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MECHANISM OF THE REACTIONS OF METHOXYCARBONYLCARBENE STUDIED BY CIDNP. IV.[1)]

DOES NOT METHOXYCARBONYLCARBENE INSERT INTO THE C-Br BONDS OF BROMOMETHANES ?

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The main products of the photochemical reactions of methyl diazoacetate with $CBrCl_3$ and CBr_2Cl_2 have been unambiguously characterized as $CCl_3CHBrCO_2CH_3$ and $CBrCl_2CHBrCO_2CH_3$, respectively. These results, together with the ^1H and ^{13}C CIDNP spectra, support the formation of these products by recombination of radical pairs $\overline{CXCl_2\cdot \quad \cdot CHBrCO_2CH_3}$ which in turn are formed by preferential attack of carbene $:CHCO_2CH_3$ on the bromine atom.

Photolysis of methyl diazoacetate(MDA) in polyhalomethanes gives methyl polyhalopropionates. Originally explained as a radical chain process,[2)] none of the experimental results such as the low quantum yield,[3)] the lack of inhibition[3)] and the formation of completely different products in benzoyl peroxide-induced decomposition[4)] supported the idea and a carbene insertion mechanism was postulated as the next possibility.[3),4)] In former papers,[1)] we reported the CIDNP aspects of the reaction with chloromethanes and uncovered that methoxycarbonylcarbene attacks chlorine atom to give a geminate radical pair which then undergoes recombination to give the apparent insertion products. The mechanism appears, however, to be in trouble when applied to reactions with bromine-containing polyhalomethanes. Whereas abstraction of bromine is generally easier than that of chlorine and application of the mechanism results in the location of bromine at C(2), the main products in the reactions with $CBrCl_3$ and CBr_2Cl_2 are reported to be methyl 3-bromo-2,3,3-trichloro-2) and 3,3-dibromo-2,3-dichloropropionates,3c) respectively. Thus we have reinvestigated the reaction of MDA with the above two polyhalomethanes and found that the assignment of the products in the literature are in error and the non-radical chain mechanism is applicable to the present cases as well.

Irradiation of a 2.6 mol % solution of MDA in CBrCl$_3$ with a high-pressure mercury arc lamp gave three tetrahalopropionates,5) **1a**(20 %), **2a**(9 %), **3a**(< 3 %), methyl dibromoacetate(7 %) and methyl 3,3-dichloroacrylate(7 %) (yields are based on nmr peak heights). Similarly a 2.7 mol % solution of MDA in CBr$_2$Cl$_2$ gave three tetrahalopropionates, **1b**(25 %), **2b**(5 %), **3b**(trace), methyl dibromoacetate(20 %) and methyl 3,3-dichloroacrylate(5 %). Independent syntheses of some tetrahalopropionates disclosed the identity of **2a** and **3b** as 3-bromo-2,3,3-trichloro-, **3a** as 2,3,3,3-tetrachloro-, **1b** as 2,3-dibromo-3,3-dichloro- and **2b** as 3,3-dibromo-2,3-dichloropropionates. Thus the main product **1a** cannot be 3-bromo-2,3,3-trichloropropionate. The 2-bromo-3,3,3-trichloropropionate structure of **1a** was established by its conversion to 2-bromo-3,3-dichloroacrylamide (mp 124 ~ 125°C. Satisfactory anal. as C$_3$H$_2$BrCl$_2$NO) on hydrolysis with aqueous barium hydroxide followed by successive action of thionyl chloride and ammonia. ^{13}C chemical shifts (Table 1) and ^{13}C spin-lattice relaxation times of **1a** in reference to those of other tetrahalopropionates are also consistent with the structural assignment. The ^{13}C shift of C(2) is either δ *ca.*68 or 57 depending on whether C(2) carries a chlorine or bromine atom, respectively. The C(3) shifts of CCl$_3$-, CBrCl$_2$- and CBr$_2$Cl- are 95, 76 and 56, respectively.6) ^{13}C spin-lattice relaxation times were measured by the progressive saturation technique on a solution of approximately equimolar mixture of three propionates **1a**, **2a** and **3a** in CBrCl$_3$ deaerated with argon. Considerably shorter relaxation time ($11._5$ sec) for C(3) of **2a** as compared to 65 and 73 sec for C(3)'s of **1a** and **3a**, respectively, indicates the location of bromine on C(3) in **2a**.7)

Table 1. ^{13}C chemical shifts of methyl 2,3,3,3-tetrahalopropionates dissolved in $CBrCl_3$(shifts in ppm downfield from internal TMS).

