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Photofragmentation and photoisomerization of *O*-acyl-α-oxooximes Quantum yields and mechanism

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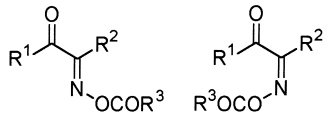
Abstract

Fourteen *O*-acyl-α-oxooximes with the general formula $R^1CO–C(R^2)=N–OCOR^3$, all but one (*E*)-isomers, with R^1 methyl (series **1**) or phenyl (series **2**), R^2 methyl, and different aliphatic or aromatic R^3 groups, have been prepared to study their radical photogeneration efficiency in acetonitrile solution under irradiation with 313 nm light. The quantum yields for the photolysis process, Φ_p, that includes radical photofragmentation and *E/Z* photoisomerization, were in the range 0.60–1.05 in the presence of oxygen, and for five tested compounds similar values were observed under inert atmosphere. The (*Z*)-isomer ***Z*-2e** (R^3 phenyl) was different, with Φ_p values of 0.41 under air and 0.77 under nitrogen. No correlation could be found between Φ_p values and the above acyloxooxime substituents. In the case of **2e** (R^3 phenyl, (*E*)-isomer) Φ_p values larger than unit have been observed, supporting the existence of dark chain processes of acyloxooxime disappearance. The quantum yields of photoisomerization, Φ_i, determined for acyloxooximes **1e** (R^3 phenyl, (*E*)-isomer), **2e** and ***Z*-2e** have shown that this process competes with photofragmentation, becoming the only one in **2e** under triplet sensitized irradiation. It is proposed that in this compound the radical photofragmentation takes place from the excited singlet state, while the photoisomerization reaction occurs through the triplet state. In addition, the photoproducts generated in the direct irradiation of **2e** in different solvents have been analysed, and radical mechanisms for their formation by reaction with the solvent molecules are suggested.

Keywords: *O*-Acyloxooximes; Quantum yields; Photofragmentaton; Photoisomerization; Photoproducts

1. Introduction

Under UV irradiation, simple *O*-acyl-α-oxooximes (AO) predominantly undergo homolitic fragmentation into radicals and/or *E/Z* isomerization, the relative importance of each process depending on the irradiated acyloxooxime [1]. Only photofragmentation has been observed in some (*E*)-AO with R^1 and R^2 alkyl groups (see formula), while photoisomerization is a competitive reaction when R^1 and/or R^2 are aryl groups [2,3]. In general, AO that are efficient photogenerators of radicals are also efficient type I (unimolecular) photoinitiators for radical polymerization of unsaturated monomers, and many AO with different substituents have been tested looking for better photoinitiators [4,5]. [1] Without exceptions, AO with R^2 alkyl are more efficient photoinitiators than those with R^2 phenyl, while the influence of the type of substituent R^3 seems to be negligible [6,7]. Nevertheless, the relationship between photoinitiator efficiency and structure, including *E/Z* configuration, has not been definitively clarified, likely as a result of the complex radical reactions involved.



All the experimental evidence suggests that AO photofragmentation mainly takes place via N–O bond fission [8–11], because the corresponding primary radicals have been detected in the irradiated solutions [6,12], as well as products clearly derived from thermal reactions of said radicals [13,14]. The reactive excited state from which AO generate these radicals is still unknown, although unpublished laser flash photolysis results support a short-lived triplet state [4], and the same state seems to be involved in the photofragmentation of *O*-acyloximes without α-carbonyl group

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[1] See also [1] for related acyloxooxime patents.

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[15,16], both under direct irradiation or by sensitization with aromatic ketones, in the latter case likely through an excited encounter complex [acyloxime-sensitizer] [17]. On the contrary, the photofragmentation of *O*-alkyl-α-oxooximes possibly proceeds through the (n,π*) excited singlet state, because triplet sensitized irradiations only produce *E/Z* isomerizations [10,18,19]. The presence of AO in photoinitiator systems for radical polymerization under visible light irradiation gives rise to a clear enhancement in the polymerization rate, and we have formerly elucidated the mechanism of this effect, with the AO as additive to the system dye-amine, or with the *O*-acyl-α-oxooxime chromophore covalently bond to the dye molecule [20,21].

The main purpose of the present work was to elucidate the influence of the substituents R^1 and R^3, and of the *E/Z* configuration, on the radical generation efficiency of several AO under UV (313 nm) irradiation. For this aim we have prepared two series of AO with R^1methyl (series **1**) or phenyl (series **2**), with different R^3 groups, and with a common R^2 group (methyl), and their photolysis quantum yields have been determined. We have included four AO with two *O*-acyl-α-oxooxime chromophores and, hence, with two possible radical-generating groups per molecule. Besides, the quantum yields of photoisomerization of three selected AO have been determined. In addition, the triplet sensitized photofragmentation and photoisomerization processes of the representative acyloxooxime **2e** (R^3 phenyl), as well as the photoproducts generated in its direct irradiation in different solvents, have been also studied. In this way we have been able to show that under direct irradiation both photoreactions compete, and that in the case of **2e** photofragmentation and photoisomerization take place from the excited singlet and triplet states, respectively.

2. Experimental

2.1. Materials

All solvents used were of the highest purity available (>99%). Acetophenone and benzophenone (both Aldrich) were purified by distillation and crystallization, respectively. The α-oxooximes (*E*)-3-hydroxyiminobutan-2-ona (**1a**) and (*E*)-1-phenyl-2-hidroxyiminopropan-1-ona (**2a**) (both Aldrich, 99%) were used as received. (*E*)-AO **1b**–**g** and **2b**–**h** (see formulas in Table 1) were obtained from oximes **1a** and **2a** by reaction with the appropriate acyl chloride, as described elsewhere [22]. Methyl 5-chloroformylpentanoate was obtained by the reaction of adipoyl chloride with one equivalent of methanol, and was purified by vacuum distillation, b.p. 69°C/0.5 Torr, 48% yield. The final AO were purified by distillation or by crystallization from hexane or its mixtures with ethyl acetate, except otherwise noted. The (*Z*)-isomer ***Z*-2e** was obtained by photoisomerization of the corresponding (*E*)-isomer **2e** [23]. Fig. 1 shows the absorption spectra of both *E/Z* isomers. All AO gave a single spot on TLC plates with several eluents, a single signal in HPLC and correct microanalytical data. See Appendix A for the relevant data of all the AO herein studied. Benzoylacetonitrile was obtained as described in [24].

