

## 24. CIDNP.-Investigation of Photoinduced Polymerization<sup>1)</sup>

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### *Summary*

The photochemistry and some initiator characteristics of the polymerization initiators  $\omega, \omega$ -dimethoxy- $\omega$ -phenyl-acetophenone (**A**),  $\omega, \omega$ -diethoxy-acetophenone (**B**) and  $\omega, \omega$ -diisopropoxy-acetophenone (**C**) have been studied by <sup>1</sup>H- and <sup>13</sup>C-chemically-induced nuclear polarization (CIDNP.) experiments. The primary reaction of initiator **A** is a *Norrish*-type I cleavage, while for **B** and **C** *Norrish*-type I and *Norrish*-type II cleavages are of comparable importance. Three different recombination products could be detected for initiator **A** which correspond to the three canonical resonance forms of the substituted benzyl radical.

In a number of polymerization experiments the competition between reactions among initiator radicals and reactions of initiator radicals with the monomer acrylic acid methyl ester was studied at low concentrations of the monomer. These experiments give insight into the first steps of the polymerization process.

The positive sign of the  $\alpha$ -hydrogen hyperfine couplings of the dimethoxymethyl- and the diisopropoxymethyl-radicals could be established, in agreement with the deviation of these radicals from planarity.

A slow square-wave light-modulation technique has been employed in <sup>13</sup>C-FT.-experiments to measure absolute CIDNP.-intensities.

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**1. Introduction.** - Ultraviolet (UV.) induced polymerization processes have become increasingly important during the last few years, particularly in the curing of organic coatings. Reviews of recent developments are found in [1], [2] and [3]. The initiation of the polymerization process is controlled by the photoinitiator or photosensitizer. Upon absorption of UV. radiation the sensitizing system produces radicals, which initiate polymerization.

The photochemistry of the initiator and the polymerization products are usually studied by chemical means [4] [5]. In the photochemical reactions of the initiator, as well as during the polymerization process, radical cage reactions (reactions

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<sup>1)</sup> In part presented at the conference on chemically induced magnetic polarization, St. Pierre de Chartreuse, France, May 21-23, 1975.

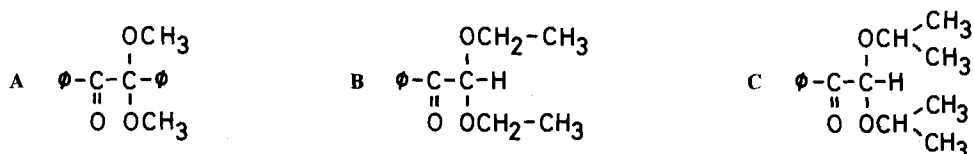
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within a radical pair), play an important role. Some of the cage reactions lead to intensities in the nuclear magnetic resonance (NMR.) spectrum of the reaction products which deviate strongly from their thermal equilibrium values. This effect of chemically induced nuclear polarization (CIDNP.), discovered ten years ago by *Bargon, Fischer & Johnsen* [6] and *Ward & Lawler* [7], is therefore well-suited for obtaining insight into the photoreactions of the photoinitiator and the process of polymerization. CIDNP.-experiments are complementary to electron-spin-resonance (ESR.) investigations, where the radicals present during the polymerization process are characterized directly. The CIDNP.-technique however, combines both high sensitivity and high resolution.

In the present work the CIDNP.-technique is first applied to study the photochemistry of:

$\omega, \omega$ -Dimethoxy- $\omega$ -phenyl-acetophenone (**A**),  $\omega, \omega$ -diethoxy-acetophenone (**B**) and  $\omega, \omega$ -diisopropoxy-acetophenone (**C**). The structures of the three initiators are given in *Scheme 1*.

Scheme 1. Structure of initiators A, B and C



In a second set of experiments, described in section 4, the photochemistry is studied when the monomer acrylic acid methyl ester (AME) is added at increasing amounts to the solution of the initiator. The competition between photoreactions of the initiator and reactions of initiator radicals with the AME-monomers changes the CIDNP.-intensities and gives insight into the first steps of the polymerization process.

In many CIDNP.-experiments, resonances which originate from reactants or products in thermodynamic equilibrium coincide or overlap with resonances whose intensities are mainly due to the CIDNP.-process. During some  $^{13}\text{C}$ -Fourier (FT.) NMR.-experiments a subtraction technique has been applied to distinguish between the two types of intensities. These experiments are described in the last section.

The interpretation of the CIDNP.-patterns, emission (E) and enhanced absorption (A), will be carried out within the radical pair diffusion model [8]. The radical pairs ( $\text{R}\cdot \cdot \text{R}'$ ) are formed in electronic singlet (S) or triplet (T) states by reaction from the precursor molecules or by encounters of freely diffusing radicals (F). Pairs in the singlet state at reencounters after diffusive displacements of the radicals  $\text{R}\cdot$  and  $\text{R}'\cdot$  may combine or disproportionate to combination products (c). Radicals which do not react in the cage may form escape products (e) by hydrogen atom abstraction or other reaction paths. The radical-pair diffusion model leads to the elegant *Kaptein* [9] rules for the phases  $\Gamma_i$  of the net polarization of a NMR.-signal of nucleus i:

$$\Gamma_i = \mu \varepsilon (g - g') a_i \begin{cases} > 0 = \text{A} \\ < 0 = \text{E} \end{cases}$$

$$\mu \begin{cases} > 0 & \text{for } T, F\text{-precursors} \\ < 0 & \text{for } S\text{-precursors} \end{cases} \quad (1)$$

$$\varepsilon \begin{cases} > 0 & \text{for } c\text{-products} \\ < 0 & \text{for } e\text{-products,} \end{cases}$$

where the parameter  $a_i$  denotes the hyperfine coupling constant of nucleus  $i$  in radical  $R$ ,  $g$  and  $g'$  are the electron spin  $g$ -values. We will not discuss multiplet effects [9], since they do not contribute further to our understanding of the present reaction mechanisms.

**2. Photochemistry.** - 2.1. *Experimental Part.* Initiators **A**, **B** or **C** were dissolved in perdeuterated benzene, methanol or toluene. Toluene solutions were used to study the temperature dependence of the photoreactions. The CIDNP,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, spectra of the three initiators were recorded during *in situ* UV. irradiation on a Varian XL-100 spectrometer equipped with a Fourier transform accessory. The UV. source was a 1 kW SP-1000 Philips mercury high-pressure lamp. The light was filtered by an aqueous solution of  $\text{NiSO}_4$  and  $\text{CoSO}_4$  [10] [11] to eliminate most of the infrared and visible light. Two quartz lenses focused the light onto the polished end of a Suprasil quartz rod which served as light guide. The probe was modified in order to irradiate the sample perpendicular to the sample tube.

2.2.  $^1\text{H}$ -CIDNP, and reaction mechanisms of initiator **A**. Some  $^1\text{H}$ -CIDNP.-parameters of initiator **A** are collected in Table 1. A typical  $^1\text{H}$ -FT.-NMR.-CIDNP. spectrum is reproduced in Figure 1. The primary reaction of initiator **A** is a Norrish-type I cleavage from the excited triplet state into a benzoyl and a substituted benzyl radical. According to Kaptein's rule (1) and the polarization assigned to the benzyl ortho protons of the recombination product **A**, a singlet precursor is excluded: The polarization did not change its phase when radical encounter pairs (F) were eliminated by adding increasing amounts of acrylic acid methyl ester (AME) to the solution, and it reached an AME independent value (E). The hyper-

Table 1. Initiator **A**: Assignments of  $^1\text{H}$ -CIDNP.-transitions

Reaction product	Assignment of proton resonance	Polarization	Chemical shift <sup>a)</sup>	Multiplet structure
Recombination product <b>A</b>	benzyl-ortho	E	7.69	<i>m</i>
Recombination product <b>A</b> <sub>1</sub>	H <sub>c</sub> <sup>b)</sup>	E	6.65	<i>d</i> × <i>d</i>
	H <sub>d</sub> <sup>b)</sup>	A	5.74	<i>d</i> × <i>d</i>
	H <sub>e</sub> <sup>b)</sup>	E	4.80	<i>m</i>
Methyl benzoate	ortho	A	8.05	<i>m</i>
Acetophenone	methyl	E	2.12	<i>s</i>
Benzaldehyde	aldehyde	E → A	9.64	<i>s</i>
Methane	methyl	E → A	0.15	<i>s</i>
	methyl	A	1.49	<i>s</i>

<sup>a)</sup>  $\delta$  in ppm vs. TMS, deuterated benzene solution. <sup>b)</sup>  $J_{cd} \approx 10$  Hz;  $J_{ce} \approx 2$  Hz;  $J_{de} \approx 4$  Hz, cf. Scheme 3.

