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Photoinitiators and photoinitiation, Part 14. N-substituted sulphamic esters of α-hydroxymethylbenzoin and α-hydroxymethylbenzoin ethers as multifunctional photo-initiators

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Abstract

Several new N-substituted sulphamic esters of α-hydroxymethylbenzoin and α-hydroxymethylbenzoin ethers have been synthesized. They are shown to release acids on irradiation, and hence to be capable of inducing the acid-catalyzed crosslinking of a melamine resin. They are also shown to photoinitiate the polymerization and crosslinking of acrylates, in all likelihood by the generation of reactive benzoyl and benzoylmethyl radicals, as concluded from a comparison with corresponding sulphonic esters of α-hydroxymethylbenzoin and its ethers. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: α-Hydroxymethylbenzoin; α-Hydroxymethylbenzoin ethers; N-Substituted sulphamic esters; Photodecomposition

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1. Introduction

Sulphonic esters of α-hydroxymethylbenzoin and α-hydroxymethylbenzoin ethers, originally designed as sulphonic acid releasing photocatalysts for acid-hardening systems [1,2], have also been shown to be capable of photoinitiating the free-radical polymerization and crosslinking of acrylates [3,4] on account of the generation of both sulphonic acids and reactive benzoyl and benzoylmethyl radicals [5,6]. In an attempt to extend this 'multifunctional photoinitiator principle' we looked for other strong acids capable of replacing sulphonic acids. Thus, it was decided to study the corresponding esters derived from *N*-alkyl-, *N*-alkoxycarbonyl-, and N-acylsulphamic acids [7].

In the present communication we report on the syntheses of these esters, and their potential as multifunctional photoinitiators.

2. Experimental details

2.1. General

The ^{1}H NMR spectra were recorded on a Bruker WH-270 spectrometer using tetramethylsilane (δ=0 ppm) as 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). The UV spectra were recorded on a Hitachi 110–80 A spectrophotometer.

2.2. Materials

α-Hydroxymethylbenzoin, and its ethyl and isopropyl ethers, and the sulphonic esters 2a-d, 4a and 6a were available from previous studies [4–6]. All other starting materials, reagents, and solvents were obtained from Aldrich unless stated otherwise.

2.3. Syntheses

The N-alkylsulphamoyl chlorides (methyl and *n*-butyl) were synthesized from the corresponding alkylamines and sulphuryl chloride according to Weiss and Schulze [8]. The higher N-alkylsulphamoyl chlorides (*n*-octyl and *n*-dodecyl) were synthesized from the corresponding alkylamines using chlorosulphonic acid and PCl_5 as described by Kloek and Leschinsky [9]. The *N*-alkoxycarbonylsulphamoyl chlorides were synthesized from the corresponding alcohols and chlorosulphonyl isocyanate according to Graf [10]. The *N*-acylsulphamoyl chlorides were synthesized from the corresponding carboxylic acids and chlorosulphonyl isocyanate as described [11,12].

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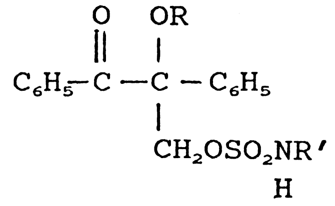
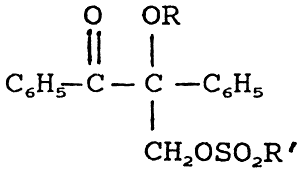
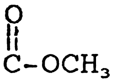
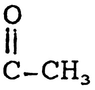
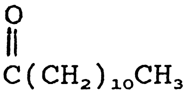
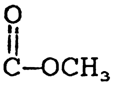
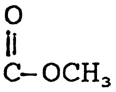
Table 1
The N-substituted sulphamic esters





R	R’	M.p. (°C)	
H	CH_3	1a 117.5–118.5	2a [5]
H	$(CH_2)_3CH_3$	1b 104.6–105.4	2b [5]
H	$(CH_2)_7CH_3$	1c 67.0–68.4	2c [5]
H	$(CH_2)_{11}CH_3$	1d 76.3–77.3	2d [5]
H	 $C(=O)OCH_3$	1e 124.3–124.5	
H	 $C(=O)CH_3$	1f 129.6–131.3	
H	 $C(=O)(CH_2)_{10}CH_3$	1g 85.0–88.0	
CH_2CH_3	CH_3	3a 106.5–107.0	4a [6]
CH_2CH_3	 $C(=O)OCH_3$	3e 93.5–95.0	
$CH(CH_3)_2$	 $C(=O)OCH_3$	5e 65.5–66.5	6e [6]

α-Hydroxymethylbenzoin, and its ethyl and isopropyl ethers were converted into the respective sulphamic esters by treatment with the appropriate sulphamoyl chlorides (mole ratio 1:1) in THF in the presence of triethylamine followed by conventional work up. The structures of the new esters were confirmed by ^1H NMR and mass spectrometry. They all showed a UV absorption maximum $\lambda \sim 320$ nm ($\log \epsilon \sim 2.30$), and are summarized in Table 1.

