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208. The Enol of Acetone during Photochemical Reactions of 3-Hydroxy-3-methyl-2-butanone and of Acetone[1]

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Summary. The enol of acetone, formed by disproportionation reactions of 1-hydroxy-1-methylethyl radicals, is detected by NMR. spectroscopy during photoreactions of 3-hydroxy-3-methyl-2-butanone in acetonitrile and of acetone in 2-propanol and slowly tautomerizes to acetone. The photolysis of 3-hydroxy-3-methyl-2-butanone is shown to proceed *via* Type I cleavage, predominantly from an excited triplet state.

1. Introduction. – Recently, the effect of chemically induced dynamic nuclear polarization (CIDNP.) has been used to determine the mechanism of photochemical radical reactions of various ketones and aldehydes in solution, by NMR. spectroscopy [1–7]. During photolysis of acetophenone [7] and of acetaldehyde and acetoin [1] the 'unstable' enols of acetophenone and acetaldehyde were detected as intermediary reaction products; it was shown that these compounds are formed in disproportionation reactions of α-hydroxyalkyl radicals of structure $R\text{–}\dot{C}(OH)CH_3$. From the previous findings we expect that the formation of enols occurs quite generally in reactions involving α-hydroxyalkyl radicals with at least one β-hydrogen atom bound to carbon.

In this paper we describe the observation of the enol of acetone formed by disproportionation reactions of 1-hydroxy-1-methylethyl radicals $CH_3\text{–}\dot{C}(OH)CH_3$ in two photochemical systems which strongly supports our assumption. The radical sources were the Type I cleavage of 3-hydroxy-3-methyl-2-butanone (**1**) [8] and the well known photoreduction of acetone in 2-propanol [9].

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2. Experimental. – Dilute solutions of the ketones were irradiated at room temperature in the modified probe of a *Varian* HA-100 D PMR. spectrometer with the light of a 1 kW high pressure mercury capillary lamp (*Philips* SP 1000 W) filtered to transmit radiation of wavelength 300 nm $\leq \lambda \leq$ 350 nm ($NiSO_4/CoSO_4$ in H_2O [8] and glass filter WG 305, *Schott & Genossen*). All chemicals used were obtained from *Fluka* in the purest form available. CIDNP.-enhancement factors per product molecules were determined from the intensity deviations during irradiation and from product transition intensities [10]. Relaxation times were measured by a rapid passage technique [11] and product yields from NMR. intensities.

3. 3-Hydroxy-3-methyl-2-butanone (1). – During irradiation of a 0.1 M solution of **1** in benzene the CIDNP. effects in Fig. 1a were obtained. The assignments of the transitions, relaxation times, phases of CIDNP. effects, enhancement factors per product molecule and product yields are given in columns 1 to 4 of Table 1. The spectrum of Fig. 1b was observed after 3 minutes photolysis and shows PMR. transitions of the starting material **1**, the major products acetone **4** and acetaldehyde **5** and the minor products biacetyl **6** and 2-propanol **7**. The products and part of the CIDNP. effects can easily be explained with the assumption of the reactions of Scheme 1.

