

Photoinitiators and photoinitiation

10. The photodecomposition of some carboxylic esters of α -hydroxymethylbenzoin

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Abstract

The photodecomposition of some carboxylic esters of α -hydroxymethylbenzoin was studied using electron spin resonance (ESR) and proton nuclear magnetic resonance-chemically induced dynamic nuclear polarization (^1H NMR-CIDNP) techniques. Exclusive α -cleavage into benzoyl and α -hydroxy- α -acyloxymethylbenzyl radicals through the triplet excited state was observed. The α -hydroxy- α -acyloxymethylbenzyl radicals mainly undergo disproportionation with the other radicals present to give benzoylmethyl carboxylates. Elimination of carboxylic acids from the α,α -disubstituted benzyl radicals occurs to some extent, but at a much lower rate than the elimination of sulphonic acids from the corresponding α -hydroxy- α -sulphonyloxymethylbenzyl radicals generated from the sulphonic esters of α -hydroxymethylbenzoin. © 1997 Elsevier Science S.A.

Keywords: α -Hydroxy- α -acyloxymethylbenzyl radicals; α -Hydroxymethylbenzoin esters; Photodecomposition

1. Introduction

The sulphonic esters of α -hydroxymethylbenzoin have recently been shown to undergo photoinduced α -cleavage into benzoyl and α -hydroxy- α -sulphonyloxymethylbenzyl radicals through a short-lived triplet state [1]. The α,α -disubstituted benzyl radicals undergo an extremely rapid heterolytic elimination of sulphonic acid to give benzoylmethyl radicals. The benzoyl and benzoylmethyl radicals readily attack the C=C double bond of 1,1-diphenylethylene used as a non-polymerizing model substrate for vinyl monomers. For these reasons, sulphonic esters of α -hydroxymethylbenzoin are suitable both as acid-releasing photoinitiators for acid-hardening resin systems [2,3] and as photoinitiators for free radical polymerization [4,5].

Carboxylic esters of α -hydroxymethylbenzoin have been claimed as photoinitiators for unsaturated polyester/styrene resin systems, i.e. for free radical polymerization processes [6]. It is perfectly reasonable to assume that these carboxylic esters will also undergo photoinduced α -cleavage into ben-

zoyl and α -hydroxy- α -acyloxymethylbenzyl radicals. Of interest is the fate of the latter radicals: will they release carboxylic acids and generate benzoylmethyl radicals, or will they undergo alternative reactions, e.g. fragmentation to acyloxy radicals and acetophenone?

In this paper, we report the photodecomposition of some carboxylic esters of α -hydroxymethylbenzoin (see Table 1), studied by electron spin resonance (ESR) and proton nuclear magnetic resonance-chemically induced dynamic nuclear polarization (^1H NMR-CIDNP) techniques, as well as by radical trapping experiments using 1-dodecanethiol, a stable nitroxyl 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) and 1,1-diphenylethylene (DPE).²

2. Experimental details

2.1. General

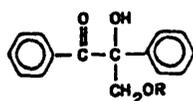
The ^1H NMR spectra were recorded on a Bruker WH-270 spectrometer using tetramethylsilane ($\delta = 0$ ppm) as internal

² Although we abandoned the use of DPE as a model substrate in favour of 1,1-di-*p*-tolylethylene (DTE) on very good grounds [7], we used DPE in this study for comparison with our previous investigation of the sulphonic esters of α -hydroxymethylbenzoin [1].

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Table 1
 α -Hydroxymethylbenzoin **1a** and some of its carboxylic esters



| Compound | R | M.p. (°C) | λ_{\max} (nm) (CH ₃ OH) ^a | log ϵ |
|-----------|---|-------------|--|----------------|
| 1a | H | 85.6–86.1 | | |
| 1b | | 100.1–100.6 | 320 ± 2 | 2.30 ± 0.02 |
| 1c | | 102.0–102.8 | 320 ± 2 | 2.30 ± 0.02 |
| 1d | | 112.3–112.9 | 320 ± 2 | 2.30 ± 0.02 |
| 1e | | 103.8–104.8 | 320 ± 2 | 2.30 ± 0.02 |

^a Only the absorption maximum beyond 300 nm, relevant to the photochemistry, is shown. It may be emphasized that the ester part neither contributes nor influences the chromophoric system.