2.2. Methods

UV absorption spectra were measured in Perkin-Elmer Lambda-2 and Shimadzu UV-265FS spectrophotometers. IR spectra were recorded in a Perkin-Elmer 681 spectrophotometer. Mass spectra (MS) were obtained in a VG 12-250 spectrometer with electron impact at 70 eV and with direct sample injection. Nuclear magnetic resonance (NMR) spectra were registered on a Varian-Gemini spectrometer (200 MHz) with tetramethylsilane as internal reference; phenyl groups 'a' and 'b' refer to PhCO–C (keto, series **2**) and PhCO–O-(benzoate esters), respectively. High performance liquid chromatography (HPLC) analyses were run at room temperature with a Waters 510 pump, a 7125 Rheodyne sample injector (20 μl), a Nova-Pak C_{18} reverse-phase column (15 cm, 5 μm), a Philips PU 4020 UV detector fixed at 254 nm, and a ChromaJet Spectra-Physics integrator, using as eluent the mixture MeCN–H_2O 45:55 (for acyloxooximes **1**) or 55:45 (for acyloxooximes **2**), at 1.2 ml min^{-1}. Retention times (t_R) and retention factors ($k = (t_R - t_M)/t_M$, being t_M the elution time of a non-retained sample) were determined for each analyte. Quantitative AO analyses were carried out by calibration with solutions of known concentrations. Combined gas chromatography/mass spectrometry (GC/MS) analyses were carried out in a Hewlett-Packard HP G1800A (GCD system) gas chromatograph equipped with a mass detector in the EI mode (ionization energy 70 eV), scanning between 40 and 425 amu, and controlled by an HP 3365 ChemStation software; a laboratory-made capillary

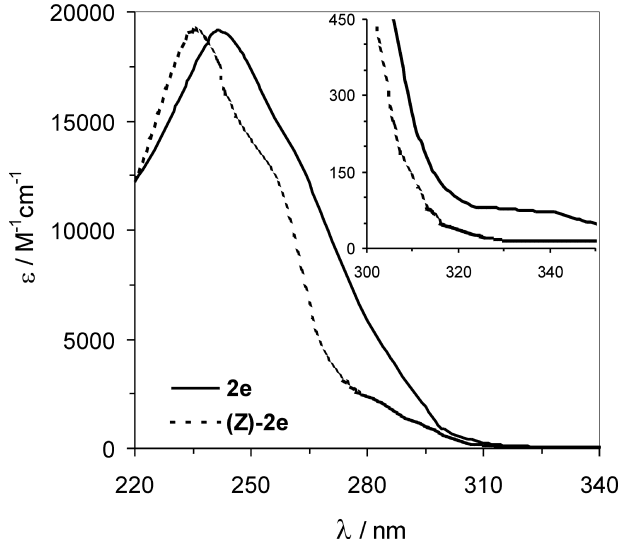


Fig. 1. UV spectra of the (*E*)-isomer **2e** and its (*Z*)-isomer ***Z*-2e** in acetonitrile solution.

column (25 m × 0.32 mm × 0.8 μm) coated with methylsilicone OV-1 was employed, with helium as carrier gas.

2.3. Irradiations

The irradiation system used in the determination of quantum yields basically consists on a high pressure Hg-lamp (Philips CS-500/2, 500 W) and a monochromator (Kratos GM-252), as well as appropriate filters and lens. Fresh AO solutions in acetonitrile (3.5 ml) were irradiated with 313 nm light in 1-cm pathlength quartz cuvettes. Different incident light intensities were obtained by changing the monochromator slits. Irradiations in the absence of oxygen were carried out in sealed cells, after bubbling nitrogen for at least 20 min. In most cases, comparative experiments (at least duplicated) were run consecutively. A merry-go-round system was used for the sensitized experiments.

For the analysis of products from the irradiation of acyloxooxime **2e** in several solvents, two methods were followed: (1) for GC/MS and HPLC analysis, 1 mM solutions of **2e** (3.5 ml) were irradiated in 1-cm quartz cell with 313 nm light (incident light intensity ca. 3×10^{-9} einstein l^{-1} s^{-1}), under nitrogen atmosphere at room temperature, analysing reaction mixtures with less than 50% **2e** disappearance; (2) for preparative irradiations, 1 mM solutions of **2e** (100 ml) were irradiated under similar conditions in an immersion-well pyrex reactor with >350 nm light (cut-off filter: 5 mM $BiCl_3$ in 0.3 M HCl). In both cases the main products were identified by chromatographic comparison with pure compounds and, when enough amount was available, by ^{1}H NMR.

2.4. Determination of quantum yields

The quantum yield of AO photolysis, Φ_p, that includes photofragmentation and *E*/*Z* photoisomerization, and the quantum yield of photoisomerization, Φ_i, have been computed from the slope of the plot of the AO concentration decrease ($\Delta[AO]_t$, mol l^{-1}), determined by quantitative HPLC analysis after irradiation for a time *t*, vs. the light intensity absorbed by the solution (I_a) for the same time for conversions lower than 30%. I_a has been calculated with the Beer law

$$I_a = I_0(1 - 10^{-Ab(t)})$$

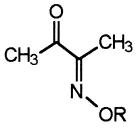
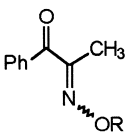
where I_0 is the incident light intensity (a value practically constant for each irradiation), determined with an International Light 700A radiometer calibrated by actinometry with Aberchrom 540 [25,26], and Ab(*t*) is the average absorbance of the solution, $\frac{1}{2}[Ab(t_2) - Ab(t_1)]$, assuming linear absorbance change along time ($t_2 - t_1$). The values of Φ_p and Φ_i so obtained were the same, within the experimental error, as the corresponding values referred to the light absorbed by the residual AO in the solution, an expected result when working with low conversions.

