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Photoinitiators and photoinitiation
Part 11. The photodecomposition of some O-acyl 2-oximinoketones

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Abstract

The photodecomposition of several O-acyl 2-oximinoketones was studied using electron spin resonance and proton nuclear magnetic resonance chemically induced dynamic nuclear polarization techniques. Primary N–O bond cleavage into α-ketoiminyl and acyloxy radicals from the triplet excited state was observed in all cases. α-Ketoiminyl radicals observable at $T < -70$ °C underwent rapid fragmentation into a benzoyl radical and a nitrile at temperatures exceeding -60 °C. Chemical evidence was provided by radical trapping using a thiol and a stable nitroxyl respectively. These experiments also showed that, for most O-acyl 2-oximinoketones **1**, $[E] \rightleftharpoons [Z]$ photoisomerization was the major process, whereas for O-acyl 2-oximinoketones **2** photodecomposition was almost exclusive. © 1997 Elsevier Science S.A.

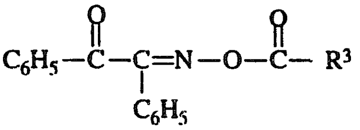
Keywords: O-Acyl 2-oximinoketones; α-Ketoiminyl radicals; Photodecomposition; Photoisomerization

1. Introduction

The sensitivity of O-acyl 2-oximinoketones to light has, in principle, been known for some time. In 1904, Werner and Piguet [1] described the sunlight-induced decomposition of a product obtained from a Beckmann type II rearrangement, which 20 years later was shown to be the [*E*] isomer of O-benzoyl 1,2-diphenyl-2-oximinoethanone **1d** [2].

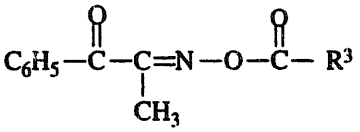
Again much later O-acyl 2-oximinoketones were shown to photoinitiate the polymerization of vinyl monomers, such as acrylamide [3,4], various acrylates [3–7] and unsaturated polyester/styrene [8].

In a preliminary screening of a number of these compounds with regard to their efficiency to photoinitiate the bulk polymerization of methyl methacrylate (MMA) and the crosslinking of trimethylolpropane triacrylate (TMPTA) in solution, it was invariably found that:



$C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{C_6H_5}{|}}{C}=N-O-\overset{\overset{O}{\|}}{C}-R^3$

1



$C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=N-O-\overset{\overset{O}{\|}}{C}-R^3$

2

1. in category **1** the efficiency appears to depend on the nature of R^3, whereas in category **2** R^3 appears to have hardly any influence;
2. compounds of category **2** are far more efficient than the corresponding compounds of category **1** without a single exception.

In order to try and explain these observations, it is necessary to take a closer look at all the events involved in these processes.

Simple O-acylketoximes have been shown to undergo N–O bond cleavage [9]. Sensitization and quenching experiments have shown that the fragmentation proceeds from a triplet excited state having an energy close to that of the parent ketone [10]. The principal reactions of the iminyl radicals

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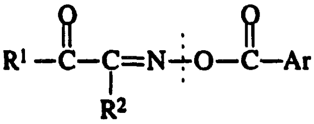
generated are the dimerization to azines, β-cleavage to give nitriles and alkyl radicals, hydrogen abstraction to form imines and aromatic (solvent) substitution [11,12].

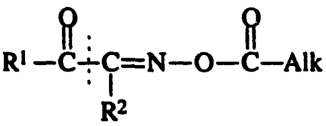
The ultimate products formed on irradiation of O-acyl 2-oximinoketones in the absence of vinyl monomers have been explained to result from a similar fragmentation sequence [4,13]. This explanation may possibly account for the influence of the nature of R^3 on the efficiency of photoinitiation found for category 1, but cannot explain the lack of influence found for category 2.

The results of a recent study [14] using laser flash photolysis indicated the influence of R^3 on the initial fragmentation mode. Thus for $R^3 \equiv$ Ar, initial N–O bond cleavage



$$R^1-\overset{O}{\overset{\|}{C}}-\underset{R^2}{\underset{|}{C}}=N\,\vdots\,O-\overset{O}{\overset{\|}{C}}-Ar$$

initial N—O cleavage



$$R^1-\overset{O}{\overset{\|}{C}}\,\vdots\,\underset{R^2}{\underset{|}{C}}=N-O-\overset{O}{\overset{\|}{C}}-Alk$$

initial α-cleavage

should take place to form the stabilized acyloxy radical. Likewise for $R^3 \equiv$ Alk, initial α-cleavage should take place using the same argument in a reverse sense, i.e. no stabilized acyloxy radical will result from initial N–O bond cleavage.

If these conclusions are correct, we would expect the nature of R^3 to affect the efficiency of photoinitiation of categories 1 and 2 in an equal manner. However, this is not the case (see below), and another explanation should be offered to account for the results.

In this paper, we report the photodecomposition of some representatives from both categories studied by electron spin resonance (ESR), proton nuclear magnetic resonance chemically induced dynamic nuclear polarization (^{1}H NMR-CIDNP) and radical trapping (using 1-dodecanethiol and 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO)) techniques.

