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THE ^{13}C CIDNP STUDIES ON THE PHOTOLYSIS OF METHYL DIAZOACETATE IN CHLORO-SUBSTITUTED METHANES

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The photolysis of methyl diazoacetate in CCl_4, $CHCl_3$, CH_2Cl_2, and $CFCl_3$ has been examined by the ^{13}C CIDNP methods. The insertion products $Cl_2XCCHClCO_2CH_3$ (X = Cl and H) show emission for the carbonyl and C-3 carbons and enhanced absorption for C-2. The cage recombination of geminate pairs $\overline{Cl_2XC\cdot \ \cdot CHClCO_2CH_3}$ formed by the cleavage of the corresponding chloronium ylides is responsible for the polarization.

On the analogy of the fully elucidated photochemistry of diazomethane in halomethanes, a radical chain mechanism was proposed by Urry and Wilt for the photolysis of diazoacetates to give the C-Cl insertion products.1) However, the overall product yields as well as the quantum yield in these reactions are usually low.2) Migita and co-workers showed that the products from the benzoyl peroxide initiated decomposition of ethyl diazoacetate in chloro-substituted methanes are different from the photochemical ones, thus providing chemical evidence in support of the nonradical chain mechanism. For the photochemical reaction, they suggested an alternative mechanism in which the alkoxycarbonyl carbene attacks a chlorine atom of the solvents to give the chloronium ylides which then undergoes intramolecular rearrangement.3) More recently Cocivera and Roth argued for the original radical chain mechanism from the ^1H CIDNP study.4) The conclusion which is based on the decay lifetime of the emission signal due to the α-proton of methyl 2,3,3,3-tetrachloropropionate was, however, found elusive.5)

We have examined the photochemical decomposition of the solutions of methyl diazoacetate in carbon tetrachloride, chloroform, dichloromethane and fluorotrichloromethane in the ^{13}C nmr cavity,[6] and have found that the CIDNP patterns are in accord with the cage recombination of geminate pairs $\overline{\mathrm{ClXYC\cdot\ \cdot CHClCO_2CH_3}}$ (X = Y = Cl; X = Cl, Y = H; X = Y = H; X = Cl, Y = F) but are inconsistent with a radical chain mechanism.

The Fourier transform pulsed nmr spectra were obtained with the aid of a Varian NV-124 computer system from the free induction decay signals accumulated during a given 800 sec span under irradiation on five batch solutions. A short radio frequency pulse of 10 μsec width was applied with the aquisition time of 0.8 sec on the 4096 data points over the 2500 Hz spectral width. In Figure 1 is shown an example of the ^{13}C nmr spectrum taken during the photolysis of a 8.5 mol % solution of methyl diazoacetate in carbon tetrachloride. We note two emission lines at - 0.7 and 67.1 ppm and an absorption signal at - 28.8 ppm in addition to absorption due to the starting material (- 42.8, OCH_3 and - 51.0 ppm, CH), the solvent[7] and hexadeuteriobenzene (31.5 ppm, triplet) employed as an internal deuterium lock. In the spectrum accumulated after irradiation was interrupted, no absorption signal is detected at the chemical shifts of the first three lines. Less than detectable amounts of the product had been formed during the limited period of irradiation of the experimental conditions. By comparison with ^{13}C chemical shifts of an authentic sample, these photo-CIDNP signals are found to be

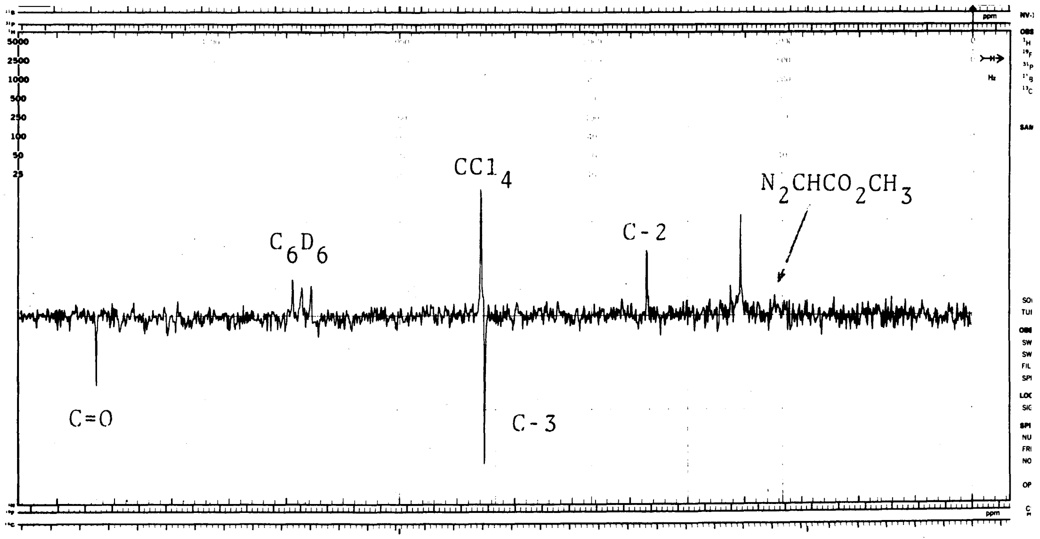

Figure 1. 15.087 MHz ^{13}C spectrum taken during photolysis of methyl diazoacetate in CCl_4 (8.5 mol %) at 56°.