3. Results and discussion

3.1. UV photolysis of O-acyl-α-oxooximes

The UV spectra in acetonitrile solution of the AO herein studied show a strong (π,π^*) absorption band at 214–239 nm

Table 1
Quantum yields of photolysis (Φ_p) and photoisomerization (Φ_i) of *O*-acyl-α-oxooximes, all but ***Z*-2e** (*E*)-isomers, in acetonitrile solution under irradiation with 313 nm light[a]

Series	Compound	R	Φ_p		Φ_i[b]	
			Air	N_2	Air	N_2
Series **1** 	**1a**	H	0.32	0.17		
	1b	COMe	0.93	0.70		
	1c	COEt	1.05	1.08		
	1d	$CO(CH_2)_4CO_2Me$	0.70			
	1e	COPh	0.74	0.71	0.44	0.45
	1f	$CO(CH_2)_2CO_2N{=}C(Me)COMe$	0.65			
	1g	$CO(CH_2)_4CO_2N{=}C(Me)COMe$	0.60			
Series **2** 	**2a**	H	0.24	0.21		
	2b	COMe	0.77	0.82		
	2c	COEt	0.83			
	2d	$CO(CH_2)_4CO_2Me$	0.99			
	2e	COPh	0.72	0.78	0.19	0.21
	***Z*-2e**	COPh	0.41	0.77	0.28	0.29
	2f	$CO(CH_2)_2CO_2N{=}C(Me)COPh$	0.74			
	2g	$CO(CH_2)_4CO_2N{=}C(Me)COPh$	0.85			
	2h	CO(*p*-CH_2Cl)Ph	0.81			

[a] I_0 ca. 10^{-6} einstein l^{-1} s^{-1}. Concentration range 2–8 mM for compounds **1**, and 0.5–1.5 mM for compounds **2**. Initial absorbances at 313 nm 0.20 ± 0.01. At least duplicated values. Conversions <30%. Relative error 15%.

[b] Only determined for compounds in which the two *E*/*Z* isomers have been characterized.

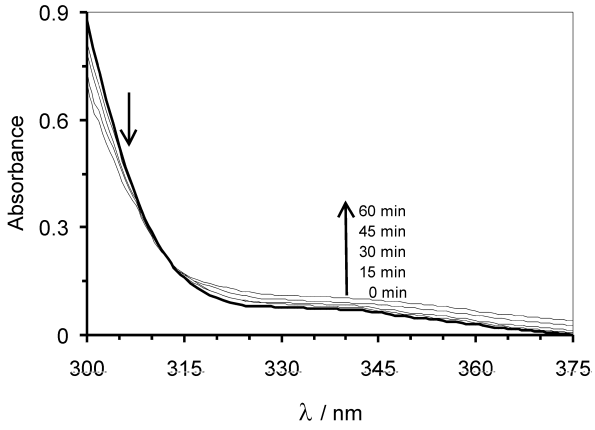


Fig. 2. Spectral changes during the photolysis of an acetonitrile solution of acyloxime **2e**. [**2e**] = 1 mM, irradiation with 313 nm light, under air.

(series **1**) or at 235–260 nm (series **2**), and a weak (n,π*) band, in some AO only detectable as a tail, at ca. 310–340 nm (Fig. 1). The photofragmentation and photoisomerization of AO and *O*-alkyl-α-oxooximes have been usually studied selectively exciting to the $S_1(n,\pi^*)$ state, i.e. irradiating with wavelengths higher than 300 nm — mainly 313 and 365 nm, two emission lines of commercial mercury lamps — in order to avoid photoreactions from higher excited states [1]. For comparative purposes, in the present work we have irradiated with 313-nm light. Under irradiation with this light, all the former AO disappeared in acetonitrile solution, both in the absence and in the presence of oxygen. The photoreaction, for ca. 30% acyloxooxime disappearance, produced absorbances changes at the irradiating wavelength of as much as ±0.05 units for initial values of 0.20 ± 0.01. In most cases an isosbestic point appeared close to 310 nm. A representative spectral change is shown in Fig. 2 for the acyloxime **2e**.

The quantum yields of photolysis, Φ_p, of all the studied AO, and those of photoisomerization, Φ_i, of **1e**, **2e** and ***Z*-2e**, the only *Z*-isomer herein studied, were graphically determined as described in Section 2. As an example, typical plots are shown for acyloxooxime **2e** in Fig. 3.

The results of the irradiation under air of 2–8 mM (series **1**) or 0.5–1.5 mM (series **2**) AO solutions (Table 1) indicate

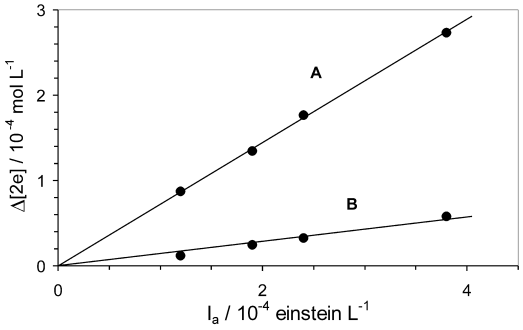


Fig. 3. Determination of quantum yields of photolysis (A) and of photoisomerization (B) of acyloxooxime **2e**. Acetonitrile solution, [**2e**] = 1 mM, irradiation with 313 nm light, under air, $I_0 = 10^{-6}$ einstein l^{-1} s^{-1}.

that these acyloxooximes undergo photolysis with high Φ_p values, in the range 0.41 (for ***Z*-2e**) to 1.05 (for **1c**), while the parent oximes **1a** and **2a** show much lower values. Similar Φ_p values have been observed under inert atmosphere for five tested compounds, indicating a low, if any, oxygen influence. An interesting exception is the acyloxooxime ***Z*-2e**, with a Φ_p value under air much lower than under nitrogen, the value under nitrogen being close to that of the isomeric (*E*)-acyloxyme **2e** under the same conditions. The different photochemical behaviour of **2e** and ***Z*-2e** in the presence of oxygen could not be studied in other couples of isomers because ***Z*-2e** was the only (*Z*)-isomer isolated in pure form. On the other hand, for each AO series and under comparative conditions no clear correlation could be deduced between Φ_p and the type of acyl group R (and hence R^3), or the type of substituent at the keto group, R^1, pointing to complex photolysis mechanisms that do not exclusively depend on the substituents. Molecules with two *O*-acyl-α-oxooxime groups (**1f**, **1g**, **2f** and **2g**) also show high Φ_p values, behaving as if they had a single chromophore.

Regarding the photoisomerization quantum yields, Φ_i, the values determined for **1e**, **2e** and ***Z*-2e** indicate that an important pathway for the photolysis of these AO is *E*/*Z* photoisomerization, with percentages of the isomerization processes on the total disappearance processes in the absence of oxygen of ca. 63, 27 and 38%, respectively. In the particular case of acyloxooxime ***Z*-2e**, photoisomerization predominates in the presence of oxygen (68%). As photoisomerization competes with the photofragmentation into radicals, the efficiency for radical generation of the (*E*)-isomer **2e** must be higher than that of ***Z*-2e**, under similar experimental conditions, because **2e** shows lower Φ_i values. Moreover, the higher Φ_i of **1e**, if compared with **2e**, again indicates a more efficient radical photogeneration process of **2e**, taking into account that both compounds show similar Φ_p values. The Φ_i values of the three AO herein studied are not affected by the presence of oxygen.

