Photo-CIDNP Studies of Hydroxy Ketones and Higher-Molecular-Weight Systems

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In memoriam Professor *Hanns Fischer*

In situ NMR spectroscopy can be applied to investigate chemical reactions during which free radicals occur as intermediates. In chemical systems of low molecular weight, nuclear-spin polarization results from the spin selectivity of free-radical reactions, because a pair of radicals has to obey the exclusion principle according to *Pauli*; therefore, this system reacts in a spin-selective manner when forming a chemical single bond. As a consequence, strong transient absorption and emission lines occur in the NMR spectra acquired during free-radical reactions. This phenomenon is known as 'chemically induced dynamic nuclear polarization' (CIDNP). However, long correlation times associated with short proton spin–lattice relaxation times T_1 render it difficult to observe CIDNP in macromolecules. Therefore, in these and in many other cases, it can be attractive to utilize the simultaneously occurring heteronuclear polarization or to selectively transfer the ^{1}H polarization to heteronuclei, since their T_1 times can be substantially shorter than those of protons.

In this paper, we present examples of how CIDNP can be observed both in low-molecular-weight systems as well as in systems exhibiting a rather macromolecular character. Also, CIDNP can assist in obtaining useful information about macromolecular systems that normally is very difficult to obtain otherwise. Since CIDNP is primarily a qualitative method by which free-radical intermediates may be identified, we have developed a procedure allowing the quantitative determination of the magnetic properties of the intermediate free radicals. This process is especially useful for very short-lived radicals, which are frequently elusive to ESR spectroscopy conducted in solution. In particular, *g* values of a variety of radical ions have been determined in this fashion by CIDNP-NMR spectroscopy. The data thus obtained provide an alternative to ESR and, hence, complement this traditional method (manuscript in preparation).

Introduction. – Ever since its accidental discovery [1][2] in the form of intense emission and enhanced absorption lines in NMR spectra *ca*. 40 years ago, the nuclear-spin-polarization phenomenon termed 'chemically induced dynamic nuclear polarization' (CIDNP) has been used to investigate a great variety of free-radical reactions. Especially attractive is its application to determine structural details of biochemically important molecules both in the steady state as well as during the progression of folding or unfolding [3]. The observation of CIDNP requires *in situ* NMR spectroscopy, which allows one to investigate chemical reactions during which free radicals occur as intermediates. At least in chemical systems of low molecular weight, nuclear-spin polarization results from the spin selectivity of free-radical reactions, because a pair of radicals

has to obey the exclusion principle when forming a chemical single bond. Also, the CIDNP phenomenon is suited to identify both the nature of intermediate radicals as well as their reaction products in macromolecular systems. However, observing CIDNP in systems of high molecular weight is intrinsically more difficult, mainly because of the very short relaxation times of the nuclei within or even in the mere presence of macromolecules. This is especially true for situations where the reaction products themselves have a high molecular weight, and it is worst in cases where the product molecules contain long molecular chains, e.g., alkyl chains. The situation is, however, not totally hopeless provided the NMR equipment is adapted to suit the required boundary conditions for investigating such reactions.

CIDNP is an indirect method to observe and characterize free radicals by means of the polarization observed in the corresponding reaction products. Since the extent of CIDNP is inversely proportional to the lifetime of the interacting paramagnetic intermediates, this spectroscopic method complements direct electron-spin-resonance (ESR) methods to investigate free radicals both in its applicability as well as in the type of results obtained.

The magnitude of CIDNP enhancements in reaction products of low molecular weight is governed by the ratio of the magnetic moment of the electron *vs.* the magnetic moments of the nuclei being observed. Thus, for H-atoms, the experimentally observed enhancements typically range in regions of one to almost three orders of magnitude, and for heteronuclei even higher. The related CIDEP effect in ESR is much smaller than typical CIDNP-NMR enhancements. The CIDEP enhancements are of the order of unity in steady-state spectra, but can reach values of up to two orders of magnitude. To detect these higher CIDEP enhancements, ESR spectrometers have to be modified to allow observation of the radicals within microseconds after their formation.

