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46. Chemically Induced Dynamic Nuclear Polarization XI[1]) Intermediary Vinyl Alcohol During Photochemical Reactions of Acetaldehyde and of Acetoin

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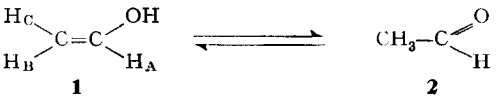
Herrn Prof. Dr. *M. Viscontini* zum 60. Geburtstag gewidmet

(11. XII. 72)

Summary. Vinylalcohol, formed by disproportionation of α-hydroxyethyl radicals, is detected by NMR. spectroscopy during photoreactions of acetaldehyde and acetoin in solution and slowly tautomerizes to acetaldehyde.

At room temperature, the equilibrium concentration of vinyl alcohol **1** has been estimated to be at least seven orders of magnitude lower than that of the keto isomer, acetaldehyde **2**, *i.e.* to be lower than the detection limit of most physical techniques [2] [3]. This has impeded the determination of spectroscopic properties of this most simple enol.



1 **2** (1)

During photolysis of **2** and of 2-hydroxybutan-3-one (acetoin, **3**) in the probe of a modified HA-100 ^{1}H-NMR. spectrometer, we detect **1** as thermally unstable radical reaction product, and observe its vinyl proton spectrum highly enhanced by chemically induced dynamic nuclear polarization (CIDNP.) [4] [5] [6]. Fig. 1 shows ^{1}H-NMR.-spectra taken at room temperature during irradiation of **2** (a) and **3** (b), 0.2 M in benzene, with the beam of a high pressure mercury capillary lamp filtered to transmit radiation of wavelength 300 nm $\leqslant \lambda \leqslant$ 350 nm. During the periods of observation conversion was less than 10%. The same CIDNP. effects were found with benzene-h_6, benzene-d_6, cyclohexane-h_{12}, cyclohexane-d_{12}, and octamethyltetrasiloxane as solvents.

The Table gives the assignments of the transitions 1 through 10 of Fig. 1 to the various reaction products together with the description of the CIDNP.-effects in the

[1]) For part X of this series: see [1].

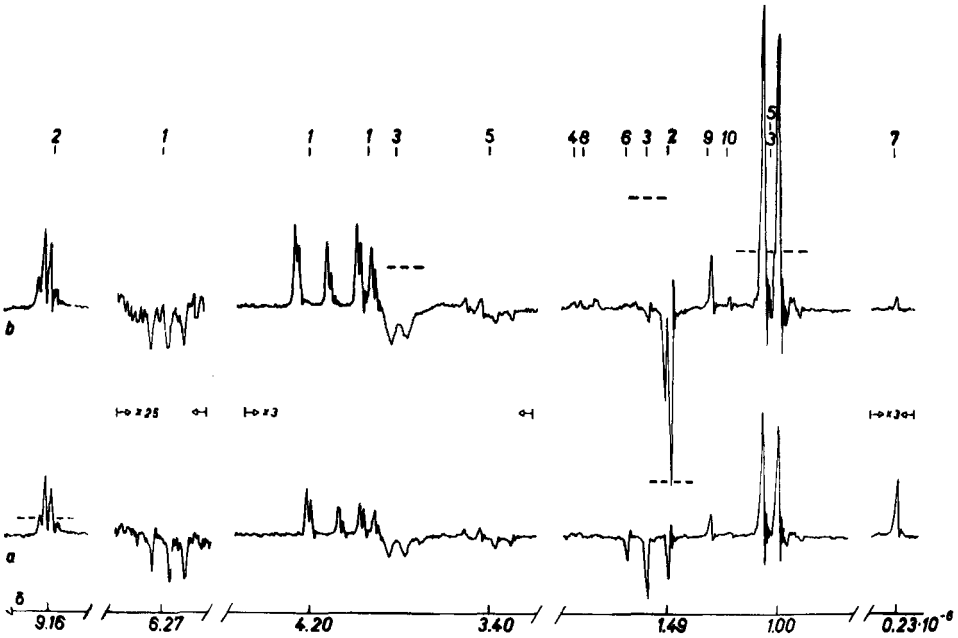


Fig. 1. *CIDNP. during photolysis of acetaldehyde (a) and acetoin (b) in benzene* (parts of the spectrum at increased sensitivity). ––– denotes line intensities before irradiation. 1 to 10 refer to line positions of reaction products, see Table.