2. Experimental details

2.1. General

The ^{1}H NMR spectra were recorded on a Bruker WH-270 spectrometer using tetramethylsilane ($\delta = 0$ ppm) as internal standard. The mass spectra were recorded on a Finnegan MAT 212 (EI) and MAT 112 (CI). Melting points (m.p.) were determined on a melting point microscope (Zeiss, equipped with a Mettler hot stage and FP 80 processor) and are corrected.

The ESR experiments were carried out with a Varian E-4 electron paramagnetic resonance (EPR) spectrometer equipped with a variable temperature accessory (E-257). Samples of the compounds (approximately 10 mg per gram of solvent) were deoxygenated by purging with helium for 30 min. In the spin trapping experiments using *N*-tert-butyl-α-phenylnitrone (PBN) and 2-methyl-2-nitrosopropane (MNP) the samples were not deoxygenated. Irradiation was performed in the cavity of the spectrometer with a Philips SO 100 Hg lamp with a glass filter (5% transmission at 320 nm). The irradiation time in the spin trapping experiments was 10–30 s. In the absence of a spin trap, the samples were continuously irradiated. The *g* values of the radicals detected were determined relative to the benzoyl radical **8** ($g = 2.0008$ [15]).

The ^{1}H NMR-CIDNP experiments were carried out at the University of Leiden (cooperation with Dr. J.A. den Hollander) A DA 60 IL NMR spectrometer equipped with a modified probe was used. The light source was a high-pressure Hg lamp (1000 W, $NiSO_4/CuSO_4$ filter).

2.2. Materials

Benzil (Merck), 4-methoxybenzoin (K&K) and anisoin (Acros Chimica) were used without purification. 2-Oximinopropiophenone (Acros Chimica) was recrystallized from hexane–ethyl acetate (m.p. 113.4–113.6 °C).

Acetyl chloride, phenylacetyl chloride, benzoyl chloride and *p*-anisoyl chloride (all Acros Chimica) were fractionated before use. 2-Cyano-2-methylpropionyl chloride was available from another study [16]. Isoamyl nitrite, methyl cyanoacetate and 1,3-dibromopropane (all Acros Chimica) were used without purification. PBN, MNP, 1-dodecanethiol and TMPO (all Acros Chimica) were used as received.

TMPTA was obtained from Akzo Nobel Resins (Bergen op Zoom).

2.3. Syntheses

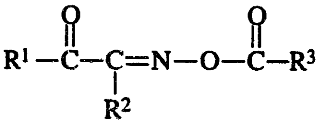
1,2-Diphenyl-2-oximinoethanones ([*E*] isomer m.p. 139.0–140.0 °C; [*Z*] isomer m.p. 110.8–112.2 °C) were synthesized according to standard procedures [17].

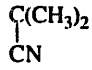
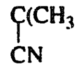
4-Methoxydeoxybenzoin (m.p. 76.4–76.6 °C) was synthesized from anisole and phenylacetyl chloride in dichloromethane [18]. 1-(4-Methoxyphenyl)-2-oximino-2-phenylethanone (m.p. 129.5–130.5 °C) was synthesized according to a standard procedure [19]. 4-Methoxybenzil (m.p. 61.5–62.5 °C) was obtained by oxidation of 4-methoxybenzoin [20]. Anisil (m.p. 131.8–132.4 °C) was similarly obtained from anisoin.

1-Cyanocyclobutane carboxylic acid was synthesized according to Hall et al. [21]. The acid chloride (b.p. 84.5–86.5 °C (16 mbar)) was obtained from the acid and thionyl chloride.

The O-acyl 2-oximinoketones (Table 1) were synthesized from the 2-oximinoketones and the appropriate acid chloride in tetrahydrofuran (THF) in the presence of triethylamine, followed by conventional work-up. Purification was achieved

Table 1
O-Acyl 2-oximinoketones synthesized[a]


$R^1{-}C({=}O){-}C(R^2){=}N{-}O{-}C({=}O){-}R^3$

R¹	R²	R³	Compound	Isomer	M.p. (°C)	Reported m.p. (°C)	Reference
C_6H_5	C_6H_5	CH_3	**1a**	[*E*] [*Z*]	61.3–62.3 77.1–78.0	61–62 78–79	[22] [22]
C_6H_5	C_6H_5	 $C(CH_3)_2CN$	**1b**	[*E*] [*Z*]	97.0–97.4 90.6–92.9		
C_6H_5	C_6H_5	 $C(CN)(CH_2)_3$	**1c**	[*E*]	103.7–104.7		
C_6H_5	C_6H_5	C_6H_5	**1d**	[*E*] [*Z*]	94.5–95.4 137.3–137.8	95–96 137.5–138	[1,2] [23]
C_6H_5	C_6H_5	*p*-$CH_3OC_6H_4$	**1e**	[*E*] [*Z*]	135.2–136.2 131.7–133.0		
C_6H_5	CH_3	CH_3	**2a**	[*E*]	33.5–34.0		
C_6H_5	CH_3	 $C(CH_3)_2CN$	**2b**	[*E*]	73.1–73.7		
C_6H_5	CH_3	 $C(CN)(CH_2)_3$	**2c**	[*E*]	69.5–70.2		
C_6H_5	CH_3	C_6H_5	**2d**	[*E*]	70.0–70.7	70–72	[24]
C_6H_5	CH_3	*p*-$CH_3OC_6H_4$	**2e**	[*E*]	128.4–129.9		
p-$CH_3OC_6H_4$	C_6H_5	CH_3	**3a**	[*E*]	84.0–85.0	85–86	[25]
p-$CH_3OC_6H_4$	C_6H_5	C_6H_5	**3d**	[*E*]	94.5–94.8	95.5–96.5	[25]