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 (10 mg g⁻¹ of solvent) were deoxygenated by purging with helium for 30 min. In the spin-trapping experiments using 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 MNP, the samples were continuously irradiated. The *g* values of the radicals detected were determined relative to the benzoyl radical **2** (*g* = 2.0008 [8]).

The ¹H 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, NiSO₄/CuSO₄ filter).

2.2. Materials

α -Hydroxymethylbenzoin **1a** and its esters **1b** and **1d** were available from previous studies [1,9].

Methyl cyanoacetate (Acros Chimica) and diphenylacetic acid (Merck) were used without purification. *p*-Anisoyl chloride (Acros Chimica) was fractionated before use. 2-Bro-

moacetophenone (Acros Chimica) was recrystallized from methanol. MNP, 1-dodecanethiol and TMPO (Acros Chimica) were used as received. DPE (Merck) was fractionated (b.p. 79–80 °C at 0.3 mbar) before use.

2.3. Syntheses

2-Cyano-2-methylpropionic acid (b.p. 102–104 °C at 2.1 mbar) was synthesized according to Ebersson and Nilsson [10]. The acid chloride (b.p. 57–59 °C at 16 mbar) was obtained from the acid and thionyl chloride. α -Hydroxymethylbenzoin **1a** was converted into esters **1c** and **1e** by treatment with the respective acid chlorides (mole ratio, 1 : 1) in tetrahydrofuran (THF) in the presence of triethylamine followed by conventional work-up [9]. Purification was achieved by recrystallization in all cases. The structures of the new esters **1c** and **1e** were confirmed by ¹H NMR and mass spectrometry (MS).

2-Bromoacetophenone was converted into benzoylmethyl acetate **10b** (m.p. 48.0–48.4 °C) [11], benzoylmethyl 2-cyano-2-methylpropionate **10c** (m.p. 64.9–65.1 °C), benzoylmethyl benzoate **10d** (m.p. 118.8–119.2 °C) [12] and benzoylmethyl *p*-anisate **10e** (m.p. 135.3–135.7 °C) [13] according to Sheehan and Umezawa [14].

2,2-Diphenylethanol (m.p. 60.3–60.6 °C), obtained by reduction of diphenylacetic acid with LiAlH₄ [15], was converted into its benzoate (m.p. 87.8–88.8 °C).

2.4. Irradiation procedures

2.4.1. General

All irradiations were conducted 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 reactions were monitored by thin layer chromatography (TLC) analysis.

2.4.2. Preparative irradiations

Solutions of the various esters (approximately 10⁻² M) in benzene were irradiated for 2–6 h in the presence of 1-dodecanethiol (2 × 10⁻² M), TMPO (3 × 10⁻² M) and DPE (2 × 10⁻² M).

The irradiation mixtures were fractionated by preparative liquid chromatography on a 5 g scale using a Chromatospec preparative liquid chromatograph equipped with a silica column (Lichroprep; particle size, 15–25 μ m; Merck). The resulting fractions were further purified on a semi-preparative column (Lichrosorb SI-60; particle size, 10 μ m; 250 mm × 22 mm i.d.; Merck). The products were identified by spectroscopic methods (¹H NMR and MS) and by comparison with authentic samples. Thus S-dodecyl thiobenzoate **16** [1,16], 2-(dodecylthio)-acetophenone **17** [1,17], 2,2,6,6-tetramethyl-1-piperidino benzoate **18** [1,18,19] and 2,2,6,6-

tetramethyl-1-piperidyloxymethyl phenyl ketone **20** [1] have already been described.

The reaction products from the photodecomposition of ester **1d** in the presence of DPE are as follows: 3,3-diphenylpropiophenone **23** (m.p. 92.3–92.9 °C) [20]; 2,2-diphenylvinyl phenyl ketone **24** (m.p. 86.9–87.4 °C) [21]; 3,3,3-triphenylpropiophenone **25** (m.p. 168.0–169.4 °C) [22]; 4,4-diphenylbutyrophenone **26** (m.p. 89.5–90.4 °C) [23]; 3,3-diphenyl-2-propenyl phenyl ketone **27** (m.p. 124.9–125.7 °C) [24]; these have also been described previously (cf. also Ref. [1]).