due to the C-3 (E, - 0.7), carbonyl (E, 67.1), and C-2 (A, - 28.8 ppm) of methyl 2,3,3,3-tetrachloropropionate.

In chloroform the polarization signals due to the insertion product, methyl 2,3,3-trichloropropionate, are observed at 88.8 (E, C=0), -6.4 (E, C-3), and - 14.9 (A, C-2).7) With all attempts under various reaction conditions, no photo-CIDNP signal is detected for methyl 2,3-dichloropropionate formed by the photolysis of methyl diazoacetate in dichloromethane. In fluorotrichloromethane, only one emission line is observed at - 1.9 ppm where the low-field part of the C-3 doublet (J_{CF} = 297 Hz) due to methyl 3-fluoro-2,3,3-trichloropropionate should appear.

These results are fully in accord with the mechanism of the ^{13}C polarization induced in singlet recombination of geminate pairs $\overline{ClXYC\cdot\ \cdot CHClCO_2CH_3}$. The g values for the radicals $\cdot CCl_3$, $\cdot CHCl_2$ and $\cdot CHClCO_2CH_3$ are 2.0091,8) 2.0083,9) and 2.0068.10) The hyperfine coupling constants for the carbon atoms of the radical center are positive and are of the order of 35 G.11) The coupling of the ester carbonyl carbon atom in $\cdot CHClCO_2CH_3$ arises through spin polarization effect and is expected to have the value of - 13 G.12) Application of Kaptein's rules for net polarization is straightforward with knowledge of these parameters.13) Since the net effects are E(-) for the carbonyl and C-3 carbons and A(+) for C-2 carbon atom of $Cl_2XCCHClCO_2CH_3$ (X = Cl and H), it is clear that these insertion products are derived from the cage recombination of geminate pairs $\overline{Cl_2XC\cdot\ \cdot CHClCO_2CH_3}$ from the singlet precursors. It is not unreasonable to expect that the g value of the radical $\cdot CH_2Cl$ may not be far from 2.007.8,9) The failure to observe CIDNP for the photolysis in dichloromethane could very probably be due to fortuitous g value equivalence in the pair $\overline{ClH_2C\cdot\ \cdot CHClCO_2CH_3}$ rather than drastic change of the reaction mechanism on going from CCl_4 and $CHCl_3$ to CH_2Cl_2. The g value for the radical $\cdot CFCl_2$ is 2.0069.14) Net polarization cannot arise from the pair $\overline{Cl_2FC\cdot\ \cdot CHClCO_2CH_3}$. The observed emission in fluorotrichloromethane should be interpreted in terms of multiplet effect of the C-3 coupling with the fluorine atoms, although enhanced absorption of the E/A pattern is obscured by overlap with the solvent absorption.

It should be noted that the presence of a radical chain cannot be established with CIDNP. Polarization ascribed to such a process 15) originates either from a memory of the previous radical pair or from a radical disproportionation reaction instead of the apparent transfer reaction.13) The memory effect is limited to appear only when the subsequent steps are very rapid, or else the nuclear spin polarization will disappear (with rates of 10^4– 10^5 sec^{-1}) in one of the intermediate radicals as a result of efficient fluctuation of the local magnetic field produced by the spins of unpaired electrons.16) Therefore a radical chain mechanism in which ·CClXY is a chain carrier is unlikely because polarization induced at the earliest stage in geminate pairs before escape out of the cage has to be retained unrelaxed during radical chain transfer steps. CIDNP at nuclei other than the C-3 in the insertion products cannot also be explained by a radical chain mechanism. The recombination of geminate pairs formed by the homolysis of chloronium ylides $ClXYC-\overset{+}{Cl}-\overset{-}{C}HCO_2CH_3$ is proposed.17)

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6) Measured at 15.087 MHz with a Varian NV-14 spectrometer. A focused beam of uv light from a Ushio USH-500D high pressure mercury arc (500 W) was introduced from the bottom of the probe to a Pyrex nmr sample tube of 8 mm o.d.
7) Shifts in ppm are relative to the respective solvent signals and are positive when they are downfield.
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17) There are many examples of the thermal 1,2-rearrangements of ylides which exhibit CIDNP. See Chapter 8 of Ref. 13.

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