[a] Beyond 300 nm, all of these compounds show an absorption shoulder around 340 nm (log $\epsilon = 2.0 \pm 0.1$).

by recrystallization in all cases. The structures of the new esters were confirmed by ^{1}H NMR and mass spectrometry.

2.4. Irradiation procedures

2.4.1. Photoinduced polymerization and crosslinking

Samples of MMA (5 g, 5×10^{-2} mol) containing the various esters (10^{-3} mol l^{-1}) in sealed Pyrex tubes (i.d. 1 cm) were irradiated in a Rayonet photoreactor (model RPR-208) equipped with 350 nm lamps. The time (gel time in minutes) to achieve complete solidification of MMA was determined.

Solutions of TMPTA (10 g l^{-1}) in 2-propanol containing the various esters (10^{-2} mol l^{-1}) were irradiated in cuvettes (polystyrene; 4 ml; from Witeg) with a high-pressure Hg lamp (90 W; Ealing Optics, No 26-2865) at a distance of 10 cm. The crosslinking (insolubilization) of TMPTA was monitored by laser nephelometry as described by Decker and Fizet [26].

The induction periods (T_{ind}) were determined as the irradiation time (s) until the onset of crosslinking. Relative rates of crosslinking (R_p) were determined from the slopes of the curves (tan α) using a calibration curve obtained by plotting the amount of polymer formed (by gravimetry) vs. the time (s), with benzoin isopropyl ether as the standard [27].

2.4.2. Photodecomposition in the presence of thiol and TMPO

Solutions of esters **1d** and **2d** (10^{-2} mol l^{-1}) in benzene in the presence of 1-dodecanethiol (10^{-2} mol l^{-1}) and TMPO (3×10^{-2} mol l^{-1}) respectively were irradiated for 4 h in a Rayonet photoreactor (model RPR-208) equipped with 350 nm lamps. The Pyrex reaction vessels were equipped with a magnetic stirrer, a gas dispersion tube and a reflux condenser. The solutions were flushed with nitrogen before and during irradiation.

The work-up procedure on a preparative scale and the quantitative analyses have been described in detail previously [16].

3. Results

3.1. Results from ESR spectroscopy

At low temperatures (from −70 to −90 °C) and in the absence of a spin trap, the ESR spectra showed the presence of radicals characterized by a *g* value of 2.0033 and $a_N = 0.89^5$ mT from esters **1a** and **1d**, and a *g* value of 2.0038, $a_N = 0.95$ mT and $a_H = 0.18$ mT from esters **2a** and **2d**. These radicals

Table 2
Radicals observed by ESR

Radical	*g*	a_N	a_H	Remarks
4	2.0033	0.89^5	–	From [*E*]-**1a** and [*E*]-**1d** at −90 °C
5	2.0038	0.95	0.18	From [*E*]-**2a** and [*E*]-**2d** at −90 °C
8	(2.0008)	–	0.12	From all esters at 20 °C
12a	2.0028	–	2.28	From [*E*]-**1a**, [*Z*]-**1a** and [*E*]-**2a** at 20 °C
12b	2.0029	0.32	2.06	From [*E*]-**1b** and [*E*]-**2b** at 20 °C
12c	2.0029	0.32	3.01 (β) 0.08 (γ)	From [*E*]-**1c** and [*E*]-**2c** at 20 °C
13	2.0061	1.43	0.45	From [*E*]-**1a**, [*E*]-**1d** and [*E*]-**2d** at 20 °C
14	2.0063	1.33	0.15	From [*E*]-**1a**, [*E*]-**1d** and [*E*]-**2d** at 20 °C
15	2.0069	0.80	–	From [*E*]-**1a**, [*E*]-**1b**, [*E*]-**1d** and [*E*]-**2d** at 20 °C
16	2.0062	0.15	1.10 [a]	From [*E*]-**1a** and [*E*]-**1b**

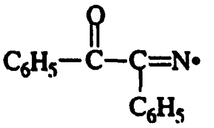
[a] Only from [*E*]-**1a**.

are assigned to the α-ketoiminyl radicals **4** and **5** respectively from a comparison of their parameters with the reported values for various dialkyliminyl and diaryliminyl radicals [28].