Experimental. – To observe and record CIDNP spectra, no modification of conventional NMR spectrometers operating in either FT or CW mode is required. The latter mode used to be typical for NMR spectrometers prior to the advent of the *Fourier* transform (FT) technology, which requires computers to generate the NMR spectrum from a free induction decay (FID). Accordingly, we have used the CW mode when recording spectra at a lower magnetic-field strength of either 60 or 100 MHz due to the availability of older CW spectrometers in our laboratory. All ^{1}H-NMR spectra recorded at 80 or 200 MHz (or higher), however, were obtained using contemporary FT-NMR spectrometers.

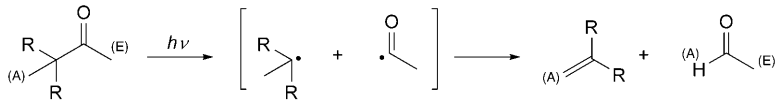
Photochemical generation of free radicals requires appropriate attachments to conventional NMR spectrometers. Appropriately modified probes were either home-built or available commercially, whereby the required light is admitted either along the axis of the static magnetic field or from the side of the spinning NMR tube. In the latter case, mirrors were used to deflect and admit the radiation through an appropriately shaped and spaced radio-frequency coil.

However, the required modifications can be minor, especially if an appropriately shaped UV-light rod built from fused quartz is used, as in our case. Such a rod of an outer diameter between 4 and 10 mm (depending on the inner diameter of the NMR tube) extends into the open spinning sample from the top with its tapered end, cut at an angle of *ca.* 45°, which, in turn, extends *ca.* 1 cm into the liquid sample. There it introduces efficient stirring agitated by the spinning, in addition to allowing sufficient UV irradiation of the continuously stirred solution. This stirring effect is especially beneficial in ^{13}C-FT-NMR spectrometers and has its merit even without accompanying UV illumination. Recording of CIDNP spectra with FT-NMR spectrometers in combination with a pulsed-light source (laser) has certain advantages over a CW spectrometer in combination with a Hg/Xe arc lamp, because, in this way, the effects of NMR relaxation can be greatly reduced or even eliminated.

Results and Discussion. – 1. *CIDNP in Macromolecular Systems.* The dilemma with CIDNP in macromolecular systems is relaxation: macromolecules, in particular those containing long alkyl chains, have notoriously short relaxation times. When investigating macromolecular systems using conventional NMR spectroscopy it is, thus, common practice to increase the temperature, typically to values exceeding 100 °C, to obtain relatively narrow resonance lines thanks to the lowered viscosity of the solution. For biological systems, however, this option is not applicable because under such conditions they would collapse and loose there activity.

An early attempt to explore the seriousness of this situation and the consequences of such relaxation processes for the nuclear-spin polarization derived from free radicals *via* CIDNP was the investigation of a number of macromolecular model systems [4], whereby the required free radicals or pairs thereof were generated photochemically according to *Scheme 1*.

Scheme 1



R = Me, Et, $[CH_2C(Me)C(O)Me]_n$

The systems (mainly ketones) studied contained appropriate chromophores to absorb UV light at a wavelength of *ca.* 300 nm. Their C=O groups can be photoexcited, upon which they undergo a variety of photoreactions, including α-cleavage and photoreduction.

In one set of experiments, we investigated the photo-induced α-cleavage of poly(methylisopropenyl ketone) (PMIK) and its low-molecular-weight model compounds 3,3-dimethylbutan-2-one (DMB) and 3-ethyl-3-methylpentan-2-one (EMP). *Scheme 1* illustrates the corresponding photoreactions of these systems.

Solutions of the ketones in CD_3CN, C_6D_6, $CDCl_3$, or CCl_4, each containing 0.1M of the model compound or 10 g/l of the polymer, respectively, were irradiated in 5-mm quartz tubes inside a modified probe of a CW-NMR spectrometer operating at 60 MHz. The probe admitted UV irradiation through a quartz light pipe from the rear. A 5-kW high-pressure Hg/Xe lamp served as the light source. The optical system consisted of a spherical mirror, two quartz lenses, and a filter of 10-cm path length containing an aqueous solution of $NiSO_4 \cdot 7\ H_2O$ (250 g/l), $CoSO_4 \cdot 6\ H_2O$ (50 g/l), and H_2SO_4 (1 g/l) to remove the IR and most of the VIS radiation. Tetramethylsilane (TMS) sealed in a capillary provided a magnetic-field lock. Chemical shifts δ were measured against internal TMS in separate runs. Both aerobic and anaerobic (deoxygenated) solutions gave identical results.

