

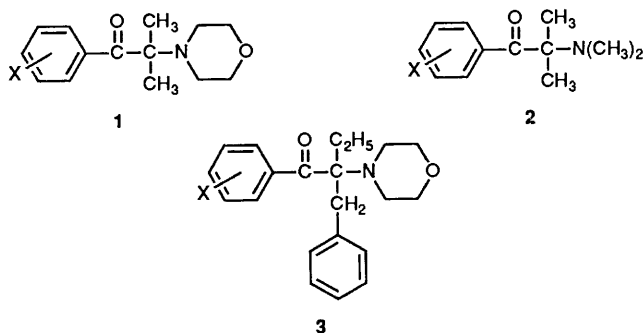
EPR Studies on the Photofragmentation of 2,2-Dialkyl-2-alkylaminoacetophenones

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Free radical reactions induced by photolysis of 2,2-dialkyl-2-alkylaminoacetophenone photocuring agents have been studied by continuous wave (CW) and time-resolved EPR spectroscopy. In all solvents α -cleavage from the triplet state is the major process. In hydrogen donor solvents it is accompanied by photoreduction followed by a rapid amine elimination from the ketyl radical intermediate. The benzoyl and α -aminoalkyl radicals resulting from α -cleavage readily add to acrylonitrile whereas radicals formed by photoreduction do not.

2,2-Dialkyl-2-alkylaminoacetophenones [**1**, **2**, **3** with X = H, *p*-OCH₃, *p*-SCH₃, *p*-N(CH₃)₂, *p*-*N*-morpholino and *m*, *p*-OCH₃] are efficient photoinitiators for the UV-curing of resins and coatings and have relatively high absorptions in the near-UV region (Irgacure 907, 369, 1185, Ciba-Geigy).¹⁻⁴



Whereas α -unalkylated α -alkylaminoketones mainly undergo Type II fragmentation and an apparent cleavage of the C _{α} -N bond⁵⁻⁸ the α -alkylated compounds (**1-3**) have been shown by CIDNP and product studies to undergo α -cleavage from the triplet state¹⁻⁴ to give benzoyl and α -aminoalkyl radicals which are expected to initiate polymerization.⁹⁻¹⁰ In addition, an unusual β -cleavage has been mentioned.¹⁻⁴ This continuation of previous work on photoinitiators^{11,12} aims at the direct detection of the radicals formed by photofragmentation of **1-3** by EPR spectroscopy, their spectroscopic characterization and the elucidation of the β -cleavage mechanism. Some auxiliary CIDNP and product studies are also reported.

Experimental

Various 2,2-dialkyl-2-alkylaminoacetophenones were obtained from Ciba-Geigy, Marly. All other chemicals were of the purest commercial forms. Solutions were always freshly prepared and freed from oxygen prior to use either by purging with helium (EPR) or *via* freeze-pump-thaw cycles (CIDNP).

In CW-EPR experiments flowing solutions of the ketones (5×10^{-3} to 5×10^{-2} mol dm⁻³) were photolysed in the cavity of the spectrometer (Bruker ESP 300) with the light of a 1000 W Hg-Xe lamp filtered with aqueous CuSO₄ (or CoSO₄/NiSO₄) to the ranges $310 \leq \lambda \leq 380$ nm or $240 \leq \lambda \leq 330$ nm, respectively. Time-resolved EPR employed the arrangement described previously^{11,13} and laser pulse photolysis at 308 nm. CIDNP studies were carried out on a 200 MHz NMR system