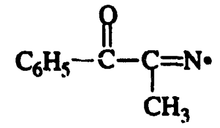
At room temperature, the spectra only showed the presence of the benzoyl radical **8** [15] and the various alkyl radicals **12a–12c** [29–31].

At room temperature and in the presence of a spin trap, the spectra showed the trapped benzoyl radical **13** (with PBN [32]) and **15** (with MNP [33]).

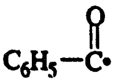
In addition, trapped acyloxy radicals **14** (with PBN [34]) and the corresponding trapped alkyl radicals **16** (with MNP [35]) were observed. In all experiments employing MNP, signals of radical **17** [36] were also detected. The radicals observed by ESR are given in Table 2.


$C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{C_6H_5}{\underset{|}{C}}=N\bullet$

4


$C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}=N\bullet$

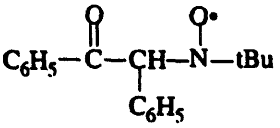
5


$C_6H_5-\overset{O}{\overset{\|}{C}}\bullet$

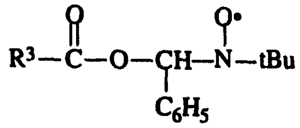
8

•R³ (alkyl)

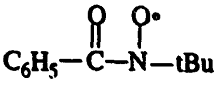
12a–c


$C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{C_6H_5}{\underset{|}{CH}}-\overset{O\bullet}{\overset{|}{N}}-tBu$

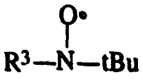
13


$R^3-\overset{O}{\overset{\|}{C}}-O-\underset{C_6H_5}{\underset{|}{CH}}-\overset{O\bullet}{\overset{|}{N}}-tBu$

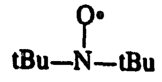
14


$C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{O\bullet}{\overset{|}{N}}-tBu$

15


$R^3-\overset{O\bullet}{\overset{|}{N}}-tBu$

16


$tBu-\overset{O\bullet}{\overset{|}{N}}-tBu$

17

3.2. *Results from ¹H NMR-CIDNP*

A number of esters were selected for the CIDNP experiments. Pronounced polarization effects were observed, particularly for esters **2**. The spectra of esters [*E*]-**1a** and [*E*]-**1d** were qualitatively similar (except of course for acetonitrile formation), but showed much weaker polarization effects.

The polarization effects observed (see Table 3) can be readily explained using the set of simple rules developed by Kaptein [39]. The net polarization is given by $\Gamma_{ne} = \mu\epsilon\Delta g A_i$, considering

1. photodecomposition from the triplet excited state ($\mu = +$);
2. the formation of products by in-cage recombination ($\epsilon = +$) or by transfer reactions after escape from the cage ($\epsilon = -$);
3. the *g* values of the respective radicals, e.g. in the case of acetophenone, the methyl radical has a larger *g* value (2.0029) than the benzoyl radical (2.0008), and hence $\Delta g > 0$;
4. the respective hyperfine coupling constants A_i.

This then leads to the series of reactions shown in Scheme 1.

3.3. *Results from polymerization and crosslinking*

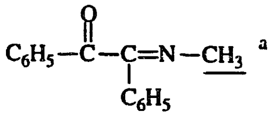
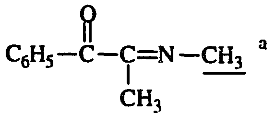
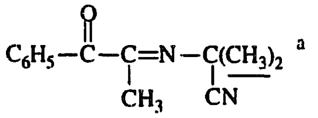
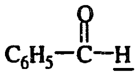
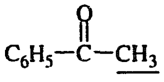
The results of both the bulk polymerization of MMA and the crosslinking of TMPTA in solution show some interesting features (see Table 4). The esters **1**, with the exception of **1b** and **1c**, have longer gel times (MMA), much longer induction periods T_{ind} and lower rates of crosslinking R_p (TMPTA) than the corresponding esters **2**. It also appears that these values depend more strongly on the nature of R³ for the esters of type **1** than for those of type **2** which show less variation.

For esters **1b** and **1c**, the values are strikingly different from those of the other esters **1**, and are more similar to the values found for the corresponding [*Z*]-*O*-sulphonyl 2-oximinoketones [40], suggesting that the acid strength may play a role.

3.4. *Results from trapping with thiol and TMPO*

Esters [*E*]-**1d** and [*E*]-**2d** were selected for the trapping experiments (see Table 5). In the presence of thiol, the ester [*E*]-**1d** is only decomposed in part (13%), giving benzal-

