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REACTIONS OF METHOXYCARBONYLCARBENE WITH ETHERS STUDIED BY ^{1}H AND ^{13}C CIDNP[1)]

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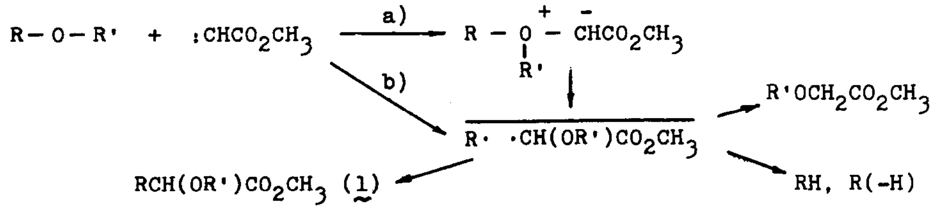
In contrast with nearly random insertion of methylene into the various C-H bonds, the reaction of electrophilic methoxycarbonylcarbene with ethers is characterized by two types of reactions, namely, the insertion reaction into the C-O bonds and the displacement reaction of one of the alkyl groups.[2)] There are two *a priori* mechanisms possible for these reactions. One is electrophilic attack of the carbene at the lone pair of electrons to form an ylide intermediate (path a of Scheme 1) which then undergoes Stevens rearrangements via the homolysis – recombination mechanism.[3,4)] The other is abstraction of an alkoxy group by the carbene to form radical pairs $\overline{R\cdot\ \cdot CH(OR')CO_2CH_3}$ directly (path b). In this communication we would like to argue for the first mechanism on the ground of the CIDNP experiments.

The proton nmr spectra obtained on a Hitachi R-20B spectrometer (60 MHz) during the thermal decomposition at 180° of *ca.* 10 vol % solution of methyl

Scheme 1



diazoacetate in dibenzyl, benzyl phenyl and benzyl ethyl ethers are shown in Figures 1a, 1b and 1c, respectively. A strong emissive doublet signal is noted in the δ 2.9 ~ 3.1 region. By comparison with the spectra of the authentic samples, these emission signals are assigned to the C-benzyl methylene protons of insertion products, 1a (R = R' = $PhCH_2$), 1b (R = $PhCH_2$, R' = Ph) and 1c (R = $PhCH_2$, R' = C_2H_5). The enhanced absorption singlet at higher field in Figures 1a ~ 1c is assigned to the methyl protons of toluene formed as an escape product. In Figures 1a and 1c we note additionally enhanced absorption at the high field side shoulder of the benzylic methylene protons of the solvents. Their chemical shifts corresponds very nicely to those of the methine protons of 1a and 1c. When the reactions are over after 20 min, all the polarized signals collapse and nothing can be seen except those of the solvents. The H_1 level and sensitivity of the recorder are adjusted so that the unpolarized products can hardly be detected.

In Figure 2 is reproduced the pulse Fourier transform ^{13}C spectrum taken on a Varian CFT-20 spectrometer (20.1 MHz). The free induction decay signal obtained by application of a short radio frequency pulse of 8 µ sec width, aquisition time of 1.023 sec and the pulse delay of 1 sec on the 8184 data points over the 4000 Hz spectral width was accumulated 1200 times on three batch solutions of 15 % methyl diazoacetate in dibenzyl ether. The emission signals at 10.8 and 68.5 ppm (down field from the benzylic carbon signal of solvent dibenzyl ether) are assigned to the α-carbon and aromatic C-1 atoms of 1a. The enhanced

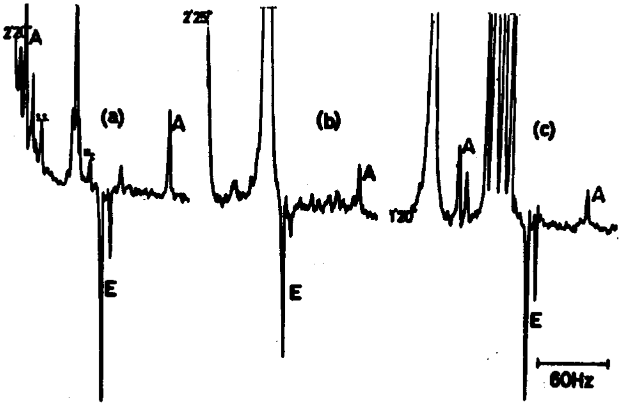


Figure 1. The 60 MHz ^1H spectra taken during thermal decomposition of methyl diazoacetate in (a) dibenzyl ether, (b) benzyl phenyl ether, and (c) benzyl ethyl ether. The time when cw scanning was started after insertion of the samples into the nmr cavity is indicated.

absorption signals at -33.2, 56.9 and 99.1 ppm are found to be due to the β, aromatic C-2 (C-6) and carbonyl carbon atoms of 1a. The enhancement factors of the polarized signals are considerably large ($\sim 10^2$).