In *Fig. 1*, the low-field portions of the CIDNP spectra observed during the photolysis of DMB (*a*), EMP (*b*), and PMIK (*c*) in CD_3CN are shown. The high-field portions of the spectra were omitted because of overlapping absorption lines of the starting materials at δ(H) 2.5 – 0 ppm. The sections of the spectra showed no lines in the absence of irradiation, but on admission of UV light, the following resonances

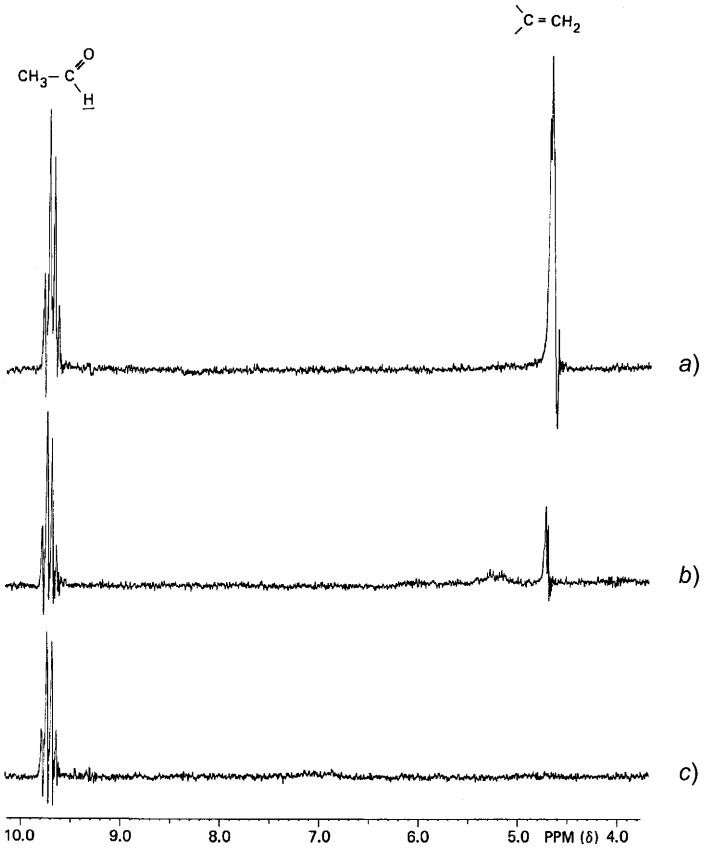


Fig. 1. *CIDNP Spectra during the photolysis of* a) *DMB,* b) *EMP, and* c) *PMIK in CD_3CN solution*

appeared and disappeared after termination of the irradiation. An intense *quadruplet* (*q*) centered at δ(H) 9.7 occurred in all three traces of *Fig. 1*, which can be attributed to the aldehyde H-atom of acetaldehyde. Furthermore, a strong *multiplet* (*m*) was observed at δ(H) 4.7 (*Fig. 1*,*a*) caused by the methylene protons of isobutylene (=2-methylprop-1-ene). In *Fig. 1*,*b*, a similar, but much weaker, *multiplet* was found, with a broad and even weaker absorption band at δ(H) 5.2–6.2. In *Fig. 1*,*c*, however, no corresponding resonance was observed in the olefinic region.

The starting materials DMB and EMP showed CIDNP themselves during irradiation, in contrast to PMIK. In C_6D_6 or other chemically inert solvents, essentially identical results were obtained. *Table 1* lists the products identified during the photolysis of PMIK in C_6D_6 solution.

Using known values for the *g* parameters and the proton hyperfine coupling constants of the radicals occurring in *Scheme 1*, it can be concluded, according to the well-established CIDNP-sign rules [5], that photodecomposition of DMB yields acetyl/*tert*-butyl radical pairs with predominant triplet character. Accordingly, DMB undergoes a *Norrish* type-I cleavage from its triplet state.

