

The Formation and Reactions of Monovalent Carbon Intermediates. III. The Reaction of Carbethoxymethyne with Olefins

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Abstract: Carbethoxymethyne ($\text{EtOCOC}\cdot$) has been generated by the short wavelength photolysis of diethylmercury bisdiazooacetate, $(\text{N}_2\text{CCO}_2\text{Et})_2\text{Hg} + h\nu \rightarrow 2\text{EtOCOC}\cdot + 2\text{N}_2 + \text{Hg}$, and its reactions with cyclohexene, *cis*-2-butene, and *trans*-2-butene were investigated. The carbyne, formed in its $^2\Pi$ ground state, adds to the olefinic π bond in a spin allowed but, according to INDO MO calculations, orbital symmetry forbidden concerted step with retention of the geometrical configuration of the parent olefin to yield a cyclopropyl radical. Parallel to addition, preferential insertion into the allylic C-H bonds also occurs yielding an alkyl radical. Thus, the basic chemical behavior of doublet ground state carbynes appears to bear a close resemblance to that of singlet carbenes. The cyclopropyl and alkyl radicals undergo free radical combination and hydrogen abstraction reactions with solvent molecules. The hydrogen abstraction reaction of cyclopropyl radicals is stereoselective and occurs from the sterically less hindered side of the ring, resulting in the preponderant formation of the less stable *endo* product. In the longer wavelength photolysis of the source compound N_2 is eliminated in a stepwise fashion and a singlet state mercury carbene, which is capable of insertion and stereospecific addition, is formed. Cleavage of the C-Hg linkage in the source compound results in the formation of ethyl diazoacetate which was detected and monitored during the photolysis by infrared spectroscopy. The effect of conversion and wavelength of photolysis on product yields and the relative importance of the various competing primary modes of decomposition were investigated and the overall mechanism is discussed.

Carbon free radicals constitute the most common and frequently encountered class of organic intermediates. The chemistry of the trivalent, divalent, and to a lesser extent of the zerovalent carbon radicals, the simplest representatives of which are $\text{H}_3\text{C}\cdot$, $\text{H}_2\text{C}\cdot$, and the free carbon atom, respectively, comprises one of the fundamental pillars of modern organic chemistry. Little, however, is known about the family of monovalent carbon radicals, the carbynes. The simplest of these is CH, which has been detected spectroscopically in extraterrestrial matter^{3,4} and under laboratory conditions in numerous energetic reactions including hydrocarbon flames,^{5,6} discharges,⁷ and photochemical systems.⁸ Its intermediacy has also been postulated in the reactions of "hot" carbon atoms⁹ with hydrocarbons, etc.¹⁰

The basic objectives of the present study were twofold: to develop a suitable photochemical source for generating carbynes under conditions amenable to quantitative kinetic-mechanistic studies, and to examine their chemistry. Diethyl mercurybisdiazooacetate (I) appeared to be a suitable source material. The synthesis of I was described by Buchner¹¹ in 1895, and in the past decade several additional diazomercurial structures were prepared.¹²

The first study of the chemistry of CH was reported by Safrany, Reeves, and Harteck⁶ in 1964. Early results on the photolysis of I have been reported in two preliminary communications by Strausz and co-workers¹³ along with some observations on the reactions of carbethoxymethyne. Preceding and concurrent to the latter studies were two articles by McNesby, Braun, Welge, and Bass^{14,15} who described the detection of CH in flash photolyzed methane by kinetic spectroscopy and derived rate constants for some of its reactions. In the intervening period a few flash photolysis-

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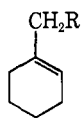
(14) W. Braun, K. H. Welge, and J. R. McNesby, *J. Chem. Phys.*, **45**, 2650 (1966).

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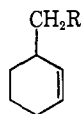
kinetic spectroscopic studies on carbynes have also been reported from other laboratories.¹⁶⁻¹⁸ Still, apart from our preliminary reports¹³ no detailed mechanistic study of a carbyne reaction has appeared to date in the literature.

Results

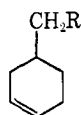
Photolysis of I in Cyclohexene Solution. Upon photolysis, nitrogen evolution, bleaching of the yellow color, and mercury precipitation became evident. In smaller diameter photolysis cells metallic mercury plated out in mirror form. In addition to N₂, mercury, and ethyl diazoacetate (II), the following retrievable products were identified



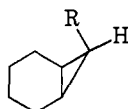
IIIa, ethyl (1'-cyclohexenyl)acetate



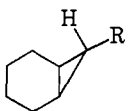
IIIb, ethyl (3'-cyclohexenyl)acetate



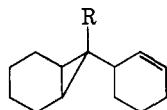
IIIc, ethyl (4'-cyclohexenyl)acetate



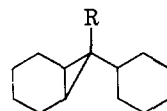
IV, ethyl *endo*-norcarane-7-carboxylate



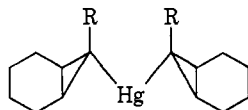
V, ethyl *exo*-norcarane-7-carboxylate



VI, ethyl norcarane-7-(3'-cyclohexenyl)-7-carboxylate



VII, ethyl norcarane-7-cyclohexyl-7-carboxylate



VIII, diethyl bis(7-norcaranyl) mercury-7,7'-dicarboxylate

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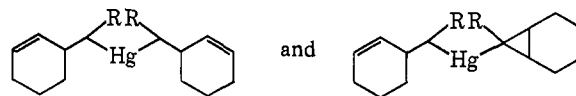
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where R is a CO₂Et group, and 3,3'-bicyclohexenyl (IX).

Gc retention times and mass spectra of these compounds are compiled in Table I and molecular weights from high resolution mass spectra and the principal peaks of the ir and nmr spectra in Table II. The data are fully consistent with the proposed structures. Also, compounds IIIa-c, IV, V, and IX were synthesized independently and found to be identical with those resulting from the photolysis of I in cyclohexene.

Examination of the nmr and mass spectra of the mother liquor after the isolation of VIII indicated the presence of at least one, and possibly two, mercury compounds in addition to residual VIII. They are tentatively assigned the structures



The yields of products III-VIII are dependent on the wavelength of the exciting radiation and were determined employing four different cut-off filters. The results are given in Table III. Each figure reported represents the average of three determinations. The scatter among parallel runs in some cases was large and some trend appeared with the size of the photolysis cell. Nonetheless, it is clear that the total yield of metallic mercury and retrievable mercury free products decreases and that of the mercury adducts increases with increasing wavelength.

In order to establish the mechanism of the formation of products III to VIII, the photolysis of VIII, the thermal stability of I, and the effect of dissolved oxygen upon the reactions were examined in auxiliary studies.

The photolysis of VIII was carried out under identical conditions and for the same time of irradiation as that of I. As in the photolysis of I, the photolysis of VIII at $\lambda > 210$ nm affords products III, IV, and V. At 53 and 93% yields of mercury the product ratio IV to V is about 20. The rate of photolysis of VIII is much slower than the rate of photolysis of I, and its occurrence during the photolysis of I is insignificant.