tetrahalopropionates	carbons			
	C(2)	C(3)	C(1)	OCH_3
$CCl_3CHClCO_2CH_3$ **3a**	67.6	95.5	163.4	53.4
$CBrCl_2CHClCO_2CH_3$ **2a**, **3b**	67.7	76.7	163.1	52.9
$CBr_2ClCHClCO_2CH_3$ **2b**	68.4	56.7	163.4	53.1
$CCl_3CHBrCO_2CH_3$ **1a**	56.3	94.4	163.7	53.3
$CBrCl_2CHBrCO_2CH_3$ **1b**	57.1	75.5	163.5	53.0
$CBr_2ClCHBrCO_2CH_3$	58.3	55.7	164.0	53.1

The proton nmr spectrum obtained on a Varian NV-14 spectrometer(60 MHz) during the photolysis of a 1.7 mol % solution of MDA in $CBrCl_3$ is shown in Figure 1. The polarized signals in the δ 4.8 ∿ 5.0 region are due to the methine protons of tetrahalopropionates. The enhanced absorption signal at the lowest field is assigned to **1a**. Similarly the emissive singlet is due to **2a** and the enhanced absorption signal at the highest field is assigned to **3a**. Methyl dichloroacrylate and methyl dibromoacetate show no polarization. In Figure 2 is reproduced the pulse Fourier transform ^{13}C spectrum taken on the same spectrometer(15.1 MHz for ^{13}C). The free induction decay signals obtained by application of a short radio frequency pulse of 10 μsec width and aquisition time of 0.8 sec on the 4096 data points over the 2500 Hz spectral width were accumulated 8000 times on eight portions of a batch solution of a 6.4 wt % MDA in $CBrCl_3$. Assignments of polarized signals due to propionates are shown in Figure 2 (see Table 1 for the chemical shift values). Polarization of C(2) of **1a** and **3a** is not clear-cut in contrast to well-defined polarization due to C(1) and C(3)(*vide infra*). Along with two emission signals at 105 and 97 of at present unknown origin, the enhanced absorption due to CBr_2Cl_2 is noted at 37.

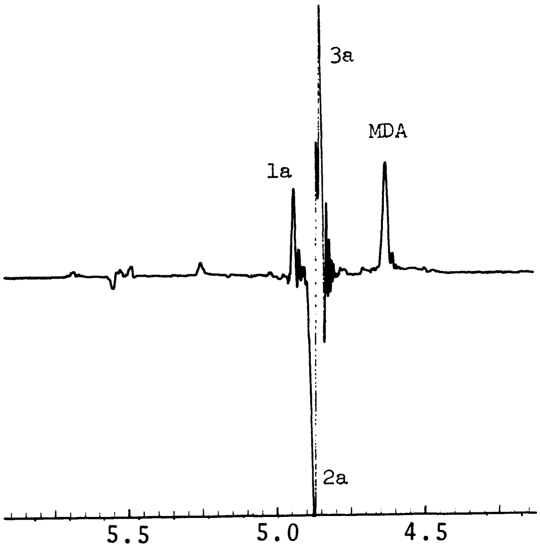


Figure 1. The 60 MHz ^{1}H spectrum taken during photolysis of MDA in $CBrCl_3$.