Table 1. *The Photoproducts and Their CIDNP Observed During Irradiation of Poly(methylisopropenyl Ketone)* (PMIK)

Product	δ(H) [ppm]	T_1 [s]	Multiplicity[a])	CIDNP[b])
$(CH_2C(Me)COMe)_n$	1.5	<0.5	br.	N
$(CH_2C(Me)COMe)_n$	1.1	<0.5	br.	N
$(CH_2C(Me)COMe)_n$	2.1	<0.5	br.	N
*Me*CHO	1.49	<20	*d*	E (+A/E)
MeC*H*O	9.7	<35	*q*	A
–CH=C(Me)	5.2–5.6	<0.5	br.	N
–CH=C(Me)	1.5	<0.5	br.	N
$-CH_2(C{=}CH_2)-$	4.8	<0.5	br.	N
MeCO–COMe	1.79	<4	*s*	A
C_6HD_5 (solvent)	7.2	–	–	N

[a]) Abbreviations: br, broad; *d*, *doublet*; *q*, *quadruplet*; *s*, *singlet*. [b]) A, enhanced absorption; E, emission; N, no CIDNP; A/E, superimposed *multiplet* effect with low-field components showing enhanced absorption (A) and high-field components showing emission (E).

If we assume that the other two radicals in *Scheme 1* have the same *g* value as $Me_3C^{\bullet}$ and a positive hyperfine coupling constant for all their β-H-atoms, it follows from the CIDNP absorption of the universal photoproduct acetaldehyde (observed throughout in *Fig. 1*) that PMIK as well as the two model compounds are cleaved in inert solvents predominantly in their photo-excited triplet state. The CIDNP spectra obtained from the polymer exhibit fewer lines than expected, which is outlined in the following: acetaldehyde is one of two simultaneously formed disproportionation products of the *Norrish* type-I decomposition of the ketones described. Hence, one would expect the H-atoms of the complementary disproportionation product (last radical in *Scheme 1*) to display CIDNP as well. However, there is no CIDNP signal from an olefin in *Fig. 1*,*c*, whereas in *Fig. 1*,*a* and *Fig. 1*,*b* the products show CIDNP for their olefinic H-atoms. Furthermore, because the acetaldehyde H-atom is in β-position in the intermediate radical and since the remaining equivalent β-H-atoms become the olefinic ones in the last olefin, both the aldehyde H-atom and the olefinic H-atoms should become *equally strong* when polarized. This, however, was not the case. Therefore, the missing CIDNP signal of the olefinic H-atoms in *Fig. 1*,*c* can be rationalized only by a relaxation phenomenon: once the initially equivalent radical nuclei become part of different reaction products, their spin polarization will decay with different rates. These rates can be measured experimentally by NMR with the aid of the proton nuclear spin–lattice relaxation times T_1. It is well-known that H-atoms of different chemical groups of the same molecule may have different relaxation times. Hence, CIDNP-intensity correlations will even be lost for nuclei that are equivalent in the intermediate radicals, but become nonequivalent in the reaction products.

For reactions yielding *macromolecular* products, it has to be considered that long-chain molecules show decreasing T_1 values with increasing chain lengths until a critical polymerization degree is reached, above which T_1 is constant. This phenomenon has been attributed to segmental motions of the macromolecules. Measurements for aqueous solutions of polyethylene oxide as a function of the polymerization degree *n* yielded

T_1 values of 5.0, 1.0, and 0.6 s for model compounds with $n=1$, 6, and 20–20,000, respectively. Similar data have been reported for the H-atoms of unbranched alkanes. From these data, it can be extrapolated that $T_1 < 0.5$ s for the products of *Scheme 1*.

The CIDNP signals for molecules with such short T_1 values could at best be weak, but are most likely undetectable. This conclusion follows from the early studies of *Bargon* and *Fischer* [6], who showed that, on shortening T_1 by addition of increasing concentrations of paramagnetic ions to systems showing CIDNP, the signal enhancements of the products could be decreased and eventually suppressed.

In the systems studied here, the proton T_1 values of the simultaneously formed disproportionation products of *Scheme 1* differ by a factor of *ca.* 2 for those derived from DMB, but by two orders of magnitude for those from PMIK. The CIDNP intensities of these products cannot be correlated in a simple way with their relative chemical yields, which is evident from *Fig. 1,a* and *Fig. 1,c*.