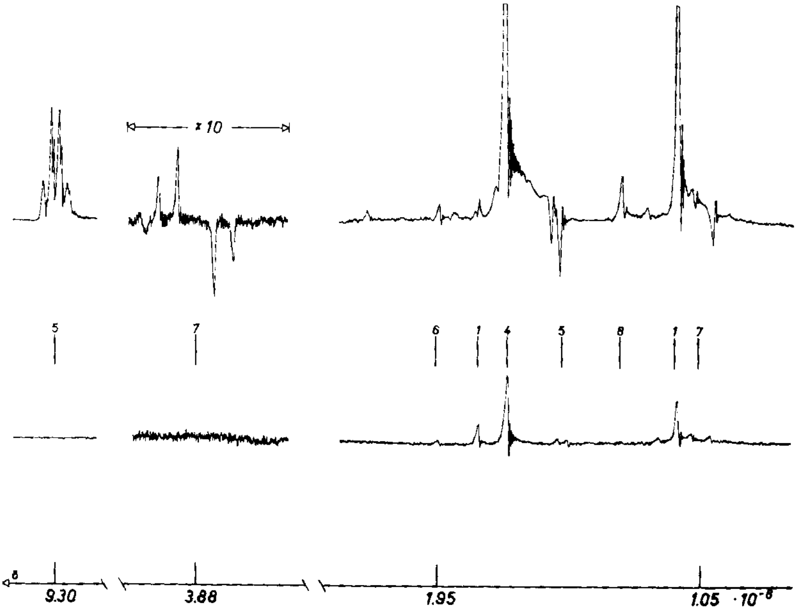


Fig. 1. *CIDNP. (a) during and (b) after 180 s photolysis of* **1** *in benzene* (Parts of spectrum at increased sensitivity)

The initial step of radical production is Type I cleavage of **1** leading to the formation of the acetyl-hydroxy-alkyl radical pair **3**. Singlet reencounters of **3** give **1** (c_2) or acetaldehyde (**5**) and acetone (**4**) (c_1), and pair escape leads to the formation of the free radicals which were also observed by ESR. spectroscopy [8]. Subsequent radical reactions yield biacetyl (**6**), additional acetone and 2-propanol (**7**). The formation of pinacol (**9**) is expected but could not be observed because of a strong

Table 1. *CIDNP.-effects during photolysis of* **1** (0.1 M)

Product	Benzene				Acetonitrile-d_3			
	$\delta \cdot 10^6$ a)	T_1 [s]	CIDNP b)	yield [mol] c)	$\delta \cdot 10^6$ a)	T_1 [s]	CIDNP b)	yield [mol] c)
1. 3-Hydroxy-3-methyl-2-butanone								
CH_3CO	1.79	11	E	0.029	2.32		E	0.024
$(CH_3)_2$	1.13	8	A (~150)		1.42	13	A (~400)	
2. Enol of acetone								
H_A					4.03		A+A/E	
H_B					3.85		A+A/E	
H_X					1.86		A+A/E	
4. Acetone	1.68	20	A (~200)	0.048	2.22	6	A (~500)	0.041
5. Acetaldehyde								
CHO	9.30	30	A (~200)	0.013	9.84	37	A (~500)	0.010
CH	1.53	27	E+A/E (~25)		2.24	11.5	E+A/E (~100)	
6. Biacetyl	1.95		A	0.002	2.36		A	0.002
7. 2-Propanol								
C*H*OH	3.88		A/E	0.009	3.65			0.006
$(CH_3)_2$	1.05		E+A/E		1.23		E+A/E	
8. unassigned	1.31		A		1.58		A	

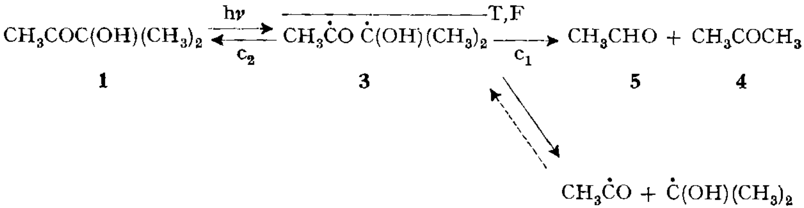
a) Referred to tetramethylsilane

b) For nomenclature, see [13]; numbers in brackets are the enhancement factors.

c) Concentrations after 250 s photolysis determined from NMR.-intensities. Proton balance ~75%.

