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Journal of Photochemistry and Photobiology A: Chemistry 121 (1999) 207–211

Journal of Photochemistry and Photobiology A:Chemistry

Photoinitiators and photoinitiation
Part 15. The photodecomposition of some [Z] *O*-sulphonyl 2-oximinoketones and some [Z] *O*-sulphamoyl 2-oximinoketones

Hendrik J. Hageman[a,*], Pieter Oosterhoff[b], Jan Verbeek[b]
[a]*The Chemical Laboratory, The University of Kent, Canterbury, Kent CT2 7NH, UK*
[b]*Akzo Nobel Central Research Arnhem, Arnhem, The Netherlands*

Received 19 October 1998; accepted 13 November 1998

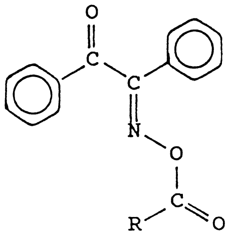
Abstract

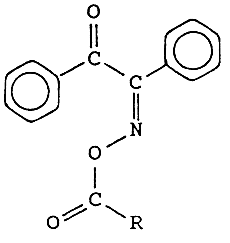
The photodecomposition of some [Z]-*O*-sulphonyl 2-oximinoketones is studied by ESR spectroscopy. At low temperatures ($T < -70°C$), α-ketoiminyl radicals are observed, indicative of initial N–O bond cleavage, implying that *O*-sulphonyl (and *O*-sulphamoyl) fragments are split off as sulphonyloxy (and sulphamoyloxy) radicals in much the same way as acyloxy radicals in the case of *O*-acyl 2-oximinoketones studied before. At room temperature in the presence of a spin-trap, the trapped benzoyl radical is observed, which must have been formed by fragmentation of the α-ketoiminyl radical. The title compounds are shown to photoinitiate the polymerization of acrylates and to photoinduce the acid-catalyzed crosslinking of a melamine resin. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: [z] *O*-Sulphonyl 2-oximinoketones; [Z] *O*-Sulphamoyl 2-oximinoketones; Photodecomposition; α-*Ketoiminyl radicals*

1. Introduction

It has been established [1] that *O*-acyl 1,2-diphenyl 2-oximinoethanones (**1**) undergo photodecomposition through initial homolytic N–O bond cleavage in addition to extensive [E] ⇌ [Z] photoisomerization irrespective of their initial configuration. *O*-Sulphonyl 1,2-diphenyl 2-oximinoethanones (**2**), however, can only be obtained in the [Z] configuration starting from [Z]-1,2-diphenyl 2-oximinoethanone, since reacting the [E]-isomer with sulphonyl chlorides in the presence of base invariably leads to a Beckmann Type-II rearrangement [2–6][1].


[E]-1


[Z]-1

It is now of interest whether **2** will undergo similar photoreactions as their *O*-acyl counterparts **1**, with particular emphasis on the fate of the *O*-sulphonyl fragment.

In principle there are two pathways for the release of the *O*-sulphonyl fragment:

1. as a sulphonate anion in a heterolytic process, e.g. a photo-induced Beckmann Type-II rearrangement, and
2. as a sulphonyloxy radical in a homolytic process as is observed for the corresponding *O*-acyl compounds **1**.

In this communication, the syntheses of some [Z]-*O*-sulphonyl and [Z]-*O*-sulphamoyl 2-oximinoketones are reported. The photodecomposition of some of these compounds is studied by ESR. The free radical polymerization and crosslinking of acrylates as well as the acid-catalyzed crosslinking of a melamine resin photoinduced by the title compounds is also reported.

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 an

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*Corresponding author.

[1] The expression ‘Beckmann’sche Umlagerung zweiter Art’ used by Werner and Piguet [3] has been incorrectly translated into ‘Beckmann rearrangement of the second order’, and ‘abnormal Beckmann rearrangement’[4–6].

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PII: S1010-6030(98)00441-9

internal standard. The mass spectra were recorded on a Finnegan MAT 212 (EI) and MAT 112 (CI) respectively. Melting points 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 EPR spectrometer equipped with a variable temperature accessory (E-257).

Samples of the compounds (~10 mg g^{-1} of solvent) were deoxygenated by purging with helium for 30 min. In the spin-trapping experiments using *N-t*-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 (**7**) ($g = 2.0008$ [7]).

