Photolysis of Diethyl Mercurybisdiazoacetate and Ethyl Diazoacetate in Chloroalkanes^{1a}

Summary: A comparison of the reaction products from the title photolytic reactions allows the preclusion of significant carboethoxycarbene participation in the carboethoxymethyne reaction.

Sir: Photolytic decomposition of diethyl mercurybisdiazoacetate² (1) at wavelengths shorter than 290 nm has been shown to be a complicated but useful source of carboethoxymethyne (A).³

$$Hg(N_2CCO_2C_2H_5)_2 \longrightarrow 2N_2 + Hg + 2:CCO_2C_2H_5$$
1
A

We have studied the photolysis reaction of 1 in several chloroalkanes and compared the reaction products with those from the photolysis of ethyl diazoacetate (2), a precursor to carboethoxycarbene (B),⁴ in the same chloroalkanes. We now communicate the results of these studies.

$$N_2CHCO_2C_2H_5 \longrightarrow N_2 + :CHCO_2C_2H_5$$

2 B

Photolysis of 1 in chloroalkanes (2.5 g in 500 ml, 450-W medium-pressure mercury lamp with a Vycor filter, 30 min at room temperature with continuous nitrogen flushing) gave the products shown in Table I.⁵ Mercuric chloride, not mercury, was isolated in nearly quantitative yield. Small amounts of mercury-containing products were observed by mass spectrometry. Decomposition of these products may partially account for the formation of mercuric chloride. Products resulting from carbon-hydrogen insertion were not observed. Photolysis of 2 (same conditions as 1) gave the products reported in Table II.⁴

Inspection of the tables shows that the major products from 1 are C–Cl insertion products leading to ethyl chloroacetate and ethyl chloroacrylate derivatives. Control experiments indicate that the unsaturated products are probably artifacts resulting from loss of chlorine from the original saturated insertion products occurring under our isolation techniques.⁶

The reaction products from 2 show little similarity to those from 1 with the only C–Cl insertion product resulting from 1,1,1-trichloroethane. No C–H insertion products were observed and most products appear to result from free-radical reactions.^{7,8}

Carboethoxymethyne (A) in chloroalkanes could conceivably abstract either a hydrogen atom giving carboethoxycarbene (B) or abstract a chlorine atom giving carboethoxychlorocarbene (ClCCO₂C₂H₅, C) with the resulting products then arising from reaction of B or C with the chloroalkanes. However, the marked differences in reaction products from 1 as compared with 2 gives strong support for the absence of any B in the photolysis of 1. The results from Table I suggest that A may be produced from 1 in yields from 63 to 83% (combined yields of ethyl chloroacetate and insertion products). This is contingent on the absence of any intervention of C or mercury-containing carboethoxycarbenes.

Table I Diethyl Mercurybisdiazoacetate-Chloroalkane Photolysis Products

Chloroalkane ^{<i>a</i>}	Products ^b	% yield ^c
CCl4	$Cl_2C = (Cl)CO_2C_2H_5$	41
•	$Cl_3CC(Cl)_2CO_2C_2H_5$	12
	Cl ₃ CCCl ₃	52
	Unidentified	~ 2
CH ₃ CCl ₃	$CH_3C(C1) = C(C1)CO_2C_2H_5^d$	35
5 5	$CH_{3}C(C1)_{2}CH(C1)CO_{2}C_{2}H_{5}$	37
	$CH_2 = CCl_2^e$	18
	Unidentified (2)	~10
$(CH_3)_2 CCl_2$	$(CH_3)_2C = C(C1)CO_2C_2H_5$	18
	$(CH_3)_2 C(C1)CH(C1)CO_2 C_2 H_5$	7
	ClCH ₂ CO ₂ C ₂ H ₅	35
	$CH_3C(Cl) = CH_2^e$	24
	Unidentified	~16
$(CH_3)_3CC1$	$C1CH_2CO_2C_2H_5$	83
	$CH_2 = C(CH_3)_2^{e}$	22

^a Commercial reagent grade chloroalkanes were used. ^b Product identity was determined from spectral data, elemental analyses, and comparison with authentic samples when possible. ^c Product yields were determined using internal standards. ^d E:Z ratio 2.2;1: M. Verny and R. Vessiere, Bull. Soc. Chim. Fr., 746 (1970). Isolated as bromine addition product.