overlap of transitions. Reactions involving the solvent, benzene, are discounted due to the lack of any changes of the effects upon using cyclohexane as solvent. We believe that the low yields of biacetyl and acetaldehyde (Table I) may be explained by photoreactions of these compounds. In order to determine the multiplicity of the excited state of **1**, which leads to the Type I cleavage, standard triplet quenchers were added to the solutions. It was found that naphthalene ($E_T = 60.9$ kcal/mol [12]) and *cis*-piperylene ($E_T = 56.9$ kcal/mol [12]) had no effect on product yields or CIDNP. effects whereas successful quenching was obtained with *trans*-stilbene (14% quenching at $3 \cdot 10^{-5}$M, $E_T = 49$ kcal/mol [12]) and anthracene ($E_T = 42.5$ kcal/mol [12]). From the slopes of the *Stern-Volmer* plots the constants $k_q\,\tau = 2 \cdot 10^3\,l\,mol^{-1}$ and $k_q \cdot \tau = 4 \cdot 10^2\,l\,mol^{-1}$, respectively, were determined. We conclude that **1** reacts predominantly from a triplet state which is unquenchable with triplet quenchers having triplet energies larger than about 50 kcal/mol.

Scheme 1



$$\underset{\mathbf{1}}{CH_3COC(OH)(CH_3)_2} \underset{c_2}{\overset{h\nu}{\rightleftarrows}} \underset{\mathbf{3}}{CH_3\dot{C}O\ \dot{C}(OH)(CH_3)_2} \xrightarrow[c_1]{T,F} \underset{\mathbf{5}}{CH_3CHO} + \underset{\mathbf{4}}{CH_3COCH_3}$$

$$CH_3\dot{C}O + \dot{C}(OH)(CH_3)_2$$

$$2\ CH_3\dot{C}O \longrightarrow \underset{\mathbf{6}}{CH_3COCOCH_3}$$

$$2\ \dot{C}(OH)(CH_3)_2 \longrightarrow \underset{\mathbf{4}}{CH_3COCH_3} + \underset{\mathbf{7}}{(CH_3)_2CHOH}$$

$$2\ \dot{C}(OH)(CH_3)_2 \xrightarrow{?} \underset{\mathbf{9}}{(CH_3)_2C(OH)C(OH)(CH_3)_2}$$

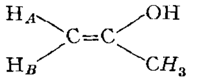
For the interpretation of the CIDNP. effects we use *Kaptein*'s rules [13] and the parameters of the free radicals: g $((CH_3)_2\dot{C}OH) = 2.00315$ [14], $a_{H_\beta}((CH_3)_2\dot{C}OH) = +1.994$ mT [14], g $(CH_3\dot{C}O) = 2.00053$ [8] and a_H $(CH_3\dot{C}O) = +0.40$ mT [8]. They give complete agreement of observed and calculated effects of **1**, **4**, **6** and **7** if the pair **3** is predominantly formed in a triplet state (T) and by free radical encounters (F). Thus these CIDNP. effects support Scheme 1 and the conclusions drawn from the triplet quenching experiments. For the formation of acetaldehyde **5** and acetone **4** from the radical pair two mechanisms may be formulated

$$CH_3\dot{C}O\ \dot{C}(OH^*)(CH_3)_2 \longrightarrow CH_3CH^*O + CH_3COCH_3 \tag{1}$$

$$CH_3\dot{C}O\ \dot{C}(OH)(CH_2H^*)CH_3 \longrightarrow CH_3CH^*O + \underset{\mathbf{2}}{(CH_3)(HO)C{=}CH_2} \tag{2}$$

Reaction (2) involves the intermediary enol **2** of acetone which would tautomerize to give acetone **4**. The strongly enhanced CIDNP. absorption of the CHO-proton of acetaldehyde along with the comparable enhancement factors of this proton and those of acetone indicate that this proton comes from a CH_3-group of the 1-hydroxy-1-methylethyl radical. Therefore, we favor reaction (2) rather than (1), though the enol intermediate **2** could not be observed in the samples utilizing benzene as solvent.