The results of the thermal studies are presented in Table IV. As seen from the data, I is thermally stable in oxygen-free cyclohexene solution up to 145° but tends to decompose even at room temperature at a measurable rate when dissolved oxygen or air is present. The decomposition yields mercury oxide and II, in yields of up to 73% of the theoretical, as well as typical oxidation products of cyclohexene including cyclohexanol, cyclohexenol, cyclohexenone, bicyclohexenyl, etc.

For the elucidation of the role of II in the photolysis of I, auxiliary studies were performed in which the concentrations of both species were continuously monitored using the sharp, characteristic infrared diazo bands of II and I at 2110 and 2075 cm⁻¹, respectively. The rate of disappearance of I and the rate of formation of II were determined from the initial slopes of the time profiles of the concentration curves shown for the photolysis with Vycor filtered light in Figure 1. The intervention of II in the early stages of the reaction was estimated to have upper limits of 8% ($\lambda > 210$ nm) and 12% ($\lambda > 240$ nm).

Table I. Gc Retention Times and Mass Spectra of Products III-IX from the Photolysis of I in Cyclohexene

Compd	t_R , min	m/e (P)	m/e and (% of base peak) ^d									
			122	94	81	80	79	61	41	32	29	18
III	18 ^a	168 (14)	(40)	(44)	(52)	(100)	(96)	(44)	(28)	(56)	(24)	(26)
IV	20.5 ^a	168 (18)	(40)	(56)	(40)	(42)	(65)	(70)	(96)	(100)	(52)	(46)
V	24 ^a	168 (40)	(56)	(70)	(57)	(97)	(77)	(84)	(68)	(75)	(65)	(100)
VI	21 ^b	248	167	81	80	79	78	44	41	32	29	28
VII	18 ^b	250 (31)	168 (12)	95 (13)	81 (23)	79 (14)	67 (16)	55 (15)	41 (20)	32 (17)	29 (16)	28 (100)
VIII	9 ^c	536 (<1)	167 (38)	93 (97)	80 (37)	79 (63)	77 (39)	41 (60)	39 (54)	81 (57)	29 (100)	27 (60)
IX	26 ^a	162 (<1)	81 (100)	80 (56)	79 (42)	77 (14)	67 (11)	55 (10)	53 (18)	41 (28)	39 (26)	27 (20)

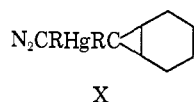
^a Column: 15 ft \times 1/8 in. packed with 20% SE30 on Chromosorb W, 30-60 mesh. Program: from 110 to 180° at 1°/min with 6 min post-injection delay; flow rate 60 cm³/min. ^b Column: as in footnote a. Program: 180° constant column temperature; flow rate 60 cm³/min. ^c Column: 10 ft \times 1/8 in. packed with 10% SE30 on Chromosorb W. Program: 240° constant temperature; flow rate 60 cm³/min. ^d Determined in an A.E.I. MS-12 mass spectrometer at 70 eV.

Table II. Molecular Weights and Ir and Nmr Spectra of Products III-IX from the Photolysis of I in Cyclohexene

Compd no.	Formula	Mol wt ^a		Ir, $\nu_{\text{max}}^{\text{CCl}_4}$, cm ⁻¹ ^b	Nmr τ (CCl ₄) ^c
		Calcd	Measd		
III	C ₁₀ H ₁₆ O ₂	168.1150	168.1153	3050 (w); 1720 (s)	8.80 (t, 3 H); 7.90-9.00 (broad m, 6 H); 7.85 (m, 2 H); 7.50 (m, 1 H); 5.93 (q, 2 H); 4.42 (m, 2 H)
IV	C ₁₀ H ₁₆ O ₂	168.1150	168.1151	3045 (w); 1725 (s)	8.80 (t, 3 H); 8.10-9.05 (broad m, 11 H); 5.95 (q, 2 H)
V	C ₁₀ H ₁₆ O ₂	168.1150	168.1151	3050 (w); 1720 (s)	8.80 (t, 3 H); 7.65-9.05 (broad m, 11 H); 6.00 (q, 2 H)
VI	C ₁₆ H ₂₄ O ₂	248.1776		3010 (s); 2930 (s); 1740 (s)	8.78 (t, 2.0 Hz, 3 H); centered around 8.08 and 8.35 (2 broad m, 19 H); 5.92 (q, 7.0 Hz, 2 H); 4.40 (m, 2 H)
VII	C ₁₆ H ₂₄ O ₂	250.1933		2930 (s); 1718 (s)	8.72 (t, 7.0 Hz, 3 H); centered around 8.25 and 8.90 (2 broad m, 21 H); 5.89 (q, 7.0 Hz, 2 H)
VIII	C ₂₀ H ₃₀ O ₄ ²⁰² Hg	536.1850	536.1856	2980 (w); 2928 (s); 2853 (s); 1700 (s)	9.82 (t, 7.0 Hz, 6 H); centered around 8.14 and 8.48 (2 broad m, 20 H); 6.00 (q, 7.0 Hz, 4 H)
IX	C ₁₂ H ₁₈	162.1409	162.1409	3020 (w); 1642 (w)	8.43 and 8.10 (2 broad m, 14 H); 4.45 (m, 4 H)

^a Determined in an A.E.I. MS-9 double-focusing mass spectrometer at 70 eV. ^b Determined in a Perkin-Elmer PE-421 ir spectrometer. ^c Recorded on Varian A-56/60 and A-100 spectrometers.

The mercury product may arise from I in a primary process or from the secondary photolysis of the intermediate diazomercury compound



In the former case the plot of the product ratio 2Hg/N₂ vs. exposure time would extrapolate at zero exposure time to a finite value, in the limit to unity, while in the latter case an induction period would appear. For this reason, in a series of experiments, using Vycor filtered light, the 2Hg/N₂ ratio was determined at different exposures and the resulting plot, given in Figure 2, was extrapolated to zero exposure time. As seen, the extrapolated value of 2Hg/N₂ is about 0.18 indicating a primary yield of Hg from I of 9-18% depending on the nature of the primary step (*vide infra*).

The role of the intermediate diazomercurial X was investigated in the Pyrex filtered photolysis of I using sequentially two different olefinic solvents for the deter-

Table III. Product Yield Variation as a Function of Wavelength of Irradiation in the Photolysis of I in Cyclohexene^a

Compd	Per cent yield for the wavelength—			
	>2100 Å (Vycor)	>2400 Å (Corex)	>2800 Å (Pyrex)	>3200 Å (uranium)
III	9	8	5	3
IV	14	7	2	1
V	2	1	1	0.3
VI	3	3	2	0.6
VII	3	2	1	0.1
ΣIII-VII →	31	21	11	5
VIII	16	27	39	38
Total product	47	48	50	43
Hg(metallic) recovered	~35	~30	~16	~4

^a Average of three experiments.

mination of the extent of conversion. Photolysis of I was carried out for different exposure times in cyclohexene, the solvent evaporated, *trans*-2-butene added, and the irradiation continued until no diazo band could be detected in the ir spectrum. After butene evapora-

Table IV. Thermolysis of I in Cyclohexene in the Absence and Presence of Oxygen

Temp, °C	Amount of oxygen	Reaction time, hr	Concn, $M \times 10^{-3}$				Per cent ^a II produced
			Initial		Final		
			I	II	I	II	
25	Nil	24	12.1	0.5	12.1	0.5	Nil
80	Nil	8	12.1	0.8	12.1	0.9	Trace?
145	Nil	3	12.1	1.0	12.0	1.2	Trace
165 ^b	Nil	1.5	11.9	1.0	<0.2	0.5	2
20	4×10^{-3} mol	1	12.1	0.5	11.6	1.2	70
80	7×10^{-3} mol	0.5	12.0	1.0	Complete decomposition		
20	Open to air	4	12.0	0.25	10.8	2.0	73
40	Open to air	4	12.0	0.25	7.2	5.25	52
60	Open to air	4	12.0	0.25	5.75	6.6	50
70	Open to air	4	12.0	0.25	4.5	8.3	54

^a Per cent II produced from decomposed I. ^b Carried out in a Carius tube.