When acetonitrile solutions of **1b**, **1e**, **2b** and **2e** with 10 times lower concentrations than those used in the former assays were irradiated under similar conditions, both in the presence and in the absence of oxygen, Φ_p and Φ_i values similar to those of Table 1 were obtained (results not shown). However, when solutions of the acyloxooxime **2e** with higher concentrations (up to 4 mM) were similarly irradiated, keeping constant the absorbed light intensity I_a by properly changing the incident light intensities I_0, a clear concentration effect was observed: the increase of the AO concentration does increase Φ_p and, to a lesser extent, Φ_i (Fig. 4).

In these cases, Φ_p values higher than the unity (2.57 and 2.29, with and without oxygen, respectively, for [**2e**] 4 mM) have been observed, indicating the existence of dark thermal chain processes by which the photogenerated radicals decompose more acyloxooxime. These chain processes also explain the clear increase of Φ_p values observed when 1 mM solutions of **2e** were irradiated with increasing light

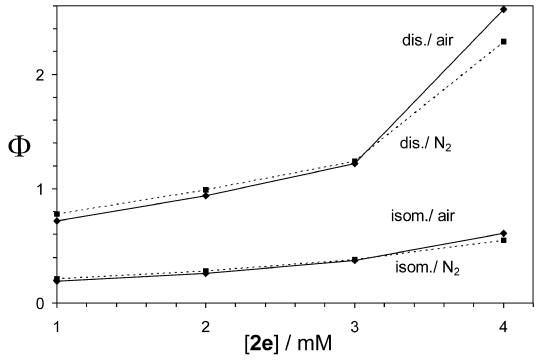


Fig. 4. Dependence of the quantum yields of photolysis (dis.) and of photoisomerization (isom.) on the initial concentration of **2e**. Acetonitrile solutions, irradiation with 313 nm light, $I_a = 2.0 \times 10^{-7}$ einstein l^{-1} s^{-1}.

intensities (Fig. 5), i.e. when the proportion of excited AO molecules able to generate radicals increases, with regard to the total number of AO molecules. This increase is more pronounced in the presence of oxygen. On the contrary, Φ_i values hardly depend on I_a, in accordance with a unimolecular process. An important consequence of the former results is that any comparison of AO photolysis ought to be carried out irradiating solutions with similar concentration in such a way as to get the same I_a values.

In order to study the nature of the excited state involved in the photolysis and photoisomerization of the representative acyloxooxime **2e**, acetonitrile solutions of this compound were irradiated in the presence of the triplet sensitizers acetophenone and benzophenone, each one used in concentration such as to absorb more than 99% of the 313 nm incident light. The triplet energy of **2e** could not be determined, no emission was detected from excited **2e** with the spectrometers available in our laboratories, even in the absence of oxygen and at 77 K, but it must be close to 65 kcal mol^{-1}, the value reported for the *O*-ethyl ether of (*E*)-3-hydroxyiminopropan-2-one [18].

The results (Table 2) indicate that under triplet sensitization only photoisomerization was observed, because very similar quantum yields values of photolysis, Φ'_p, and of photoisomerization, Φ'_i, were found. The presence of oxygen

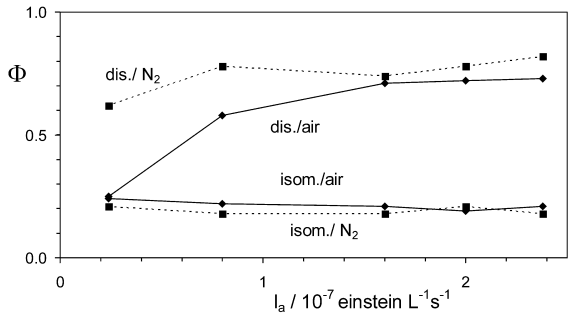


Fig. 5. Dependence of the quantum yields of photolysis (dis.) and of photoisomerization (isom.) of acyloxooxime **2e** on the absorbed light intensity. Acetonitrile solutions, irradiation with 313 nm light, [**2e**] = 1 mM.

Table 2
Quantum yields of triplet-sensitized photolysis (Φ'_p) and photoisomerization (Φ'_i) of **2e** in acetonitrile[a]

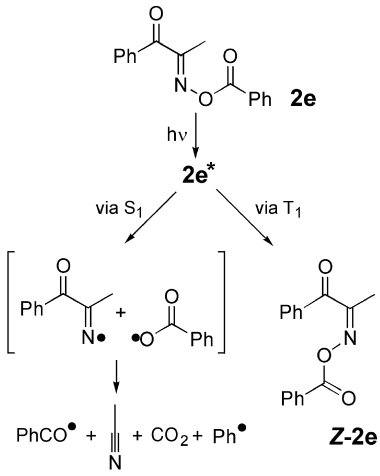
Sensitizer	E_T (kcal mol^{-1})[b]	Φ'_p		Φ'_i	
		Air	N_2	Air	N_2
Acetophenone	73.6	0.13	0.15	0.12	0.15
Benzophenone	68.6	0.03	0.12	0.03	0.07

[a] [**2e**] = 1 mM; [sensitiser] = 60 mM. Irradiation with 313 nm light. I_0 ca. 10^{-6} einstein l^{-1} s^{-1}. At least duplicated assays. Conversions <15%. Relative error 15%.
[b] E_T: triplet energy. Irradiation with 313 nm light.

produced slightly lower values, as expected when triplets are involved. The former results suggest that triplet **2e** undergoes photolysis solely through photoisomerization, likely through the rotation around the C=N bond, in accordance with theoretical calculations on oximes [27] and α-oxooximes [28], and that, therefore, **2e** photofragmentation must mainly go through the excited singlet state. *E/Z* photoisomerization of *O*-ethers of α-oxooximes also proceeds via triplet state [18,29].