Polar aprotic solvents are known to be excellent NMR. solvents for alcohols and to stabilize the enolic form of ketones [15–16]. In attempts to detect **2**, the photolysis of **1** was studied in acetonitrile-h_3 and -d_3. Fig. 2. shows an NMR. spectrum observed during the photolysis of a 0.1 M solution of **1** in CD_3CN. The CIDNP. effects of **1**, **4**, **5**, **6** and **7** are similar to those observed in benzene (Fig. 1), indicating that in both solvents the same reactions occur. This is further supported by the reaction yields given in Table 1. In addition to the transitions of Fig. 1 photolysis in CD_3CN leads to enhanced absorptions at 4.03, 3.85 and 1.86 ppm (Fig. 2). Because of the following reasons we assign these transitions to the A, B and X_3-protons of the enol of acetone **2**:



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1) The pattern is characteristic of an olefinic ABX_3-System and the parameters ($\delta_A = 4.03$, $\delta_B = 3.85$, $\delta_X = 1.86 \cdot 10^{-6}$, $|J_{AB}| \approx |J_{AX}| \approx |J_{BX}| \simeq 1$ s^{-1}) are most compatible with propenes substituted by an electron withdrawing group [17–18], and in particular with those of vinyl alcohol [1].

2) The transitions must belong to an unstable product because they were not detectable after the reactions.

3) The phases of the CIDNP.-effects are in agreement with the formation of **2** from **3** by reaction (2).

Further support for the formation of **2** in reaction (2) is obtained from experiments carried out with the hydroxyketone **1** deuterated in the alcoholic group. The deuteration was accomplished by treating **1** with D_2O and was found successful since solutions of **1** (d_1) did not show any alcoholic transitions in contrast to those of untreated **1**. The CIDNP.-effects during photoreactions of **1** (d_1) are identical with those observed for **1** (Fig. 1 and 2). In particular, the triplet, characteristic for CH_3CDO, is not observed during or after photolysis, which implies that reaction (1) is unimportant relative to (2). Generalizing this finding, we suggest that the disproportionation reaction of hydroxy-alkyl radicals of structure $R^1R^2CH\text{-}\dot{C}R^3OH$ should always involve predominantly the transfer of the CH-hydrogen atom, rather than transfer of

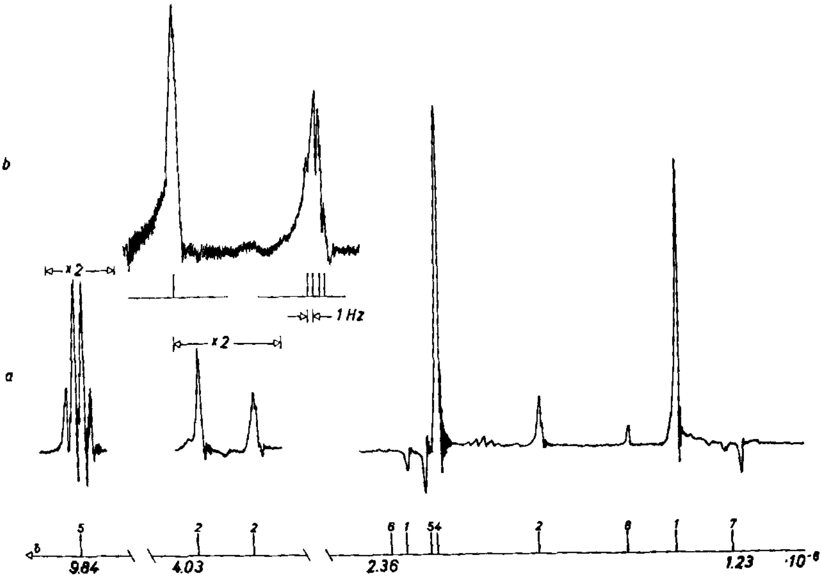


Fig. 2. (*a*) *CIDNP. during photolysis of* **1** *in* CD_3CN. (b) Resonances of **2** on expanded scale (Parts of spectrum at increased sensitivity)