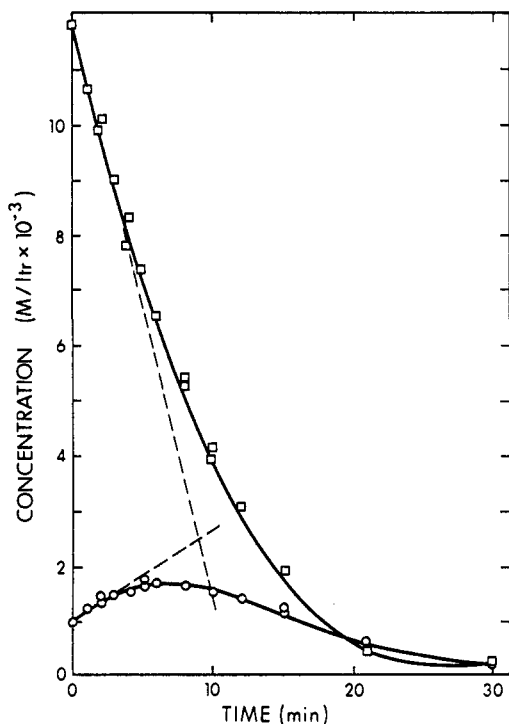
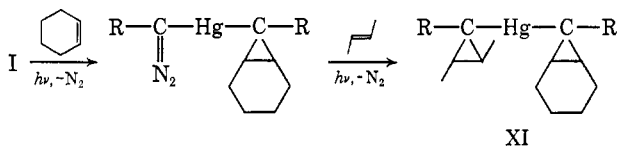


Figure 1. Concentration variation of I (□) and II (○) during the photolysis of I in cyclohexene solution with Vycor filtered light.

tion, the residues were analyzed by mass spectrometry and the parent ion intensities determined. The results are plotted in Figure 3. The presence of X is indicated by the appearance of the mixed cyclopropane adduct XI. The cyclopropylmercurydiazo compound is



formed upon the demise of I in the early stages of the photolysis and is decomposed in turn to form VIII at longer irradiation times.

The presence of X in the cyclohexene solution photolysate of I was also confirmed by direct mass spectrometric detection. Irradiation of the solution was stopped at 55% decrease in the ir diazo band intensity, the olefin was carefully removed in the dark by rotary vaporization, and the residual viscous oil was analyzed by low voltage mass spectrometry without further puri-

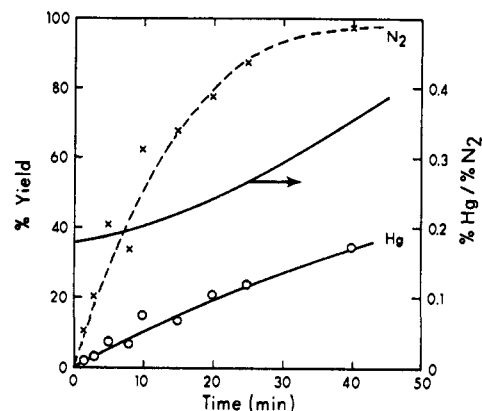


Figure 2. Variation in the per cent yield of Hg (○), N₂ (×), and their ratio (—) with exposure time.

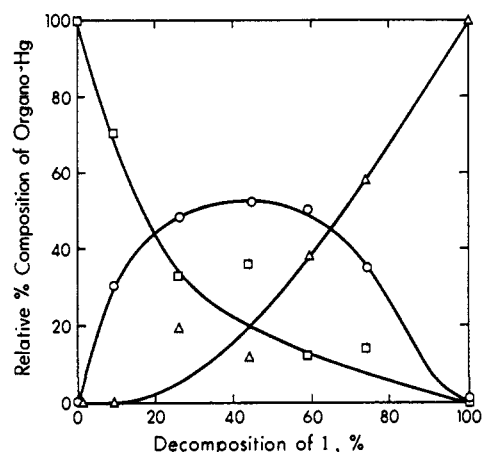


Figure 3. Variation in the relative per cent composition of organomercurial with the decomposition of I. The symbols are I, □; VIII, △; and X, ○.

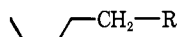
fication. Mercury isotope patterns were found at m/e (^{200}Hg) 426, 534, and 480 corresponding to the parent ions of I, VIII, and X in relative intensities of 14, 46, and 40, respectively. A partial mass spectrum of X could also be discerned: m/e (^{200}Hg) 480 (P), 452 (P-N₂), 435 (P-OEt), and 407 (P-CO₂Et).

In another series of experiments the effect of conversion was determined on the endo to exo addition and the addition to insertion product ratios in the Pyrex filtered photolysis of I in cyclohexene solution. From the data presented in Table V, significant variations appear with the extent of conversion. The photosta-

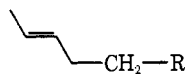
bility under the prevailing experimental conditions of products III–V and VIII has been demonstrated in control experiments in the presence and absence of I.

Photolysis of I in *cis*-2-Butene and *trans*-2-Butene. These reactants were chosen in order to elucidate the stereochemical aspects of the cyclopropane-forming reaction paths.

In addition to nitrogen, mercury, and II, the following eight products were isolated and identified



XII, ethyl *cis*-4-hexenoate



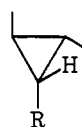
XIII, ethyl *trans*-4-hexenoate



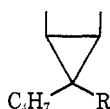
XIV, ethyl *cis*-2,3-dimethylcyclopropane-*cis*-carboxylate
(α isomer)



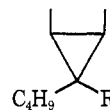
XV, ethyl *cis*-2,3-dimethylcyclopropane-*trans*-carboxylate
(β isomer)



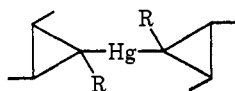
XVI, ethyl *trans*-2,3-dimethylcyclopropane-
carboxylate (γ isomer)



XVII, ethyl butenyl-2,3-dimethylcyclopropanecarboxylate



XVIII, ethyl butyl-2,3-dimethylcyclopropanecarboxylate



XIX, diethyl mercury bis(*trans*-2,3-dimethylcyclopropane-
carboxylate)

where R = CO₂Et.

The gc retention times and ir, nmr, and mass spectral data of products XII to XIX are collected in Tables VI and VII. Parallel to these studies, the photolysis of II was also carried out in order to examine the reactions of carbethoxymethylene with the butenes and also to assist product identification.