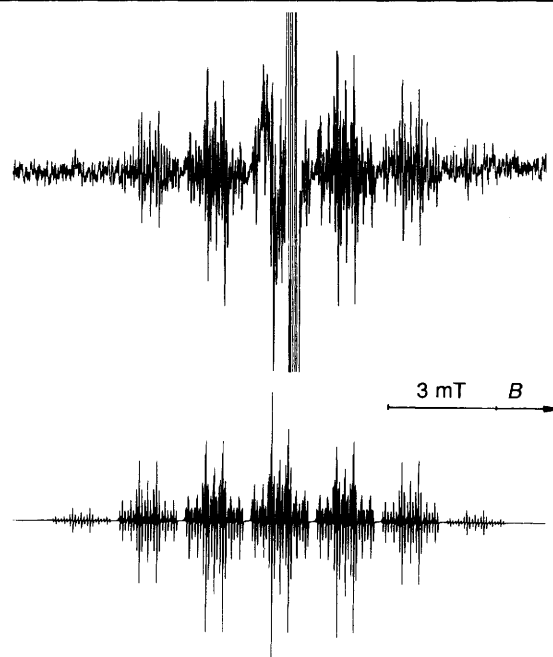


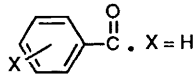
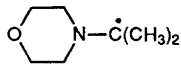
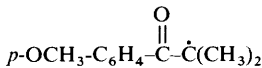
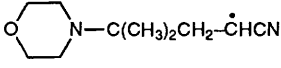
Fig. 1 EPR spectrum during photolysis of *p*-methoxy-2,2-dimethyl-2-*N*-morpholinoacetophenone (**1**, X = *p*-OCH₃) at 233 K in methyloxirane. Lower part: Simulation for 2-*N*-morpholino-2-propyl.

with 308 nm pulse photolysis.¹⁴ Product analyses involved NMR and GLC.

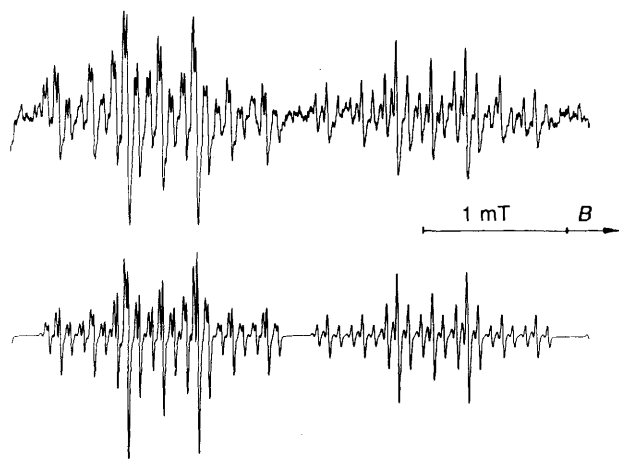
Results and Discussion

CW-EPR spectra taken during photolysis of **1** with X = H, *p*-OCH₃, *p*-SCH₃ and *p*-*N*-morpholino in methyloxirane for $220 \leq T \leq 300$ K revealed the formation of benzoyl-type species and of the 2-*N*-morpholino-2-propyl radical, *i.e.* an α -aminoalkyl species, expected from α -cleavage. For the naming and structures of the radicals we refer to Table 1. The upper part of Fig. 1 shows the spectrum obtained from the *p*-OCH₃ substituted compound with the three strong lines of the benzoyl radical and an extended line system of the α -aminoalkyl radical, part of which is blurred by a broad unidentified line near $g = 2.004$. The lower part of Fig. 1 is a spectrum simulated for the α -aminoalkyl radical with the parameters given in Table 1. Fig. 2 is an expansion of the first two high-field line groups of this radical. Similarly, Figs. 3 and 4 give experimental and simulated spectra for the radicals obtained from **2** with X = *p*-OCH₃ in methyloxirane at 233 K. For the ketones **3** also clear evidence for the formation of benzoyl type and α -aminoalkyl radicals by

Table 1 *g*-Factors and hyperfine coupling constants of benzoyl, α -aminoalkyl, α -ketoalkyl and adduct radicals observed in this work