Table II Ethyl Diazoacetate–Chloroalkane Photolysis Products

Chloroalkane ^a	Products ^b	% yield¢
CCl ₄	$Cl_2C = C(Cl)CO_2C_2H_5$	80
CH ₃ CCl ₃	$CH_3C(C1) = CHCO_2C_2H_5$	40
0 0	Cl ₂ CHCH ₂ Cl	45
(CH ₃) ₂ CCl ₂	CICH ₂ CO ₂ C ₂ H ₅	30
	CICH, CHCI,	22
	Cl ₃ CCCl ₃	26
	$[CH_3C(C1)_2CH_2]_2$	22
	or isomer	
$(CH_3)_3CC1$	13 components	

^a Commercial reagent grade chloroalkanes were used in all cases. ^b Product identity was determined from spectral data, elemental analyses, and comparison with known samples when possible. ^c Product yields were determined using internal standards.

Using an analogy from the suggested mechanism for carbon-halogen insertion reactions for carbenes,⁴ one can speculate on a novel ylide-radical intermediate (D) in the reactions of A with chloroalkanes. Intermediate D could

$$-\overset{\downarrow}{C}-\overset{\bullet}{C}1-\overset{\bullet}{C}-CO_2C_2H_5$$

D

undergo C-Cl insertion or β elimination to give the observed products.

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- (1) (a) Presented at the 10th Midwestern American Chemical Society meet-
- (1) (a) Presented at the four Midwestern American Chemical Society meeting, lowa, City, Iowa, Nov 7, 1974.
 (2) E. Buchner, *Ber.*, 26, 215 (1895), mp 104°, observed 102–104°.
 (3) O. P. Strausz, G. J. Kennepohl, R. X. Garneau, T. DoMinh, B. Kim, S. Valenty, and P. S. Skell, *J. Am. Chem. Soc.*, 96, 5723 (1974), and reference. ences cited therein.
- (4) A. P. Marchand and N. M. Brockway [*Chem. Rev.*, 74, 431 (1974)] give an excellent review on carboalkoxycarbene reactions. Their account of the reaction between carboethoxycarbene and haloalkanes shows the reaction depends on a number of factors such as the presence of initiators or inhibitors, possible heavy atom effects, wavelength, and sensitizers. Thus the observation of different reaction products from the reaction of B with tetrachloromethane or 2-chloro-2-methylpropane found by a number of workers is not particularly meaningful to our work. We emphasize here that the same experimental conditions were used for studying the photolytic decompositions of both 1 and 2.
- (5) Compound 1 in tetrachloromethane at room temperature in the absence of light showed after 40 min the precipitation of mercuric chloride and the appearance of a singlet at ca. δ 2.0 in the NMR spectrum. This reaction

did not interfere with the photolysis reactions. No product containing this NMR signal was observed.

- (6) Preparative GLC was accomplished on a Varian A-90 gas chromato-graph using either a 5 ft by 0.25 in. 20% QF-1 column or a 10 ft by 0.12 in. 10% QF-column. Yields were based on relative integration areas assuming unity response ratios for the various peaks. The injection port temperature of 185-200° required for good separation was high enough to effect elimination in the saturated insertion products. Ethyl 2,3,3-trichlorobutanoate decomposed appreciably to ethyl 2,3-dichloro-2-bute-noate under these conditions. We thank Dr. H. D. Roth for bring this to w. A. Pryor, "Free Radicals," McGraw-Hill, New York, N.Y., 1966.
- (7) (8) Solvent derived products were not observed in the absence of 2.

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