the –OH-hydrogen and lead to a transient enolic species $R^1R^2C{=}CR^3OH$. In fact, the previous observations of enols [1] [7] support this view. This leads to the further conclusion that the formation of **4** and **7** by disproportionation of two hydroxyalkyl radicals (Scheme 1) is also a two step process involving the intermediary enol **2** and

$$2\,\dot{C}(OH)(CH_3)_2 \longrightarrow \mathbf{2} + \mathbf{7} \qquad (3)$$

$$\mathbf{2} \longrightarrow \mathbf{4} \qquad (4)$$

its tautomerization. The multiplet effects (A/E) of **2** and **7** are in accord with the occurence of these reactions and indicate a negative sign for J_{AX} and J_{BX} of **2**. Thus, we may have two pathways for the formation of **2**, namely the reactions (2) and (3). It is difficult to determine the relative contributions of (2) and (3) to the yield of the enol. However, as demonstrated by Fig. 3, reaction (3) must play a major role. Here are shown computer simulations of CIDNP.-spectra based on a program developed by *Kaptein* and *den Hollander* [19–20] and modified by *Henne* [21]. The calculation utilizes the radical parameters given above, the NMR.-parameters of **2** ($\delta_A = 4.03$, $\delta_B = 3.85$, $\delta_X = 1.86 \cdot 10^{-6}$; $J_{AB} = +0.9$, $J_{AX} = -0.8$, $J_{BX} = -1.2\ s^{-1}$ and the assumptions that **2** is formed a) exclusively by reaction (3) from uncorrelated radicals, b) exclusively by reaction (2) from triplet radical pairs **3** and c) by both pathways a) and b). To obtain spectrum *c*, 75% of spectrum *a* and 25% of spectrum *b* were added. This spectrum gives the best fit to the transitions of **2** displayed in Fig. 2 and indicates that both (2) and (3) are occurring.

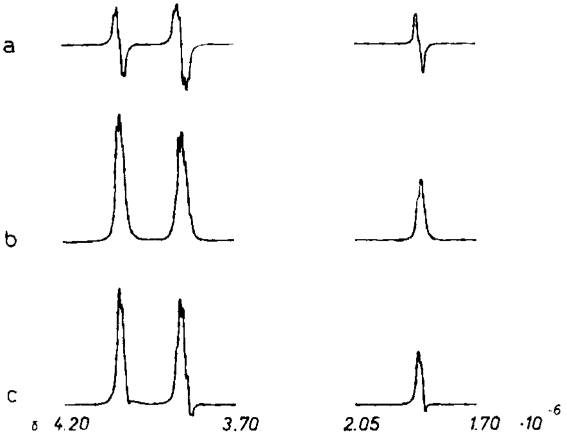


Fig. 3. *Computer simulations of CIDNP.-spectra of the enol of acetone* (**2**) (a, b, c: see text)

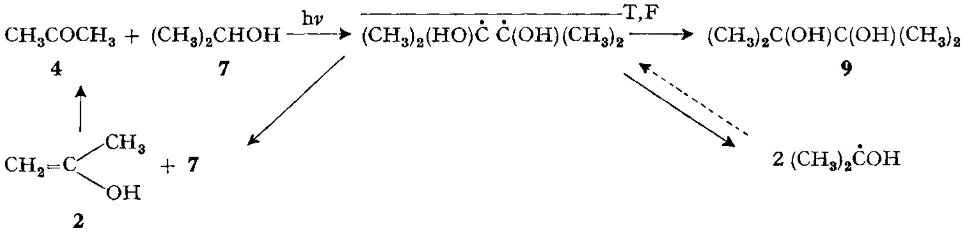
The polarization of the parent ketone **1** shows that this compound is regenerated *via* path c_2 of Scheme 1 and is consistent with the same observation in other systems [1–2] [4–5] [22]. As has been shown previously [5], the CIDNP.-intensities of the products of two competing reactions of the primary pairs, such as those of reactions c_2 and c_1 of Scheme 1, allow a determination of the ratio of the reaction probabilities $f(c_2)$ and $f(c_1)$. For this determination one compares the polarizations of the nuclei of products c_1 and c_2 which reside in the same radical moiety of the pair. In the present case equation (8) of Ref. [5] and the polarizations of the CH_3-protons of

