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The photoinduced α-cleavage of α-bromomethylbenzoin: the generation and behaviour of β-bromoketyl radicals

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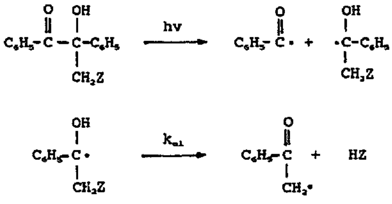
Abstract

The photodecomposition of α-bromomethylbenzoin was studied by electron spin resonance and by radical trapping using 1-dodecanethiol and a stable nitroxyl (TMPO) respectively. Photoinduced α-cleavage into benzoyl and α-hydroxy-α-bromomethylbenzyl (β-bromoketyl) radicals is observed. The β-bromoketyl radicals are found to undergo an extremely fast elimination of hydrogen bromide to give benzoylmethyl radicals. These β-bromoketyl radicals are also generated by hydrogen-abstraction from 2-bromo-1-phenyl-ethanol using triplet excited benzophenone. The only products observed are 'unchanged' benzophenone, acetophenone and hydrogen bromide. The same result is obtained on irradiation of 2-bromoacetophenone in the presence of benzhydrol. Possible mechanisms and implications are discussed. © 1997 Published by Elsevier Science S.A.

Keywords: α-Bromomethylbenzoin; Photodecomposition; β-Bromoketyl radicals

1. Introduction

Both sulphonic esters [1] and carboxylic esters [2] of α-hydroxymethylbenzoin have been shown to undergo photoinduced α-cleavage into benzoyl and α-hydroxy-α-sulphonyloxymethylbenzyl and α-hydroxy-α-acyloxymethylbenzyl radicals respectively. The α,α-disubstituted benzyl radicals, which may also be regarded as β-(Z)ketyl radicals, have been found to undergo subsequent heterolytic elimination of HZ, generating benzoylmethyl radicals at rates k_{el} depending in all likelihood on the nucleofugality [3] of the group Z, i.e. $Z = -OSO_2R \gg Z = -OCOR$.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{CH_2Z}{\overset{OH}{C}}-C_6H_5 \xrightarrow{h\nu} C_6H_5-\overset{O}{\overset{\|}{C}}\cdot + \cdot\underset{CH_2Z}{\overset{OH}{C}}-C_6H_5$$

$$C_6H_5-\underset{CH_2Z}{\overset{OH}{C}}\cdot \xrightarrow{k_{el}} C_6H_5-\underset{CH_2\cdot}{\overset{O}{\overset{\|}{C}}} + HZ$$

In the present communication we report on the photodecomposition of α-bromomethylbenzoin as studied by electron spin resonance (ESR) as well as by qualitative radical trapping experiments using 1-dodecanethiol and 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO). Anticipating an initial α-cleavage into benzoyl and α-hydroxy-α-bromomethylbenzyl (β-bromoketyl) radicals we also included alternative routes expected to generate the latter radicals, such as hydrogen-abstraction from 2-bromo-1-phenylethanol using triplet excited benzophenone, and the photoreduction of 2-bromoacetophenone using benzhydrol.

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 melting points were determined on a melting point microscope (Zeiss, equipped with a Mettler FP 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 (type E-257). Samples of the compounds (~10 mg/g 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 deoxygen-

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ated. 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 ($g = 2.0008$ [4]).

2.2. *Materials*

1-Phenyl-1,2-propanedione, styrene, *N*-bromosuccinimide (NBS), and *trans*-1,2-dibenzoylethylene (Acros Chimica) were used without purification. 2-Bromoacetophenone, benzophenone, and benzhydrol (Acros Chimica) were recrystallized before use. 2-Methyl-2-nitrosopropane (MNP), 1-dodecanethiol, and 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) (Acros Chimica) were used as received.

2.3. *Syntheses*

2.3.1. *3-Bromo-1-phenyl-1,2-propanedione*

This was synthesized by brominating 1-phenyl-1,2-propanedione in dioxane-ether in the presence of a catalytic amount of $AlCl_3$, b.p. 69–70 °C at 0.11 mbar.

2.3.2. *α-Bromomethylbenzoin (1)*

This was synthesized from 3-bromo-1-phenyl-1,2-propanedione according to Wegmann and Dahl [5], m.p. 92.6–93.6 °C.

2.3.3. *2-Bromo-1-phenylethanol (15)*

This was synthesized by treating styrene with NBS in water according to Winstein and Ingraham [6], b.p. 65–66 °C at 0.13 mbar.

