CIDNP STUDY OF THE PHOTOCLEAVAGE OF BENZYL DERIVATIVES

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<u>Summary</u>. Evidence of the mechanistic pathways involved in the acetone sensitized homolytic photocleavage of benzyltrialkylammonium salts and other benzyl derivatives is obtained by CIDNP.

Recent papers by McKenna and coworkers on the photochemical cleavage of benzylammonium compounds ( $\emptyset$ -CH<sub>2</sub>-NR<sub>3</sub><sup>+</sup>) and other benzyl derivatives ( $\emptyset$ -CH<sub>2</sub>-X) provided good insight into the mechanistic pathways involved in their unsensitized and acetone-sensitized homolysis and/or heterolysis.<sup>1</sup>

In spite of the large amount of experimental data, some discrepancies remain between McKenna's work and papers by other authors.<sup>2</sup>

Since the homolytic pathway yields radical pairs, a CIDNP study should reveal further details about the reaction mechanism. Because of our interest in the behaviour of radical ions in polar solvents, we investigated the photolysis of many benzyl derivatives under conditions essentially similar to those of our previous photoinduced electron transfer CIDNP studies between tertiary aliphatic amines and a variety of acceptors in polar solvents.<sup>3</sup> Therefore,  $CD_3CN$  and  $CD_3OD$  were chosen as solvents. Since our high pressure mercury-xenon lamp (Hanovia 977-B-1, 290 <  $\Lambda$  < 330 nm) did not allow direct excitation of any benzyl compound, we limited our experiments to their sensitized photolysis. As a sensitizer, acetone ( $E^T = 79-81$  kcal/mole) gave the best results, whereas both acetophenone ( $E^T = 74$ ) and benzophenone ( $E^T = 69$ ) failed in generating any polarization in the system during photolysis; this could suggest that triplet energy for those benzyl derivatives which show CIDNP upon acetone sensitization, lies in the range  $91 < E^T < 74$  kcal/mole.

As a model compound for our studies on benzyltrialkylammonium derivatives we chose  $\oint -CH_2 - N(CH_3)_3^+ PF_6^-$ , due to its good solubility in organic solvents.  $10^{-4}$  Molar solutions were photolized directly in the modified probe of a 60 MHz spectrometer in the spinning quartz NMR tube. The spectra recorded in  $CD_3CN$  and  $CD_3OD$  (in the presence of 3%  $CD_3COCD_3$ ) respectively are shown in Figure 1 The Table lists the CIDNP found in products and reactants.

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Fig. 1. 60 MHz <sup>1</sup>H NMR spectra observed during the irradiation of  $C_{6}H_{5}CH_{2}\overline{N}(CH_{3})_{3}PF_{6}^{-}$  in  $CD_{3}CN$  (*b*),  $CD_{3}OD$  (*c*), and the dark spectrum in  $CD_{3}CN$  (*a*).

Table NMR and CIDNP data of starting material and reaction products showing CIDNP<sup>3</sup>

Compound	$c_5^{H_5} - c_{H_2} - \dot{N}(c_{H_3})_3$			с <sub>6</sub> н <sub>5</sub> — сн <sub>3</sub>		$(CH_3)_2^{\dagger} = CH_2$		$(CH_3)_2 N - CH_2 - OR$		
CIDNP	Ew	Ew	Ew	Am	As	As	As	As	As	-
Chemical shift (ppm)(d	5)7.5	4.4	3.0	7 2	2 3	3.7	7.9	2.7	4 5	

<sup>8</sup>A = Enhanched absorption (+); E = emission (-), s =strong, m = medium; w = weak. Further details partaining to the NMR spectra of iminium ions have been given elsewhere.<sup>4</sup>

According to the Kaptein sign rules for CIDNP,<sup>5</sup> the phase of the CIDNP resonance is governed by four parameters radical pairs multiplicity ( $\mu$ ), type of products ( $\epsilon$ ), g value difference (Ag) and hyperfine coupling constants (a). The sign of CIDNP lines found in the reaction products are consistent with the expected one from triplet radical pairs ( $\mu$  > 0) resulting from the photocleavage of the initial photoexcited triplet state of the salt as iscutlined further in the following. for the aminylium radical ( $\Delta g$  > 0 relative to benzyl)  $a_{\rm H}$  of the  $\alpha$ -protons is large and positive, for benzyl radical ( $\Delta g$  < 0)  $a_{\rm H}$  of the CH<sub>2</sub> protons as well as those of the ortho and para protons are negative. Furthermore, for an in cage process  $\epsilon$  > 0, and thus  $\mu$  must be positive, *i.e.* the radical pairs have triplet precursors Accordingly, Scheme I is consistent with McKenna's suggestions. 1a



Similar results were obtained using bromide, chloride, acetate or  $SbF_6$  as anion in the salt, but not with iodide. Possibly, lack of CIDNP in the latter case could be due to the suggested triplet quenching behaviour of iodide anions.<sup>1a</sup>

In addition to the products showing CIDNP and listed in the Table, evidence for the following products was found in the darb spectrum after irradiation times of 20 minutes bibenzyl, dimethylamine and trimethylamine, all lacking CIDNP however.