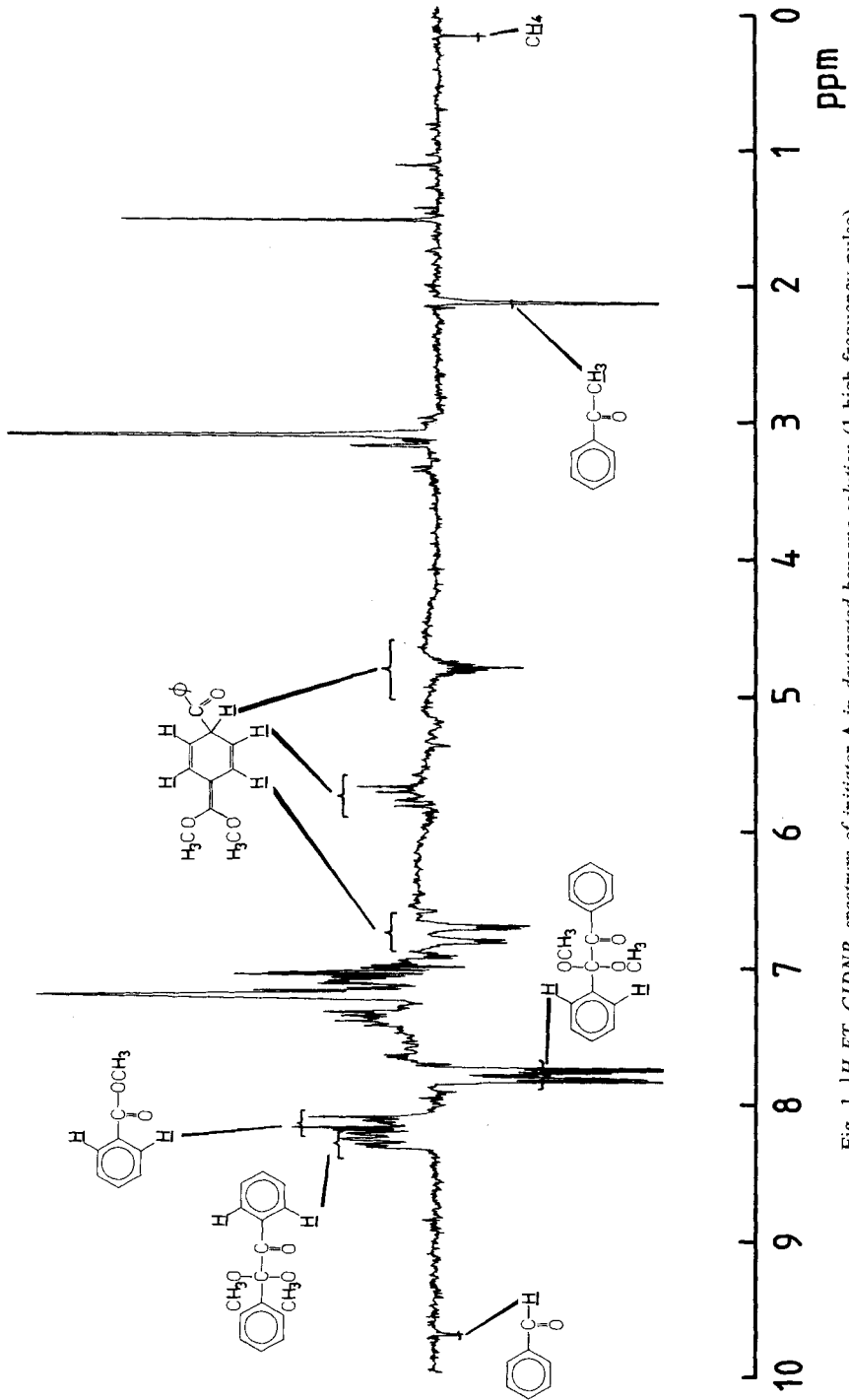
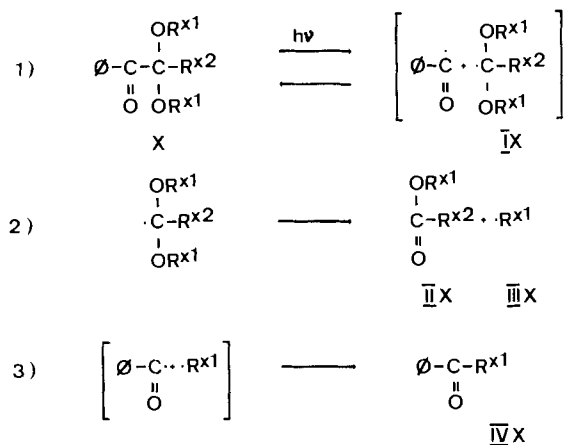


Fig. 1.  $^1\text{H}$ -FT-CIDNP-spectrum of initiator A in deuterated benzene solution (1 high-frequency pulse)

fine coupling of the benzyl ortho protons in the initial radical pair is negative [12] and the  $g$ -value of the benzoyl radical (2.0006) [13] is smaller than of the benzyl radical (approx. 2.0026 [13]). This leads to a positive value for  $\mu$ .

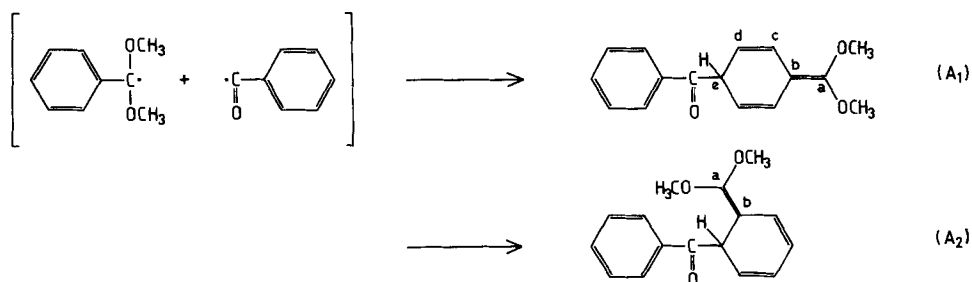
Norrish-type I cleavage and two secondary reactions of initiators **A**, **B** and **C** are represented in *Scheme 2*. In a temperature-controlled reaction which becomes important above room temperature, the substituted benzyl radical may decay into a highly reactive secondary methyl radical and methyl benzoate. Acetophenone is formed in a cage reaction as shown by the (E)-type polarization of the methyl group. These main photoproducts, as well as benzil and benzaldehyde, have been characterized in [5] by chemical means.

Scheme 2. Norrish-type I cleavage of initiators  $X = \mathbf{A}$ ,  $\mathbf{B}$  or  $\mathbf{C}$  and two main secondary reactions (for structures of R cf. *Scheme 1*)



The two primary benzoyl and benzyl radicals may recombine in three different ways: The two radicals may collapse to the recombination product **A** or form the unstable semibenzenes **A1** and **A2** shown in *Scheme 3*.