2.3.4. *1,2-Dibenzoylethane*

This was synthesized by reduction ($SnCl_2$/CHI) of *trans*-1,2-dibenzoylethylene according to Bailey and Lutz [7], m.p. 144.8–145.3 °C.

2.4. *Irradiation procedures*

All irradiations were carried out 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 reactions were monitored by TLC analysis.

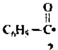
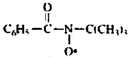
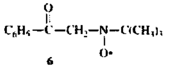
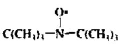
Solutions of α-bromomethylbenzoin **1** (10^{-2} M) in benzene in the presence of 1-dodecanethiol (2×10^{-2} M) and TMPO (3×10^{-2} M) respectively were irradiated for 4 h.

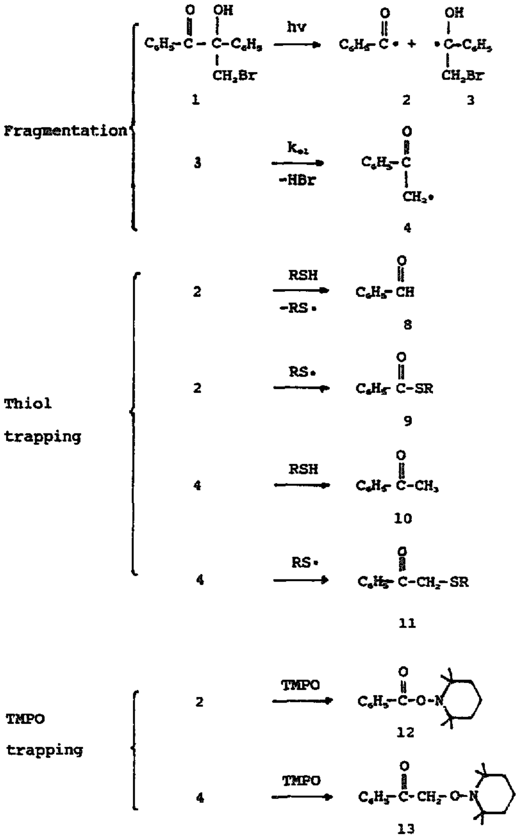
A solution of 2-bromo-1-phenylethanol **15** (3×10^{-2} M) in benzene in the presence of benzophenone **14** (10^{-2} M) was irradiated for 4 h.

A solution of 2-bromoacetophenone **17** (10^{-2} M) in benzene in the presence of benzhydrol **18** (3×10^{-2} M) was irradiated for 4 h.

The irradiation mixtures were fractionated by preparative liquid chromatography on a 5 g scale using the Chromatospec Preparative Liquid Chromatograph equipped with a silica column (Lichroprep. particle size 15–25 μm, from Merck). The resulting fractions were further purified on a semi-preparative column (Lichrosorb SI-60, particle size 10 μm, 250 × 22 mm i.d., from Merck). The products were identified by ^1H NMR and by comparison with authentic samples. Thus *S*-dodecyl thiobenzoate **9** [1,8], 2-(dodecylthio)acetophenone **11** [1,9], 2,2,6,6-tetramethyl-1-piperidino benzoate **12** [1,10,11], and 2,2,6,6-tetramethyl-1-piperidyloxymethyl phenyl ketone **13** [1] have already been described.

Table 1
Radicals observed by ESR from α-bromomethylbenzoin **1**

	g	a_N	a_H	Remarks
 $C_6H_5-\overset{O}{\overset{\|}{C}}\cdot$ **2**	(2.0008)		0.11	at −90 °C [4]
 $C_6H_5-\overset{O}{\overset{\|}{C}}-\underset{O\cdot}{\underset{\|}{N}}-C(CH_3)_3$ **5**	2.0063	0.80		at 20 °C in the presence of MNP [12]
 $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-\underset{O\cdot}{\underset{\|}{N}}-C(CH_3)_3$ **6**	2.0057	1.43	0.77	at 20 °C in the presence of MNP [13]
 $C(CH_3)_3-\overset{O\cdot}{\overset{\|}{N}}-C(CH_3)_3$	2.0056	1.56		from MNP [14]