3.2. Products from the photolysis of *O*-acyl-α-oxooxime **2e**

According to the accepted AO photofragmentation process, the irradiation of **2e** must generate the radicals shown in Scheme 1. It has been reported [8] that the irradiation of **2e** in benzene or carbon tetrachloride produces acetonitrile, biphenyl, benzoic acid, benzoic anhydride and phenyl benzoate, all products being explained through secondary reactions of the primary radicals. From the products detected in irradiated solutions of **2e** in other solvents (see Section 2) we have concluded that some of these radicals are also formed. Thus, the detection of methyl benzoate and ethyl benzoate in the irradiations in methanol and ethanol, respectively (ca. 6% each, estimated by ^{1}H-RMN, for ca. 40% **2e** disappearance) suggests the photogeneration of the radical PhCOO•,



Scheme 1. Mechanism of the photolysis of acyloxooxime **2e**.

solvent-H + $R^{\bullet}$ ⟶ solvent$^{\bullet}$ + R-H (1)

solvent$^{\bullet}$ + $PhCO^{\bullet}$ ⟶ PhCO-solvent (2)

$R^{\bullet}$ = $PhCOO^{\bullet}$ and/or $Ph^{\bullet}$

solvent-H	detected products
MeOH	PhCOOMe, PhCOOH
EtOH	PhCOOEt, PhCOOH
C_6H_{12}	$PhCOC_6H_{11}$
MeCN	$PhCOCH_2CN$, PhCOCOPh, PhCOOH
EtCN	PhCOCH(Me)CN

Scheme 2. Possible mechanism for the appearance of the detected products in the irradiation of **2e** in different solvents. The isomer ***Z*-2e** was also present in all the irradiated solutions.

that after H-abstraction from the solvent (Scheme 2, reaction (1)) would yield benzoic acid (detected as traces in both solvents), the esterification of which would produce the observed esters. The isomer ***Z*-2e** (ca. 25%, based on chromatographic peak areas) was also found in the former solvents.

In addition, the appearance of cyclohexylphenylketone, benzoylacetonitrile, and 2-benzoylpropionitrile in the irradiations in cyclohexane, acetonitrile and propionitrile solution, respectively (6–10% each, for 40–50% **2e** disappearance), points to the photoformation of the radical $PhCO^{\bullet}$, that after coupling with a solvent radical would yield the observed products (Scheme 2, reaction (2)). In these three solvents the isomer ***Z*-2e** was again the main reaction product (23–28%). A representative HPLC analysis of the irradiated acetonitrile solution of **2e** is: benzoic acid 6%, benzil 3%, isomer ***Z*-2e** 25%, benzoylacetonitrile 6%, and residual **2e** 60% (products in order of increasing t_R).

In acetonitrile solution, benzoylacetonitrile is formed by the coupling of $PhCO^{\bullet}$ with $^{\bullet}CH_2CN$ (reaction (2)), the latter radical likely coming from the solvent via H-abstraction by radicals from **2e**. Although radical $^{\bullet}CH_2CN$ could also proceed from the cleavage of the iminyl radical $PhCOC(Me)=N^{\bullet}$ [8], this is unlikely because benzoylacetonitrile has not been detected in the irradiation of **2e** in the other solvents.

H-abstraction from the solvents could be carried out, in principle, by any of the radicals from **2e** (Scheme 1). However, the results of some comparative experiments have shown that this is not the case for $PhCO^{\bullet}$ because: (a) benzoylacetonitrile was clearly detected when a mixture of benzil (PhCO–COPh) (0.075 M) and benzoyl peroxide (PhCOO–OCOPh) (0.075 M) was heated in acetonitrile, i.e. when the H-abstracting species $PhCOO^{\bullet}$ and/or $Ph^{\bullet}$ (both from benzoyl peroxide) and the radical $PhCO^{\bullet}$, (likely from the homolitic cleavage of benzil induced by other radicals in the medium) were simultaneously present in the solvent; (b) on the contrary, benzoylacetonitrile was not detected when $PhCO^{\bullet}$ radicals alone were generated by irradiating benzil in acetonitrile [30]; and (c) benzoylacetonitrile was not detected either when radicals $PhCOO^{\bullet}$ and $Ph^{\bullet}$ were generated in the medium, but in the absence of $PhCO^{\bullet}$, by heating benzoyl peroxide alone in acetonitrile. Summarising, when acyloxooxime **2e** is irradiated, hydrogen abstraction from the solvent seems to proceed by the radicals $PhCOO^{\bullet}$ and/or $Ph^{\bullet}$, both from the AO photofragmentation, and a latter reaction between the generated solvent radical and $PhCO^{\bullet}$ would yield the observed products.

4. Conclusions

All the *O*-acyl-α-oxooximes herein studied undergo photolysis in acetonitrile solution under irradiation with 313 nm light. Under comparative conditions, the photolysis quantum yields, Φ_p, that include the disappearance through *E/Z* photoisomerization, are in the range 0.60–1.05, and these values are scarcely influenced by the presence of oxygen. An exception is the (*Z*)-isomer ***Z*-2e**, with a much lower Φ_p value under air, indicating a more efficient oxygen quenching of the precursor excited state. No correlation could be found between these yields and the type of substituents in the chromophore –CO–C(Me)=N–O–CO– of Table 1, suggesting photolysis mechanisms where these substituents play a limited role. When the representative (*E*)-isomer **2e** was irradiated at constant concentration (1 mM) but with higher incident light intensity, or at higher concentration and constant absorbed light intensity, an increase in the photolysis quantum yield values was observed, up to values higher than the unity, indicating the existence of thermal processes where the photogenerated radicals can decompose more acyloxooxime **2e**.

The photoisomerization quantum yields of three *O*-acyl-α-oxooximes have shown that photoisomerization competes with the photofragmentation into radicals, in some cases becoming the main process. These yields are not affected by the presence of oxygen. Sensitized irradiations of the (*E*)-isomer **2e** with acetophenone or benzophenone support that the radical photofragmentation takes place from the excited singlet state, while photoisomerization proceeds from the **2e** triplet state.

The products found in the irradiation of solutions of **2e** in several solvents are clearly formed through H-abstraction from each solvent by the photogenerated radicals from **2e** $PhCOO^{\bullet}$ and $Ph^{\bullet}$, and through addition to the solvent radicals of the benzoyl radical $PhCO^{\bullet}$ from the photocleavage.

All these *O*-acyl-α-oxooximes have shown to be good photoinitiators for radical polymerization of unsaturated monomers, as will be reported in a future paper.