2.4.3. Quantitative irradiations

The analyses of samples withdrawn from the irradiation mixtures were carried out on a modular high performance liquid chromatography (HPLC) system (Waters) equipped with two model 6000 A pumps, a model 720 system controller, a WISP automatic sample processor, a 730 M data module and a model 440 UV-absorbance detector ($\lambda = 254$ nm).

For the quantitative analysis of the photodecomposition of ester **1d** in the presence of DPE, both normal- and reversed-phase HPLC were used. Normal-phase separations were carried out on a Lichrosorb SI-60 column (particle size, 5 μ m; 250 mm \times 4 mm i.d.; Merck) using a hexane–ethyl acetate mixture (ratio, 95 : 5 v/v) as the solvent system. For the reversed-phase separations, a Lichrosorb PR-1 column (particle size, 5 μ m; 250 mm \times 4 mm i.d.; Merck) was used with a solvent system consisting of methanol and water in various ratios.

3. Results

3.1. ESR spectroscopy

At low temperatures (from -70 to -90 °C) and in the absence of a spin trap, the ESR spectra of esters **1b–1e** all show the presence of the benzoyl radical **2** [8] (see Table 2). In addition, at low temperature (-90 °C), the spectra of esters **1d** and **1e** in particular show the presence of a radical which can be assigned to the respective α -hydroxy- α -acyloxymethylbenzyl radical **3** by comparison of the parameters with the reported values for the α -hydroxy- α -ethylbenzyl radical [25].

At room temperature, the ESR spectra of esters **1b–1e** all show the presence of the benzoylmethyl radical **4** [26]. At room temperature and in the presence of MNP, the ESR spectra of esters **1b–1e** all show the presence of the trapped benzoyl radical **5** [27] and the trapped benzoylmethyl radical **6** [28]. In addition, the trapped phenyl radical **7** [29] is observed in both benzene and toluene. The origin of the phenyl radical is not known with certainty. However, it seems that its appearance is connected with the occurrence of radical **4**. The phenyl radical may be formed from radical **4** through the elimination of ketene, which may well be a side reaction of the neophyl-like rearrangement and subsequent decarbonylation of radical **4** [26].

Interestingly, the elimination of ketene from radical **4** has recently been assumed to occur in order to explain the formation of small amounts of biphenyl during the photolysis of ester **1b** [30].

Table 2
Radicals observed by ESR during the photolysis of esters **1**

| | | | | | | | |
|---------------|---------------------------------|-------------------------|-------------------------|---------------------------|--------------------|---------------|-------------------------|
| | | | | | | | |
| g 2.0008 | $a_{H(m)}$ 0.11 ² | g 2.0031 | $a_{H(\alpha)}$ 1.02 | $a_{H(\alpha,p)}$ 0.46 | $a_{H(m)}$ 0.16 | g 2.0046 | $a_{H(\alpha)}$ 1.96 |
| | | | | | | | |
| g 2.0069 | a_N 0.8 | g 2.0062 | a_N 1.44 | $a_{H(\alpha)}$ 0.77 | | g 2.0061 | a_N/a_H n.d. |
| | | | | | | | |
| g 2.0054 | a_N 2.98 | $a_{H(\alpha)}$ 0.09 | | | | | |

Table 3
Assignments of ^1H NMR-CIDNP transitions of ester **1b**

| Product assignment | Chemical shift | Polarization |
|---|----------------|--------------|
| $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{OH}}{\underset{\text{CH}_2\text{OCOCH}_3}{\text{C}}}-\text{C}_6\text{H}_5$ (recombination) | 4.35 (s) | E |
| <i>o</i> -benzyl (recombination) | 7.50 (m) | E |
| $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}$ 12 | 9.65 (s) | A |
| $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{OCOCH}_3$ 10b | 4.80 (s) | E |
| $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ 11 | 2.05 (s) | A |
| $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$ 13 | 3.20 (s) | A |

In the ESR spectra of esters **1d** and **1e** in particular, a radical can be observed which, in all likelihood, is radical **8** ($R' \equiv \text{C}_6\text{H}_5$ [31]), since it only appears when toluene is used as solvent.