2.4. Irradiation procedures

2.4.1. Photoinduced crosslinking of TMPTA in solution

Solutions of TMPTA (trimethylolpropane triacrylate) ($10\ g\ l^{-1}$) 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 cross-linking (insolubilization) of TMPTA was monitored by laser nephelometry as described by Decker and Fizet [13]. Induction periods (T_{ind}) were determined as the irradiation time (in seconds) until the onset of the cross-linking. Relative rates crosslinking were determined from the slope of the curves (tgα) using a calibration curve obtained by plotting the amount of polymer formed (by gravimetry) vs. time (in seconds) benzoin isopropyl ether (BIPE) being the standard [14]. The results are summarized in Table 2.

2.4.2. Photoinduced acid generation

Solutions of some esters ($10^{-2}\ mol\ l^{-1}$) in CH_3CN/H_2O (1:1) were irradiated 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 the irradiation. The pH was determined of samples withdrawn at regular intervals. The results are summarized in Table 3.

2.4.3. Photocuring of a melamine resin

The equipment consisted of a high-pressure Hg-lamp (Philips HOK-6, 80 W cm^{-1}) mounted (15 cm in distance) over a conveyor belt. The belt had a variable speed and had been calibrated so that speed (in $m\,min^{-1}$) and the irradiation time (in seconds) could be determined.

Table 2
Crosslinking of TMPTA in solution

Ester	T_{ind} (s)	tgα	10^{-3} R_p (mol l^{-1} s^{-1})
1a	26.0	9.1	4.06
1b	26.1	9.1	4.06
1c	27.6	8.5	3.79
1d	24.6	8.5	3.79
1e	25.8	9.1	4.06
1f	24.4	9.3	4.15
1g	25.1	9.1	4.06
2a	25.3	11.2	5.00
2b	25.5	11.0	4.90
2c	25.6	10.8	4.81
2d	24.9	11.0	4.90
3a	18.5	8.4	3.74
3e	18.1	8.3	3.71
4a	16.2	8.3	3.71
5e	18.8	8.2	3.66
6e	18.4	8.1	3.62
BIPE[a]	35.5	7.8	3.48

[a] Benzoin isopropyl ether, the calibrated standard applied [14].

Table 4
Melamine curing by photoinduced generated acids from some esters

	Pendulum hardness (s)			
	Film thickness 30 μm		Film thickness 80 μm	
Ester	Δ[a]	hv/Δ[b]	Δ[a]	hv/Δ[b]
1a	Wet film	324		
1b	Wet film	307		
1c	Wet film	330		
1d	Wet film	314		
1e	Wet film	333	Wet film	264
1e	Wet film	368		
1g	Wet film	365		
2a	Wet film	356	Wet film	312
2d	Wet film	346		
3a	Wet film	320		
3e	Wet film	330		
4a	Wet film	345	Wet film	320
5e	Wet film	325		
6a	Wet film	340	Wet film	311

[a] Baking for 30 min at 100°C without prior irradiation
[b] Irradiation (4 S) followed by baking for 30 min at 100°C

The formulation consisted of: 37.5 g of diesterdiol (an experimental composition consisting of equal parts by weight of (a) di(monodecanoic acid ester of trimethylolpropane) isophthalate and (b) a mixture of 1 part of di(neopentylglycol) isophthalate and 2 parts of di(neopentylglycol) phthalate) [15,16] $+10^{-3}$ mol of initiator 10 g of Cymel-303 (hexamethoxymethylmelamine), and 10 g of ethyleneglycol monoacetate.

The formulations were applied onto Bonder steel plates using Erichsen rods resulting in thin films of 30 and 80 μm thickness respectively. The plates were then passed under the light source at 2 mmin^{-1} (irradiation time of 4 s) and baked for 30 min at 100°C in an oven. The pendulum hardness of the films was determined after 24 h (Erichsen 299 and 300). The results are summarized in Table 4.