2.2. Materials

[Z]-1,2-Diphenyl 2-oximinoethanone (mp 110.8–112.2°C) was available from a previous study [1]. [E]-2-Oximinopropiophenone (Aldrich) was recrystallized before use (m.p.113.2–113.4°C). Methanesulphonyl chloride, *p*-toluenesulphonyl chloride, and 1-hexadecanesulphonyl chloride (Aldrich) were used without purification. 1-Hexadecanesulphonyl chloride (Aldrich) were used without purification. 1-Octanesulphonyl chloride, and 1-dodecanesulphonyl chloride were available from a previous study [8]. The *N*-alkylsulphamoyl chlorides were also available from a previous study [9]. *N-t*-Butyl-α-phenylnitrone (PBN), and 2-methyl-2-nitrosopropane (MNP) (Aldrich) were used as received. Trimethylolpropane triacrylate (TMPTA) was obtained from Akzo Nobel Resins.

2.3. Syntheses

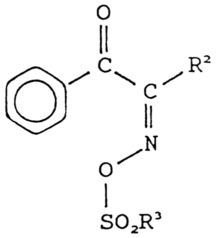
[Z]-2-Oximinopropiophenone,m.p.57.5–58.5°C, was obtained from its [E]-isomer as described [6]. The [Z]-2-oximinoketones were converted into the respective sulphonic and *N*-alkylsulphamic esters by treatment with the appropriate sulphonyl and *N*-alkylsulphamoyl chloride (mole ratio 1 : 1) in THF or chloroform in the presence of of triethylamine or pyridine followed by conventional work up. The structures of the new esters were confirmed by ^{1}H NMR and MS. They all showed a UV absorption at $\lambda \sim 340$ nm ($\log \epsilon \sim 2.10$) and are summarized in Table 1.

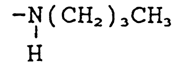
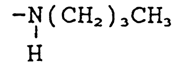
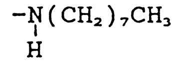
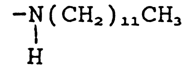
2.4. Irradiation procedures

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 min) to achieve complete solidification of MMA was determined.

Table 1
The [Z]-*O*-sulphonyl and *O*-sulphamoyl 2-oximinoketones synthesized



Ester	R^2	R^3	mp (°C)
2a	$-C_6H_5$	$-CH_3$	123.8–124.2
2c	$-C_6H_5$	$-(CH_2)_7CH_3$	104.4–106.0
2d	$-C_6H_5$	$-(CH_2)_{11}CH_3$	111.6–112.2
2e	$-C_6H_5$	$-(CH_2)_{15}CH_3$	108.8–110.2
2f	$-C_6H_5$	$-C_6H_4-CH_3$	109.3–109.8[a]
3f	$-CH_3$	$-C_6H_4-CH_3$	70.7–71.6[b]
4b	$-C_6H_5$	 $-\underset{H}{N}(CH_2)_3CH_3$  $-\underset{H}{N}(CH_2)_3CH_3$	97.8–98.0[c] 143.9–144.9
4c	$-C_6H_5$	 $-\underset{H}{N}(CH_2)_7CH_3$	70.8–71.5
4d	$-C_6H_5$	 $-\underset{H}{N}(CH_2)_{11}CH_3$	57.7–58.7

[a] Pure compound. Repeated recrystallization, however, failed to get mp of our compound anywhere near the reported [6] value of 113–115°C.
[b] Reported [6] mp 75–77°C.
[c] Crystallized immediately after melting, giving a 'new' and higher mp.

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 [10].

3. Results

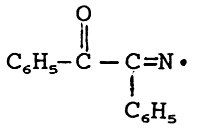
3.1. ESR spectroscopy

The ESR spectra of [Z]-2f and [Z]-3f recorded at low temperatures (from −70°C to −90°C) and in the absence of a spin trap showed the presence of the radicals previously assigned to the α-ketoiminyl radicals **5** and **6** respectively in the case of the corresponding *O*-acyl derivatives [1] (cf. Table 2).

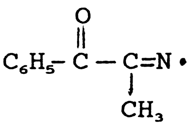
The ESR spectra recorded at room temperature showed the benzoyl radical **7**, and in the presence of spin traps, the trapped benzyol radicals **8** and **9** respectively.