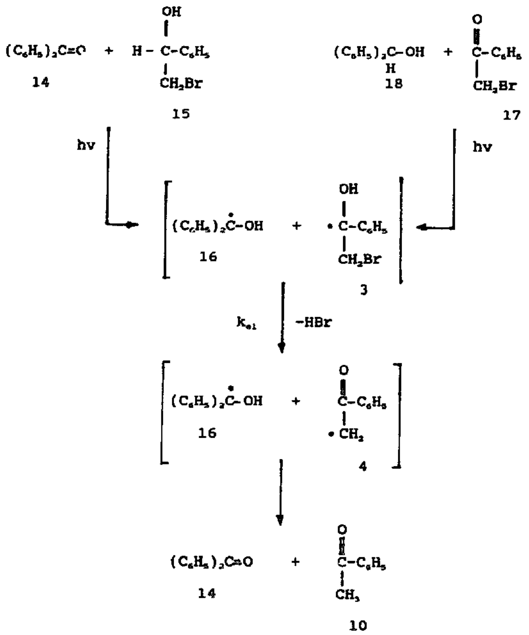
Scheme 1.

3. Results and discussion

The ESR spectra of α-bromomethylbenzoin **1** at low temperature ($T \sim -90$ °C) clearly showed the benzoyl radical **2**. At room temperature in the presence of MNP both the trapped benzoyl radical **5** and the trapped benzoylmethyl radical **6** were observed (cf. Table 1), which indicates a photoinduced α-cleavage as expected [1,2]. Moreover the presence of the trapped benzoylmethyl radical **6** indicates a fast elimination of hydrogen bromide from the α-hydroxy-α-bromomethylbenzyl radical **3**.

The irradiation of α-bromomethylbenzoin **1** in the presence of 1-dodecanethiol as scavenger for non-cage benzoyl radicals [12] resulted in the formation of benzaldehyde **8** (cf. Scheme 1) as expected. The benzoyl radicals **2** were also in part scavenged by the thiyl radicals formed in the process to give *S*-dodecyl thiobenzoate **9** as observed before [1]. Products resulting from the α-hydroxy-α-bromomethylbenzyl radical **3** were acetophenone **10** and hydrogen bromide. The benzoylmethyl radicals **4** were similarly in part scavenged by the thiyl radicals to give 2-(dodecylthio)acetophenone **11**.

The irradiation of α-bromomethylbenzoin **1** in the presence of TMPO resulted in the formation of 2,2,6,6-tetramethyl-1-piperidino benzoate **12**, the coupling product of benzoyl radicals **2** and TMPO. In addition there were formed 2,2,6,6-tetramethyl-1-piperidyloxymethyl phenyl ketone **13**, the coupling product of benzoylmethyl radicals **4** and TMPO, and hydrogen bromide, suggesting a rate of elimination of



Scheme 2.

hydrogen bromide from the β-bromoketyl radicals 3 $k_{el} > 10^8$ s^{-1}, as previously observed for the elimination of sulphonic acids from the corresponding β-sulphonyloxyketyl radicals [1].

Benzil (dimerization of benzoyl radicals) and 1,2-dibenzoylethane (dimerization of benzoylmethyl radicals) were not observed, implying complete trapping of these radicals by thiol/thiyl and TMPO respectively.

The irradiation of benzophenone **14** in benzene in the presence of a three-fold molar amount of 2-bromo-1-phenylethanol **15** resulted in 'unchanged' benzophenone **14**, acetophenone **10** and an abundant liberation of hydrogen bromide. 2-bromo-1-phenylethanol **15** being completely consumed. No other products were detected (cf. Scheme 2). From the absence, notably of benzpinacol, it is tentatively concluded that an in-cage hydrogen-transfer from the benzophenone ketyl radical **16** to the benzoylmethyl radical **4** occurs, forming acetophenone **10** and 'regenerated' benzophenone **14**.

Corroborating evidence is provided by the irradiation of 2-bromoacetophenone **17** in benzene in the presence of a three-fold molar amount of benzhydrol **18**, which should lead to the same radical pair as obtained through hydrogen-abstraction from 2-bromo-1-phenylethanol **15** by triplet excited benzophenone **14**.

Again the formation of benzophenone **14** and acetophenone **10**, accompanied by an abundant liberation of hydrogen bromide, was observed, 2-bromoacetophenone **17** being completely consumed. Only towards the end of the irradiation some benzpinacol formation was observed.

Thus the behaviour of the β-bromoketyl radical **3** appears to represent an example of a more general reaction, i.e. the elimination of HZ from β-(Z)ketyl radicals as has been observed for Z = –OSO_2R [1], for Z = –OCOR [2], and for Z = –ONO_2 [15].

An interesting consequence of this reaction is that generation of β-(Z)ketyl radicals inevitably leads to the liberation of HZ. Preliminary experiments using peroxide decomposition in the presence of 2-bromo-1-phenylethanol **15** indeed liberated vast amounts of hydrogen bromide.

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