3. Results and discussion

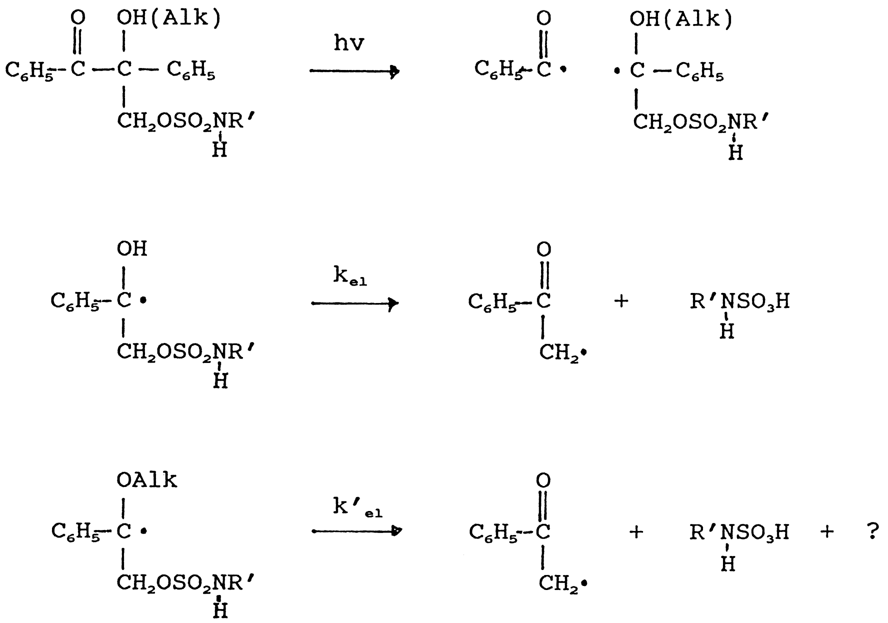
The crosslinking of TMPTA in solution (cf. Table 2) shows that the N-substituted sulphamic esters are also capable of initiating the free-radical polymerization of acrylates in much the same way as the corresponding sulphonic esters included for comparison, e.g. esters 1 showing an average $T_{ind}\sim25.7$ s and an average $R_p\sim4.0$ as compared with an average $T_{ind}\sim25.3$ s and an average $R_p\sim4.9$ of corresponding esters 2, and esters 3 and 5 showing an average $T_{ind}\sim18.5$ s and an average $R_p\sim3.7$ as compared with an average $T_{ind}\sim17.3$ s and an average $R_p\sim3.67$ of the corresponding esters 4 and 6.

Table 3
Photoinduced generation of acid from some esters

	Irradiation time			
	1 min		5 min	
Ester	pH	[H$^+$]	pH	[H$^+$]
1a	3.89	1.3×10^{-4}	2.96	1.1×10^{-3}
2a	3.25	5.6×10^{-4}	2.81	1.6×10^{-3}
3a	3.39	4.1×10^{-4}	2.77	1.7×10^{-3}
4a	3.78	1.7×10^{-4}	2.85	1.4×10^{-3}

The pH measurements vs. irradiation time (cf. Table 3) clearly show that the N-substituted sulphamic esters 1a and 3a release acid on irradiation, again in much the same way as the corresponding sulphonic esters 2a and 4a. Corroborating evidence for the photoinduced release of acid is provided by the acid-catalyzed curing of a melamine resin (cf. Table 4). The irradiation of the formulations containing the N-substituted sulphamic esters followed by baking for 30 min at 100°C leads to cured films comparable to the formulations containing the corresponding sulphonic esters, whereas baking without prior irradiation only results in unchanged wet films.

Considering now the close resemblance to the corresponding sulphonic esters, the conclusion is justified that the N-substituted sulphamic esters undergo a very similar photodecomposition (cf. Scheme 1), i.e. a primary α-cleavage into a benzoyl and an α-hydroxy(alkoxy)-α-sulphamoyloxymethylbenzyl radical pair. The α-hydroxy-α-sulphamoyloxymethylbenzyl radical must subsequently undergo a rapid heterolytic elimination of N-substituted sulphamic acid simultaneously generating the benzoylmethyl radical. The α-alkoxy-α-sulphamoyloxymethylbenzyl radical must also release the N-substituted sulphamic acid, simultaneously generating the benzoylmethyl radical as was previously observed for the corresponding α-alkoxy-α-sulphonyloxymethylbenzyl radicals [6], the fate of the alkyl ether part still being obscure, however.



in which $k'_{el} < k_{el}$ (cf.[6])

Scheme 1.

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