In all experiments employing MNP, signals of radical **9** [31] are also detected.

3.2. ^1H NMR-CIDNP

Acetic ester **1b** was selected for the CIDNP experiments. The polarization effects observed (see Table 3) can be readily explained using the set of simple rules developed by Kaptein [32]: net polarization $T_{nc} = \mu\epsilon\Delta gA_i$, considering

1. photodecomposition from a triplet excited state ($\mu = +$);
2. 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. the g value of radical **3** (2.0031) is larger than the g value of radical **2** (2.0008), and hence $\Delta g = +$ for the protons (OH and *o*-benzyl) of radical **3** in the in-cage recombination;
4. the hyperfine coupling constants A_i .

This then leads to the reactions shown in Scheme 1.

3.3. Trapping with 1-dodecanethiol

Carboxylic esters **1b–1e** were irradiated in benzene solution in the presence of 1-dodecanethiol as a scavenger for non-cage benzoyl radicals **2** [33]. Benzaldehyde **12** proved to be the major product in all cases. The major products resulting from the respective radicals **3** which could be iden-

tified were the benzoylmethyl carboxylates **10** and acetophenone **11**.

The benzoyl radicals **2** and the benzoylmethyl radicals **4** resulting from radicals **3** were also scavenged in part by the 1-dodecanethiol radicals to form small amounts of *S*-dodecyl thiobenzoate **16** and 2-(dodecylthio)acetophenone **17** respectively as observed previously [1].

3.4. Trapping with TMPO

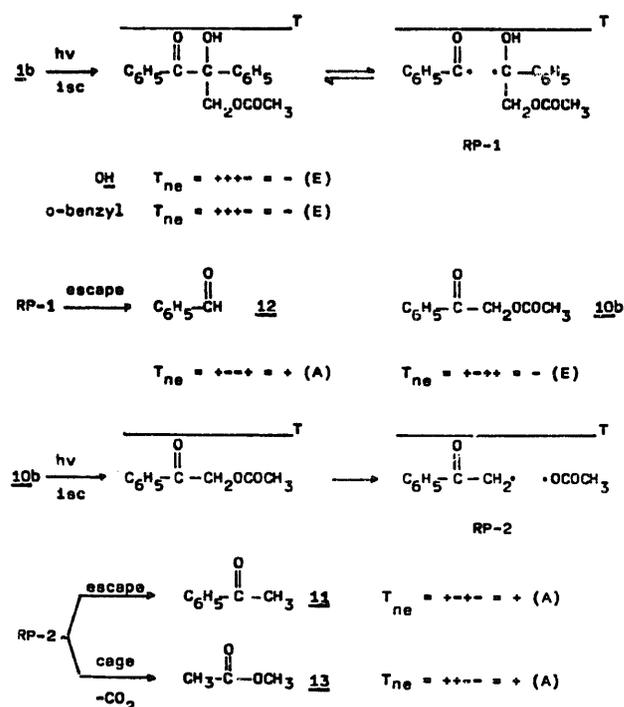
Carboxylic esters **1b–1e** were irradiated in benzene solution in the presence of TMPO as described previously [1,19]. In all cases, 2,2,6,6-tetramethyl-1-piperidino benzoate **18** [1,18,19], resulting from the coupling of radicals **2** and TMPO, was formed. In addition, other products, resulting from the reaction of radicals **3** with TMPO, were found. Thus benzoylmethyl carboxylates **10** were formed, together with 1-hydroxy-2,2,6,6-tetramethyl piperidine **19**, by a redox reaction between radicals **3** and TMPO, as observed previously for benzoin [19], α -hydroxymethylbenzoin **1a** [1] and 2-hydroxyisobutyrophenone [34].