Table 3
Assignments of ^1H CIDNP transitions

Ester	Product assignment	Chemical shift	Polarization
[*E*]-**1a**	 $C_6H_5-\overset{\overset{O}{\Vert}}{C}-\underset{\underset{C_6H_5}{\vert}}{C}=N-\underline{CH_3}$ [a] **18a**	3.10 (s)	A
[*E*]-**2a**	 $C_6H_5-\overset{\overset{O}{\Vert}}{C}-\underset{\underset{CH_3}{\vert}}{C}=N-\underline{CH_3}$ [a] **19a**	2.85 (s)	A
[*E*]-**2b**	 $C_6H_5-\overset{\overset{O}{\Vert}}{C}-\underset{\underset{CH_3}{\vert}}{C}=N-\underset{\underset{CN}{\vert}}{C}\underline{(CH_3)_2}$ [a] **19b**	1.75 (s)	A
[*E*]-**1a**	 $C_6H_5-\overset{\overset{O}{\Vert}}{C}-\underline{H}$ **26**	9.70 (s)	A
[*E*]-**1d** [*E*]-**2a** [*E*]-**2b** [*E*]-**2d** [*E*]-**2a**	$\underline{CH_3}-CN$ **10**	0.95 (s)	E(→A) [b]
[*E*]-**2b** [*E*]-**2d** [*E*]-**1a**	 $C_6H_5-\overset{\overset{O}{\Vert}}{C}-\underline{CH_3}$ **30**	2.05 (s)	E
[*E*]-**2a** [*E*]-**1a** [*E*]-**2a**	CH_4 and $CH_3-\underline{CH_3}$ **31** **32**	0.20/0.80 (both s)	A (both)

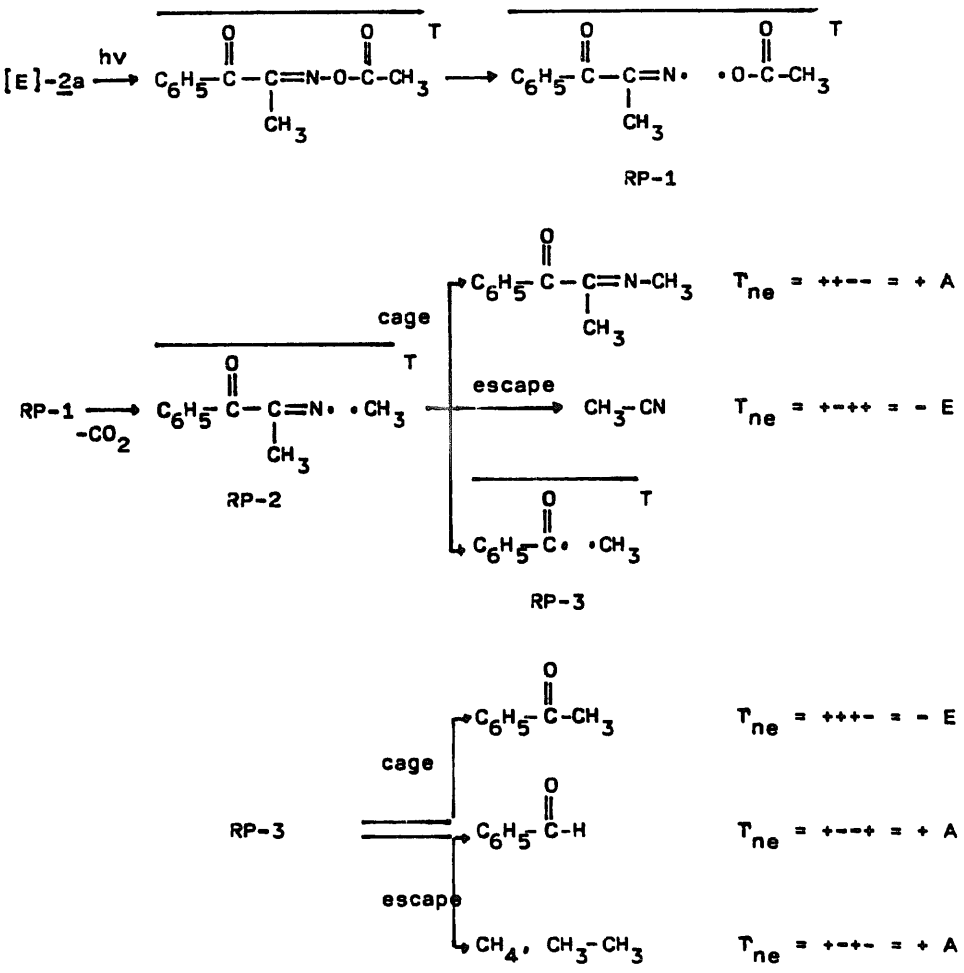
[a] Assignment based on the observed formation of *N*-alkylamines on irradiation of O-acyl ketoximes [12,37,38].
[b] Emission rapidly overshadowed by absorption due to product formation.

dehyde **26**, benzonitrile **9**, surprisingly (see Section 4) some benzil **21** and benzoic acid **28d**, with the major "product" being the geometric isomer [*Z*]-**1d**. Under similar irradiation conditions, the ester [*E*]-**2d** is completely decomposed, giving benzaldehyde **26** (major product), acetonitrile **10**, surprisingly (see Section 4) some phenylpropanedione **23** and benzoic acid **28d** (major product).

The TMPO trapping experiments merely confirm the results of the thiol trapping experiments, i.e. ester [*E*]-**1d** mainly undergoes isomerization to its geometric isomer [*Z*]-**1d**, the decomposition products being 2,2,6,6-tetramethyl-1-piperidino benzoate **29** (the TMPO-trapped benzoyl radical [41]), benzonitrile **9** and benzoic acid **28d**, and ester [*E*]-**2d** undergoing complete decomposition to give **29**, acetonitrile **10** and benzoic acid **28d**.