Nevertheless, the fact that the reaction product acetaldehyde shows CIDNP, independent of the type and the size of its partner radical in *Scheme 1*, suggests that, in principle, CIDNP can be generated in macromolecular systems as well as in reactions of small radicals. Thus, it appears that in the intermediate free radicals the proton and electron spin–lattice relaxation times are quite insensitive to the chain length of the substituent R. Once the CIDNP is transferred to the reaction products, however, the nuclei in the macromolecules will experience a fast decay of their polarization, whereas those in small molecules retain it much longer. Because of this, it is not surprising that CIDNP spectra recorded during photolysis of polymers do not reflect the relative significance of alternate decomposition pathways correctly. In PMIK, it is known that 'side-group scissions' (for which we found exclusive evidence) are indeed of only minor significance. The main photoreaction of PMIK is instead 'main-chain cleavage', which typically yields only long-chain molecules and, hence, no CIDNP. Furthermore, the reaction mechanism of this main-chain cleavage is not known in detail, but is thought to proceed *via* biradical intermediates and, therefore, may not cause CIDNP in the first place. CIDNP from 1,4-biradical intermediates is unlikely to be detected at the field strength of 1.4 T of our NMR spectrometer, because the exchange interaction does not match with the electronic *Zeeman* energies.

2. *Photolysis in Reactive Solvents.* – Small product molecules alone can, nevertheless, reflect useful information in CIDNP spectra. To demonstrate this, we have investigated the photolysis of PMIK and its model compounds in $CDCl_3$ solution. In *Fig. 2*, the corresponding CIDNP spectra observed during irradiation are shown for the region $\delta(H) > 2.5$ ppm. Again, the sections $0 < \delta < 2.5$ of the spectra were masked by the intense CIDNP lines of the ketones. Thus, PMIK shows three broad resonances in $CDCl_3$: at $\delta(H)$ 1.00 the Me groups, at $\delta(H)$ 1.86 the CH_2 groups, and at $\delta(H)$ 2.12 the Ac H-atoms. The onset of the polymer absorption is evident at the right end of *Fig. 2,c*. The photoproducts identified are acetaldehyde ($\delta(H)$ 9.8), $CHCl_3$ (7.3), $CDHCl_2$ (5.3), AcCl (2.7), $AcCCl_3$ (2.5), and individual olefins (*e.g.*, $H_2C{=}CMe_2$ at $\delta(H)$ 5.3; *Fig. 2,a*).

From these products, it can be concluded that PMIK, as well as the two model ketones, undergoes α-cleavage yielding acetyl and tertiary-alkyl radicals. These primary radicals attack the solvent ($CDCl_3$) and abstract D- or Cl-atoms. Thus, the CCl_3 and $CDCl_2$ moieties being generated encounter other free radicals in the system yield-