Table 2
Radicals observed by ESR from esters [Z]-**2f** and [Z]-**3f**

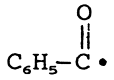
Radical	g	a_N	a_H	Remarks
5	2.0033	0.89	–	from [Z]-**2f** at −90°C
6	2.0037	0.94	0.18	from [Z]-**3f** at −90°C
7	2.0008	–	0.12	from [Z]-**2f** and [Z]-**3f** at 20°C
8	2.0061	1.43	0.45	from [Z]-**2f** and [Z]-**3f** at 20°C in the presence of PBN
9	2.0069	0.8	–	from [Z]-**2f** and [Z]-**3f** at 20°C in the presence of MNP


$C_6H_5-C(=O)-C(C_6H_5)=N\bullet$

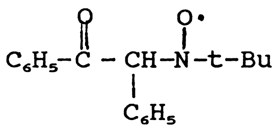
5


$C_6H_5-C(=O)-C(CH_3)=N\bullet$

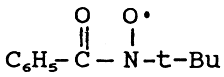
6


$C_6H_5-C(=O)\bullet$

7


$C_6H_5-C(=O)-CH(C_6H_5)-N(O\bullet)-t\text{-}Bu$

8


$C_6H_5-C(=O)-N(O\bullet)-t\text{-}Bu$

9

3.2. Polymerization and crosslinking

The *O*-sulphonyl 2-oximinoketones all showed the same gel time in the bulk polymerization of MMA within the limits of accuracy, which is much shorter than shown by most of the corresponding *O*-acyl derivatives [1] (cf. Table 3).

The *O*-sulphonyl 2-oximinoketones also showed considerably shorter induction periods (T_{ind}) and higher rates of polymerization (R_p) in the crosslinking of TMPTA in solution than most of the corresponding *O*-acyl derivatives [1].

The *O*-sulphamoyl 2-oximinoketones showed more or less the same results in the crosslinking of TMPTA.

3.3. Melamine curing

Both the *O*-sulphonyl and the *O*-sulphamoyl 2-oximinoketones on irradiation followed by baking at 100°C apparently induce the curing of a melamine formulation, which is known to be an acid-catalyzed process (cf. Table 4).

4. Discussion

From the ESR spectra, it is concluded that the photodecomposition of the [Z]-*O*-sulphonyl 2-oximinoketones, and hence also of the [Z]-*O*-sulphamoyl 2-oximinoketones

Table 3
[Z]-*O*-sulphonyl and [Z]-*O*-sulphamoyl 2-oximinoketones as photoinitiators for free radical polymerizations

Ester	Polymerization of MMA	Crosslinking of TMPTA		
	Gel time (min)	T_{ind} (s)	tg α	10^{-3} R_p (mol^{-1} s^{-1})
2a	47	43.0	4.3	1.92
2c	45	n.d.	–	–
2d	45	n.d.	–	–
2e	46	n.d.	–	–
2f	45	37.0	5.1	2.28
4b	n.d.	60.0	7.3	3.26
4c	n.d.	55.8	7.3	3.26
4d	n.d.	55.2	6.4	2.86
BIPE[a]	55	35.5	7.8	3.48

[a] Benzoin isopropyl ether, the calibrated standard applied [11].

Table 4
[Z]-*O*-sulphonyl and [Z]-*O*-sulphamoyl 2-oximinoketones as photocatalysts for the acid-catalyzed crosslinking of a melamine resin

Ester	Pendulum hardness (sec)[a]	
	Δ[b]	*hν*/Δ[c]
2a	Tacky film	346
2f	Tacky film	354
4b	Tacky film	331
4c	Tacky film	316
4d	Tacky film	296

[a] Film thickness 30 μm.

[b] Baking for 30 min at 100°C without prior irradiation.