4. Discussion

The ESR experiments carried out at room temperature in the absence of spin traps showed the presence of the benzoyl radical **8**, as well as the alkyl radicals **12a**–**12c** formed through rapid decarboxylation of the corresponding acyloxy radicals **7a**–**7c** (Scheme 2, reactions (1), (2) and (7)). This was confirmed using spin traps, the observed radicals being **13** ("8-PBN"), **14** ("7-PBN"), **15** ("8-MNP") and **16** ("12-MNP"). These experiments failed to indicate the initial bond cleavage (C–CO α-cleavage or N–O bond cleavage), but similar experiments carried out at temperatures of less than −70 °C provided the desired evidence, showing for the first time the presence of the α-ketoiminyl radicals **4** and **5** formed from the esters **1** and **2** respectively (Scheme 2, reactions (1) and (2)).



Scheme 1.

Table 4
O-Acyl 2-oximinoketones as photoinitiators

Ester	Bulk polymerization of MMA Gel time (min)	Crosslinking of TMPTA in solution		
		T_{ind} (s)	tan α	$10^{-3}R_p$ (mol l^{-1} s^{-1})
[*E*]-**1a**	72	222	1.43	0.64
[*Z*]-**1a**		263	1.54	0.69
[*E*]-**1b**	43	63	4.33	1.93
[*Z*]-**1b**		57	5.14	2.29
[*E*]-**1c**	45			
[*E*]-**1d**	77	329	1.28	0.57
[*Z*]-**1d**	72			
[*E*]-**1e**	90	344	1.54	0.69
[*E*]-**2a**	43	61	7.60	3.39
[*E*]-**2b**	40	18	8.14	3.63
[*E*]-**2c**	45			
[*E*]-**2d**	42	48	7.12	3.18
[*E*]-**2e**	42	67	6.31	2.82
BIPE [a]	55	35.5	7.80	3.48

[a] Benzoin isopropyl ether, the calibrated standard applied [27].

Table 5
Radical trapping with thiol and TMPO [a]

Product	Amount (mmol)			
	With RSH		With TMPO	
	[*E*]-**1d**	[*E*]-**2d**	[*E*]-**1d**	[*E*]-**2d**
[*E*]-ester	2.50	0	1.80	0
[*Z*]-ester	6.20	0	4.60	0
Benzaldehyde **26**	1.00	9.80	–	–
Benzoyl-TMPO **29**	–	–	3.60	10.00
Benzonitrile **9**	1.00	–	3.60	–
Acetonitrile **10**	–	n.d.	–	n.d.
Benzil **21**	0.20!	0	0	0
Phenylpropanedione **23**	–	0.20!	–	0
Benzoic acid **28d**	1.30	9.70	3.32	9.52
[*E*]/[*Z*] p.s.s.	0.40	–	0.39	–