Table V. Variations in Product Ratios IV/V and (IV + V)/III with the Extent of Decomposition of I^a

% decrease in ir absorption of I	IV/V	(IV + V)/III
0	0.0	0.0
4	0.4	5.8
17	0.5	2.5
37	0.6	
67	1.0	
91	1.7	1.2
~100	2.0	0.8

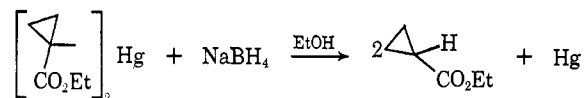
^a $\lambda > 280$ nm.

The mercury adduct XIX could only be isolated with *trans*-butene, in the form of a white crystalline solid (mp 109–110°). Mass spectral analysis of the high boiling mother liquid indicated the presence of further mercury adducts.

The structural distinction between the isomeric α - and β -addition products, XIV and XV, is based on the assumption that, owing to steric hindrance, the catalytic hydrogenation of ethyl 2,3-dimethylcyclopropene-carboxylate should give predominantly the all-*cis* product. Standard samples of XIV were prepared by the photolysis of II in 2-butyne followed by the catalytic hydrogenation¹⁹ of the resultant ethyl 2,3-dimethylcyclopropenecarboxylate.

Results of the photolysis of 0.1-g samples of I or II in 25 ml of 2-butene using Pyrex filtered light, presented in Table VIII, indicate a highly stereospecific path for cyclopropane formation. As expected, *cis*-butene gives as major addition products the α and β isomers, XIV and XV, while *trans*-butene yields only the γ isomer, XVI. More detailed quantitative studies with regard to the effect of wavelength on product distribution were undertaken for *trans*-butene only. The data reported in Table IX show an increase of the cycloaddition products, XVI + XVII + XVIII, with increasing energy of the exciting light and at the same time a decrease in the yield of the mercury adduct, XIX, a trend that was also observed in the cyclohexene system. A solution of XIX in *trans*-butene showed no significant decomposition when irradiated under the same conditions and for the same length of time as required to photolyze an equivalent amount of I.

Sodium borohydride reduction of the entire post-photolysis residues of I in 2-butene gave a further yield of 40–60% Hg and 45–50% cyclopropanes.

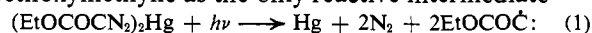


Approximately 5% total C–H insertion product was found after this reduction. The data are shown in Table X.

Discussion

The primary steps that can be envisaged in the photolysis of I are as follows.

(a) Simultaneous rupture of the carbon–nitrogen and carbon–mercury bonds leading to the formation of carbethoxymethylene as the only reactive intermediate



(19) W. von Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

Table VI. Gc Retention Times and Mass Spectra of Products XII–XIX from Photolysis of I in *cis*- and *trans*-2-Butene

Compd no.	t_R , min	m/e (P)	m/e and (% of base peak)									
			142	127	97	71	69	68	55	41	39	29
XII	15.5 ^a	142 (34)	142 (34)	127 (45)	97 (55)	71 (28)	69 (100)	68 (60)	55 (38)	41 (90)	39 (25)	29 (43)
XIII	14.0 ^a	142 (32)	142 (32)	127 (50)	99 (35)	97 (50)	69 (100)	41 (96)	39 (22)	29 (50)	28 (96)	18 (26)
XIV	12.2 ^a	142 (5)	127 (100)	114 (10)	99 (60)	97 (65)	69 (70)	43 (15)	41 (80)	39 (16)	29 (30)	27 (15)
XV	14.6 ^a	142 (15)	142 (15)	127 (88)	114 (20)	99 (40)	97 (90)	69 (97)	41 (100)	39 (20)	29 (37)	27 (18)
XVI	9.8 ^a	142 (8)	127 (100)	114 (11)	99 (55)	97 (68)	69 (73)	43 (14)	41 (80)	39 (17)	29 (30)	27 (15)
XVII	18 ^b	196	181	169	151	141	123	95	81	67	53	41
XVIII	17 ^b	198 (7)	183 (12)	181 (24)	169 (100)	153 (25)	123 (55)	95 (46)	69 (35)	55 (35)	41 (50)	29 (60)
XIX	38 ^c	454	439 (1)	142 (41)	141 (93)	114 (23)	113 (86)	95 (100)	67 (51)	45 (30)	41 (35)	29 (33)

^a Column: 15 ft \times 1/8 in., packed with 12% XE60 on Chromosorb W, 30–60 mesh. Program: 50 cm³/min helium, 80°. ^b Column and flow rate as in footnote a, 110°. ^c Column as in footnote a, flow rate 75 cm³/min, 180°.

Table VII. Molecular Weights and Ir and Nmr Spectra of Products XII–XIX from the Photolysis of I in *cis*- and *trans*-2-Butene

Compd no.	Formula	Mol wt		Ir, $\nu_{\max}^{\text{C-Cl}}$, cm ⁻¹	Nmr, τ (CCl ₄)
		Calcd	Meas		
XII	C ₈ H ₁₄ O ₂	142	142	1710 (s); 2980 (w)	8.90 (t, 3 H); 8.5 (m, 3 H); 7.87 (m, 4 H); 6.10 (q, 2 H); 4.75 (m, 2 H)
XIII	C ₈ H ₁₄ O ₂	142	142	1730 (s); 2980 (s)	8.86 (t, 3 H); 8.44 (d, 3 H); 7.83 (m, 4 H); 6.05 (q, 2 H); 4.7 (m, 2 H)
XIV	C ₈ H ₁₄ O ₂	142	142	1770 (s); 2980 (s)	8.95 (m, 9 H); 8.88 (5h, 3 H); 6.14 (q, 2 H)
XV	C ₈ H ₁₄ O ₂	142	142	1720 (s); 2980 (s)	9.0 (m, 9 H); 8.92 (5, 3 H); 6.15 (q, 2 H)
XVI	C ₈ H ₁₄ O ₂	142	142	1720 (s); 2980 (s)	9.1 (m, 9 H); 9.05 (t, 2 Hz, 3 H); 6.24 (q, 7 Hz, 2 H)
XVII	C ₁₂ H ₂₀ O ₂	196.1463	196.1455	1715 (s)	8.82 (t, 3 H); 8.7–9.2 (m, 15 H); 6.06 (q, 2 H); 5.1–5.3 (m, 2 H)
XVIII	C ₁₂ H ₂₂ O ₂	198	198	1715 (s)	8.81 (t, 3 H); 8.5–9.2 (m, 17 H); 6.05 (q, 2 H)
XIX	C ₁₆ H ₂₆ O ₄ Hg	484.1532	484.1530	1705 (s)	8.84 (t, 7.2 Hz, 6 H); 8.89 (d, 1.4 Hz, 6 H); 8.86 (m, 2 H); 8.83 (d, 1.4 Hz, 6 H); 8.24 (m, 2 H); 5.98 (q, 4 H)

Table VIII. Yields of Products XII–XVI from the Photolysis of II and I in *cis*- and *trans*-2-Butene^{a, b}

Product	Relative yield			
	<i>cis</i> -2-Butene		<i>trans</i> -2-Butene	
	II ^c	I ^d	II	I
XII	10	17	Nil	Nil
XIII	Nil	Trace	13	17
XIV	19	39	Nil	Trace
XV	73	57	Nil	Trace
XVI	Nil	Trace	70	82
XIV/XV	0.25	0.69		

^a $\lambda > 280$ nm (Pyrex). ^b 15–20% Hg at 100% N₂ evolution. ^c Total yield of XII–XVI is ca. 55% (theoretical). ^d Total yield of XII–XVI is ca. 2% (theoretical).