Scheme 3. Initiator **A**: Recombination products **A1** and **A2**



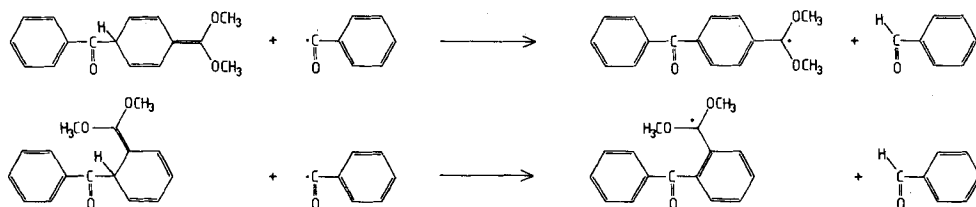
The three products correspond to the three canonical resonance forms of the benzyl radical. The para product **A1** leads to very strong CIDNP.-intensities in the  $^1\text{H-NMR}$ -spectrum. They decay rapidly when UV.-radiation is interrupted. The

ortho product, because of its lower symmetry, could not be detected by  $^1\text{H-NMR}$ -spectroscopy (*cf.* section 3). The polarizations obey *Kaptein's* rules [9] for a recombination process in a geminate pair. Similar cage products have been detected during the photoreaction of dibenzylketone [14a], and have been formed in dimerization reactions of other substituted benzyl radicals [14b].

Immediately after beginning the *in situ* irradiation, the benzaldehyde resonance appears in emission (E) (*Fig. 1*). Later, when tertiary reactions become important, the polarization changes to enhanced absorption (A). The photoproduct methane exhibits the same behaviour. Deuteration of the methyl groups of initiator A does not affect the benzaldehyde emission signal. Therefore the benzaldehyde hydrogen atom of the initially formed benzaldehyde is abstracted from the six-membered rings of the initiator.

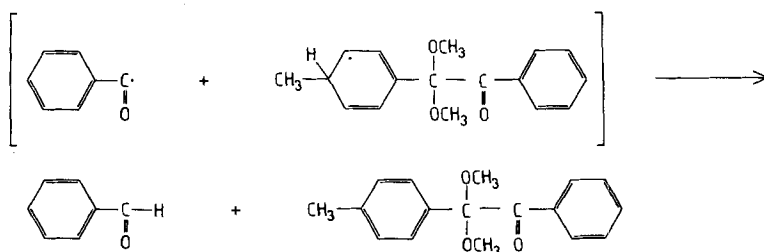
The spin densities near the protons in the  $\sigma$ -type benzoyl radical are too small to account for the aldehyde emission [13]. However, any fast abstraction of hydrogen atoms whose nuclear spin populations have been polarized in the primary pair benzyl ortho or para positions would explain the weak initial (E)-type polarization. Such an abstraction process from products **A1** and **A2** is indicated in *Scheme 4*. After formation of **A1** and **A2** the nuclear spin polarizations of these unstable products decay with the nuclear relaxation times  $T_1$ . Replacing the benzoyl radical in *Scheme 4* by the methyl radical would lead to a reaction explaining the initial polarization of methane.

Scheme 4. Formation of benzaldehyde leading to (E)-type polarization for the aldehyde proton



Three different methyl substituted benzoates (one product at higher concentration than the other two) have been detected by a GC./MS.-analysis of the reaction mixture. Formation of methyl substituted initiator A which may eventually react to the substituted benzoate and benzaldehyde is illustrated in *Scheme 5*. Cage processes involving  $\beta$ -hydrogen-atom abstraction could contribute to the weak

Scheme 5. Formation of benzaldehyde and methyl substituted initiator A



enhanced absorption (A) observed for benzaldehyde when quasi steady state conditions are reached. Similar cage reactions have been proposed for the formation of benzaldehyde in the photoreactions of benzoine ethers and halogen-substituted initiator A [15].

2.3.  $^1\text{H}$ -CIDNP. and reaction mechanisms of initiators **B** and **C**. *Norrish*-type II cleavage products of initiator **B** have been discussed in [3]. The CIDNP.-experiments show that *Norrish*-type I and *Norrish*-type II pathways are of comparable importance for both initiators **B** and **C** in benzene, toluene and methanol solutions. The relative rates depend on the solvent. A  $^1\text{H}$ -CIDNP.-spectrum of initiator **B** is given in Figure 2. The *Norrish*-type II reaction for the two initiators is illustrated in Schemes 6 and 7. In the first step a biradical is formed (Scheme 7) which may decay directly to the reaction products in Scheme 6 or form an oxetanol intermediate as shown in Scheme 7 for initiator **C**. The  $^1\text{H}$ -NMR.-integrals of a typical reaction mixture of initiator **B** in perdeuterated benzene at room temperature, after relaxation of the CIDNP.-effect, lead to the following approximate relative weights: (*Norrish*-type I products):(*Norrish*-type II products):(oxetanol)  $\approx 2:1:2$ .

*Norrish*-type I cleavage for initiator **C** is slightly more important than for initiator **B**. The products related to *Norrish*-type II cleavage do not exhibit any polarization effects.

The *Norrish*-type I cleavage and secondary reactions of initiators **B** and **C** are very similar to the reactions of **A** and are illustrated in Schemes 2 and 8. The  $^1\text{H}$ -CIDNP.-parameters of the two initiators are collected in Tables 2 and 3. The polarization effects observed for the initiator photoproducts together with polymerization scavenging experiments (section 4) show that the  $\alpha$ -cleavage occurs from the

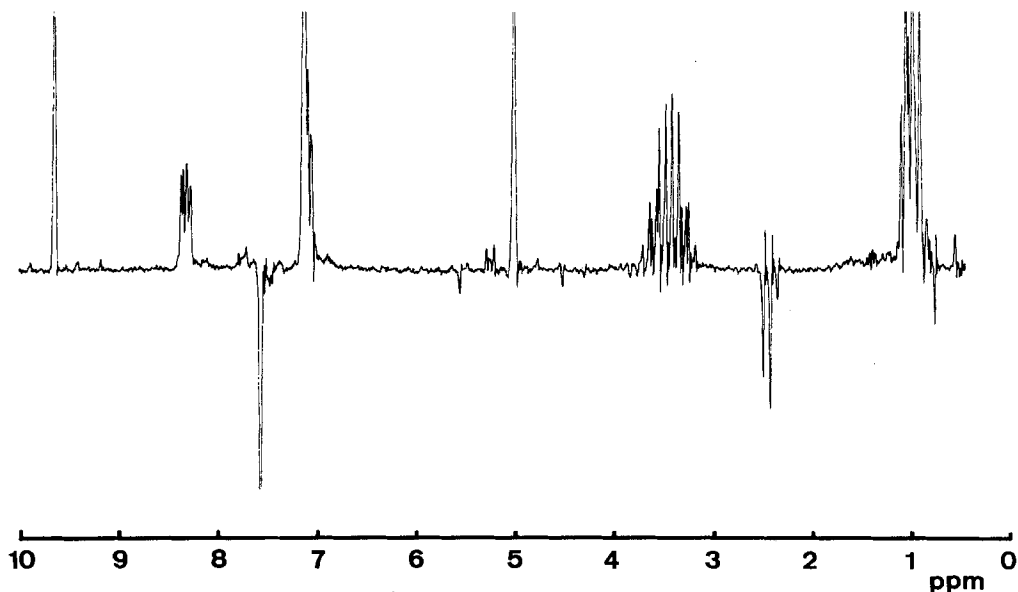
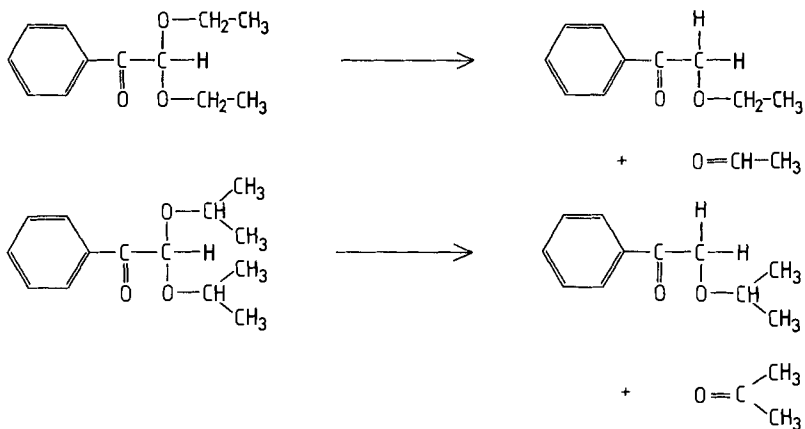
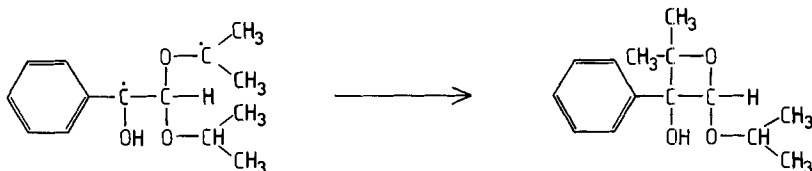
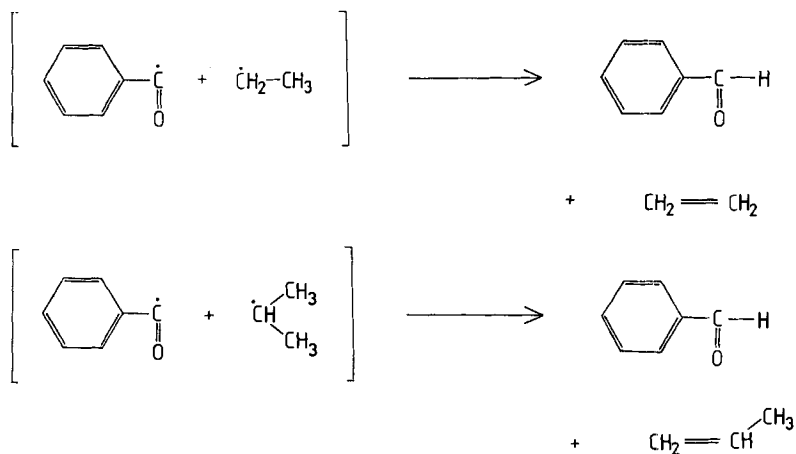


