¹): 2960, 2930, 2880, 1680, 1565, 1460, 1375, 1350, 1310, 1280, 1080, 935, 840. MS (70 eV, *m/z*): 169 (M[±]), 43 (base, MeC=O⁺). Accurate mass obsd.: 169.1103, calcd. for C₉H₁₅NO₂: 169.1103. UV [λ_{max} (nm), (ϵ) (1 · mol⁻¹ · cm⁻¹)]: cyclohexane, 259 (6500), 320 (30); ethanol 261 (6900), 320 (25).

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- ⁶ The stereochemistry of the present compounds is quite complex, since the configuration of C=N and the conformation of the central C-C and the N-O bonds of the C-O-N=C-C=N-O-C moiety have all to be taken into account. Experimental evidence^{7,8} has shown that the C=N-O-H moiety of oximes is planar with the O-H and C=N in antiplanar orientation and a similar orientations has been proposed for the corresponding *O*-alkyl ethers⁹.
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- ³² On performing the irradiation of (E,E)-3 with λ 254 nm in the presence of a hydrogen (atom) donor such as 2-propanol or 1-dodecanethiol, the degree of formation of the corresponding α -oxo oxime ether 10, which results rapidly from the unstable α -oxo imine 9 by hydrolysis²⁷, was not enhanced. This behaviour differs from that of the isoxazoline derivative (E)-6 (see Results and discussion).
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