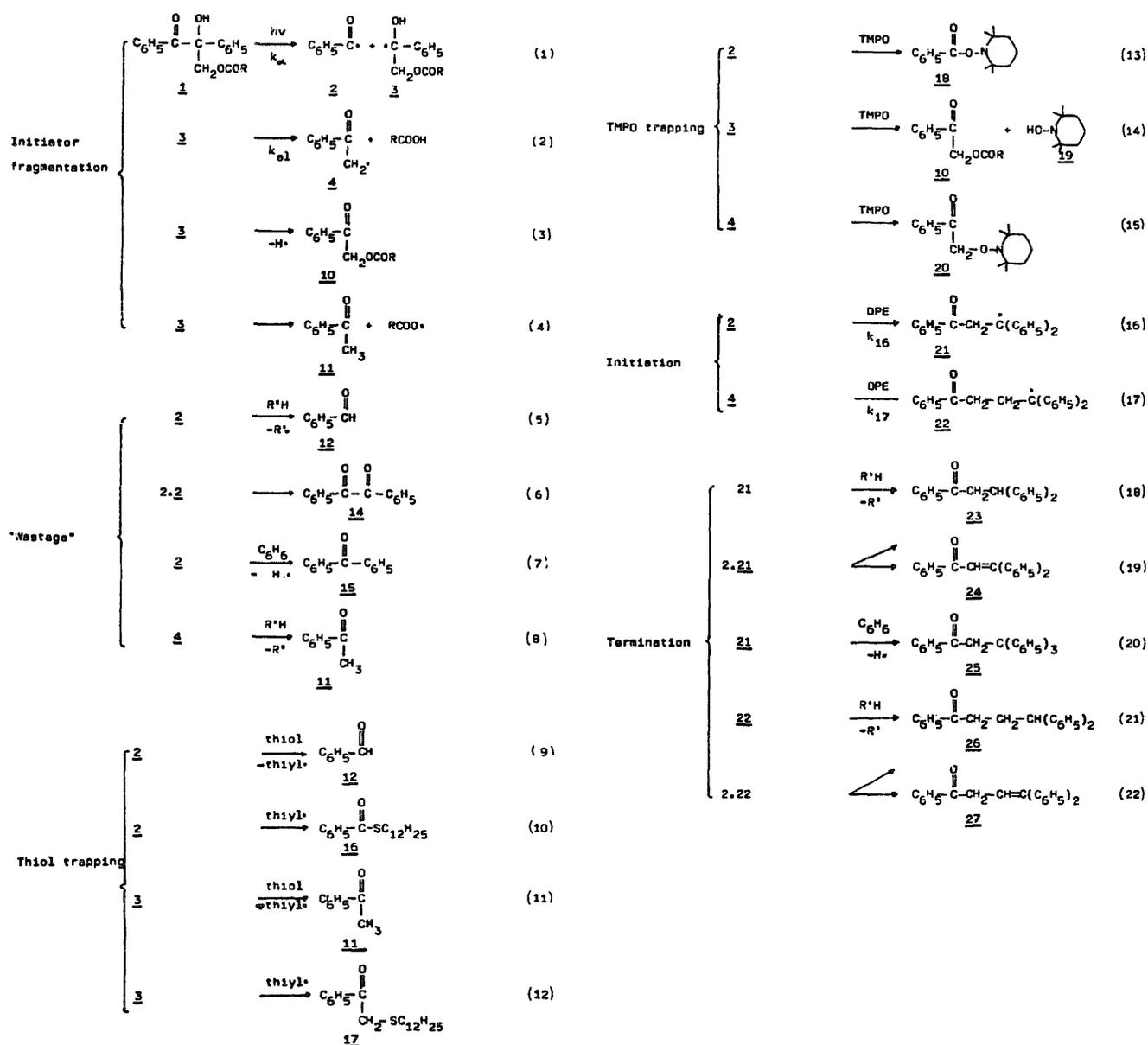
In the case of ester **1c**, an additional product was isolated, 2,2,6,6-tetramethyl-1-piperidylmethyl phenyl ketone **20**, resulting from the coupling of radical **4** and TMPO, as observed previously for the sulphonic esters of **1a**.

It should be emphasized that no other products were formed on irradiation of esters **1b–1e** in benzene in the presence of TMPO (e.g. 1-alkoxy-2,2,6,6-tetramethylpiperidines resulting from the coupling of alkyl radicals and TMPO).