Fig. 2.  $^1\text{H}$ -CIDNP.-spectrum of initiator **B**

Scheme 6. Norrish-type II cleavage for initiators **B** and **C**

Scheme 7. Oxetanol intermediate

Scheme 8. Formation of benzaldehyde for initiators **B** and **C** by  $\beta$ -hydrogen-atom abstraction

excited triplet state. Benzaldehyde (*Scheme 8*) is formed partly as a cage  $\beta$ -abstraction product between secondary radicals **III B** or **III C** and the benzoyl radical. The magnitude of the  $\beta$ -coupling in the ethyl- and isopropylradicals is larger than of the  $\alpha$ -coupling and the methyl groups of the escape products ethane (*Scheme 5*) and propane show emission (E)-type polarization. The CIDNP-effects and the benzal-



Table 2. Initiator B: Assignment of  $^1\text{H}$ -CIDNP.-transitions (Norrish-type I cleavage)

Reaction product	Assignment of proton resonance	Polarization	Chemical shift <sup>a)</sup>	Multiplet structure
Recombination product B	methine	A	5.05	<i>s</i>
Propiophenone	methylene	E	2.47	<i>qa</i>
	methyl	A	1.05	<i>t</i>
Ethyl formate	ester	E	7.62	<i>s</i>
Benzaldehyde	aldehyde	A	9.64	<i>s</i>
Ethane <sup>b)</sup>	methyl	E	0.84	<i>s</i>

a)  $\delta$  in  $10^{-6}$  vs. TMS, deuterated benzene solution. b) Tentative assignment.

Table 3. Initiator C: Assignment of  $^1\text{H}$ -CIDNP.-transitions (Norrish-type I cleavage)

Reaction product	Assignment of proton resonance	Polarization	Chemical shift <sup>a)</sup>	Multiplet structure
Recombination product C	methine	A	5.19	<i>s</i>
$\omega, \omega$ -Dimethyl-acetophenone	methine	E	3.19	<i>m</i>
Propyl formate	ester	E	7.67	<i>s</i>
Benzaldehyde	aldehyde	A	9.64	<i>s</i>
Propylen	<i>trans</i>	} A	~ 5.0	<i>m</i>
	<i>cis</i>			
	vicinal	E	5.66	<i>m</i>
	methyl	A	1.60	<i>m</i>
Propane <sup>b)</sup>	methyl	E	0.84	<i>t</i>

a)  $\delta$  in  $10^{-6}$  vs. TMS, deuterated benzene solution. b) Tentative assignment.

dehyde formation prove that the major part of ethyl formate and propyl formate do not result from a cleavage of the oxetanol four-membered ring.

3.  $^{13}\text{C}$ -CIDNP., assignment of  $^{13}\text{C}$ -resonances by CIDNP.-effects and relative formation rates of recombination products A1, A2 and A. - Lippmaa *et al.* [16] were the first to demonstrate that  $^{13}\text{C}$ -CIDNP. benefits from the relatively large spin densities at the  $C_\alpha$  and  $C_\beta$  radical carbon atoms. In the reactions of initiators A, B and C, the spin densities at the carbon nuclei do not produce sufficiently large intensities to compensate completely for the smaller sensitivity of  $^{13}\text{C}$  as compared with  $^1\text{H}$ -NMR.-spectroscopy. A  $^{13}\text{C}$ -CIDNP.-spectrum of initiator A is reproduced in Figure 3. The spectrum is the result of accumulating  $10^3$  free induction decays. Some  $^{13}\text{C}$ -CIDNP.-data of initiators A and C are summarized in Tables 4 and 5. The  $^{13}\text{C}$ -data of initiator B are analogous to the data of initiator C and confirm the results from  $^1\text{H}$ -CIDNP.

Among the radicals formed during the photoreactions of the three initiators, the benzoyl radical exhibits the smallest *g*-value ( $g = 2.0006$ ) [13]. As will be shown the hyperfine coupling constant of the carbonyl carbon atom in the benzoyl radical is positive. In all photoproducts of benzoyl radicals the carbonyl CIDNP.-signal

Table 4. *Initiator A: Assignment of <sup>13</sup>C-CIDNP.-transitions*

Reaction product	Assignment of resonance	Polarization	Chemical shift <sup>a)</sup>
Recombination product A	carbonyl	E	194.6
	C <sub>s</sub> <sup>b)</sup> benzyl	E	138.3
	C <sub>s</sub> <sup>b)</sup> benzoyl	E	135.7
	C <sub>2</sub>	A	105.7
Recombination product A <sub>1</sub>	C <sub>a</sub>	A	156.7
	C <sub>b</sub> <sup>d)</sup>	E	99.1
Recombination product A <sub>2</sub>	C <sub>a</sub>	A	157.6
	C <sub>b</sub> <sup>d)</sup>	E	99.3
Acetophenone	carbonyl	E	197.1
	C <sub>s</sub> <sup>b)</sup>	E	137.2
	methyl	A	26.2
Methyl benzoate	carbonyl <sup>c)</sup>	E	166.5

<sup>a)</sup>  $\delta$  in 10<sup>-6</sup> vs. TMS, deuterated benzene solution. <sup>b)</sup> Substituted aromatic carbon atom. <sup>c)</sup> 95°, deuterated toluene solution. <sup>d)</sup> Tentative assignment.