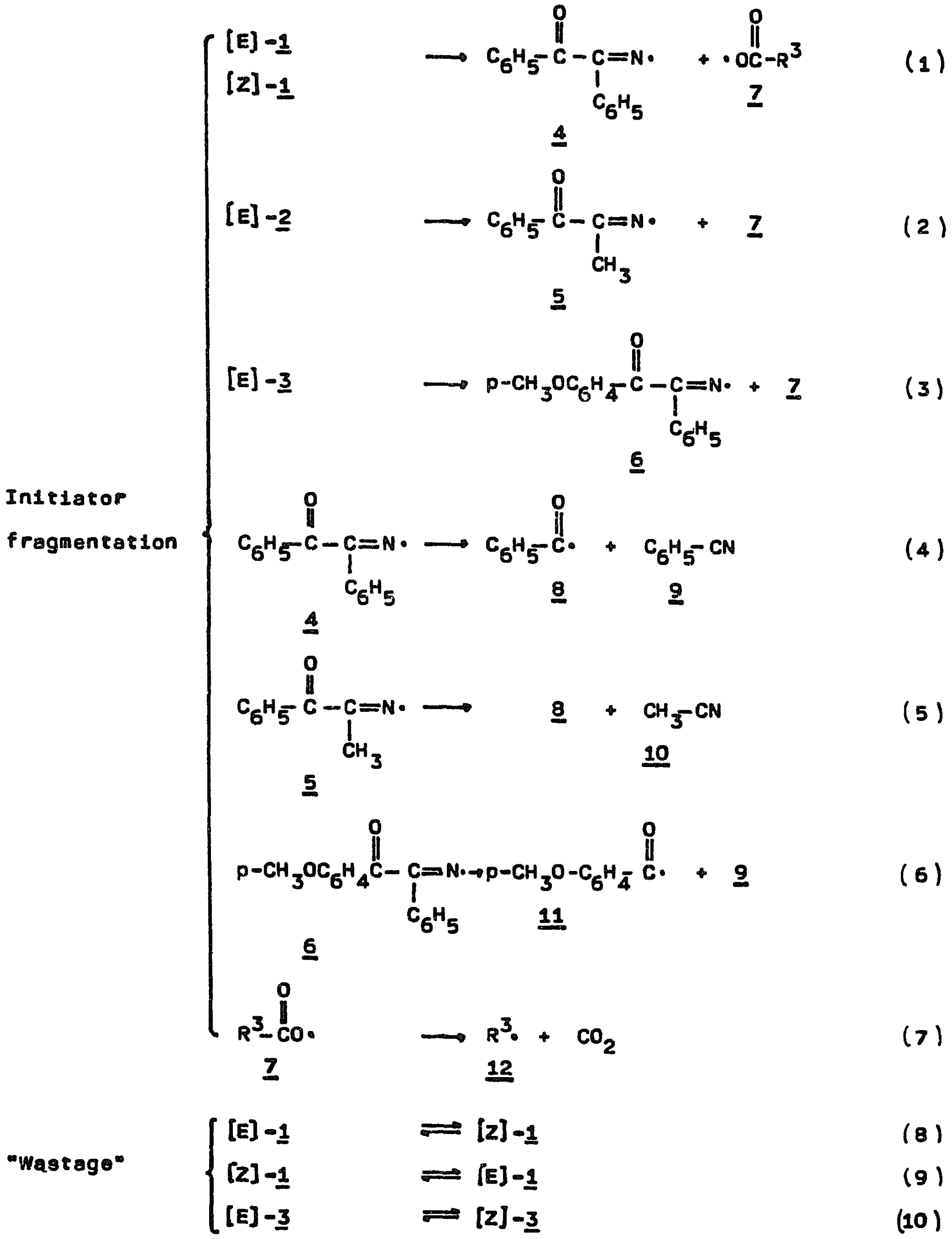
[a] Starting solutions contained 10 mmol of [*E*]-ester, 20 mmol of thiol and 30 mmol of TMPO. Irradiation time, 4 h.

There appeared to be no difference between the aliphatic and aromatic esters in either category, i.e. in all cases the initial bond cleavage was that of the N–O bond. This opposes earlier conclusions from laser flash photolysis experiments [14] concerning the influence of the acyl group (aliphatic vs. aromatic) on the initial cleavage process. However, those experiments were carried out at room temperature, and we now know that the primary α-ketoiminyl radicals **4** and **5** are only sufficiently long lived to be observed at temperatures of less than −70 °C.

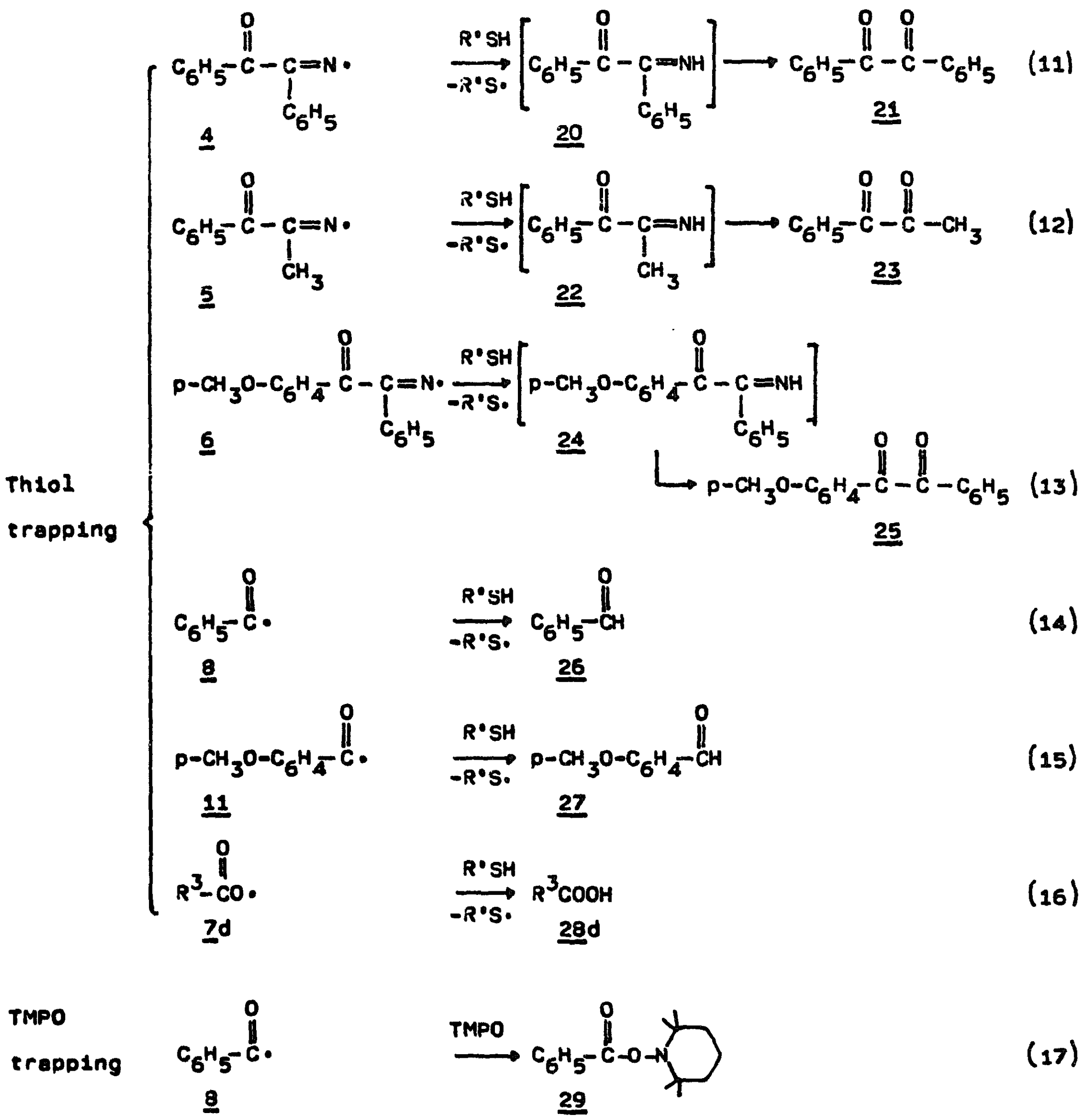
Laser flash photolysis of esters [*E*]-**1d** and [*E*]-**2d** showed the excited state involved to be short lived, which was corroborated by the failure to quench the photoreactions of ester [*E*]-**2d** with naphthalene [14]. From the polarization effects observed in the ^{1}H NMR-CIDNP experiments, we conclude that this short-lived excited state is the triplet state.