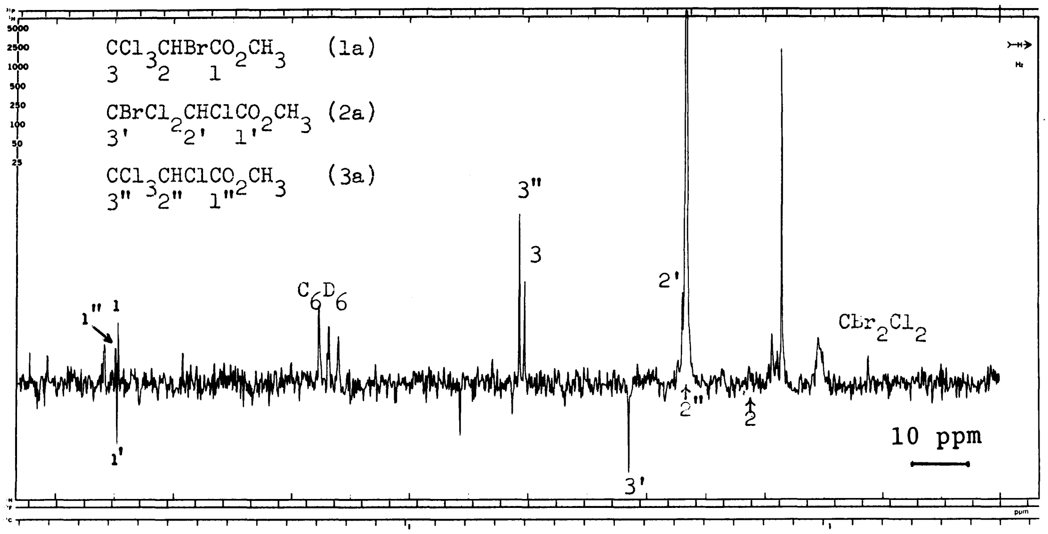
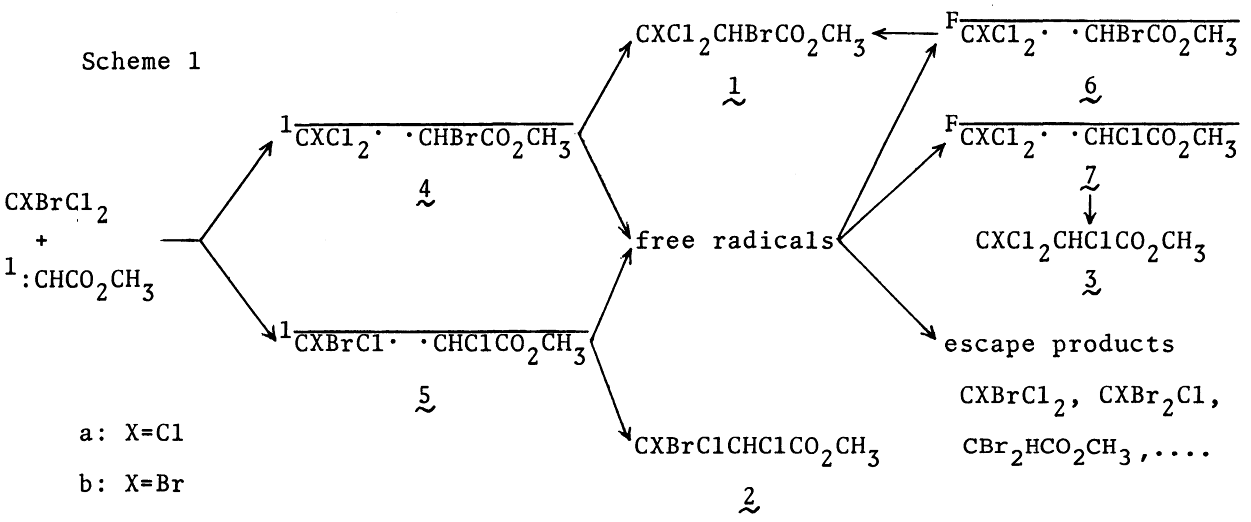


Figure 2. The 15.1 MHz ^{13}C spectrum taken during photolysis of MDA in $CBrCl_3$.

All the results including the structures of the products and the signs of ^{1}H and ^{13}C CIDNP are satisfactorily explained in terms of a mechanism similar to that for chloromethanes. Methoxycarbonylcarbene mainly attacks the bromine atom to form singlet radical pairs $^{1}\overline{CXCl_2\cdot\ \cdot CHBrCO_2CH_3}$ (4, a: X=Cl, b: X=Br) and their cage recombination leads to C-Br insertion products 1. A part of the carbene, however, attacks the chlorine atom to give $^{1}\overline{CXBrCl\cdot\ \cdot CHClCO_2CH_3}$(5) whose recombination produces products 2. Free encounter of the radicals $\cdot CXCl_2$ and $\cdot CHClCO_2CH_3$ forms radical pairs $^{F}\overline{CXCl_2\cdot\ \cdot CHClCO_2CH_3}$(7). Recombination results in the formation of products 3(Scheme 1). Naturally we must also consider free

Scheme 1



encounter pairs $^F\overline{CXCl_2\cdot\ \cdot CHBrCO_2CH_3}$(6) which may be responsible for the observed weak polarization of 1a by partial cancellation of polarization due to 4. The unknown g-value of $\cdot CBrCl_2$ is in all probability larger than 2.019 of $\cdot CHBrCO_2CH_3$.[8] Application of the Kaptein's rule[9] for net polarization predicts, for example, emission for the methine proton of 1b as long as it is formed by the recombination of 4b. The observed enhanced absorption is more appropriately considered to be due to a larger contribution of recombination of the free encounter pair 6b to polarization. Chemical yield of 1b is, however, considered to be dominated by the former process. The contribution of free encounter pairs $^F\overline{CXBrCl\cdot\ \cdot CHClCO_2CH_3}$(8) and $^F\overline{CXBrCl\cdot\ \cdot CHBrCO_2CH_3}$(9) is considered to be small because of lower concentration of $\cdot CXBrCl$ than that of $\cdot CXCl_2$. Correspondingly the formation as well as polarization of the recombination products of 9 can not be detected by nmr.

Thus methoxycarbonylcarbene does "insert" into the C-Br bond of $CBrCl_3$ and CBr_2Cl_2. The contribution of the induced decomposition appears to be larger here than in the reaction with chloromethanes. Methyl dichloroacrylate is not detected by nmr in the latter reactions but a considerable amount of it is formed in the present cases. The presence of such a process (Scheme 2) is thus indicated.

Scheme 2

$$CXCl_2\cdot \;+\; N_2CHCO_2CH_3 \xrightarrow{-N_2} CXCl_2\dot{C}HCO_2CH_3 \xrightarrow{-X\cdot} CCl_2{=}CHCO_2CH_3$$

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