Table 5. *Initiator C: Assignment of <sup>13</sup>C-CIDNP.-transitions*

Reaction product	Assignment of resonance	Polarization	Chemical shift <sup>a)</sup>
Recombination product C	carbonyl	E	194.3
	C <sub>s</sub> <sup>b)</sup>	E	134.0
	methine	A	103.8
Benzaldehyde	carbonyl	E	191.2
	C <sub>s</sub> <sup>b)</sup>	E	135.7
$\omega, \omega$ -Dimethyl-acetophenone	carbonyl	E	202.8
	C <sub>s</sub> <sup>b)</sup>	E	137.1
	methine	A	35.7
	methyl	E	19.2
Propyl formate	carboxyl	E	160.0

<sup>a)</sup>  $\delta$  in 10<sup>-6</sup> vs. TMS, deuterated benzene solution. <sup>b)</sup> Substituted aromatic carbon atom.

appears in emission. According to *Kaptein's* rule [9] these products may be understood therefore as combination or disproportionation products in a pair generated from a triplet precursor or by a free radical encounter.

In the <sup>13</sup>C-CIDNP.-spectrum of initiator A (*cf. Fig. 3 and Table 4*) two enhanced resonances appear in the region between 150 and 160 ppm. They are assigned to carbon atoms a (*Scheme 3*) of the initiator recombination products A<sub>1</sub> and A<sub>2</sub>; no other products have been detected which lead to resonances in this chemical shift region. The two carbon atoms are identical in the polarizing pair. If we assume that the longitudinal nuclear relaxation times and contributions to the NMR.-intensities from the *Overhauser* effect are equal for the two product carbon atoms, the <sup>13</sup>C-intensity ratio of 4-5:1 measured in perdeuterated benzene solutions represents

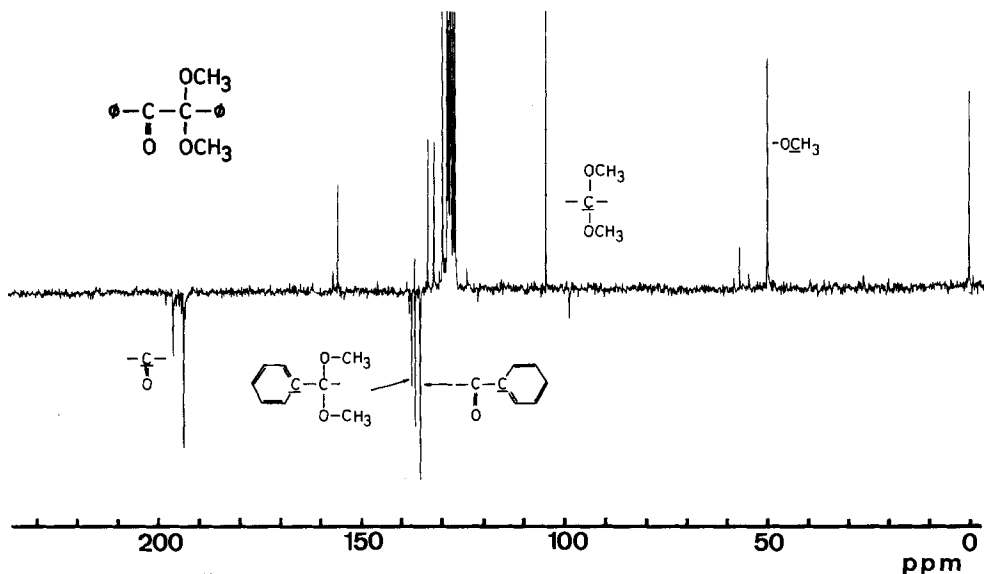


Fig. 3.  $^{13}\text{C}$ -FT-CIDNP.-spectrum of initiator A in perdeuterated benzene solution

the product ratio of A1 and A2. We conclude from the  $^1\text{H}$ -CIDNP.-spectrum that product A1 predominates. In perdeuterated methanol (Fig. 4) the CIDNP.-intensity ratio is about 2:1. The  $^{13}\text{C}$ -NMR.-intensities assigned to carbon atoms b (Scheme 3) yield similar ratios. Specific radical-solvent interactions may influence the formation rates of A1 and A2. The  $^{13}\text{C}$ -spectrum in Figure 4 shows in a good approximation absolute CIDNP.-intensities. Contributions from educt and product molecules in thermal equilibrium are suppressed by a subtraction technique (cf. section 5). The resonances assigned in Figure 4 permit a rough estimate for the relative formation rates of A1 and A2 and A. As the reaction temperature is increased the formation of methyl benzoate becomes faster and the resonances assigned to A1 and A2 decrease in intensity.

In some special cases the relative values of CIDNP. lead to the assignment of  $^{13}\text{C}$ -resonances. It is not straightforward, for example, to distinguish between the  $^{13}\text{C}$ -resonances of the two substituted aromatic carbon atoms of initiator A,  $\text{C}_s$  (benzoyl) =  $\text{C}_{\text{bo}}$  and  $\text{C}_s$  (benzyl) =  $\text{C}_{\text{be}}$ :

In proton decoupled  $^{13}\text{C}$ -CIDNP.-spectra of recombination products R-R' which contain no magnetic nuclei other than natural abundance  $^{13}\text{C}$  and  $^1\text{H}$ , the ratio of the CIDNP.-intensities  $I_u$  and  $I_v$  of the two carbon atoms u (radical R) and v (radical R') depends, within the pair diffusion model [8], on three kinds of parameters: the difference in the  $g$ -values,  $g$  and  $g'$ , of the radicals, the hyperfine parameters  $a_u$  and  $a_v$  of the two nuclei, and their longitudinal relaxation times  $T_{1u}$  and  $T_{1v}$  via the equation

$$\frac{I_u}{I_v} = \frac{T_{1u}}{T_{1v}} \cdot \frac{\sqrt{\left| (g-g')\beta H + \frac{1}{2}a_u \right|} - \sqrt{\left| (g-g')\beta H - \frac{1}{2}a_u \right|}}{\sqrt{\left| (g'-g)\beta H + \frac{1}{2}a_v \right|} - \sqrt{\left| (g'-g)\beta H - \frac{1}{2}a_v \right|}} \quad (2)$$

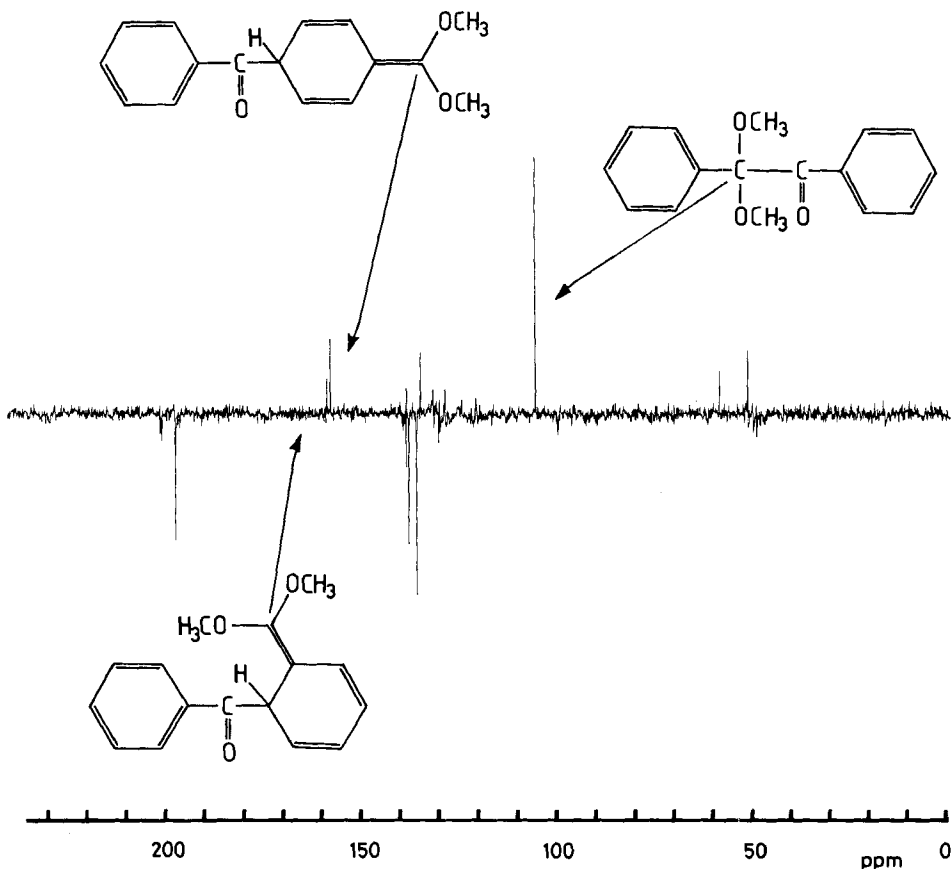


Fig. 4.  $^{13}\text{C}$ -FT-CIDNP-spectrum of initiator A in perdeuterated methanol solution (absolute CIDNP-intensities)