$\dot{C}(OH)(CH_3)_2$ which appear as CH_3-protons in **1** and as the CHO-proton in **5** lead to $f(c_2)/f(c_1) = 2.3 \pm 0.3$ (benzene solvent). The same result is obtained under conditions in which the formation of **3** from uncorrelated radicals (F) is quenched by the action of a free radical scavenger. Low concentrations of CCl_4 (<0.02 M) in benzene solutions of **1**, were found to scavenge the free radicals but did not interfere with the primary triplet process leading to **3**. For a CCl_4-concentration of 0.013 M it was possible to obtain $f(c_2)/f(c_1)$ both from the CH_3-protons of $\dot{C}(OH)(CH_3)_2$ (CH_3-protons of **1** and CHO-proton of **5**) and from the CH_3-protons of $CH_3\dot{C}O$ (CH_3CO-protons of **1** and **5**). The values are $f(c_2)/f(c_1) = 2.56 \pm 0.20$ and $f(c_2)/f(c_1) = 2.58 \pm 0.20$. Obviously, combination of **3** is more favored than disproportionation. Since acetaldehyde **5** is formed only *via* c_1 its chemical yield (Table 1) combined with the ratio $f(c_2)/f(c_1)$ indicates that c_2 is a major reaction of the pair **3**. This suggests a possible formation of **3** from excited singlet **1**, but since the phases of the polarizations are dominated by the triplet reaction it seems as yet impossible to firmly establish this point. At concentrations of CCl_4 larger than 0.2 M a singlet reaction (5) which is known for other ketones [3] interferes with the reactions of Scheme 1, and becomes dominant:

$$\mathbf{1} + CCl_4 \xrightarrow{h\nu} CH_3COCl + \overline{Cl_3\dot{C}\quad \dot{C}(OH)(CH_3)_2}^{\,S}$$
$$\downarrow$$
$$CCl_3CH + \mathbf{4} \qquad (5)$$
$$(\text{at } [CCl_4] \gg 0.2\,\text{M})$$

4. Acetone and 2-Propanol. – The photochemistry of mixtures of ketones and alcohols finds its roots in the work of *Ciamician & Silber* [23] who reported in 1911 [23c] that only one product, pinacol, results from the exposure of a mixture of acetone and 2-propanol to sunlight. As in the photolysis of aromatic ketones in similar solvents [9] [24], [25] it is believed that the reaction is initiated by the ketone in an excited triplet state abstracting a hydrogen of 2-propanol to give two 1-hydroxy-1-methylethyl radicals which combine to give pinacol.

Scheme 2



From the observation of the enol of acetone **2** during the disproportionation of pair **3**, we expect that **2** is also formed in the photoreduction of acetone in 2-propanol (or other hydrogen donor media) so that the full mechanism would be as given in Scmehe 2. To prove this mechanism, solutions of **4** in **7** were irradiated in the NMR.-spectrometer and the CIDNP. effects were recorded. In fact, solutions diluted with

CD_3CN show the characteristic resonances of **2** and a typical spectrum is displayed in Fig. 4a. The assignments of the resonances are:

2: H_A $\delta = 3.69$, H_B $\delta = 3.47$, H_X $\delta = 1.86$;
4: $\delta = 2.22$;
7: C*H*OH $\delta = 3.65$, CH_3 $\delta = 1.23$;
9: CH_3 $\delta = 1.26 \cdot 10^{-6}$.

Fig. 4b shows a part of a spectrum taken under double resonance conditions to decouple the CH_3-groups of **7** from the CH-group. The phases of the CIDNP.-effects of **7** and **2** are pure A/E as is expected from *Kaptein*'s rules [13], the formation of **2** and **7** from a pair of equal radicals produced in the T-or F-mode and the radical and product parameters given previously. Furthermore, the CIDNP.-pattern of **2** is in complete agreement with the pattern calculated (Fig. 3a).