In CD<sub>3</sub>OD as a solvent, or even in CD<sub>3</sub>CN upon addition of few drops of CD<sub>3</sub>OH, the enhanched absorption due to the iminium salt (3) disappears, while lines of similar intensities arise which appear to be due to the addition product  $(CH_3)_2NCH_2OCD$ ,<sup>2a</sup> which also explains the formation of dimethylamine through the reaction.

7 (3) + ROD 
$$\longrightarrow$$
 (CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>OR + D<sup>+</sup>  $\xrightarrow{\text{ROD}}$  (CH<sub>2</sub>)<sub>2</sub>ND<sub>2</sub> + CH<sub>2</sub>(OR)<sub>2</sub>  
4. 5.

Similarly, water or other alcohols (ROH,  $R = CH_3$ ,  $C_2H_5$ ,  $1so-C_3H_7$ ) when added to the  $CD_3CN$  solution of the benzylammonium salt, caused the enhanched absorption due to (3) to disappear, thereby producing (4), showing a alight difference in chemical shift of the methylene protons

When the bulky tert-butyl alcohol is added, however, no changes in the resonance lines of  $\binom{3}{3}$  are noticed. The steric requirements for the nucleophilic addition of ROH to C=N<sup>+</sup> bond can also be seen in the photolysis of  $\[mu]CH_2 \[mu](C_2H_5)_3 \]PF_6^-$  in CD<sub>3</sub>OD. In this system the enhanced absorption due to the iminium cation  $(C_2H_5)_2 \[mu]N=CHCH_3^6$  does not disappear in spite of the fact that CD<sub>3</sub>OD is present in large concentration.

Finally, a brief mention should be made of the small enhanced absorption shown by  $N(CH_3)_3$  (Figure, singlet at 2.8 ppm), which was proven in separate experiments to be due to the second-ary reaction of the amine with triplet acetone.<sup>7</sup>

Furthermore, the small but detectable emission of the starting compounds  $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$  in our opinion is due to the secondary reaction (Scheme I, reaction  $\theta$ ) of the radical pair carrying the polarization typical for cage escape. Due to the opposite character of  $ØCH_2$ . (nucleophilic) and  ${}^{+}NR_3$  (electrophilic),<sup>8</sup> the recombination reaction 6 is most likely fast enough to avoid complete relaxation.

We have also investigated the acetone photosensitized photolysis of  $ØCH_2^{-X}$  (X = Br, Cl, I, CN, OMe, OTs) in  $CD_3^{-}CN$ : poor CIDNP signals were obtained for X = Cl or Br, but only when some  $CH_3^{-}OH$  was present in the system. Universally, the observed polarization stems from the product  $ØCH_2^{-}OH$  and appears in A/E mode. Even at higher sensitivities no other polarization was detected.

Clearly, 2-phenylethanol stems from an in cace recombination in F pairs, according to Scheme II.

$$s^{3} + \&CH_{2}-C1 \longrightarrow s + \overleftarrow{\&CH_{2} \cdot C1}^{T} \xrightarrow{dlffusion} \&CH_{2} \cdot + \cdot C1$$
  

$$\cdot C1 + CH_{3}OH \longrightarrow HC1 + \cdot CH_{2}OH$$
  

$$\overrightarrow{\&CH_{2} \cdot \cdot CH_{2}OH} \xrightarrow{F} \&CH_{2}CH_{2}OH$$
  

$$2 \&CH_{2} \cdot \longrightarrow \&CH_{2}CH_{2}\emptyset \quad (no \text{ polarization})$$

## Scheme II

Due to the triple multiplicity of the mimary radical pairs and the unavailability of in cage reaction in this system, it is reasonable to assume that the main homolytic product<sup>1C</sup> derives from combination of escaped radicals. Owing to the fast triplet/singlet intersystem crossing<sup>9</sup> of the radical pairs

$$\overrightarrow{\phi_{\text{CH}_2} \cdot c1} \xrightarrow{\text{T}} \overrightarrow{\phi_{\text{-CH}_2} \cdot c1} \xrightarrow{\text{S}} \phi_{\text{CH}_2\text{-}c1}$$

we expected some polarization in the starting compounds also. The lack of CIDNP however should suggest that the intersystem crossing is slower than diffusion from the cage.

The lack of CIDNP for other products unfortunately does not allow conclusive evidence about the electron transfer between the radical pairs to form a ion pair, nor does it yield any information about the possibility of direct population of the ion pairs from the excited triplet benzyl chloride

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