The parameter  $H$  represents the magnetic field strength and  $\beta$  the Bohr magneton. This equation neglects the influence of the longitudinal relaxation times and the *Overhauser* effect on the free induction decay and FT.-NMR.-intensities. As may be seen in *Table 4* and *Figure 3*, the resonances of both carbon atoms in the recombination product of initiator A appear in emission. Consequently, if we follow *Kaptein's* rule [9] or equation (2), the hyperfine coupling constants  $C_{\text{bo}}$  and  $C_{\text{be}}$  must have opposite signs. For the unsubstituted benzyl radical, *Pople et al.* [17] have calculated a carbon hyperfine coupling constant  $a_{\text{be}} = -12.3$  Gauss. According to experiments by *Paul & Fischer* [11] [13], this hyperfine parameter does not vary much with oxysubstituents at the alkyl carbon atom. We are not aware of any theoretical or experimental parameters for the spin density at the  $C_{\text{bo}}$  carbon atom. The hyperfine coupling constants of the  $\beta$ -carbon atom in the acetyl, phenacetyl and isobutyl radicals have very similar values between +46 and +51 Gauss [11] [18]. According to *Bennett* [18] and *Adrian* [19], the structure  $\text{R} \cdot : \text{CO}$  makes an important contribution to the hyperfine value of the  $\beta$ -carbon atom.

The hyperfine coupling constant of the  $C_{bo}$  carbon atom therefore should be approximately  $+(40-50)$  Gauss.

Within the error of our experiment, the two longitudinal relaxation times  $T_{1bo}$  and  $T_{1be}$  are the same. The  $180^\circ - \tau - 90^\circ$ -pulse method leads to the values:

$$T_{1bo} = 19.2 \pm 1.5 \text{ s}$$

$$T_{1be} = 18.8 \pm 1.5 \text{ s}$$

in perdeuterated benzene solution.

Since the magnitude of the nuclear polarization increases with increasing magnitude of the hyperfine coupling, the more intense signal must be assigned to  $C_{bo}$ .

Rough estimates of relative hyperfine coupling constants may be derived from (2) and relative CIDNP.-intensities. The experimental ratio of the two polarizations of  $\sim 3.0$ , as determined by the subtraction experiment described in section 5, with corrections of the FT.-NMR.-intensities for the influence of the *Overhauser* effect and unresolved differences of the two  $T_1$  values, an estimated difference of the two  $g$ -values  $g_{be} - g_{bo} \approx 2.3 \cdot 10^{-4}$  [13] and the hyperfine coupling  $a_{be} = -12.3$  Gauss lead to an approximate benzoyl hyperfine coupling  $a_{bo} \approx +34$  Gauss, in reasonable agreement with prediction.

**4. Polymerization experiments.** - In order to get an insight into the radical reactions during the polymerization process, 0.1 M benzene solutions of initiators **A** and **B** were irradiated in the presence of the monomer acrylic acid methyl ester (AME).

At low monomer concentration reactions of the initiator radicals compete with reactions between radicals and the AME monomer. The  $^1\text{H}$ -CIDNP.-intensities of some initiator photoproducts as a function of the initial monomer concentrations should reflect the first steps of the polymerization process.

One should keep in mind, that in the experiments with initiator **A** only radicals produced by *Norrish*-type I cleavage induce polymerization. With initiator **B** radicals generated by *Norrish*-type I cleavage and according to [3], despite of its short lifetime, the biradical in the *Norrish*-type II pathway are responsible for polymerization.

Diagrams for the  $^1\text{H}$ -CIDNP.-intensities of some photoproducts of initiators **A** and **B** as a function of the AME concentration are given in *Figures 5* and *6*. These CIDNP.-intensities correspond to quasi steady state conditions. The polymerization experiments can be described by the following main features:

- a) The CIDNP.-intensities of the free radical combination products, acetophenone and propiophenone, disappear at small AME concentrations;
- b) The resonances of the photoproducts methyl benzoate and ethyl formate reach intensities which are independent of AME concentration;
- c) The CIDNP.-intensities of recombination products **A** and **B** show an AME dependence similar to that of the ester products (dependence represented for initiator **B** only);
- d) The CIDNP.-intensities of the escape products methane and ethane disappear at small AME concentrations;

e) The benzaldehyde CIDNP.-intensity of initiator **A** varies strongly with concentration of AME. As the AME concentration increases, the aldehyde resonance changes from emission to enhanced absorption. At higher AME concentrations the polarization passes a maximum and decreases slowly as the AME concentration is further increased.

There has been a great deal of discussion about the geometry and the related sign and magnitude of the  $\alpha$ -hydrogen atom hyperfine coupling of difluoro- and dioxisubstituted methyl radicals [20]. The asymptotic enhanced absorption (A) assigned to the methine proton in the recombination product of initiator **B** (C) establishes the positive sign of this hyperfine coupling in the dimethoxy-methyl-radical (and the diisopropoxy-methyl-radical), in agreement with a strong deviation of these radicals from planarity:

According to equation (1) and the CIDNP.-phase (A) the product ( $\mu_{\text{methine}}$ ) must have a positive sign. The CIDNP.-phases  $\Gamma$  of initiator **B** do not change as the AME-independent CIDNP.-intensities are reached. This, together with the

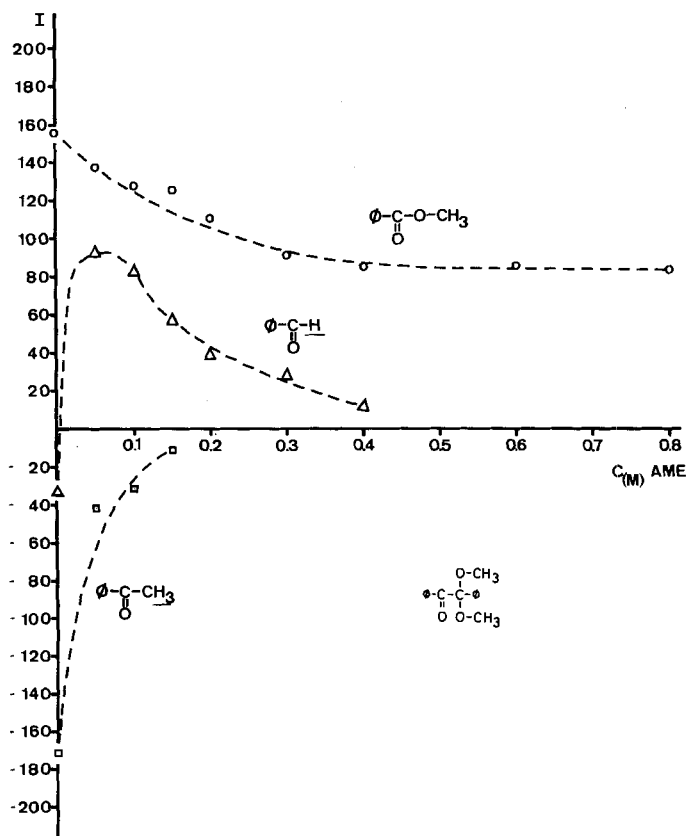


Fig. 5. Initiator **A**:  $^1\text{H}$ -CIDNP.-intensities as a function of initial AME concentration. Positive values (A), negative values (E). Observed protons underlined. Methyl benzoate: Ortho protons.