Table IX. Product Yield Variation as a Function of Wavelength of Irradiation in the Photolysis of I in *trans*-2-Butene

Compd no.	% yield (theoretical) for λ		
	>2100 Å (Vycor)	>2800 Å (Pyrex)	>3200 Å (uranium)
XVI	10	2	1
XVII	2	<1	<1
XVIII	1	<1	<1
XIX	20	34	40

If all products are formed in their ground state then the enthalpy change of the corresponding dark reaction can

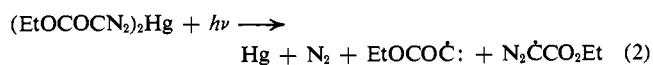
Table X. Photolysis of I in 2-Butene^a

Product	<i>cis</i> -2-Butene % theoretical		<i>trans</i> -2-Butene % theoretical	
	Before NaBH ₄	After NaBH ₄	Before NaBH ₄	After NaBH ₄
XII	0.05	4		
XIII			0.1	5
XIV	0.2	26		
XV	0.2	16		
XVI	Trace	Trace	0.6	44
WR <i>cis</i>	0.4			
WR <i>trans</i>			0.5	
Hg	21	61	15	41

^a $\lambda > 280$ nm.

be estimated^{20, 21} to be approximately 100 kcal/mol and consequently step 1 would become possible at wavelengths shorter than 290 nm.

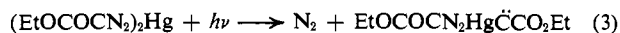
(b) Simultaneous cleavage of one carbon–nitrogen bond and both carbon–mercury bonds yielding carbethoxymethyne and the ethyl diazoacetate radical as reactive intermediates



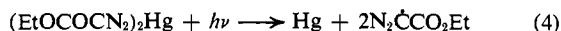
(20) D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1768 (1970).

(21) A. C. Lalonde and S. J. W. Price, *Can. J. Chem.*, **49**, 3367 (1971).

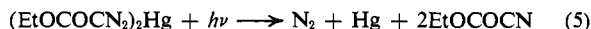
(c) Single carbon–nitrogen rupture to give a mercury carbene intermediate



(d) Elimination of mercury to yield two diazo ester radicals

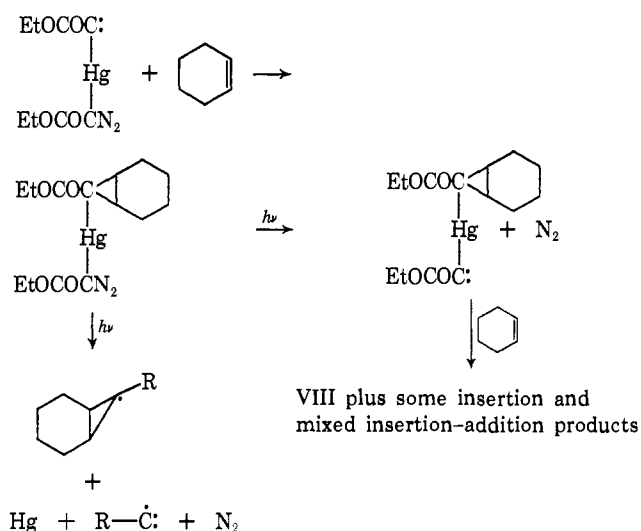


(e) And, finally, elimination of nitrogen between diazo groups to give molecular products



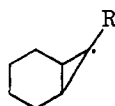
Steps 1 to 4 are concordant with the nature and distribution of observed products. Step 5 can be discounted on the grounds that nitrogen recovery is complete and carbethoxynitrile cannot be detected among the products. Also, although step 4 cannot be discounted, it is regarded as of low probability because C–Hg bond cleavage without cleavage of the weaker C=N₂ bond of the chromophore moiety of the molecule is unlikely. Of the remaining three steps which probably occur in parallel and competition, steps 2 and 3 are feasible within the entire absorption region used in this work, whereas step 1 is only feasible at shorter wavelengths. The relative importance of steps 1 to 3 should then be wavelength dependent, in agreement with the observed trends in product yields.

The combined yield of steps 1 and 2 (in cyclohexene and with Vycor filtered light) lies between 0.09 and 0.18 comprising 25–50% of the total yield of mercury. The rest of the mercury must come from the secondary photolysis of the diazomercurial product X.



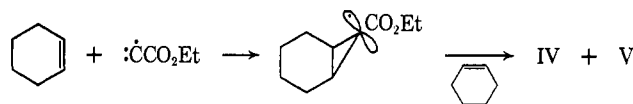
This sequence is supported by the formation of VIII, as the major reaction product, the direct mass spectrometric detection of X, and the production of the mixed mercury adduct XI in the sequential photolysis of I in cyclohexene and *trans*-2-butene.

The principal mercury free reaction products found in 31% yield can then be derived from the reactions of carbethoxymethylene, the cyclopropyl radical



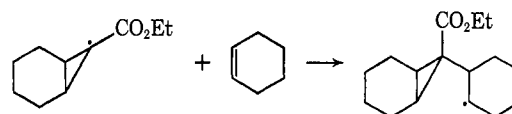
and the diazo ester radical, EtOCOCN₂. The latter undergoes hydrogen abstraction with the solvent in at

least 73% yield (Table IV) to give ethyl diazoacetate, the intermediacy of which was detected by ir spectroscopy. Photolysis of ethyl diazoacetate produces carbethoxymethylene, which has been shown before to give III–V with cyclohexene in a ratio of IV to V of ~0.5.^{22,23} This leads to an upper limit for the yield of mercury free products arising *via* the intervention of carbethoxymethylene of 4–5%. Of the remaining 26–27%, not more than one-third can arise from the cyclopropyl radical, the rest must come from the reaction of carbethoxymethylene with cyclohexene

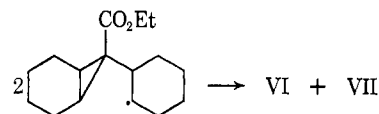


The hydrogen abstraction step of the cyclopropyl radical is highly stereoselective and the steric hindrance in the strongly hindered endo position of the cyclopropyl radical confers the less stable endo configuration on the final product, Table III. This stereoselectivity of the hydrogen abstraction process has been verified in auxiliary experiments where the cyclopropyl radical, produced by the photolysis of the mercury adduct VIII in oxygen free cyclohexene solution, afforded nearly exclusively the endo isomer IV.