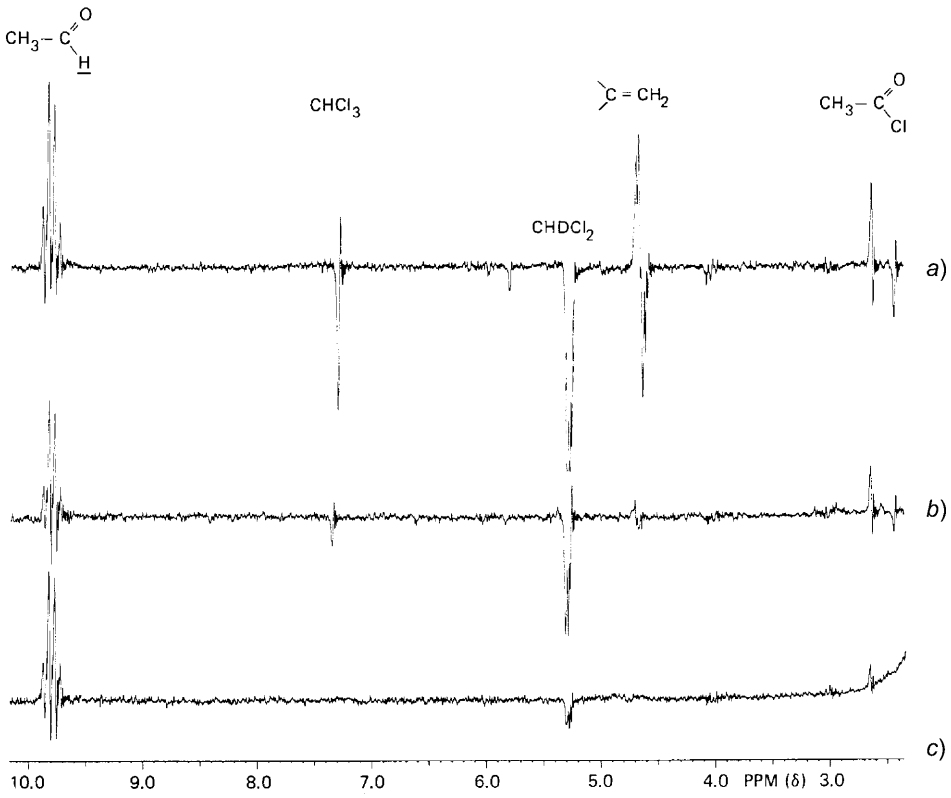


Fig. 2. *CIDNP Spectra during the photolysis of* a) *DMB,* b) *EMP, and* c) *PMIK in* $CDCl_3$ *solution*

ing a variety of secondary radical pairs. Many of these pairs contain a tertiary-alkyl radical as one component. All can produce one identical alkene by disproportionation, and for the precursor DMB, all radical pairs containing *tert*-butyl radicals can yield isobutylene. Therefore, the CIDNP found for the isobutylene H-atoms stem from a variety of radical pairs and, hence, correspond to the sum of individual contributions from the primary *t*-Bu/Ac radical pair and all appropriate secondary radical pairs. For all systems studied here, it has been deduced from the CIDNP studies in inert solvents (*Fig. 1*) that both primary as well as secondary radical pairs have predominantly electronic triplet multiplicities. If we assume that the same holds true for the reactive solvent ($CDCl_3$), the CIDNP phase of the isobutylene H-atoms depends only on the *g* values of the partner radicals (S) in the pairs of the type *t*-Bu/S. A series of combinations are possible giving rise to the following phase patterns, where B and S refer to tertiary-alkyl and partner radical, respectively:

a) $g(S) < g(B) \rightarrow$ absorption
b) $g(S) > g(B) \rightarrow$ emission
c) $g(S) = g(B) \rightarrow$ multiplet effect

In *Fig. 2*,*a*, the isobutylene H-atom resonances reflect a pure multiplet effect, with no superimposed absorption or emission. We rationalize this as resulting from a cancellation of an equally strong emission and enhanced absorption from both pairs of patterns *a* and *b*. Hence, the remaining multiplet effect must stem from pairs of type *c*.

The only choice for a partner radical S to give radical pairs of type *c* is another tertiary-alkyl radical (S = B). All other radicals have inappropriate *g* values, as can be seen from *Table 2*. Similar conclusions have been reached when studying the photoreactions of di(*tert*-butyl) ketone (= 2,2,4,4-tetramethylpentan-3-one) in $CDCl_3$ solution. From the cancellation of the CIDNP stemming from pairs *a* and *b*, one is tempted to determine their relative concentrations. However, because the magnitude of a CIDNP signal is a complex function of numerous parameters, including a series of almost unknown rate constants, this effort has to be postponed. According to our rough estimate, the concentration of the *a*-type radical pairs appears to dominate over that of type *b*.

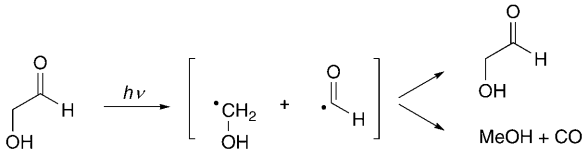
Table 2. *ESR Data of Selected Free Radicals*

Radical	*g* Value	Proton hyperfine coupling (a_H)
Ac$^{\bullet}$	2.005	5.3
$Me_3C^{\bullet}$	2.0025	22.72
$Cl_2(H)C^{\bullet}$	2.0083	– 16.79
$Cl_3C^{\bullet}$	2.0091	–

3. *CIDNP from the Photolysis of Steroids.* During the photolysis of steroids containing appropriate chromophores such as an α-hydroxy ketone, enhanced absorption was observed for the aldehyde H-atom of the low-molecular-weight fragment glycolaldehyde. In contrast, the complementary fragment, namely the steroid framework containing a C=C bond, failed to exhibit any detectable CIDNP, at least not in its ^{1}H-NMR spectrum. This failure to detect any evidence of nuclear-spin polarization from the steroid has been attributed to efficient relaxation processes quenching any polarization.