Assignments of CIDNP. transitions

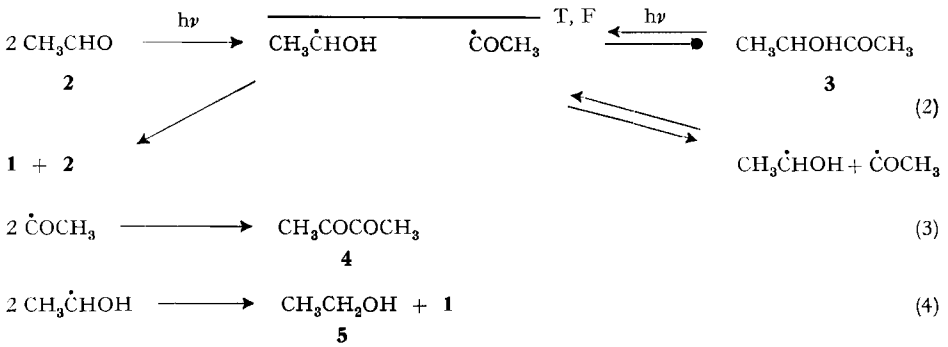
Transition	position[a])	CIDNP.	product
1	6.27 q	E+A/E	**1** (see text)
	4.13 q	A+A/E	**1** (see text)
	3.91 q	A+A/E	**1** (see text)
2	9.16 q	A+A/E	**2** CH_3–CHO
	1.49 d	E+A/E	**2** CH_3–CHO
3	3.80 q	E+A/E	**3** $CH_3CHOHCOCH_3$
	1.57 s	E	**3** $CH_3CHOHCOCH_3$
	1.03 d	A+A/E	**3** $CH_3CHOHCOCH_3$
4	1.92 s	A	**4** $CH_3COCOCH_3$
5	3.41 q	A+A/E	**5** CH_3 CH_2OH
	1.02 t	E+A/E	**5** CH_3 CH_2OH
6	1.65 s	E	CH_3COCH_3
7	0.23 s	A	CH_4
8	1.87 s	A	unassigned
9	1.30 s	A	unassigned
10	1.22 s	A	unassigned

[a]) δ in 10^{-6} *vs* TMS, benzene solvent; see Fig. 1.

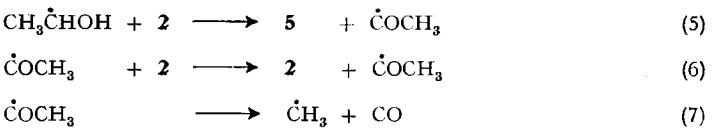
usual nomenclature (A = enhanced absorption, E = emission, A/E = absorption/emission type multiplet effect) [4] [5] [6]. For transitions 2–7 the assignments are based on comparisons with authentic material. 8–10 denote yet unidentified products. Transitions 1 are assigned to the vinyl protons A, B, C of vinyl alcohol **1** because of the following reasons: The pattern is characteristic for an olefinic ABC-system, and the parameters ($\delta_A = 6.27$, $\delta_B = 3.91$, $\delta_C = 4.13$; $J_{AB} = 6.5$, $J_{AC} = 14.0$, $J_{BC} = 1.8\ s^{-1}$) are compatible best with an oxygen substituted vinyl group [7] [8]. The transitions must belong to an unstable product since they were not detectable after reaction, and, further, addition of traces of *p*-toluenesulfonic acid or other acids prevents their intermediary detection as anticipated for **1** because acids increase the rate of tautomerization (1).

Application of the rules of CIDNP., based on the radical pair theory [4] [5] [6], and using the literature values [9] [10] for the *g*-factors and hyperfine splittings of the α-hydroxyethyl and acetyl radicals, demonstrates that all major CIDNP. effects are consistent with the reactions of the Scheme.

Scheme



Thus, based on the similarity of the CIDNP. effects of Fig. 1, we propose that solutions of **2** and **3** undergo the same primary radical reactions. In the case of acetaldehyde reaction of excited with ground state **2** (or of an excimer) serves as initiation, while the hydroxyketone **3** suffers Type I cleavage on photo-activation. Both processes lead to the same α-hydroxyethyl-acetyl primary radical pair. Reactions like (5)–(7) of the primary radicals, leading to the products **2**–**5**, acetone, methane and the unidentified products are likely, but do not contribute to the CIDNP. effects.



In accord with the formation of **1** by the disproportionation reactions (2) and (4) of α-hydroxyethyl radicals, the polarization of the hydroxyproton of **1** cannot be observed since this proton is only weakly coupled with the electron spin in the hydroxyethyl radical precursor [9].

Apart from the CIDNP. effects, the reactions of the scheme are supported by observation of **3**, **4** and **5** as products after photolysis of **2** and of **2**, **4** and **5** as products after photolysis of **3**. Furthermore, α-hydroxyethyl radicals have been detected by electron spin resonance during irradiation of **2** and **3** [9] [11], the Type I cleavage of **3** has been established previously [12] and the bimolecular reaction of excited aldehyde to give α-hydroxyethyl has also been proposed [9].