Radical	Solvent ^a / <i>T</i> ^b	<i>g</i>	<i>a</i> /mT
Benzoyl radicals			
 X = H	M/233, D/293	2.000 58	2H _m :0.120 2H _o :0.019
X = <i>p</i> -OCH ₃	M/233, D/293	2.000 70	2H _m :0.110 2H _o :0.017
X = <i>m</i> , <i>p</i> -OCH ₃	M/233, D/293	2.000 67	H _m :0.080 2H _o :0.010
X = <i>p</i> -SCH ₃	M/233, D/293	2.000 65	2H _m :0.110 2H _o :0.016
X = <i>p</i> -N(CH ₃) ₂	M/233, D/293	2.000 76	2H _m :0.110
X = <i>p</i> - <i>N</i> -morpholino	M/233, D/293	2.000 73	2H _m :0.110 2H _o :0.023
α-Aminoalkyl radicals			
	M/233	2.002 7	6CH ₃ :1.850 N :0.237 2CH ₂ , ax.:0.475 2CH ₂ , eq.:0.075
(CH ₃) ₂ N-C(CH ₃) ₂	M/233	2.002 6	6CH ₃ :1.775 N :0.240 6CH ₃ , γ :0.280
α-Ketoalkyl radical			
	D/293	2.004 12	3CH ₃ :2.05 3CH ₃ :1.85
Acrylonitrile adducts			
X-C ₆ H ₄ -CO-CH ₂ -C \dot{C} HCN, X = H	M/233	2.003 0	2CH ₂ :2.32 CH :2.04 N :0.34
X = <i>p</i> -OCH ₃	M/233	2.002 9	2CH ₂ :2.37 CH :2.04 N :0.34
X = <i>p</i> -SCH ₃	M/233	2.002 9	2CH ₂ :2.35 CH :2.04 N :0.34
	M/233	2.002 9	2CH ₂ :2.15 CH :2.04 N :0.34
Acrolein adduct			
<i>p</i> -OCH ₃ -C ₆ H ₄ -CH ₂ -C \dot{C} HCHO	M/233	2.004 6	2CH ₂ :2.05 CH :1.78 CHO :0.09

^a M = methyloxirane, D = decan-1-ol. ^b Temperature in K.

**Fig. 2** Expanded high-field part of Fig. 1

α -cleavage was obtained for methyloxirane solutions. However, the complexity of the spectrum of the aminoalkyl species prevented its complete analysis.

The upper part of Fig. 5 shows an EPR spectrum obtained 900 ns after laser pulse photolysis of **1** with X = *p*-OCH₃ in methyloxirane at 233 K with the benzoyl triplet (*a*) and weak features of the 2-*N*-morpholino-2-propyl radical (*b*). At these short times the spectrum is purely emissive which proves α -cleavage from a short-lived triplet precursor as found for other ketone photocuring agents.^{11,13} The time dependence of the signals (*a*) and (*b*) given in the lower section of Fig. 5 indicates a simultaneous formation of both radicals and a similar decay rate of their electron spin polarization by relaxation and termination reactions.

The *g*-factors and hyperfine coupling constants of the benzoyl radical derivatives and of the two new α -aminoalkyl radicals detected in methyloxirane (Table 1) are normal and deserve little comment. So far, α -aminoalkyl species have seldom been observed directly in liquids,^{15,16} though often in solid mat-

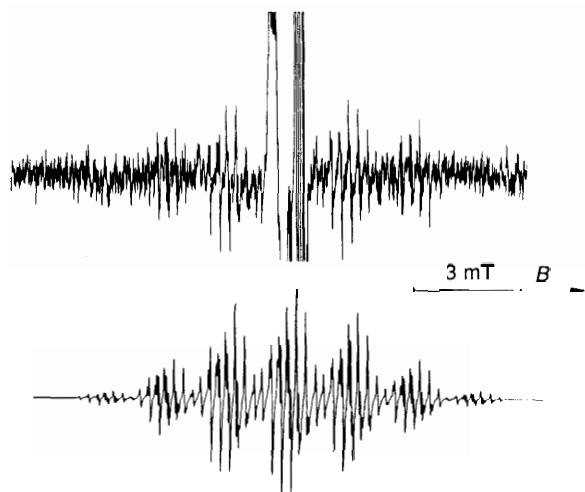


Fig. 3 EPR spectrum during photolysis of *p*-methoxy-2,2-dimethyl-2-dimethylaminoacetophenone (2, X = *p*-OCH₃) at 233 K in methyloxirane. Lower part: Simulation for 2-dimethylamino-2-propyl.