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Appendix A. Data of *O*-acyl-α-oxooximes

(E)-3-Oxobutan-2-iminyl acetate (**1b**). BP 103-5°C/20 Torr; HPLC data: t_R 1.79 min, k 1.71. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 217 (9600) (ε at 313 nm: 23 mol l^{-1} cm^{-1}). IR (neat): ν_{max} (cm^{-1}): 1790, 1710. MS, *m/z* (%): 143 (M$^+$, <1), 128 (<1), 101 (9), 43 (100). ^{1}H NMR ($CDCl_3$): δ 2.08 (s, 3H, C*H*$_3$C=N), 2.30 (s, 3H, C*H*$_3$CO ester), 2.51 (s, 3H, C*H*$_3$CO keto). ^{13}C NMR ($CDCl_3$): δ 10.2 (*C*H$_3$C=N), 19.6 (*C*H$_3$CO$_2$), 25.6 (*C*H$_3$CO), 160.7 (*C*=N), 167.9 (ester *C*O), 196.2 (keto *C*O).

(E)-3-Oxobutan-2-iminyl propionate (**1c**). BP 68°C/1 Torr; HPLC data: t_R 2.49 min, k 3.26. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 215 (10 900) (ε at 313 nm: 22 mol l^{-1} cm^{-1}). IR (neat) ν_{max} (cm^{-1}): 1790, 1710. MS, *m/z* (%): 157 (M$^+$, <1), 130 (5), 57 (100), 43 (99). ^{1}H NMR ($CDCl_3$): δ 1.27 (t, J = 7.5 Hz, 3H, C*H*$_3$CH$_2$), 2.08 (s, 3H, C*H*$_3$C=N), 2.51 (s, 3H, C*H*$_3$CO), 2.57 (q, J = 7.5 Hz, 2H, C*H*$_2$CH$_3$). ^{13}C NMR ($CDCl_3$): δ 8.8 (*C*H$_3$CH$_2$), 10.2 (*C*H$_3$C=N), 25.7 (*C*H$_3$CO), 26.2 (*C*H$_2$CH$_3$), 160.7 (*C*=N), 171.3 (ester *C*O), 196.3 (keto *C*O).

Methyl (E)-3-oxobutan-2-iminyl adipate (**1d**). BP 140°C/2 Torr; HPLC data: t_R 3.00 min, k 3.54. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 215 (11 600) (ε at 313 nm: 35 mol l^{-1} cm^{-1}). IR (neat), ν_{max} (cm^{-1}): 1790, 1740, 1705. MS, *m/z* (%): 243 (M$^+$, <1), 143 (66), 115 (17), 111 (63), 43 (100). ^{1}H NMR ($CDCl_3$): δ 1.75 (m, 4H, 2 × C*H*$_2$), 2.08 (s, 3H, C*H*$_3$C=N), 2.38 (t, J = 7.5 Hz, 2H, C*H*$_2$CO$_2$N), 2.51 (s, 3H, C*H*$_3$CO), 2.56 (t, J = 7.5 Hz, 2H, C*H*$_2$CO$_2$C), 3.68 (s, 3H, C*H*$_3$OCO). ^{13}C NMR ($CDCl_3$): δ 10.3 (*C*H$_3$C=N), 24.2, 24.1 (2 × *C*H$_2$), 25.7 (*C*H$_3$CO), 32.5, 33.6 (2 × *C*H$_2$CO$_2$), 51.6 (*C*H$_3$OCO), 160.9 (*C*=N), 170.1 (CH$_2$*C*O$_2$N), 173.2 (CH$_3$O*C*O), 196.3 (keto *C*O).

(E)-3-Oxobutan-2-iminyl benzoate (**1e**). MP 118–119°C (from methanol); HPLC data: t_R 5.22 min, k 6.91. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 239 (19 400) (ε at 313 nm: 27 mol l^{-1} cm^{-1}). IR (KBr), ν_{max} (cm^{-1}): 1760, 1705. MS, *m/z* (%): 205 (M$^+$, <1), 105 (100). ^{1}H NMR ($CDCl_3$): δ 2.23 (s, 3H, C*H*$_3$C=N), 2.60 (s, 3H, C*H*$_3$CO), 7.52 (m, 2H, H-3b/H-5b), 7.66 (tt, J = 7.5 and 1.3 Hz, 1H, H-4b), 8.12 (dq, J = 8.4 and 1.3 Hz, 2H, H-2b/H-6b). ^{13}C NMR ($CDCl_3$): δ 10.5 (*C*H$_3$C=N), 25.8 (*C*H$_3$CO), 128.1, 128.7, 129.8, 133.9 (aromatic *C*), 161.6 (*C*=N), 163.0 (ester *C*O), 189.6 (keto *C*O).

(Z)-3-Oxobutan-2-iminyl benzoate (***Z*-1e**). It was obtained by direct irradiation of **1e** with >350 nm light [23]; it could not be isolated as a pure compound. HPLC data: t_R 3.30 min, k 4.00. The absorption spectrum in MeCN could be deduced from that of a known mixture of *E*/*Z* isomers in solution in the same solvent, knowing the absorption spectrum of the (*E*)-isomer **1e**. At any wavelength λ_i the following expression holds:

$$\varepsilon_Z = \frac{\{Ab_m - (\varepsilon_E[(E)\text{-isomer}])\}}{[(Z)\text{-isomer}]},$$

where ε_Z and ε_E are the molar absorption coefficients of (*Z*)- and (*E*)-isomers at λ_i, and Ab_m is the absorbance of the solution of the mixture at the same wavelength. The concentration of the (*Z*)-isomer can be deduced from the ratio [(*E*)-isomer]/[(*Z*)-isomer] (0.25 in the present case, from the ^{1}H NMR spectrum of the mixture) and the sum ([(*E*)-isomer] + [(*Z*)-isomer]), a value known from the initial concentration of the (*E*)-isomer, and assuming that isomerization is the only photoprocess. At 254 nm, ε_E = 8670 mol l^{-1} cm^{-1}, and consequently, the ε_Z value at the same wavelength is 1690 mol l^{-1} cm^{-1}.