Additional confirmation is obtained from CIDNP. experiments using benzene solutions of **2** or **3** containing carbon tetrachloride, which should act as efficient radical scavenger.

$$CH_3\dot{C}HOH + CCl_4 \longrightarrow CH_3CHClOH + \cdot CCl_3 \quad (8)$$

$$CH_3CHClOH \longrightarrow \mathbf{2} + HCl \quad (9)$$

$$\dot{C}OCH_3 + CCl_4 \longrightarrow CH_3COCl + \cdot CCl_3 \quad (10)$$

As expected from (10), in the presence of 0.05 M CCl_4 acetylchloride ($\delta = 1.73 \cdot 10^{-6}$, *s*, A) is found as a major product and polarized species. In agreement with expectation, reactions (8) and (9), the CIDNP. intensities of **2** are stronger and **1** cannot be observed. Also, the intermediate transitions 4–10 of Fig. 1 are not detectable. Consequently, it is evident that the corresponding compounds (Table) are in fact formed by reactions of free radicals. The results allow several further conclusions. Firstly, the Type I cleavage of acetaldehyde known from gas phase photochemistry [13] is not important for solutions of concentrations 0.1 M or higher. Here, the photoreduction of excited aldehyde by oxidation of another aldehyde molecule is predominant. We have evidence that the same mechanism applies for other aliphatic aldehydes in solution [14] and it has been previously found to hold also for benzaldehyde [15]. Secondly, the line width of the ^{1}H-NMR. transitions of about 1 s^{-1} indicates a life time of vinyl alcohol of 1 s or longer in acid free solutions. Therefore, the tautomerization of **1** (1), if not catalyzed, is rather slow. Finally, the detection of vinyl alcohol reveils the potential of CIDNP. as a tool for the observation of unstable reaction products as a consequence of the large signal enhancements. Another example of this application of CIDNP. is the recent detection of the enol of acetophenone by *Ward et al.* [16].

A full account of the experimental details, reaction product yields, other mechanistic studies on photoreactions of aldehydes and computer simulations of the CIDNP. effects which further support the conclusions of this paper will be published later in this Journal.

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47. Synthese von Haschisch-Inhaltsstoffen

5. Mitteilung[1])

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(23. IX. 72)

Summary. A (–)-Δ^8-6a,10a-*trans*-tetrahydrocannabinol analogue, with a methyl-(3-dimethylamino-propyl)-amino side-chain instead of the *n*-pentyl radical in the naturally occurring product, has been synthesized by condensing 5-methylamino-resorcinol tosylate with (+)-*trans*-*p*-2,8-menthadien-1-ol.

1. Einleitung. - (–)-Tetrahydrocannabinol (im folgenden THC genannt), das aktive Prinzip des *Haschisch*, weist neben den allgemein bekannten halluzinogenen Eigenschaften eine ganze Reihe weiterer pharmakodynamischer Wirkungen auf.

Nachdem einerseits durch unsere Synthese [1] das tricyclische Gerüst des THC leicht zugänglich gemacht worden war und anderseits durch *Rapoport* [2] auch basische Produkte mit halluzinogener Wirkung aus *Marihuana* isoliert worden waren, stellten wir uns die Aufgabe, stickstoffhaltige THC-Analoga zu synthetisieren.

In dieser und in der folgenden Arbeit [3] beschreiben wir zwei ausgewählte Beispiele solcher THC-Analoga, wobei im ersten Fall die *n*-Amyl-Seitenkette des natürlich vorkommenden THC durch den in zahlreichen klassischen Psychosedativa enthaltenen Methyl-(3-dimethylamino-propyl)-amino-Rest und im zweiten Fall durch die N-Methyl-3-propyl-pyrrolidin-3-yl-Gruppe ersetzt wurde, welche interessante analgetische Eigenschaften besitzen soll [4].

Beide Beispiele sind zugleich eine Illustration für die Verallgemeinerungsfähigkeit unserer THC-Synthese [1].

2. Darstellung von 5-Monomethylamino- bzw. 5-Dimethylamino-resorcin. - Als Ausgangsmaterial für die geplante Kondensation benötigten wir geeignet substituierte Alkylaminoderivate des Resorcins. Es ist längst bekannt, dass sich Phloroglucin sowohl mit Ammoniak als auch mit primären und sekundären Aminen umsetzt und dabei je nach den Reaktionsbedingungen, insbesondere der Temperatur, eine oder mehrere Hydroxylgruppen austauscht [5]. Mit Ammoniak [6] wird die erste Hydroxylgruppe bereits bei Raumtemperatur ausgetauscht, die zweite bei erhöhter Temperatur, die dritte erst in Gegenwart eines Katalysators, etwa wie bei einem einfachen Phenol. Unsere eigenen Versuche mit Monomethylamin und Dimethylamin

[1]) 4. Mitt. s. [1].