The pronounced polarized signal in the spectra of esters [*E*]-**1a**, [*E*]-**2a** and [*E*]-**2b**, attributed to the respective *N*-alkyl 2-oximinoketones **18a**, **19a** and **19b**, deserves special attention. Sakuragi et al. [12] argued that the *N*-alkylimines found on irradiation of O-acylketoximes must be formed through encounter reactions between iminyl radicals and the respective alkyl radicals after escape from the cage. However, it can be concluded that the *N*-alkyl 2-oximinoketones formed in the present study must result from geminate coupling (cage reaction) due to the nature of the polarization observed (enhanced absorption, see Table 3 and Scheme 1).

The trapping experiments using thiol and TMPO showed some interesting features. Firstly, both sets of experiments clearly showed that ester [*E*]-**1d** undergoes [*E*] ⇌ [*Z*] photoisomerization as the major pathway (see Scheme 2, reaction (8)), photodecomposition being only a minor process. The ratio of these two processes may well be governed by the nature of the acyl (R^3) group (see Table 4). In contrast, ester [*E*]-**2d** undergoes photodecomposition exclusively.



Scheme 2. (*continued*)



Scheme 2.

Secondly, from previous studies [16,30,42,43], it is known that the non-cage benzoyl radicals **8** are efficiently scavenged by any thiol present (Scheme 2, reaction (14)). Under these conditions, the dimerization of radicals **8** to benzil **21** is completely suppressed. Therefore the conclusion is justified that when benzil **21** is formed in the presence of thiol it must stem from another reaction sequence. Scavenging of the α-ketoiminyl radical **4** [6,7] by thiol to form the α-ketoimine **20** [24,26], followed by hydrolysis (due to the presence of adventitious water on the column) to benzil **21** [25,27] (see Scheme 2, reactions (11)–(13)), is a plausible reaction sequence. Indeed, this can be confirmed by irradiating esters [*E*]-**3a** and [*E*]-**3d** in the presence of thiol. In both cases, the unsymmetrical 4-methoxybenzil **25** is formed. Formation of the symmetrical *p*-anisil (from the dimerization of *p*-methoxy-benzoyl radicals **11**) is not observed. The formation of *p*-anisaldehyde **27** and benzonitrile **9** (in approximately equal amounts) may be attributed to the fragmentation of the short-lived α-ketoiminyl radical **6** to some extent even in the presence of thiol.

The theoretically interesting question of whether photodecomposition proceeds equally well from both isomers or preferentially from one of the isomers still remains to be answered. From an experimental study on the photodecomposition of three cyclic O-methyl 2-oximinoketones [44], primary N–O bond cleavage only occurs on excitation of the [*E*] isomers; this was further confirmed by ab initio calculations on a related model compound [45].

5. Conclusions

O-Acyl 2-oximinoketones have been shown to undergo [*E*] $\rightleftharpoons$ [*Z*] photoisomerization and/or photodecomposition depending on the substituent R^2 residing at the methine carbon atom. For $R^2 \equiv$ aryl, photoisomerization is the major process, whereas for $R^2 \equiv$ alkyl, photodecomposition is the exclusive process. This explains the observed differences in efficiency as photoinitiators between the two types of O-acyl 2-oximinoketone [3–8].

The photodecomposition has been shown to occur through initial N–O bond cleavage from a short-lived triplet excited state in all cases.

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