Products VI and VII arise from the addition of the cyclopropyl radical to cyclohexene



followed by disproportionation of the resultant radical



Products IIIa–c come largely from the insertive attack of carbethoxymethylene on the C–H bonds of cyclohexene, followed by hydrogen abstraction of the resulting radical. The distribution of the isomeric insertion products IIIa–c from the independent photolyses of I and II in cyclohexene is compared to that resulting from the photolysis of diazomethane in Table XI. Carbethoxymethylene and carbethoxymethylene

Table XI. Isomeric Distribution of Insertion Products

Isomer	Statistical %	% from I	% from II	% from CH ₂ N ₂ ^a
IIIb	40	50	45	42
IIIc	40	41	44	42
IIIa	20	10	11	16

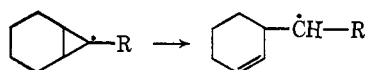
^a K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 1015 (1962).

both show a slight preference for the weak allylic position as compared to methylene which is nondiscriminative and gives a statistical product distribution. The intervention of other mechanisms such as insertion

(22) W. R. Moser, *J. Amer. Chem. Soc.*, **91**, 1135 (1969).

(23) P. S. Skell and R. M. Etter, *Proc. Chem. Soc., London*, 443 (1961).

of carbethoxymethylene or isomerization of the cyclopropyl radical

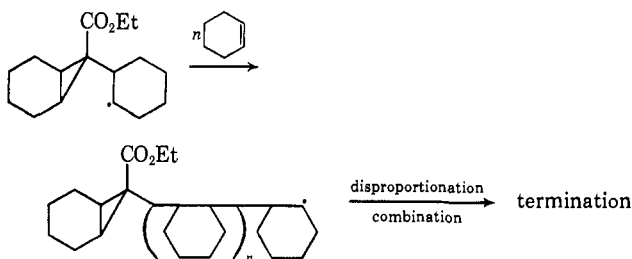


as a major source of III can be discounted. That carbethoxymethylene is capable of C-H bond insertion has also been demonstrated by auxiliary experiments in which the photolysis of I was carried out in paraffinic and alcoholic solutions.^{13, 24}

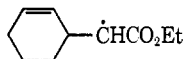
The α -mercury carbene reacts with cyclohexene mainly by addition, insertion being less than 5%. This is consistent with the observation that methylmercury carbomethoxycarbene adds almost exclusively to the double bonds of olefins.²⁵ Also, sodium borohydride reduction of the organomercury containing residue resulting from the photolysis of I in either *cis*- or *trans*-2-butene produced only 4–5% insertion product.

The formation of ethyl diazoacetate, II, is attributed to the hydrogen abstraction reaction of the diazo radical formed *via* primary steps 2 and 4. During the photolysis of I the concentration of II varies and goes through a maximum owing to secondary photolysis which produces carbethoxymethylene. The latter adds to cyclohexene yielding endo and exo addition products in the ratio of IV/V = 0.63²³–0.53.²² The intermediacy of the diazo radical therefore reduces the endo to exo product ratio obtained from the photolysis of I. The increasing trend in the relative yield of diazo radical with increasing wavelength is reflected in the more than twofold concurrent decrease in the ratio IV/V. At least 73% of the diazo radicals appear to undergo hydrogen abstraction (*vide infra*) and the rest lead to polymeric or other nonretrievable products.

The total yield of mercury free products in the Vycor filtered photolysis is 31% and that of metallic mercury is ~35%. The loss in mercury free products, ~4%, is partly due to the free radical initiated polymerization of the solvent olefin.



Similar reactions could occur with the



and $N_2\dot{C}CO_2Et$ radicals. In addition, Wolff rearrangement of carbethoxymethylene to the ethoxyketyl radical



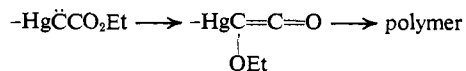
followed by hydrogen abstraction, combination, or addition to cyclohexene and subsequent polymerization or photolysis could contribute to the loss. Small quantities of CO, ~1%, presumably from the photolysis of the ketene, were detected in the noncondensable products. The low overall yield of products is not surprising in view of the reported value of retrievable products, III + IV + V ~47%, from the photolysis of

(24) M. Frater and O. P. Strausz, to be submitted for publication.

(25) P. S. Skell and S. J. Valenty, *J. Amer. Chem. Soc.*, **95**, 5042 (1973).

II in cyclohexene.^{22, 23} The occurrence of Wolff rearrangement in the latter reaction has also been observed.²⁶

The deficiency in the mercury balance, 100 - (16 + 35) = 49%, is due to the incomplete recovery of VIII and its isomers. The uncharacterized residue could have also contained some polymeric material formed *via* the Wolff rearrangement of the mercury carbene



by analogy with ethoxyketene which in nonreactive solvent has been shown to give isomeric mixtures of tetramers.²⁷

The photolysis of I in 2-butene solutions exhibits the same characteristics as in cyclohexene. The nature and distribution of products indicate that the same basic mechanism applies here as well. Products XII and XIII arise mainly from allylic C-H bond insertion and XIV–XVIII from the cycloaddition of carbethoxymethylene. XIX is the addition product of the mercury carbene.

The most important facet of this reaction is its stereochemical information content. The observed high stereoselectivity of the cyclopropane-forming reaction is a clear manifestation that doublet, ground state carbethoxymethylene, and most likely all doublet ground state carbynes, add to olefins in a concerted, although as molecular orbital computational results²⁸ suggest, orbital symmetry forbidden step. In this sense the behavior of doublet ground state carbynes parallels that of singlet carbenes. The analogy can be further extended to the reactivity with respect to the C-H bond; both species are capable of concerted, insertive attack.

Methylene is isoelectronic with the nitrogen atom but unlike the ground state of nitrogen which is a quartet its ground state is a doublet.²⁹ The lowest quartet state, $^4\Sigma^+$, which to date has not been observed experimentally, has been estimated to lie ~28 kcal/mol above the $^2\Pi$ ground state.³⁰ In fact, the ground state of all the other carbynes, CF, CCl, and CBr, whose uv spectra have been observed, is a $^2\Pi$ state. Substituents could conceivably alter the orbital energy levels and invert the energies of the $X^2\Pi$ ground state and the lowest $^4\Sigma^+$ state. In the case of carbenes, methylene has a triplet ground state, but the introduction of a single halogen atom, carbalkoxy, or aryl group raises the energy of the first virtual orbital to such an extent that the orbitally excited triplet state energy is above the lowest singlet. These relations for carbenes are expressed by Hoffmann's empirical rule³¹ which states that when the optimum σ^2 configuration has an EHMO energy less than 1.5 eV below the σp configuration at the same $>C:$ angle, then the ground state is likely to be the

(26) J. Shafer, P. Barnowsky, R. Laursen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1966); H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **90**, 4088 (1968); O. P. Strausz, T. DoMinh, and H. E. Gunning, *ibid.*, **90**, 1660 (1968); **91**, 1261 (1969); T. DoMinh and O. P. Strausz, *ibid.*, **92**, 1766 (1970).

(27) G. O. Schenck and A. Ritter, *Tetrahedron Lett.*, 3189 (1968); G. J. A. Kennepohl, G. Frater, and O. P. Strausz, unpublished results.

(28) R. K. Gosavi and O. P. Strausz, to be submitted for publication.