(E)-type polarization of the carbonyl carbon atom in the recombination product **B**, prove that  $\mu$  is positive (*Norrish*-type I cleavage from the excited triplet state) and lead to the positive sign of  $a_{\text{methine}}$ .

The CIDNP.-intensities of methyl benzoate, ethyl formate and the recombination products **A** and **B** unquenched by the polymerization process are due to reactions in the geminate primary pair during the first  $10^{-9}$ – $10^{-7}$  s after the  $\alpha$ -cleavage. According to their CIDNP.-characteristics the two esters are escape products. The CIDNP.-intensity of methyl benzoate in the presence of AME decreases to about 50%, the intensity of ethyl formate to about 16% of its original value. These percentages do not represent the fractions of ester formed in the geminate pair. The nuclear polarization of the substituted benzyl- and methyl-radicals built up in the primary pair disappears with the nuclear relaxation time. The ester products formed at later times contribute much less to the CIDNP.-intensity than products formed in the geminate pair. Simultaneous  $\alpha$ -cleavage and ester formation (*Scheme 2*) would not lead to the observed CIDNP.-effects. The CIDNP.-enhancements prove

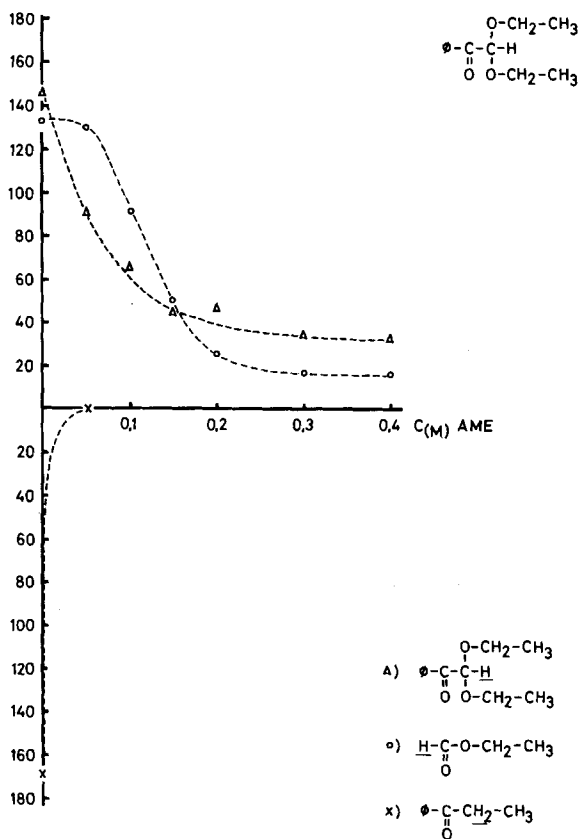


Fig. 6. Initiator **B**:  $^1\text{H}$ -CIDNP.-intensities as a function of initial AME concentration. Positive values (A), negative values (E). Observed protons underlined.

that, at least for part of the initiator molecules,  $\alpha$ -cleavage occurs before stabilization of the substituted benzyl- and methyl-radicals to the ester products.

The diagrams in *Figures 5 and 6* show clearly that primary and secondary radicals which are not eliminated by a reaction in the geminate pair, react with AME or AME radicals (AME after addition of an initiator radical). The temperature controlled formation of the very reactive secondary radicals eliminates part of the primary substituted benzyl- and methyl-radicals as potential initiators or terminators of the polymerization reactions. This secondary cleavage not only forms a reactive initiator, but also reduces the probability for the recombination of the two primary radicals.

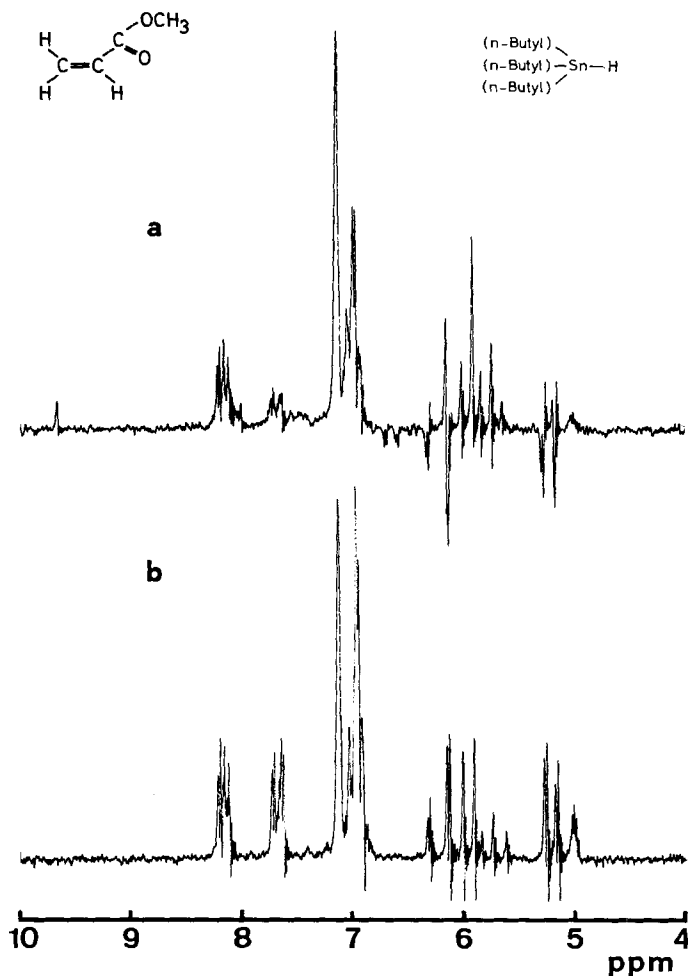


Fig. 7. Polymerization experiment in the presence of tri-*n*-butyl-tinhydride.  $^1\text{H-NMR}$ -spectra a) with UV-irradiation, b) without UV-irradiation. Chemical shifts: AME geminal protons 6.24 ppm and 5.20 ppm, vicinal proton 5.87 ppm.



The increase of enhanced absorption of the benzaldehyde proton at low AME concentrations is probably due to a  $\beta$ -hydrogen atom transfer from an AME radical to a benzoyl radical in a cage reaction. At increasing AME concentration, the ratio of AME to AME-radicals becomes unfavourable for this cage reaction and the signal intensity of benzaldehyde decreases.

Much more extensive reversible addition of radicals to AME was observed when the polymerization experiment was carried out in the presence of the proton donator, tributyl-tinhydride. Two  $^1\text{H-NMR}$ -spectra of initiator A, the AME monomer and tributyl-tinhydride with and without UV-irradiation are reproduced in *Figures 7a* and *b*. The resonances of the two geminal AME protons appear in emission (E), the resonance of the single vicinal proton exhibits enhanced absorption (A). The CIDNP.-pattern and the dependence of the CIDNP.-intensity on the tributyl-tinhydride concentration are consistent with a reversible addition of a stannyl radical to AME. The addition occurs most likely at the unsubstituted AME carbon atom. After the addition, the stannyl radical is abstracted in a cage reaction by a radical species with an electron  $g$ -value larger than that of the AME radical, *i.e.* probably a second stannyl radical with  $g \approx 2.017$  (tri-methyl-tin radical [21]). The CIDNP.-intensities in combination with the radical pair diffusion model [8] show clearly that the AME radical has a classical structure and should not be considered as a  $\pi$ -complex.

**5. Light modulation experiments.** - In order to estimate electron-nuclear hyperfine couplings or follow the kinetics of a photochemical reaction, it is important to measure absolute CIDNP.-intensities. For most CIDNP.-spectra contributions from reactants and products in the thermodynamic equilibrium overlap with CIDNP.-resonances; in the case of recombination products, the two types of intensities coincide.

In  $^{13}\text{C-FT-NMR}$ -experiments we have recorded difference spectra, subtracting free induction decays without UV-irradiation of the sample from free induction decays during excitation of the chemical reactions. A detailed description of the FT.-NMR.-technique is given in [22] and the modulation experiment is represented in *Figure 8*.