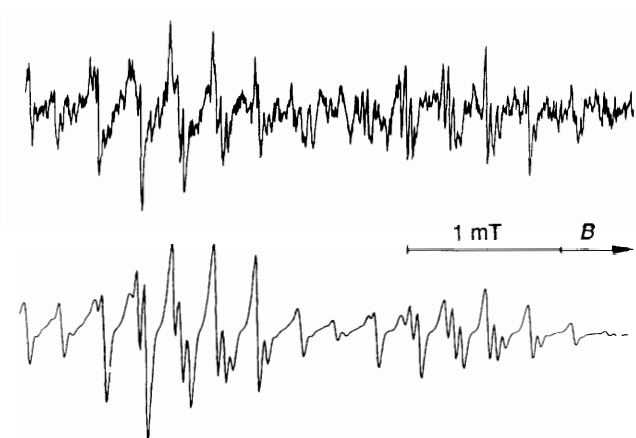


Fig. 4 Expanded high-field part of Fig. 3

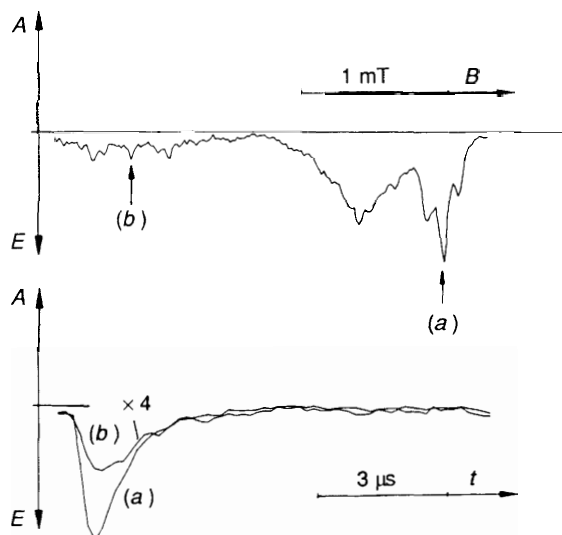


Fig. 5 Time-resolved EPR spectrum after pulse photolysis of **1**, X = *p*-OCH₃ in methyloxirane at 233 K (top) and time profiles (bottom) for the benzoyl (a) and the 2-*N*-morpholino-2-propyl radical (b). Part of the CW-spectrum range of Fig. 1.

rices.^{17,18} Our coupling constants compare well with the literature data. The substantial difference of coupling constants of the -N-CH₂-protons in the 2-*N*-morpholino-2-propyl radical demonstrates a chair conformation of the morpholine ring.

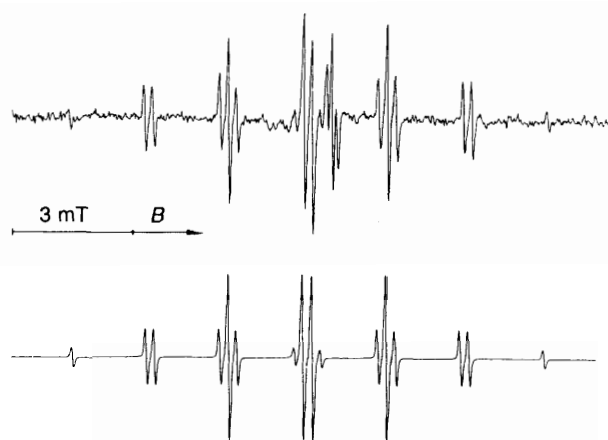


Fig. 6 EPR spectrum during photolysis of *p*-methylthio-2,2-dimethyl-2-*N*-morpholinoacetophenone (**1**, X = *p*-SCH₃) at 293 K in decan-1-ol. In the central region a broad unidentified line (*cf.* Fig. 1) was subtracted. Bottom part: Simulation for *p*-CH₃S-C₆H₄CO(C(CH₃)₂).