(29) G. Herzberg, "The Spectra and Structure of Simple Free Radicals," Cornell University Press, Ithaca, N. Y., 1971, p. 32.

(30) W. M. Huo, *J. Chem. Phys.*, **49**, 1482 (1968).

(31) R. Hoffmann, G. D. Zeiss, and G. W. von Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

triplet. The computed EHMO energy difference for methyne²⁸ is somewhat above 1.5 eV and since the ground state is known to be a doublet it seems that Hoffmann's rule is also applicable to carbynes. On this basis the ground state of carbethoxymethyne, which is the main concern of the present study, should be the ²II state and the lowest excited quartet state should lie at least 28 kcal/mol above the ground state.

The excited quartet methyne would presumably exhibit a chemical reactivity reminiscent to that of triplet ground state methylene in that addition to olefins would be nonstereospecific and attack upon the C-H bonds would lead to abstraction rather than insertion.

The reactivities of carbenes and their structural analogs the group VIa atoms, imines, etc., are basically determined by their electron deficient structure. These species behave as distinct electrophiles in their addition reactions. Recent studies on CCl¹⁷ and CBr¹⁸ suggest a similar electrophilic character for the reactivity of these species.

From the present data it is seen that singlet carbethoxymethylene from the photolysis of II also adds stereospecifically to *cis*- and *trans*-butene. Interestingly the *endo* to *exo* addition ratio from the *cis*-butene reaction, 0.25, is lower than that from the cyclohexene reaction, 0.53–0.63. This is in line with the data of Doering and Mole¹⁹ who found a value of 0.4 for the *endo* to *exo* product ratio from the photolysis of methyl diazoacetate in *cis*-butene and this seems to suggest that the rigid ring structure in cyclohexene exerts a less severe steric interference with the carbalkoxy group of the incoming carbene than the freely rotating methyl groups in *cis*-2-butene.

Another point of interest in this connection is the difference in the stereoselectivity of the hydrogen abstraction reaction of the cyclopropyl radicals from the cyclohexene and *cis*-2-butene reactions. The *endo* to *exo* product ratios for the two solvents in Pyrex filtered photolyses are about 2 and 0.7, respectively. Thus, it seems that the cyclohexyl ring structure is much more efficient in preventing hydrogen abstraction in the *endo* position than the methyl groups in 2-butene. Nonetheless, the value of the *endo* to *exo* product ratio from the photolysis of I in *cis*-2-butene is higher, 0.69, than from the photolysis of II, 0.25, which again indicates that the major precursor to XIV and XV is carbethoxymethyne.

The total yields of mercury free retrievable products from the butene reactions have not been determined, but they are lower than those from the cyclohexene reaction. This follows the trend found in the photolysis of II in cyclohexene, 47%,^{22,23} and in the photolysis of methyl diazoacetate in 2-butene, 33–39%.¹⁹

The thermal stability of I is quite good. In the pure state decomposition occurs above 100° but in cyclohexene solution only above 145°. Small quantities of dissolved oxygen, however, can initiate decomposition even at or below room temperature. The activation energy of the latter reaction is estimated to be 10–15 kcal/mol. The most probable mechanism giving II and HgO as principal final products is

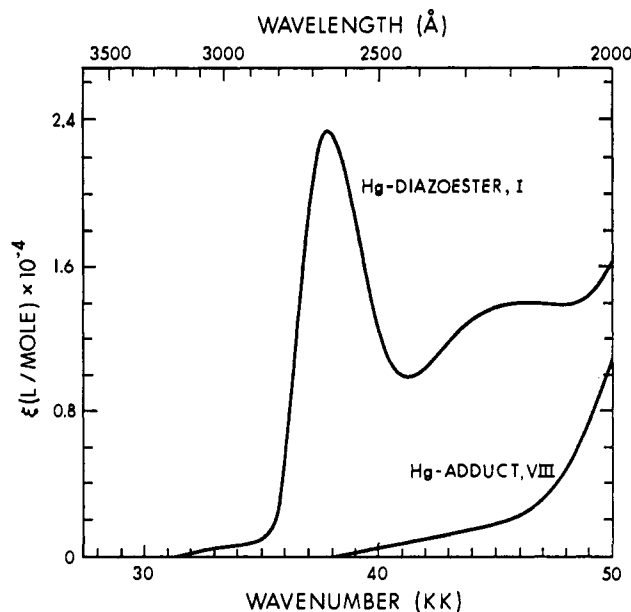
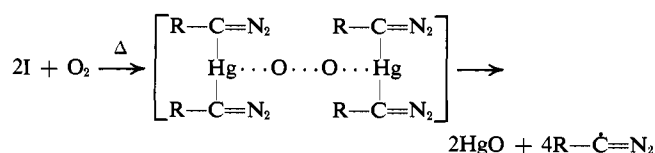
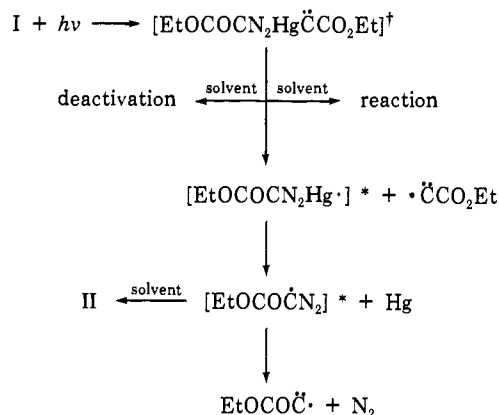


Figure 4. Uv spectra of I and VIII in ethanol solution.

Around room temperature the yield of II was as high as 73%, lending support to the above mechanism and indicating that at least 73% of the diazo radicals abstract hydrogen from the solvent at room temperature.

Finally, it should be mentioned that in the photolysis of I the observed effect of wavelength on product yields can be attributed simply to changes in the amounts of excitation energy or the nature of the electronic states involved, which in turn are directly related to the relative importance of steps 1 to 4. The uv spectrum of I, Figure 4, exhibits the general characteristics of diazoalkanes featuring two major absorption bands corresponding to a weak (n, π^*) transition $\lambda_{\text{max}}^{\text{EtOH}}$ 380 m μ (ϵ 107) and an intense (π, π^*) transition $\lambda_{\text{max}}^{\text{EtOH}}$ 264 m μ (ϵ 22,000). In any event the multifragmentation steps 1 and 2 must occur stepwise rather than concertedly and it appears that electronically excited carbenes are involved.



With a decreasing amount of excitation energy the extent of secondary fragmentation falls off, increasing the relative importance of primary steps 3 and 4 over that of steps 2 and 1. However, an exact evaluation of the relative importance of the individual primary steps is not possible because of the complex nature of the overall reaction and the scatter in the analytical data.

It is interesting to note that the photofragmentation

of the diazomercurial X is more facile than that of the bisdiazomercurial I and in the $\lambda > 280$ nm photolysis it is probably X that produces metallic mercury and the precursors of III-V rather than I. This is suggested by the ratio of the yields of primary mercury to total mercury in the $\lambda > 210$ nm photolysis and the variation of the product ratios IV/V and (IV + V)/III in the $\lambda > 280$ nm photolysis, Table IV. The latter results can be explained if it is assumed that in the initial stages of the photolysis it is only the ubiquitous II which produces III-V, and as the reaction progresses the carbyne and the cyclopropyl radical take over.