Di[(E)-3-oxobutan-2-iminyl] succinate (**1f**). MP 82–83°C; HPLC data: t_R 2.80 min, k 3.26. UV (CH_3CN): λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 214 (25 200) (ε at 313 nm: 70 mol l^{-1} cm^{-1}). IR (KBr), ν_{max} (cm^{-1}): 1775, 1705. MS, *m/z* (%): 284 (M$^+$, not observed), 184 (<1), 143 (<1), 101 (4), 43 (100). ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 6H, 2 × C*H*$_3$C=N), 2.51 (s, 6H, 2 × C*H*$_3$CO), 3.00 (s, 4H, 2 × C*H*$_2$CO). ^{13}C NMR ($CDCl_3$): δ 10.4 (2 × *C*H$_3$C=N), 25.7 (2 × *C*H$_3$CO), 27.6 (2 × *C*H$_2$), 161.2 (2 × *C*=N), 169.3 (2 × *C*OO), 196.0 (2 × *C*OMe).

Di[(E)-3-oxobutan-2-iminyl] adipate (**1g**). MP 85–86°C; HPLC data: t_R 4.13 min, k 5.26. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 215 (23 100) (ε at 313 nm: 69 mol l^{-1} cm^{-1}). IR (KBr), ν_{max} (cm^{-1}): 1780, 1680. MS, *m/z* (%): 328 (M$^+$, not observed), 228 (<1), 129 (4), 43 (100). ^{1}H NMR ($CDCl_3$): δ 1.85 (m, 4H, 2 × C*H*$_2$), 2.08 (s, 6H, 2 × C*H*$_3$C=N), 2.51 (s, 6H, 2 × C*H*$_3$CO), 2.60 (t, J = 7.5 Hz, 4H, 2 × C*H*$_2$COO). ^{13}C NMR ($CDCl_3$): δ 10.3 (2 × *C*H$_3$C=N), 24.0 (2 × *C*H$_2$CH$_2$CO), 25.8 (2 × *C*H$_3$CO), 32.4 (2 × CH$_2$*C*H$_2$CO), 160.9 (2 × *C*=N), 169.8 (2 × ester *C*O), 196.3 (2 × keto *C*O).

(E)-1-Phenyl-1-oxopropan-2-iminyl acetate (**2b**). MP 32–33°C; HPLC data: t_R 2.59 min, k 3.11. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 259 (9200) (ε at 313 nm: 161 mol l^{-1} cm^{-1}). IR (neat), ν_{max} (cm^{-1}): 1785, 1670. MS, *m/z* (%): 205 (M$^+$, <1), 163 (35), 105 (86), 43 (100). ^{1}H NMR ($CDCl_3$): δ 2.27 (s, 3H, C*H*$_3$CO), 2.30 (s, 3H, C*H*$_3$C=N), 7.48 (m, 2H, H-3a/H-5a), 7.61 (tt, J = 7.4 and 1.3 Hz, 1H, H-4a), 8.09 (m, 2H, H-2a/H-6a). ^{13}C NMR ($CDCl_3$): δ 12.6 (*C*H$_3$C=N), 19.5 (*C*H$_3$COO), 128.4, 130.8, 133.8, 134.8 (aromatic *C*), 161.0 (*C*=N), 168.0 (ester *C*O), 190.0 (keto *C*O).

(E)-1-Phenyl-1-oxopropan-2-iminyl propionate (**2c**). BP 76–78°C/2 Torr; HPLC data: t_R 3.60 min, k 4.71. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 259.5 (9200) (ε at 313 nm: 160 mol l^{-1} cm^{-1}). IR (neat), ν_{max} (cm^{-1}): 1780, 1670. MS, *m/z* (%): 219 (M$^+$, <1), 164 (4), 163 (32), 105 (59), 57 (100). ^{1}H NMR ($CDCl_3$): δ 1.26 (t, J = 7.5 Hz, 3H, C*H*$_3$CH$_2$), 2.30 (s, 3H, C*H*$_3$C=N), 2.57 (q, J = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 7.48 (m, 2H, H-3a/H-5a), 7.61 (tt, J = 7.3 and 1.4 Hz, 1H, H-4a), 8.10 (m, 2H, H-2a/H-6a). ^{13}C NMR ($CDCl_3$): δ 8.9 (*C*H$_3$CH$_2$), 12.9 (*C*H$_3$C=N), 26.2 (*C*H$_2$CH$_3$), 128.4, 130.9, 133.9, 134.9 (aromatic *C*), 161.1 (*C*=N), 171.5 (ester *C*O), 190.2 (keto *C*O).

Methyl (E)-1-phenyl-1-oxopropan-2-iminyl adipate (**2d**). MP 30–31°C; HPLC data: t_R 3.93 min, k 5.24. UV (MeCN), λ_{max} (ε, mol l^{-1} cm^{-1}): 259 (9200) (ε at 313 nm:

158 mol l^{-1} cm^{-1}). IR (neat), ν_{max} (cm^{-1}): 1780, 1740, 1675. MS, *m/z* (%): 305 (M^+, <1), 262 (<1), 247 (<1), 163 (1), 143 (100), 115 (26), 111 (82), 105 (97). ^{1}H NMR ($CDCl_3$): δ 1.75 (m, 4H, 2 × CH_2), 2.29 (s, 3H, CH_3C=N), 2.36 (t, J = 7.5 Hz, 2H, CH_2CO_2N), 2.55 (t, J = 7.5 Hz, 2H, CH_2CO_2Me), 3.67 (s, 3H, CH_3OCO), 7.49 (m, 2H, H-3a/H-5a), 7.61 (tt, J = 7.4 and 1.3 Hz, 1H, H-4a), 8.12 (m, 2H, H-2a/H-6a). ^{13}C NMR ($CDCl_3$): δ 13.0 (CH_3), 24.3, 24.1 (2 × CH_2), 32.4, 33.6 (2 × CH_2COO), 53.1 (CH_3OCO), 128.5, 130.9, 133.9, 134.8 (aromatic C), 161.2 (C=N), 170.2 (CO_2N=), 173.6 (CO_2Me), 190.1 (keto CO).