At the beginning of each second pulse delay time (PDT), the light beam is interrupted by a shutter and reopened at the end of the subsequent signal accumulation time (AT). The low frequency phase of the free induction decay is modulated synchronously with the UV.-light. As indicated in *Figure 8* in the last two rows, this procedure inverts the  $^{13}\text{C}$ -intensities corresponding to alternate free induction decays.

Long pulse delay times of the order of 10-15 s are needed both to reach quasi-state polarization and to let the polarization be destroyed before the subsequent radiofrequency pulse.

By this procedure, contributions to the magnetic resonance signal from particles which do not react during a set of two pulse experiments are cancelled. A very small fraction of thermal equilibrium intensity does not vanish, since the NMR.-intensities of some disappearing reactant molecules and newly created reaction products which have relaxed to thermal equilibrium do not sum up to zero in one

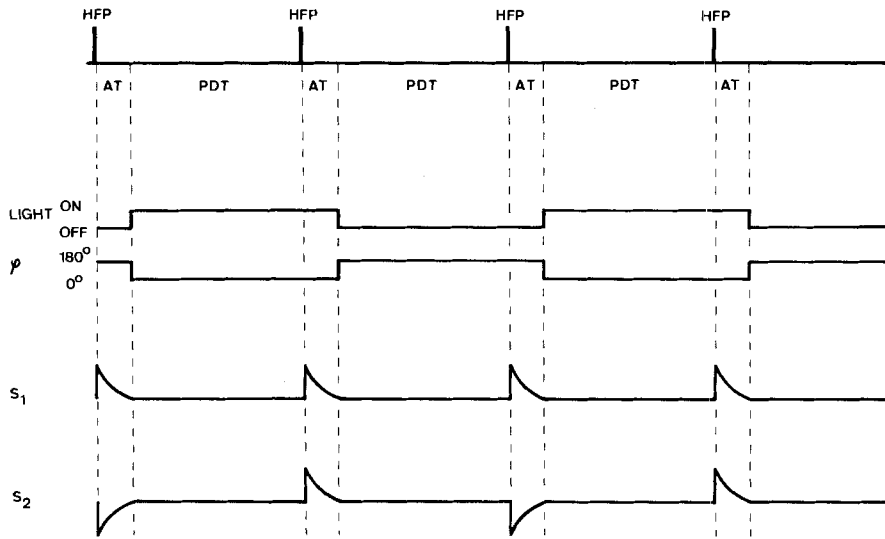


Fig. 8. UV.-modulation experiment

HFP: high frequency pulse; AT: accumulation time; PDT: pulse delay time;  $\phi$ : phase of NMR.-signal;  $S_1$ : free induction decays without phase modulation;  $S_2$ : free induction decays with phase modulation.

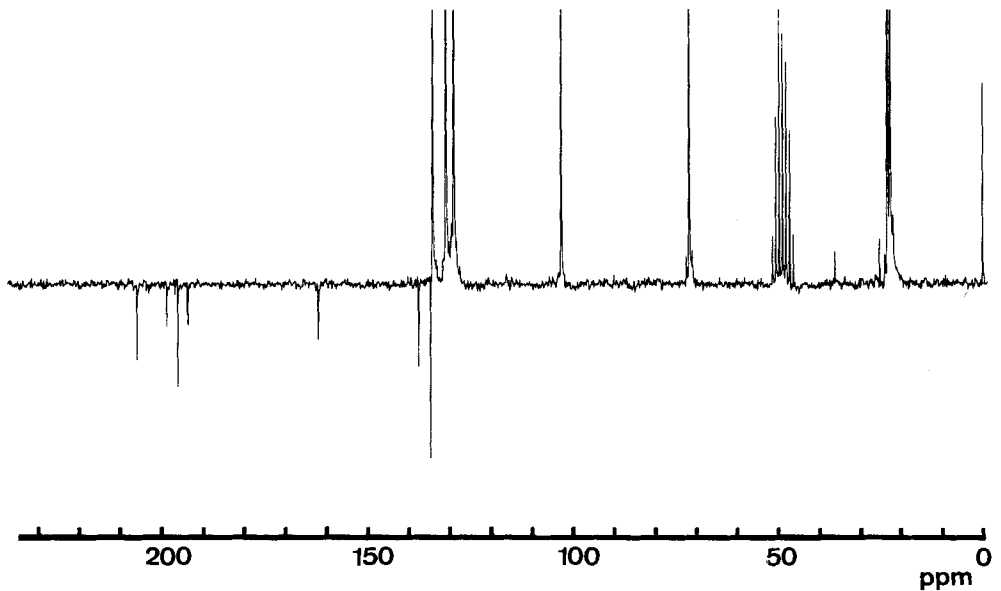


Fig. 9.  $^{13}\text{C}$ -FT.-CIDNP.-spectrum of initiator C in deuterated methanol with continuous UV.-irradiation

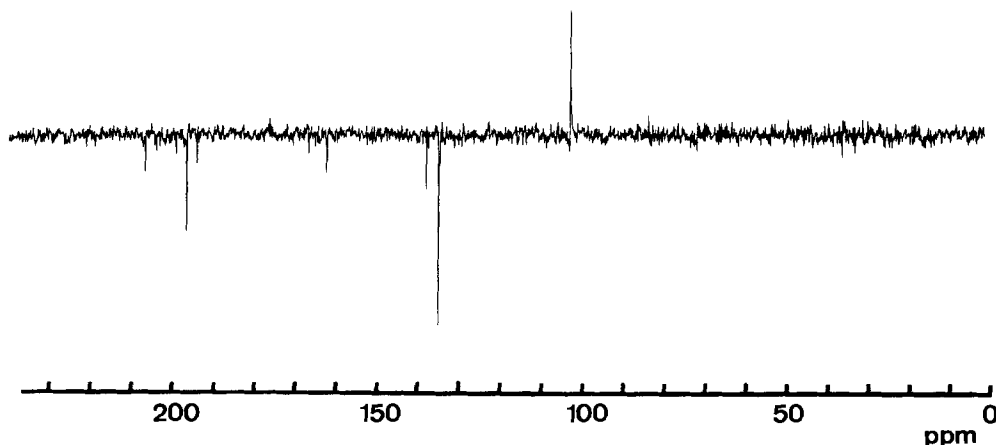


Fig. 10.  $^{13}\text{C}$ -FT-CIDNP.-spectrum of initiator C in deuterated methanol with modulated UV.-irradiation

set of two compensating pulse experiments. This residual intensity can be neglected for CIDNP.-resonances with enhancement factors larger than  $10^2$ .

An application of the square wave modulation technique is illustrated in *Figures 9 and 10*. The  $^{13}\text{C}$ -spectrum of initiator C in a methanol solution during continuous irradiation is shown in *Figure 9*; *Figure 10* exhibits the same spectrum applying modulated light. Both spectra result from the accumulation of  $10^3$  free induction decays. In *Figure 10*, only every second free induction decay contributes to the photosignal, but every decay contributes to the noise.

The modulation shows clearly which carbon atoms in the radical pair preceding the photo product carry appreciable spin density. Removal of the solvent signal demonstrates that, in this particular experiment, the nuclei of the solvent are not polarized by the photochemical process.

The subtraction experiment is related to a technique by *Fischer & Laroff* [23] where separation of CIDNP.- and thermal equilibrium intensities is achieved in continuous-wave experiments by very slow light-modulation and demodulation of the NMR.-signal in a lock-in amplifier.

The subtraction method cannot be applied to experiments where the irradiating light changes the field homogeneity and/or the chemical shift values of reactant and products. The technique did not lead to good results in  $^1\text{H}$ -experiments, but it worked well in  $^{13}\text{C}$ -spectroscopy. In [24], *Schäublin, Wokaun & Ernst* discuss elegant pulse experiments to overcome the forementioned difficulties.

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