3.5. Photodecomposition in a model substrate (DPE)

Carboxylic ester **1d** was photolysed in benzene solution in the presence of DPE as described previously for some sul-





Scheme 2.

phonic esters of **1a** [1] and some common photoinitiators [35]. The products formed fall into two categories:

1. products not containing the DPE moiety, i.e. products of "wastage" from the viewpoint of initiation, such as benzaldehyde **12**, benzil **14**, benzophenone **15**, benzoylmethyl benzoate **10d** (major product) and acetophenone **11**;
2. products resulting from the addition of radicals **2** and **4** to the C=C double bond of DPE; both primary adduct radicals **21** and **22** undergo the usual termination reactions, such as hydrogen abstraction and disproportionation as indicated in Scheme 2.

A satisfactory material balance was obtained for the benzoyl radical **2** (approximately 84%) and the benzoylmethyl radical **4** (approximately 84%) generated from **1d** (see Table 4). The initiating efficiencies f_p , defined as the fraction

of the generated radicals that initiate polymerization, can be calculated from the products.

Thus, for radical **2**, $f_{p2} = \Sigma(23, 24, 25)/1d_{\text{conv.}} = 0.61$, which is in excellent agreement with previous results obtained with the sulphonic esters of **1a** ($f_{p2} = 0.59$ [1]).

Likewise, for radical **4**, $f_{p4} = \Sigma(26, 27)/1d_{\text{conv.}} = 0.25$, which is much lower than that observed for the sulphonic esters ($f_{p4} = 0.56$ [1]). Since radicals **2** and **4** were shown to be equally reactive towards the C=C double bond of DPE, the drop in f_{p4} must be attributed to the smaller amount of radicals **4** generated owing to disproportionation (Scheme 2, reaction (3)) of radicals **3**.

As a consequence, the overall initiating efficiency $f_p = (f_{p2} + f_{p4})/2 = 0.43$ is also lower than that observed for the sulphonic esters ($f_p = 0.58$ [1]).

Table 4
The photodecomposition of **1d** in the presence of DPE ^a

| Product | Amount of product (mmol) | Corresponding amount (mmol) of | | |
|------------|--------------------------|--------------------------------|------|-----|
| | | 2 | 4 | DPE |
| 1d | 12.7 | 12.7 | 12.7 | |
| 12 | Trace | Trace | | |
| 14 | 0.4 | 0.8 | | |
| 15 | 4.0 ^b | 1.0 | | 3.0 |
| 10d | 6.6 | | 6.6 | |
| 11 | 1.5 | | 1.5 | |
| DPE | 2.2 | | | 2.2 |
| 23 | 5.8 | 5.8 | | 5.8 |
| 24 | 4.2 | 4.2 | | 4.2 |
| 25 | 0.5 | 0.5 | | 0.5 |
| 26 | 2.1 | | 2.1 | 2.1 |
| 27 | 2.2 | | 2.2 | 2.2 |

^a The starting solution contained 30 mmol of **1d** and DPE. Irradiation time, 6 h.

^b The relatively large amount of **15** is mostly due to oxidation of DPE during the entire operation (irradiation and subsequent analysis).

4. Discussion

From the spectroscopic results, it can be concluded that carboxylic esters **1b–1e** undergo photoinduced α -cleavage into the radical pair **2** and **3** through the triplet excited state, thus paralleling the behaviour of the corresponding sulphonic esters [1] as expected. Our interest, as already mentioned (see Section 1), was also focused on the behaviour of radicals **3** compared with the corresponding α -hydroxy- α -sulphonyloxymethylbenzyl radicals generated from the sulphonic esters.

The ESR spectra unmistakably indicate further fragmentation of radicals **3**, generating the benzoylmethyl radical **4** (Scheme 2). We have not been able to detect acyloxy radicals using spin trapping, nor the corresponding alkyl radicals (after the loss of CO₂ from the acyloxy radicals) in the absence of the spin trap. This strongly suggests that reaction (4) (Scheme 2) is not an important fragmentation pathway for radicals **3**.³

Supporting evidence comes from ¹H NMR-CIDNP results obtained with ester **1b**, i.e. the appearance of a polarized signal (E) due to the α -protons of acetophenone **11** and the absence of a polarized signal due to methane and ethane.⁴

Moreover, the polarized signal (E) due to the α -protons of benzoylmethyl acetate **10b** suggests that hydrogen transfer (Scheme 2, reaction (3)) is the major process of radicals **3**.