(E)-1-Phenyl-1-oxopropan-2-iminyl benzoate (**2e**). MP 71–72°C; HPLC data: t_R 6.83 min, k 9.84. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 243 (19 200) (ε at 313 nm: 206 mol L^{-1} cm^{-1}). IR (KBr), ν_{max} (cm^{-1}): 1760, 1680. MS, *m/z* (%): 267 (M^+, <1), 226 (6), 198 (20), 105 (100). ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3H, CH_3), 7.53–7.51 (m, 4H, H-3a/H-5a,H-3b/H-5b), 7.63 (tt, J = 7.6 and 1.4 Hz, 1H, H-4b or H-4a), 7.66 (tt, J = 7.8 and 1.5 Hz, 1H, H-4a or H-4b), 8.20, 8.13 (two m, 4H, H-2a/H-6a,H-2b/H-6b). ^{13}C NMR ($CDCl_3$): δ 13.1 (CH_3), 128.3 (C-1b), 128.5, 128.7, 129.8, 131.0 (C-2a/C-6a, C-3a/C-5a, C-2b /C-6b, C-3b/C-5b), 133.8, 133.9 (C-4a, C-4b), 134.9 (C-1a), 162.0 (C=N), 163.1 (ester CO), 189.9 (keto CO). Compound **2e** is thermally stable in cyclohexane or MeCN solution (50 μM), at room temperature or at 50°C, at the irradiation times herein used (HPLC analysis). Rate constant of the first order thermal disappearance in dry ethanol (0.1 mM solution) at 22 ± 2°C: 1.6 × 10^{-5} s^{-1}; detected products after in dark refluxing for 2 h in this solvent: oxime **2a**, benzoic acid, ethyl benzoate and traces of isomer ***Z*-2e**.

(Z)-1-Phenyl-1-oxopropan-2-iminyl benzoate (***Z*-2e**). MP 67–68°C; HPLC data: t_R 4.08 min, k 5.48. UV (CH_3CN): λ_{max} nm (ε, mol l^{-1} cm^{-1}): 238 (19 200) (ε at 313 nm: 83 mol l^{-1} cm^{-1}). IR (KBr), ν_{max} (cm^{-1}): 1760, 1685. EM, *m/z* (%): 267 (M^+, <1), 225 (15), 164 (13), 105 (100). ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3H, CH_3), 7.26 (m, 2H, H-3b/H-5b), 7.47 (tt, J = 7.4 and 1.3 Hz, 1H, H-4b), 7.55 (m, 4H, H-2b/H-6b, H-3a/H-5a), 7.67 (tt, J = 7.3 and 1.3 Hz, 1H, H-4a), 7.95 (m, 2H, H-2a/H-6a). ^{13}C NMR ($CDCl_3$): δ 17.6 (CH_3), 128.4 (C-1b), 127.9, 128.4, 129.1, 129.5 (C-2a/C-6a, C-3a/C-5a, C-2b/C-6b and C-3b/C-5b), 132.9 (C-1a), 133.4, 135.0 (C-4a and C-4b), 163.0, 163.4 (ester CO and C=N), 192.7 (keto CO).

Di[(E)-1-phenyl-1-oxopropan-2-iminyl] succinate (**2f**). MP 134–135°C; HPLC data: t_R 7.09 min, k 10.25. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 259.5 (18 000) (ε at 313 nm: 368 mol l^{-1} cm^{-1}). IR (KBr), ν_{max} (cm^{-1}): 1770, 1665. MS, *m/z* (%): 408 (M^+, not observed), 302 (<1), 246 (<1), 204 (1), 122 (11), 105 (100). ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 6H, 2 × CH_3), 2.97 (s, 4H, 2 × CH_2CO), 7.48 (m, 4H, 2 × H − 3a/H − 5a), 7.61 (tt, J = 7.4 and 1.3 Hz, 2H, 2 × H − 4a), 8.09 (m, 4H, 2 × H − 2a/H − 6a). ^{13}C NMR ($CDCl_3$): δ 13.1 (2 × CH_3), 27.6 (2 × CH_2), 128.5, 130.9 (2 × C − 2a/C − 6a and 2 × C − 3a/C − 5a), 134.0 (2 × C − 4a), 134.7 (2 × C − 1a), 161.6 (2 × C=N), 169.5 (2 × ester CO), 189.9 (2 × keto CO).

Di[(E)-1-phenyl-1-oxopropan-2-iminyl] adipate (**2g**). MP 116–117°C; HPLC data: t_R 10.43 min, k 16.35. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 259 (18 200) (ε at 313 nm: 364 mol l^{-1} cm^{-1}). IR (KBr), ν_{max} (cm^{-1}): 1765, 1670. MS, *m/e* (%): 436 (M^+, not observed), 198 (<1), 131 (<1), 105 (53), 51 (100). ^{1}H NMR ($CDCl_3$): δ 1.85 (m, 4H, 2 × CH_2), 2.30 (s, 6H, 2 × CH_3C=N), 2.60 (t, J = 7.5 Hz, 4H, 2 × CH_2CO), 7.48 (m, 4H, 2 × H − 3a/H − 5a), 7.61 (tt, J = 7.4 and 1.3 Hz, 2H, 2 × H − 4a), 8.10 (m, 4H, 2 × H − 2a/H − 6a). ^{13}C NMR ($CDCl_3$): δ 13.0 (2 × CH_3), 24.1 (2 × $COCH_2CH_2$), 32.4 (2 × $COCH_2CH_2$), 128.5, 130.9, 133.9, 134.9 (2 × aromatic C), 161.3 (2 × C=N), 170.2 (2 × ester CO), 190.1 (2 × keto CO).

(E)-1-Phenyl-1-oxopropan-2-iminyl p-(chloromethyl)benzoate (**2h**). It was obtained as described [20]. MP 98–99°C; HPLC data: t_R 7.14 min, k 9.66. UV (MeCN), λ_{max}, nm (ε, mol l^{-1} cm^{-1}): 248.5 (27 300) (ε at 313 nm: 220 mol l^{-1} cm^{-1}). IR (KBr), ν_{max} (cm^{-1}): 1740, 1665. MS, *m/e* (%): 315 (M^+, <1), 280 (M^+–Cl, 6), 155 (96), 153 (100), 105 (95), 77 (96). ^{1}H NMR ($CDCl_3$): δ 2.43 (s, 3H, CH_3), 4,64 (s, 2H, CH_2Cl), 7.57–7.47 (m, 4H, H-3a/H-5a,H-3b/H-5b), 7.62 (tt, J = 7.8 and 1.4 Hz, 1H, H-4a), 8.11 and 8.18 (m, 4H, H-2a/H-6a, H-2b/H-6b). ^{13}C NMR ($CDCl_3$): δ 13.2 (CH_3), 45.1 (CH_2Cl) 128.1 (C-1b), 128.5, 128.8, 130.2, 131.0 (C-2a/C-6a, C-3a/C-5a, C-2b/C-6b, C-3b/C-5b), 134.0 (C-1a), 143.2 (C-4a), 162.1 (C=N), 162.6 (ester CO), 189.9 (keto CO).

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