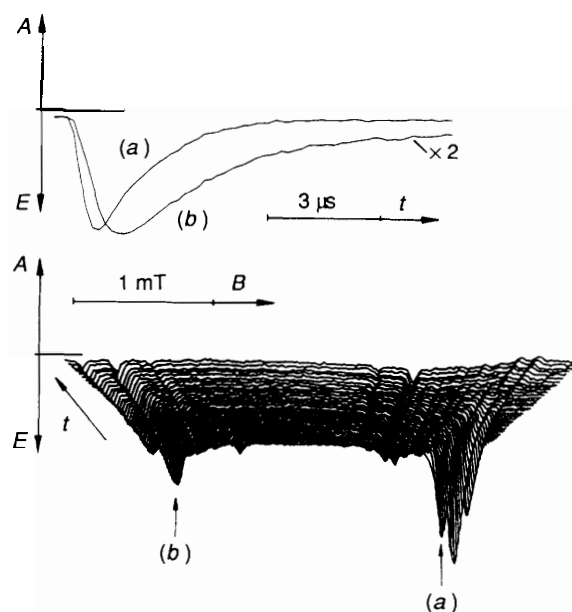


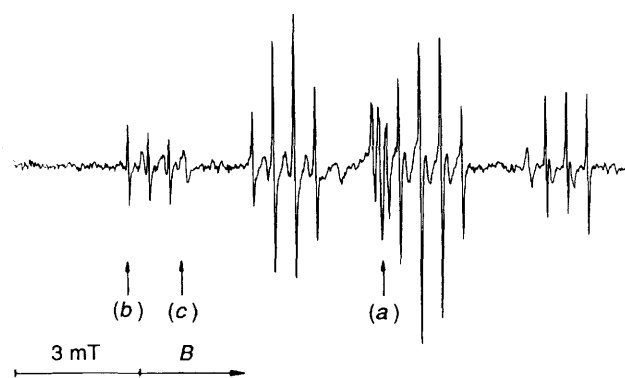
Fig. 7 Time-resolved EPR spectrum after pulse photolysis of **1**, X = *p*-OCH₃ in propan-2-ol at 233 K (bottom) for delay times of 0–4 μs and the time dependences of benzoyl (a) and α-keto radical (b) signals (top). Part of the spectral range of Fig. 6.

In the H-donor solvents decan-1-ol and propan-2-ol the 2-aminoacetophenones **1–3** also undergo α-cleavage, as is evident from the appearance of benzoyl-type radicals, but to a much lower extent than in methyloxirane. In addition, another process takes place which leads to the formation of 2-keto-substituted 2-propyl radicals, like C₆H₅COĊ(CH₃)₂, *i.e.* the result of a formal β-cleavage of the parent compounds. Fig. 6 displays a CW-EPR spectrum obtained during photolysis of **1** with X = *p*-SCH₃ in decanol at room temperature. Besides the low *g*-triplet of the benzoyl radicals one observes the widespread features of the α-keto radical CH₃SC₆H₄COĊ(CH₃)₂ which are simulated in the lower part of the figure with *g*-factor and couplings agreeing with abundant literature data¹⁹ (Table 1). There is no evidence for the formation of an aminyl species as would be expected for a direct β-cleavage process.

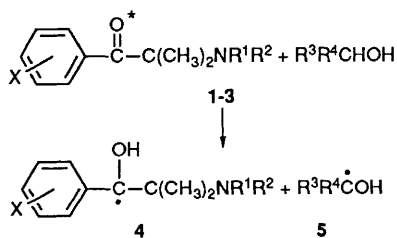
Hints to the reaction forming the α-keto radical follow from time-resolved EPR. The lower part of Fig. 7 shows the central portion of spectra after laser pulse photolysis of **1** with X = *p*-OCH₃ in propan-2-ol for early times and lines of the benzoyl (a) and the α-keto radical (b). The emission indicates a triplet

