Photochemistry of Methyl Diazoacetate in Chloro-Substituted Methanes. Evidence for a Chain Mechanism from Nuclear Polarization Studies

Sir:

We have uncovered evidence indicating that the photoinduced decomposition of methyl diazoacetate ($N_2CHCOOCH_3$) in chloro-substituted methanes involves a radical-chain mechanism. This conclusion was derived from nmr spectra recorded during and immediately after ultraviolet irradiation. Such nmr studies are possible when free radical intermediates are involved in the reaction, because the unpaired electrons can cause nuclear spin polarization. The polarization is retained in the diamagnetic product and is observed as enhanced nmr absorption and/or emission.[1-3] In the case of methyl diazoacetate, we found that the products give nmr emission lines which decay at rates slower than the nuclear spin relaxation rates. We interpret this slower rate as evidence for a chain mechanism.

The products of the photochemical decomposition of diazomethane and methyl diazoacetate in halomethanes were rationalized by Urry and coworkers as involving radical chain mechanisms.[4,5] Such a mechanism was convincingly established for the reactions of diazomethane because of high quantum yields.[6] However, in the reaction of methyl diazoacetate, the low overall product yields and quantum yield seemed inconsistent with a radical chain mechanism.[7,8]

We studied the photoinduced decomposition of methyl diazoacetate in solutions of carbon tetrachloride and deuteriochloroform.[9] The nmr spectra for these solutions, both before and during irradiation, are given in Figure 1. Figures 1a and 1c give the spectra for solutions (10% mol/mol) of methyl diazoacetate in carbon tetrachloride and deuteriochloroform, respectively. The higher field line can be assigned to the ester methyl group, the line at lower field to the single proton in the α position to the diazo group. Figures 1b and 1d give the spectra during ultraviolet irradiation of the carbon tetrachloride and deuteriochloroform solutions, respectively. In both cases one new signal appears as an emission line which has been assigned to the hydrogen atoms α to the ester groups of the reaction products, methyl 2,3,3,3-tetrachloropropionate (A) and methyl 3-deuterio-2,3,3-trichloropropionate (B-d_1), respectively.[10] The resonance lines for the ester protons of A and B are not observed, most likely
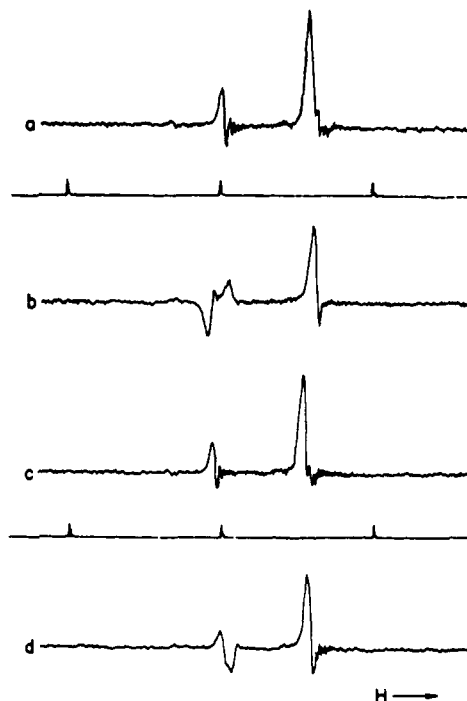

Figure 1. The proton nmr spectra (60 MHz) of methyl diazoacetate (10% mol/mol) in CCl_4 (a, b) and in $CDCl_3$ (c, d) before (a, c) and during (b, d) ultraviolet irradiation. All spectra are time averages of two passes. Frequency scales are given below traces a and c; the markers are separated by 100 Hz. The field increases from left to right.

because they are weak and have nearly the same chemical shift as the much more intense line due to the ester protons of the diazo compound. After irradia-

A

B-d_1
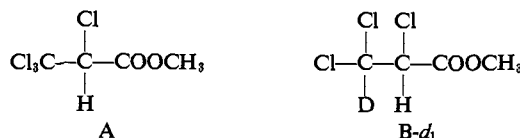
tion is stopped, the emission lines decay in about 3 min. Spectra taken 5 min after the end of irradiation appear identical with those recorded before. In particular, no absorption lines due to A or B-d_1 can be detected. Obviously, only small amounts of products have been formed during the 1-min period of irradiation. Consequently, the observed emission lines represent large polarizations.