4. *CIDNP Studies of Low-Molecular-Weight α-Hydroxy Ketones.* Upon investigating the photolysis of glycolaldehyde (= 2-hydroxyacetaldehyde) in an inert, aprotic solution ($CDCl_3$), we found that, in this case, the aldehyde H-atom displays emission upon UV irradiation at 300 nm (*Scheme 2*). In *Fig. 3*, the effects observed in the ^{1}H-NMR CDNP spectra during the photolysis are shown, recorded at a resonance frequency of 100 MHz. Photolyzing glycolaldehyde in, *e.g.*, D_2O, gave rise to much more complicated results because the glycolaldehyde may either occur in the form of different isomeric dimers or in its hydrated form.

Scheme 2. *Photolysis of Glycolaldehyde*



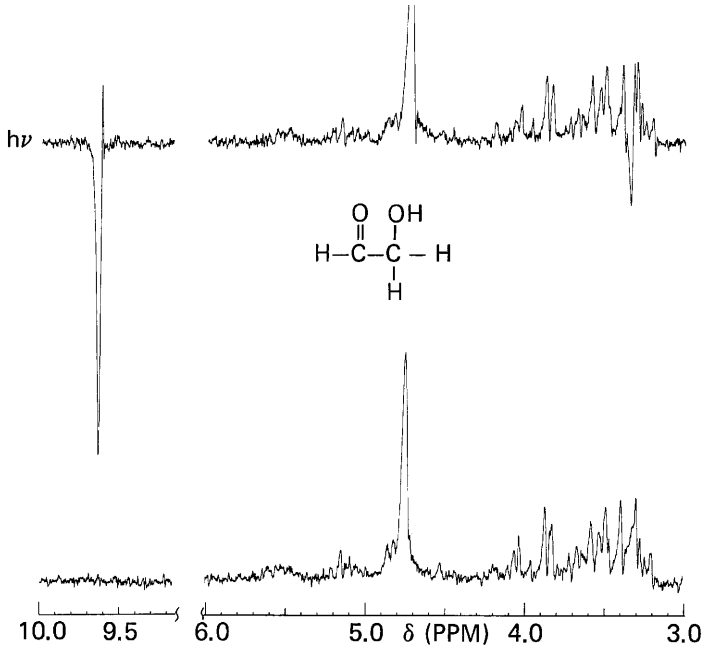


Fig. 3. *100-MHz ^{1}H-CIDNP Spectrum recorded during the photolysis of glycolaldehyde*

Similar results were obtained in the photolysis of higher α-hydroxy ketones, as is evident from the ^{1}H-NMR CIDNP spectrum recorded during the photolysis of 1,3-dihydroxyacetone (=1,3-dihydroxypropan-2-one; *Fig. 4*).

The higher homologues of α-hydroxy ketones frequently yield the enols of a variety of ketones *via* disproportionation of the intermediate radicals[1]). *Fig. 5* displays the ^{1}H-NMR CIDNP spectrum of the enol form of acetone obtained in this fashion from an appropriate precursor during the photolysis in CD_3CN solution. Normally, the NMR spectra of enols, especially of the simplest ketones, are elusive since the concentration of the tautomeric enols typically remains below the NMR detection limit. Whether the resonances of these enols appear in either enhanced absorption (A) or emission (E), or whether they display the multiplet effect, depends on the types of radical pairs from which they result. When the *g* values of the two radicals have the same value, the multiplet effect results (*Fig. 5*, *a*), but when the *g* values differ, the resonances display pure emission or absorption (*Fig. 5*, *b*).

Conclusions. – The examples outlined above demonstrate convincingly that ^{1}H-CIDNP can be observed very readily in low-molecular-weight products, even when these products result from macromolecular systems due to the cleavage of a side group. The complementary macromolecular products, even when formed from the very same radicals as the low-molecular-weight fragments, typically fail to display

[1]) CIDNP has also been used extensively by the late Prof. *Hanns Fischer* and his group to detect short-lived enols arising during the radiation of various ketones, see for example [7].