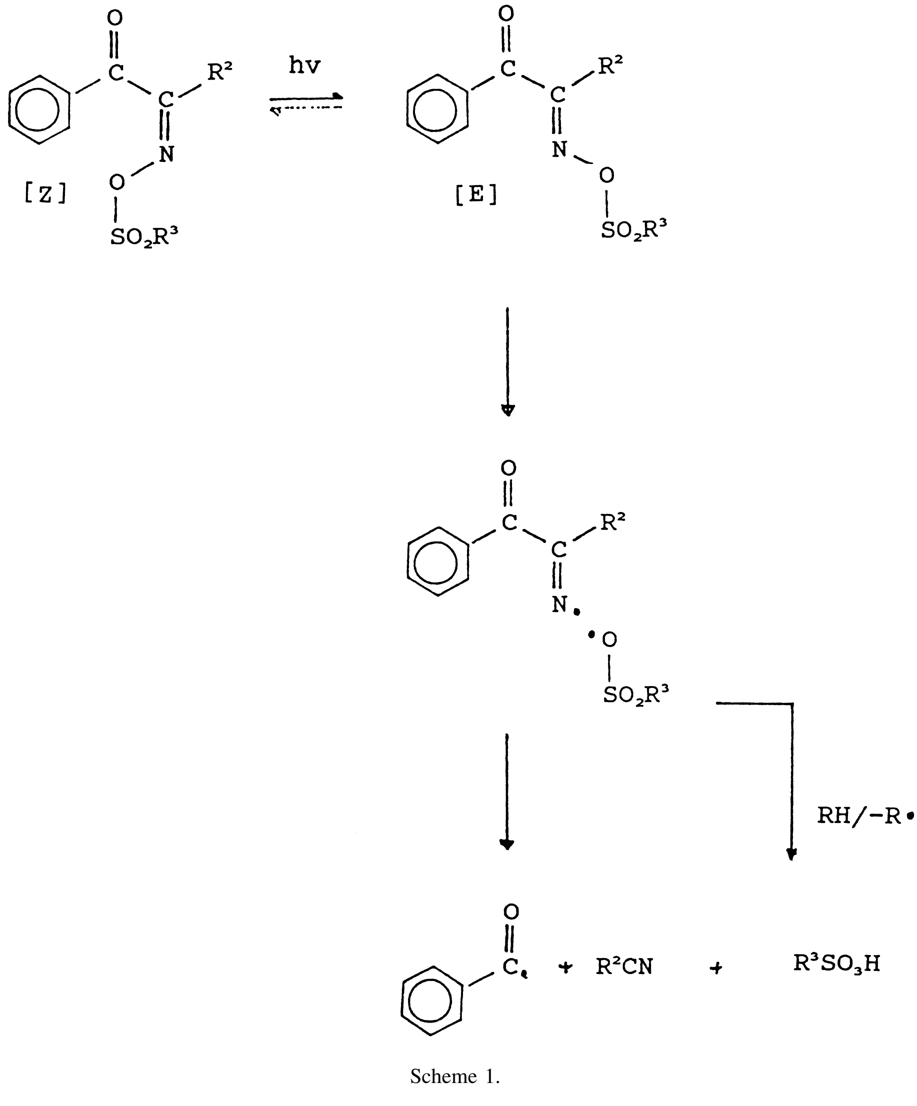
[c] Irradiation (4 s) followed by baking for 30 min at 100°C.

occurs through primary homolytic N–O bond cleavage, giving α-keto-iminyl and sulphonyloxy (sulphamoyloxy) radicals, i.e. showing a similar fragmentation pattern as the corresponding *O*-acyl 2-oximinoketones [1].

The question of whether the photodecomposition proceeds preferentially from one of the isomers ([E] or [Z] has been touched upon previously [1]. An experimental study of three cyclic *O*-methyl 2-oximinoketones [12] showed that the primary N–O bond cleavage only occurred on excitation of the [E]-isomer, which was further confirmed by ab initio calculations on a related model compound [13].

Therefore, it may well be that in the present case the sequence of events is a photoisomerization of the [Z] to the [E]-isomer followed by rapid N–O bond cleavage (cf. Scheme 1).

The polymerization and crosslinking experiments with MMA and TMPTA respectively confirm the formation of radicals capable of initiating radical polymerization processes, i.e. the benzoyl radical **7** from both the *O*-sulphonyl and the *O*-sulphamoyl 2-oximinoketones. However, considering the relatively long induction periods and the low rates of polymerization (average $T_{\mathrm{ind}} \sim 50$ s, and $R_{\mathrm{p}} \sim 2.7$), it must be concluded that these compounds are inferior to



Scheme 1.

common benzoin ethers (e.g. BIPE) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiators for radical polymerization processes [14].

The crosslinking of the melamine formulation, being an acid-catalyzed process, is indicative of the photoinduced release of strong acids, i.e. sulphonic and *N*-substituted sulphamic acids, which must have been formed from sulphonyloxy and sulphamoyloxy radicals respectively by hydrogen-abstraction from a suitable hydrogen donor (presumably the diesterdiol) present in the formulation. However, it is seen that even without prior irradiation, baking leads to tacky films, which may indicate undesired thermal decomposition of the initiator implying insufficient thermal stability. For this reason, these compounds are also unsuitable as photocatalysts for acid-hardening systems.

In any case, the present results confirm what has been claimed before, e.g. the thermal ($T \sim 130°C$) [15,16] and the photoinduced [17] generation of sulphonic acids from these compounds (the *O*-sulphonyl 2-oximinoketones).

However, it should be emphasized once more that the chemistry involved in these (thermochemical and photochemical respectively) processes leading to the release of acid is fundamentally different.

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