Table 2 Relative yields of benzoyl and α -keto radicals during photolysis of 2,2-dialkyl-2-alkylaminoacetophenones in decan-1-ol at 293 K

Compound	Total	Benzoyl	Benzoyl/ α -Keto
1 X = H	26	7	0.37
= <i>p</i> -OCH ₃	37	24	1.9
= <i>p</i> -SCH ₃	64	12	0.23
= <i>p</i> - <i>N</i> -morpholino	61	10	0.20
2 X = H	29	3	0.11
= <i>p</i> -OCH ₃	38	28	2.6
= <i>p</i> -SCH ₃	31	11	0.53
= <i>p</i> -N(CH ₃) ₂	49	15	0.71
3 X = H	69	35	1.0
= <i>m</i> , <i>p</i> -OCH ₃	37	31	5.4
= <i>p</i> - <i>N</i> -morpholino	26	22	≥ 5.4

**Fig. 8** EPR spectrum during photolysis of *p*-methoxy-2,2-dimethyl-2-*N*-morpholinoacetophenone (1, X = *p*-OCH₃) at 233 K in methyloxirane containing 2×10^{-2} mol dm⁻³ acetonitrile. (a) Benzoyl radical, (b, c) adduct radicals.

reaction as found earlier for the α -cleavage (Fig. 5). The upper part of Fig. 7 exhibits a different time dependence of the benzoyl and α -keto radical signals. Whereas the former appears immediately after the laser pulse, the latter develops and decays markedly more slowly. This points to an additional intermediate for the α -keto species with a lifetime of *ca.* 1 μ s. Since the α -keto radicals can only be observed in alcohols which are known to effectively photoreduce ketone triplets we suggest that 1–3 can undergo photoreduction besides α -cleavage from their triplet states.



The ketyl intermediate 4 rearranges to the α -keto radical by amine elimination in analogy to similar radicals with a quaternary ammonium cation in the β -position^{20,21} or to radicals formed by α -cleavage for *p*-toluenesulfonic esters of α -(hydroxymethyl)benzoins where the sulfonic acid eliminates.²² For such a system the ketyl intermediate was detected by time-resolved EPR spectroscopy, and the α -keto product had a very similar time profile as that found here.²³ As in other cases,²⁴ the alcohol derived radicals 5 transfer their OH hydrogen rapidly to the parent aromatic ketone which explains their absence in the

CW-EPR spectra (*cf.* Fig. 6). Additional evidence for the photoreduction was sought from product analysis and CIDNP studies on the photolysis of morpholino compounds 1. The photoreduction products morpholine and *p*-OCH₃C₆H₄-COCH(CH₃)₂ were found for alcohol solvents, but morpholine was also obtained in non-hydrogen donors, presumably because of secondary reactions of α -cleavage products. Geminate and non-geminate nuclear polarizations of α -cleavage products agreed with those reported by Rist.^{1-4,25} Under photoreducing conditions the CIDNP effects were too small for analysis which supports the involvement of two ketyl type radicals (4, 5) in the primary pairs. They will have very similar *g*-factors and are not expected to generate large polarizations.

With respect to the use of 2,2-dialkyl-2-alkylaminoacetophenones as photocuring agents the following findings are noteworthy. Firstly, use of the long wavelength photolysis window (310–380 nm) gave slightly, but significantly, larger radical concentrations in the CW-experiments than photolysis in the shorter UV-wavelength region (240–330 nm) even for comparable total absorbed energies. This agrees with the suitability of 1–3 for pigmented and absorbing resists,¹⁻⁴ and suggests that there are nonradical energy wasting channels in the short UV-region. Secondly, a relative measure for the efficiency of α -cleavage and photoreduction was determined from the relative integrals of the benzoyl and the α -keto radical signals during photolysis of various derivatives in decanol at room temperature using long wavelength irradiation and equal initial concentrations (Table 2). There are differences in detail which correlate with curing efficiencies but grossly all compounds yield similar total radical concentrations. As with other ketones²⁶ increased α -branching of the derivatives of 3 causes a predominance of α -cleavage over photoreduction.