All the results are consistent with formation of the singlet radical pair followed by cage recombination to give the insertion products 1a ~ 1c. Let us examine briefly the signs of the CIDNP signals in terms of the first order treatment of Kaptein.[4)] The signs of net polarization (Γ_{ne}, + for absorption and - for emission) are given by $\Gamma_{ne} = \mu\varepsilon\Delta g\, A_i$ where μ, ε and A_i labels indicate the multiplicity of the precursor (- for singlet precursors), the type of the products (+ for cage recombination) and the sign of hyperfine coupling of the nucleus i under consideration, respectively. Radicals $\cdot CH(OR')CO_2CH_3$ are assumed to have a g-value not far from 2.0036 of analogous radical $\cdot CH(OH)CO_2H$,[5)] while the g-value of benzyl radicals are 2.0025. The CH_2 protons of insertion products 1, for example, reside in the component of the pair which has smaller g-value and their hyperfine coupling constant is negative (-16.3 gauss).[6)] Therefore their polarization is predicted to be emission when the insertion products are formed by the cage recombination (ε, +) of the singlet radical pair (μ, -). The agreement between the theory and the observed signs of CIDNP is satisfactory as summarized in Table 1. Thus there is no doubt about the intermediacy of a radical pair for the formation of the insertion products. The product analyses by vpc are relevant to the remaining question where the radical pairs are coming from. While insertion products 1a and 1c are formed nearly in equal amounts in

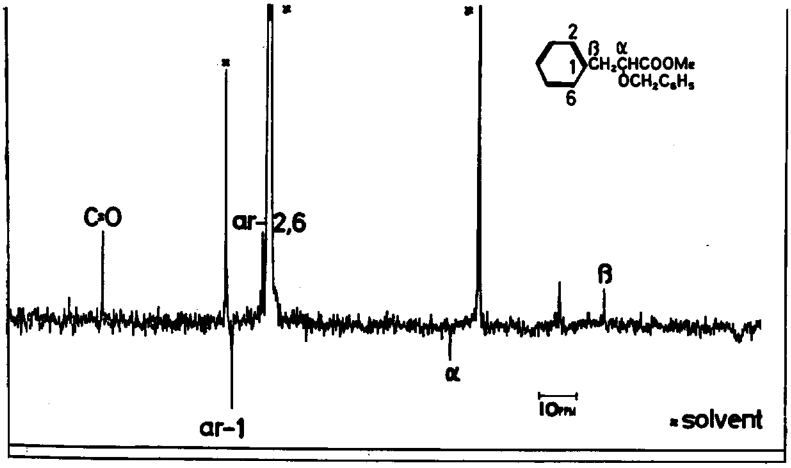


Figure 2. The 20.1 MHz C-13 spectrum taken during the thermolysis of a 15 % solution of methyl diazoacetate in dibenzyl ether.

Table 1. The theoretical and observed signs of CIDNP.

product	nucleus	μ	ε	Δg	A_i	signs theoret	signs observed
$PhCH_2CHCO_2CH_3$ | OR'	CH	-	+	+	-	A (+E/A)	A (+E/A)
	CH_2	-	+	-	-	E (+E/A)	E (+E/A)
	α-C	-	+	+	+	E	E
	β-C	-	+	-	+	A	A
	ar C-1	-	+	-	-	E	E
	ar C-2	-	+	-	+	A	A
	C=O	-	+	+	-	A	A
$PhCH_3$	CH_3	-	-	-	-	A	A

dibenzyl and benzyl ethyl ethers, respectively, the yield of methyl benzyloxyacetate is more than twice higher in the latter than in the former. The benzyloxyacetate is produced considerably more than methyl ethoxyacetate in benzyl ethyl ether. The results indicate that the ethyl group is more easily cleaved than the benzyl. Since the C-O bond energies are practically governed by the stability of the C-radicals, the observed ease of the ethyl elimination as well as the failure to detect any CIDNP on the benzyloxyacetate are not consistent with path b in Scheme 1. Formation of the ylide intermediate followed by the Hoffmann-type β-elimination of ethylene by a non-radical path is one of the most reasonable explanation for the observed results. Homolysis of the same ylide is considered to give radical pair $\overline{R\cdot\ \ \cdot CH(OR')CO_2CH_3}$.

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