These results have been corroborated by a recent report by Askerov et al. [30] on the photolysis of ester **1b** in various solvents. Benzoylmethyl acetate **10b** (approximately 30%

yield) was found to be the major product in all solvents. The formation of acetophenone **11** was found to be strongly dependent on the solvent (5% in benzene and approximately 40% in 2-propanol).

The trapping experiments using 1-dodecanethiol, TMPO and DPE are in agreement with the spectroscopic results, i.e. the primary formation of radicals **2** and **3**.

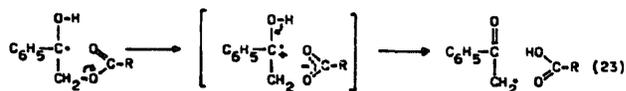
The TMPO trapping experiments provided valuable information on the relative importance of the subsequent reactions of radicals **3** as observed previously [1]. Firstly, the absence of 1-alkoxy-2,2,6,6-tetramethylpiperidines among the products should be mentioned. These products should have been formed if reaction (4) (Scheme 2) was a significant fragmentation pathway of radicals **3**.

It is also concluded that fragmentation reaction (2) (Scheme 2) of radicals **3**, generating radical **4**, is a slow process compared with the redox reaction (14) (Scheme 2) between radicals **3** and TMPO ($k_{\text{red}} \sim 5 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ [37,38]) giving benzoylmethyl carboxylates **10** and the reduced nitroxyl **19**.

In the case of ester **1c**, interestingly, some 2,2,6,6-tetramethyl-1-piperidyloxymethyl phenyl ketone **20** [1] was also formed. This indicates that fragmentation reaction (2) of radical **3c** is fast enough to at least compete with redox reaction (14).

The fact that 2-cyano-2-methylpropionic acid is a much stronger acid ($\text{p}K_{\text{a}} \sim 2.4$ [39]) than all the other acids used in this study may be significant.

The elimination of acid from the α -hydroxy- α -acyloxy-methylbenzyl radical **3** may well be related to the 1,2-rearrangement reaction



of β -acyloxyalkyl radicals, which has recently been shown [40–43] to occur through a charge-separated transition state. In the kinetic experiments, a pronounced influence of both solvent polarity (water > hydrocarbons) and the electron-attracting character of the substituent R (CF₃ > CH₃) on the rate of the rearrangement was observed [41]. Such a detailed kinetic study of the influence of both the solvent polarity and electron-attracting character of the R group on the fragmentation reaction (2) of radicals **3**, which should provide information on the possible occurrence of a charge-separated transition state, is well beyond the scope of the present work.

The trapping experiments using DPE are also in agreement with the conclusions reached so far. Similar product mixtures were obtained as found previously [1] for the sulphonic esters of **1a**, except for the appearance of substantial amounts of benzoylmethyl carboxylates **10**. As a consequence, the contribution of radical **4** to the initiation (products **26**, **27**, etc.) is far less than for the corresponding sulphonic esters [1], e.g. the ratio $f_{\text{p}2}/f_{\text{p}4}$ (carboxylic ester) ~ 2.4 vs. $f_{\text{p}2}/f_{\text{p}4}$ (sulphonic ester) ~ 1.0 .

³ Acyloxy radicals (with spin trapping) and the corresponding alkyl radicals (without spin trapping) have been observed by ESR during the photolysis of O-acyl α -oximonoketones under similar conditions [36].

⁴ ¹H NMR-CIDNP effects have been observed for methane and ethane (A) during photolysis of O-acyl α -oximonoketones [36].

The absence of termination products resulting from the coupling and cross-coupling of the primary adduct radicals **21** and **22**, as observed in the case of the corresponding sulphonic esters [1], is not clear. The absence of 2,2-diphenylethyl benzoate in the irradiation mixture of **1d** in the presence of DPE once again indicates the insignificance of fragmentation reaction (4) of radicals **3**.

It may finally be relevant to mention that long-chain carboxylic esters of α -hydroxymethylbenzoin **1a** (e.g. the laurate, m.p. 62.1–62.4 °C) failed to exhibit [44] a similar performance to the corresponding long-chain sulphonic esters [4,5] in the photocuring of acrylate resins in thin films; the reason, in all likelihood, is the much smaller amount of surface-active long-chain alkali metal (e.g. lithium) carboxylate generated.

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