It seems of some interest to estimate the lifetime of the enol **2**, in particular, with respect to its low equilibrium concentration of about 10^{-4}M in pure acetone at room temperature [26]. First, we note that the line-widths of the individual transitions of **2** are about 1 s^{-1} (Fig. 2 and 4), so that the lifetime cannot be shorter than 1 s. Secondly, we studied the time dependence of the polarization of the CH_3-transitions of **2** in CD_3CN after interruption of the irradiation and found a first order decay with a characteristic decay constant k = 0.214 s^{-1}.

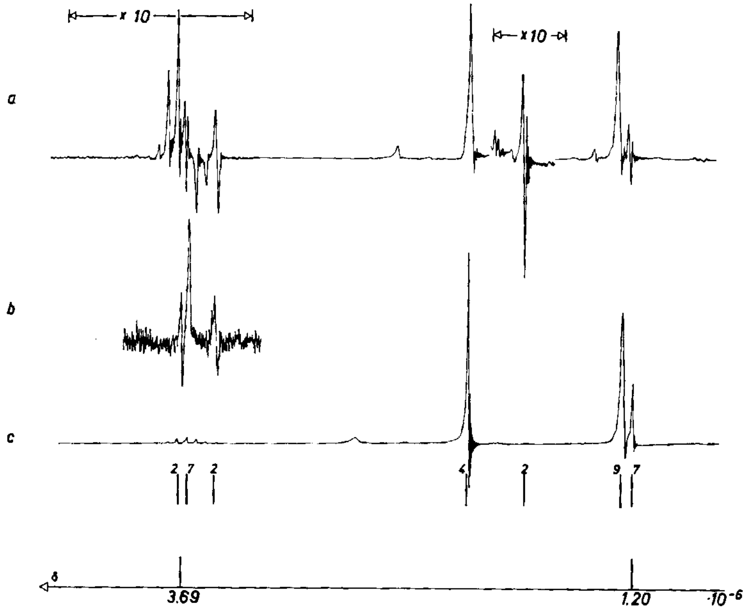


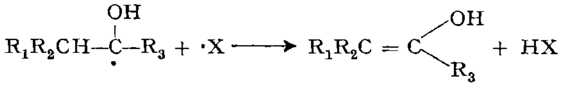
Fig. 4. *CIDNP: a) and b) during and c) after 180 s photolysis of acetone with 2-propanol in CD_3CN*
(Parts of spectrum at increased sensitivity, b: see text)

Since

$$k = \frac{1}{T_1} + \frac{1}{\tau} \tag{6}$$

where τ is the desired lifetime and T_1 is the longitudinal relaxation time [22], τ must be larger than $k^{-1} = 4.7$ s. Assuming that **2** has a T_1 similar to that of its alkene analog, isobutylene, in CD_3CN which is $T_1 = 7$ s (6) finally leads to the estimate of $\tau \approx 14$ s. Under similar conditions vinyl alcohol has $\tau \approx 25$ s [22]. We believe that these values are strongly influenced by acid impurities in our systems and do not represent the inherent lifetimes of the species. In fact, *McMillan et al.* have observed **2** in the gas phase photolysis of 2-pentanone and have determined the half-life of **2** as 3.34 ± 0.11 min. [27].

5. Concluding Remarks. – The present study confirms the generality of a disproportionation reaction of hydroxy-alkyl radicals leading to an enolic species by transfer of a β-hydrogen atom



$$R_1R_2CH-\overset{OH}{\underset{\bullet}{C}}-R_3 + \cdot X \longrightarrow R_1R_2C=C\begin{smallmatrix}OH\\R_3\end{smallmatrix} + HX \qquad (7)$$

Except for the previous CIDNP.-studies [1] [7] we have not found any formulation of this reaction in the extensive literature dealing with free radical chemistry though the reaction is a simple analog of the disproportionation of alkyl radicals leading to alkanes and alkenes. We believe that (7) has simply been overlooked because of the instability of the enolic species.