To decide which radicals initiate polymerization, 1 with X = *p*-OCH₃ was photolysed in methyloxirane and decanol solutions containing the monomer acrylonitrile. Fig. 8 shows a CW-EPR spectrum obtained at 233 K with 2×10^{-2} mol dm⁻³ acrylonitrile in methyloxirane. In comparison to Fig. 1 the 2-*N*-morpholino-2-propyl radical has disappeared and the lines of benzoyl (a) are markedly decreased. Two adduct radicals (b, c) to the CH₂-group of acrylonitrile appear which are ascribed to the benzoyl (b) and the α -amino-2-propyl adducts (Table 1). Obviously, both fragments of α -cleavage add to acrylonitrile. For our photolysis conditions the overall radical termination lifetime is *ca.* 1 ms and competes with the addition of the benzoyl species. Hence, its rate constant for addition to acrylonitrile must be of the order of 10^5 to 10^6 dm³ mol⁻¹ s⁻¹ which agrees with previous findings.¹² The 2-*N*-morpholino-2-propyl radical must add even faster. This is in accord with the very low ionization potentials of such radicals²⁷ which renders them very nucleophilic. Fig. 9 shows the result of corresponding experiments for decan-1-ol solutions where photoreduction competes with α -cleavage. Addition of 2×10^{-2} mol dm⁻³ acrylonitrile causes the appearance of benzoyl and other minor adduct radicals. However, the signals of the α -keto radical are not decreased which means that it adds to acrylonitrile with a rate constant of at most 10^4 dm³ mol⁻¹ s⁻¹. The carbonyl substituent makes this radical less nucleophilic and lowers the addition rate to the electron deficient alkene. For the related α -carboxy substituted radical (CH₃)₃COOC $\dot{\text{C}}\text{H}_2$ with less steric hindrance the rate constant for addition is 5×10^5 dm³ mol⁻¹ s⁻¹ at room temperature.²⁸ Similar results were obtained for the additions to acrolein and (*E*)-dicyanoethene and data for the adduct radicals are also given in Table 1.

In summary, the present results support the common interpretation¹⁻⁴ of the action and advantages of 2-branched and 2-amino-substituted acetophenones as UV-curing agents with the novel aspects of a possible interference by photoreduction and a fast fragmentation of β -amino-substituted ketyl radicals.

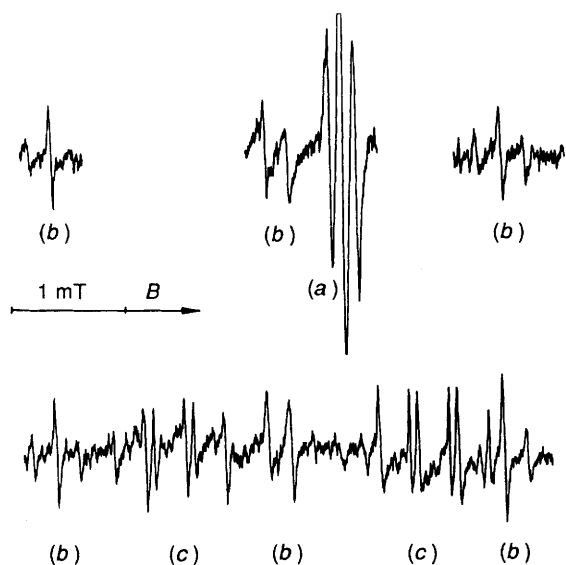


Fig. 9 EPR spectrum during photolysis of *p*-methoxy-2,2-dimethyl-2-*N*-morpholinoacetophenone (**1**, X = *p*-OCH₃) at 293 K in decan-1-ol. Top: lines of benzoyl (*a*) and α -keto-radicals (*b*). Bottom: solution with 2×10^{-2} mol dm⁻³ acrylonitrile with lines of α -keto-radicals (*b*) and benzoyl adducts (*c*).

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