Assuming that the signal intensity decays exponentially and that the line width is constant during the decay (*i.e.*, that the intensities are proportional to the heights of the lines), one obtains a relaxation time of about 70 sec. This value is much larger than the spin–lattice relaxation times of A and B-d_1 (1.05 and 1.04 sec, respectively, at 30 MHz).[11] The presence of radicals in the solution can be expected to shorten these nuclear spin relaxation times, since the radicals are paramagnetic.[12] Furthermore, the enhanced absorption or emission lines of other systems studied by this technique decay to normal absorption signals within seconds after the irradiation is discontinued.[2]

(1) For a review see H. Fischer and J. Bargon, *Accounts Chem. Res.*, 2, 110 (1969). Photochemically induced nuclear polarization has also been observed. See ref 2 and 3.

(2) M. Cocivera, *J. Amer. Chem. Soc.*, 90, 326 (1968); M. Cocivera and A. M. Trozzolo, *ibid.*, 92, 1772 (1970).

(3) G. L. Closs and L. E. Closs, *ibid.*, 91, 4549, 4550 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, 91, 4554 (1969).

(4) W. H. Urry and J. R. Eiszner, *ibid.*, 73, 2977 (1951); 74, 5822 (1952).

(5) W. H. Urry and J. W. Wilt, *ibid.*, 76, 2504 (1954).

(6) W. H. Urry, J. R. Eiszner, and J. W. Wilt, *ibid.*, 79, 918 (1957).

(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 272.

(8) J. W. Wilt, Ph.D. Dissertation, University of Chicago, 1964.

(9) Experimental details may be found in ref 2.

(10) Pertinent nmr data are as follows: (a) 10% solutions (v/v) in CCl_4–$N_2CHCOOCH_3$, τ 5.24 (s, 1 H), 6.28 (s, 3 H); Cl_3C–$CHCl$–$COOCH_3$, τ 5.05 (s, 1 H), 6.10 (s, 3 H); (b) 10% solutions (v/v) in $CDCl_3$–$N_2CHCOOCH_3$, τ 5.20 (s, 1 H), 6.21 (s, 3 H); Cl_2HC–$CHCl$–$COOCH_3$, 3.92 (d, 1 H), 5.33 (d, 1 H), 6.10 (s, 3 H).

(11) The authors are indebted to Mr. D. Davis for the determination of these data.

(12) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, 34, 842 (1961).

The slow decay of the emission signals due to A and B-d_1 can be rationalized by the assumption that products are still being formed after the irradiation is stopped. This could conceivably occur in two ways: (1) *via* a one-step reaction of intermediate paramagnetic species which have relatively long lifetimes, or (2) by way of a radical-chain mechanism.

The one-step reactions which could conceivably occur are the insertion of carbomethoxycarbene into a carbon–chlorine bond or the combination of a pair of radicals, chlorocarbomethoxymethyl and trichloromethyl (or dichloromethyl-d_1), which are originated by the abstraction of a chlorine atom by carbomethoxycarbene. However, the limited selectivity of carbomethoxycarbene in reactions with hydrocarbons[13] as well as the fast combination rates reported for the trichloromethyl radical[14] are inconsistent with the relatively slow decay rate of the emission lines. We, therefore, favor the alternative, radical chain mechanism, involving a reaction sequence similar to the one proposed by Urry and Wilt.[5]

Our experimental observations cannot rule out the possibility that product formation also occurs *via* competing mechanism such as the insertion, in one or two steps, of the intermediate carbene into carbon–chlorine bonds. At the present time, studies are under way to further elucidate the mechanism of the reactions discussed and the electronic spin state of the divalent-carbon intermediate.

(13) Photolytically generated carbomethoxycarbene was found to insert into the aromatic carbon–hydrogen bonds of benzene and toluene: H. D. Roth, manuscript in preparation.

(14) Reference 7, pp 247–272.

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Stereoselectivity in the Boron Trifluoride Catalyzed Rearrangement of a 1,1-Disubstituted Ethylene Oxide

Sir:

For the boron trifluoride catalyzed rearrangement of epoxides 1 stereochemical data have been obtained[1-4] which are most satisfactorily interpreted in terms of the intermediacy of the discrete carbonium ion 2.
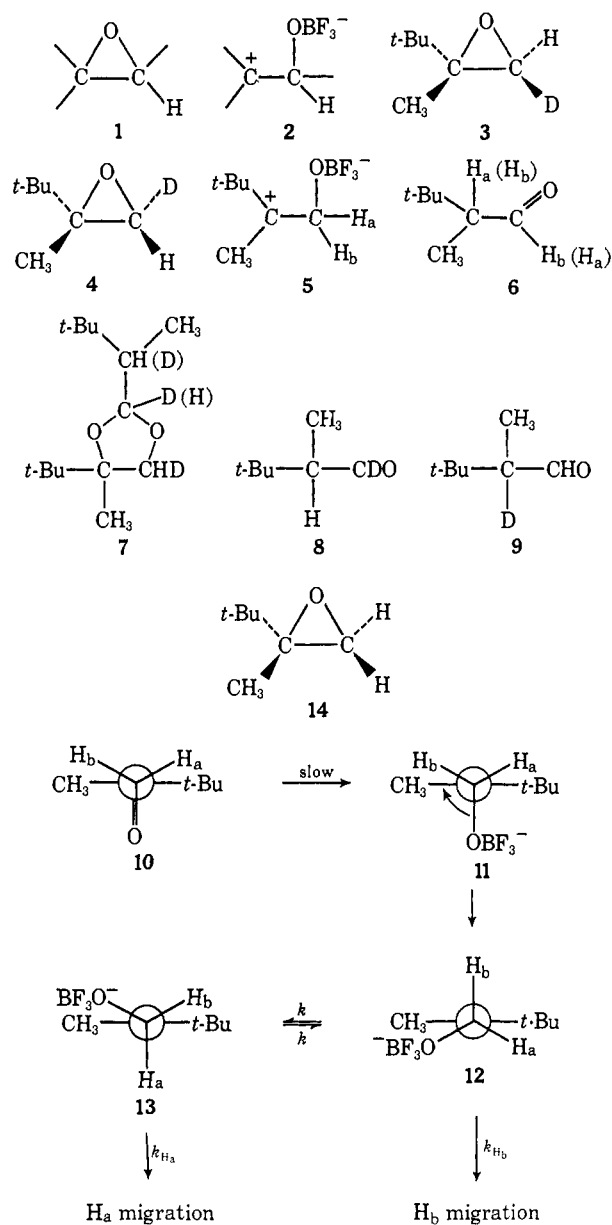
As part of an attempt to identify the factors which influence the rearrangement of the intermediate carbonium ion we examined the rearrangement of the monodeuterated epoxides 3 and 4. The intent was to determine whether or not the selection of the migrating hydrogen atom in the carbonium ion 5 → aldehyde 6 reaction depends upon the stereochemical

(1) J. M. Coxon, M. P. Hartshorn, and B. L. S. Sutherland, *Tetrahedron Lett.*, 4029 (1969).

(2) B. N. Blackett, J. M. Coxon, M. P. Hartshorn, and K. E. Richards, *Tetrahedron*, 25, 4999 (1969).

(3) J. M. Coxon, M. P. Hartshorn, and C. N. Muir, *ibid.*, 25, 3925 (1969), and references cited therein.

(4) B. N. Blackett, J. M. Coxon, M. P. Hartshorn, B. L. J. Jackson, and C. N. Muir, *ibid.*, 25, 1479 (1969).

origin of the proton relative to the bulky *t*-butyl group and the smaller methyl group.

The stereochemistry of the deuterated epoxides 3 and 4 followed not only from the synthetic routes used[5] but also the nmr spectra (60 Mc): epoxide 3,[6] 0.90 (s, 9 H, *t*-butyl), 1.21 (d, $J_{CH_3,H} = 0.8$ cps, 3 H, methyl), 2.64 ppm (q, $J_{H,CH_3} = 0.8$ cps, 1 H); epoxide 4,[7] 0.91 (s, 9 H, *t*-butyl), 1.22 (s, 3 H, methyl), 2.27 ppm (s, $W_{h/2} = 2.1$ cps, 1 H). In particular the long-range CH$_3$–H coupling[5,8] in epoxide 3 and its absence in epoxide 4 confirm the stereochemical assignments.

Reaction of each epoxide, 3 and 4, with boron trifluoride in carbon tetrachloride at 0° gave, in addition to dioxolanes (7; 50%) and an unidentified component (12%) of high boiling point, mixtures (*ca.* 33%) of

Scheme I

(5) B. N. Blackett, J. M. Coxon, M. P. Hartshorn, and K. E. Richards, to be published.

(6) Deuterium content 99.5%; isomer 3 93.4%, isomer 4 6.6%.

(7) Deuterium content 98.2%; isomer 4 96.3%, isomer 3 1.8%, undeuterated epoxide 14 1.8%.

(8) *Cf.* N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, New York, N. Y., 1964, p 115 ff.