In this and the previous CIDNP.-studies [1] [7], the enols were detected because they show large signal enhancements. This demonstrates the possibilities of CIDNP. as a mechanistic probe, particularly in the detection of intermediary products [28].

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209. Zur Kenntnis der 4-Thioglucose

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Zusammenfassung. Die aus 1,6;3,4-Dianhydro-D-galaktopyranose (**2**) erstmals hergestellte 4-Thio-D-glucose, welche fast ausschliesslich in der Thiophanoseform **19** vorliegt, ist hygroskopisch, oxydationsempfindlich und zersetzlich. Die wässerigen und äthanolischen Lösungen der 4-Thio-D-glucose sind besser haltbar, ebenso das in der Pyranoseform vorliegende Natriummercaptid **15**.

1,6;3,4-Dianhydro-D-galaktopyranose (**2**) ist in Gegenwart von äquimolekularen Mengen Natriummethylat aus 1,6;3,4-Dianhydro-2-O-tosyl-D-galaktopyranose (**1**) durch Photolyse [1] der methanolischen Lösung im 254-nm-Bereich mit den dazu besonders geeigneten handelsüblichen Niederdruck-Entkeimungslampen einheitlich, in ausgezeichneter Ausbeute und wesentlich einfacher als beschrieben [2] zugänglich. Bei länger dauernder Bestrahlung entstand, offenbar über das primäre Reaktionsprodukt **2** unter Anlagerung von Methanol, in beträchtlichen Mengen die 1,6-Anhydro-4-O-methyl-D-glucose (**11**).

Umsetzung der Dianhydroverbindung **2** mit Natriumbenzylsulfid in Methanol führte recht einheitlich zur 1,6-Anhydro-S-benzyl-4-thio-D-glucose **3**, deren Acetylderivat **4** im NMR.-Spektrum 6 Acetylprotonen in 2 Singuletten bei 2,06 und 2,12 ppm, die Methylenprotonen als Singulett bei 3,94 ppm und die 5 Phenylprotonen bei 7,3 ppm zeigte. H(4) erschien bei 2,62 ppm mit $J_{4,3} = 3$ Hz und $J_{4,5} = 2$ Hz. Die weiteren Kopplungen $J_{1,2} = 1,5$ Hz und $J_{2,3} = 2,5$ Hz waren ebenfalls für die Glucosekonfiguration charakteristisch. Entkopplungsversuche bestätigten die Anordnung der Benzylthiogruppe am C(4).

Reduktive Entfernung des Benzylrests aus **3** erfolgte mit Natrium in flüssigem Ammoniak. Die Reindarstellung des Mercaptans **7**, das im IR.-Spektrum die Thiolschwingung bei 2575 cm^{-1} aufwies, geschah über das Triacetylderivat **5**, welches im IR. durch die S-Acetylbande bei 1685 cm^{-1} und im NMR. durch das S-Acetylsingulett bei 2,38 ppm, das H(4) Proton bei 3,72 und Kopplungskonstanten der Ringprotonen von 1–3 Hz, entsprechend der Glucosekonfiguration, charakterisiert war. Das Mercaptan **7** oxydierte sich beim Stehen an der Luft, wobei das als krist. Acetylderivat **9** isolierte Disulfid **8** als Hauptprodukt entstand. Für ein weiteres, ebenfalls als Acetylderivat isoliertes Zersetzungsprodukt erscheint die Bis-thioäther-Struktur **10** möglich.

Durch Acetolyse in Gegenwart katalytischer Mengen konz. Schwefelsäure wurde aus dem 1,6-Anhydro-triacetylderivat **5** glatt und einheitlich die 1,2,3,6-Tetra-O-