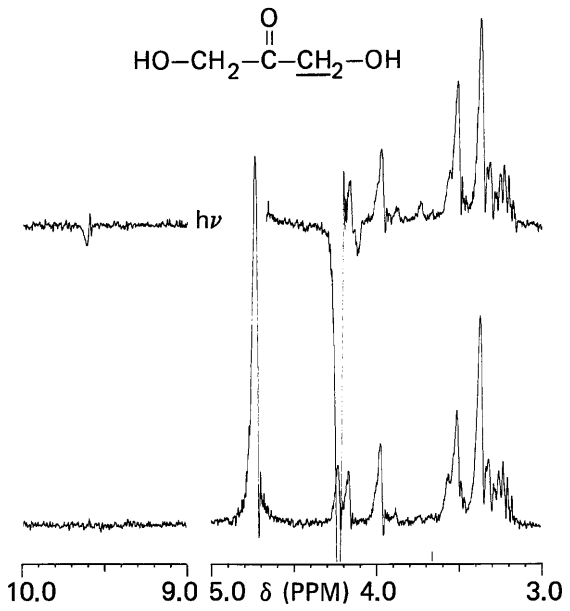


Fig. 4. *100-MHz ^{1}H-CIDNP Spectrum recorded during the photolysis of 1,3-dihydroxyacetone*

CIDNP, at least in the ^{1}H-NMR spectra. We attribute this phenomenon to the different T_1 nuclear-relaxation times, which are known to be short for macromolecular systems. A quite promising, potential alternative is to transfer the CIDNP-derived initial ^{1}H spin polarization to heteronuclei, in particular to ^{13}C. For certain heteronuclei, notably for ^{13}C, the T_1 nuclear-relaxation times are considerably longer than those of the corresponding protons. Hence, we have investigated the feasibility and rules for transferring nuclear polarization from ^{1}H to ^{13}C or to ^{19}F, respectively. For this purpose, we have used another and much more efficient source of initial ^{1}H spin polarization, namely the so-called 'parahydrogen-induced polarization'. In this latter case, the mechanisms leading to nuclear polarization are quite different. However, the subsequent behavior of the polarized spin system is identical to those where the initial polarization was attained by exploiting the CIDNP phenomenon. Various systems have been investigated in great detail, where we have successfully transferred the initial ^{1}H polarization to ^{13}C and, alternatively, to ^{19}F. For this purpose, we have also developed the appropriate pulse sequences, which differ significantly from those used typically for nonpolarized spin systems. The results of all of these studies have been published [8–13].

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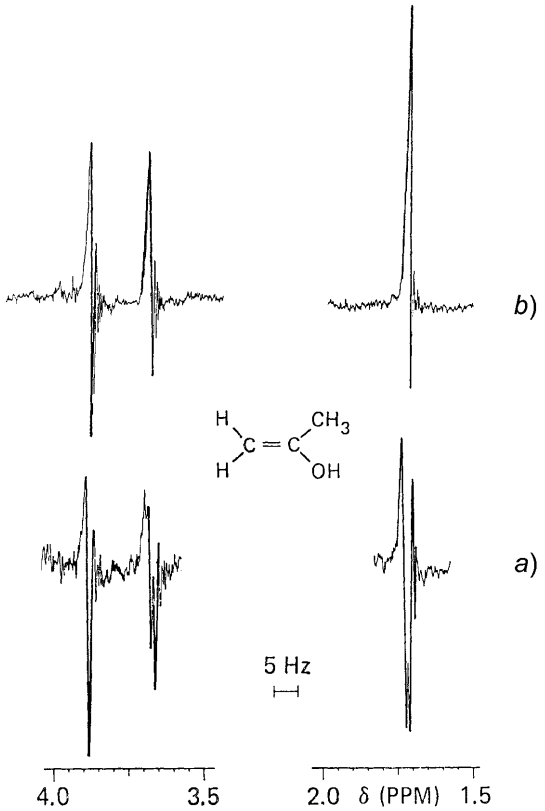

Fig. 5. *100-MHz ^{1}H-CIDNP Spectra of the enol form of acetone displaying the multiplet effect* (a) *or appearing in enhanced absorption* (b)

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