Further studies are in progress.

Experimental Section

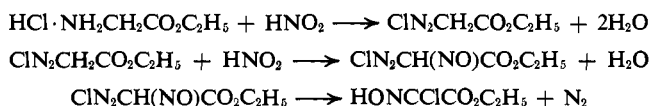
General. A conventional high vacuum apparatus was used for handling gaseous products, degassing low boiling solvents, and vacuum distillation. Noncondensable products (N_2 , CO) were measured in a gas buret and transferred under vacuum to a Gow-Mac TR2B thermal conductivity gc for analysis on a 10-ft molecular sieve 13X column.

Photolyses in most cases were effected by a Hanovia 450W medium pressure arc (No. 679A36) using an immersion well assembly³² with appropriate cylindrical filter sleeves. Provision was made for cooling, purging with nitrogen, and magnetic stirring. The experiments for monitoring the concentration variation of the diazo esters during photolysis were carried out in a vacuum tight quartz vessel containing a small ir cell and a magnetic stirrer.

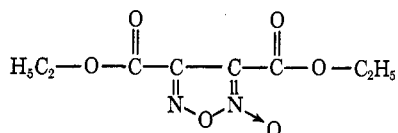
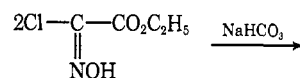
A Varian aerograph (90P) gc was used for preparative purposes and a Hewlett-Packard 5750B or 7620A instrument for analyses. Uv spectra were obtained with a Cary 14 or 15 instrument.

Materials. Commercial reagent grade chemicals were used without further purification. The purity of all solvents was checked by ir and gc analyses. *cis*- and *trans*-butene (Matheson) contained less than 0.1% contaminant and were used without purification. Cyclohexene (BDH) was dried over potassium hydroxide pellets and distilled in a spinning band column. The freshly distilled material contained less than 0.1% cyclohexanol, cyclohexanol, and cyclohexanone as impurities.

Preparation of II. The procedure described in the latest edition of "Organic Syntheses"³³ was followed. The method quotes "high boiling esters" as major contaminants in the product fraction and it was observed that the most important "high boiling ester" was dicarbethoxyfuroxan. The formation of this by-product in the synthesis of ethyl diazoacetate by the action of sodium nitrite on glycine ethyl ester hydrochloride can be understood from the following considerations. Skinner³⁴ found that in the presence of hydrochloric acid glycine ester hydrochloride and sodium nitrite form the ester of chlorooximino acid



According to Wieland³⁵ chlorooximino acetate condenses in the cold to dicarbethoxyfuroxan with great facility when treated with sodium bicarbonate.



The gc retention time of dicarbethoxyfuroxan on a 12% XE60 on

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(33) "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 424.

(34) G. S. Skinner, *J. Amer. Chem. Soc.*, **46**, 731 (1924).

(35) G. Wieland, *Justus Liebigs Ann. Chem.*, **367**, 52 (1909).

40-60 mesh Chromosorb W column was 26 min at 170° and 60 cm³/min He. Reported³⁶ and observed properties were in good agreement: bp 90° (0.1 Torr); mass spectra, *m/e* 29 (base), 230 (parent), 215 (P - CH₃), 200 (P - 2CH₃ and P - NO), 185 (P - OC₂H₅); ir (CCl₄) 1740 cm⁻¹ (C=O), 1620 cm⁻¹ (C=N); nmr (CCl₄) τ 8.63 and 8.59 (t, CH₃), 5.58 and 5.54 (quartet, -CH₂-). Distilled EDA purchased from Aldrich Chemical Co. did not contain a detectable amount of dicarbethoxyfuroxan. The initiation of the reaction with purchased or stored II appeared difficult and often took more than 3 hr.

Preparation of I. The reaction of yellow mercuric oxide and II as described by Buchner¹¹ was used to prepare I in 85% yield. It was noticed that the exclusion of air, moisture, and light enhanced the stability of freshly formed I in solution. Violent and almost instant decomposition occurred several times when the heat of reaction was not adequately controlled. A crystalline product of sulfur-yellow color was obtained by recrystallization from ethyl ether. Analytical data: mp 103-104°; mass spectra, *m/e* 428 (parent), *m/e* 85 (base); ir (KBr) 2075 cm⁻¹ (C=N₂), 1670 cm⁻¹ (C=O); nmr (CDCl₃) τ 8.75 (t, CH₃), 5.80 (quartet -CH₂-).

Preparation of Isomeric Ethyl Cyclohexeneacetates, IIIa. This compound was synthesized by the acidic ethanolysis of 1-cyclohexenylacetonitrile obtained from the pyrolysis of the condensation product of cyanoacetic acid with cyclohexanone.^{37,38} 1-Cyclohexenylacetonitrile: 70% yield, bp 73-74° (4 Torr) (lit.³⁷ bp 74-75° (4 torr)). Ethyl cyclohexene-1-acetate: 30% yield, bp 81-83° (7 Torr) (lit.³⁸ bp 120° (40 Torr)). The ester was purified by preparative gc.

IIIb was obtained *via* a malonic ester synthesis starting with 3-bromocyclohexene in an overall yield of 20% bp 80° (5 Torr).

IIIc was prepared by esterification of the acid resulting from the Jones reagent oxidation³⁹ of 2-(4-cyclohexenyl)ethanol. This alcohol was synthesized by disiamyl hydroboration of 4-vinylcyclohexene.⁴⁰ The overall yield of ester based on vinylcyclohexene was 31%.

Analytical separation of the three isomeric esters was achieved using a Perkin-Elmer F-11 gc and a tricresyl phosphate support coated capillary column: 50 ft \times 0.20 in., 100°, 5.5 psi He. The retention times were: for IIIa, IIIb, and IIIc, 16.0, 15.0, and 15.6 min, respectively.

Procedure. Photolyses were carried out at slightly below or room temperature. Excessive irradiation was avoided to minimize secondary decomposition. The thermolyses were performed in the quartz vessels used for photolyses by placing them in temperature controlled water or oil baths. In a few cases the decompositions were effected in sealed Carius tubes. The thermogravimetric experiment was done in a Du Pont apparatus.

Analyses. Products III to VII and IX were fractionated by bulb-to-bulb distillation at 100-110° (0.01 Torr) and then isolated from the distillate by preparative gc. The fraction distilling at 175-200° (0.01 Torr) contained the mercury adduct VIII which partially decomposed. Upon cooling, the fraction gave a crystalline, white compound (mp 126-127°, recrystallization from *n*-pentane).

For the isolation of the products from the butene reaction the photolysates of 0.5 g of I and 1.0 g of II in 100 ml of butene were subjected to bulb-to-bulb distillation. Products XII to XVIII were recovered from the fraction distilling at 80-95° (0.5 Torr). They were subsequently separated by preparative gc. At 175° (0.5 Torr) a heavy colorless oil began slowly to distil which, upon extended heating, released mercury. In the samples from *trans*-butene + I, the heavy distillate crystallized upon addition of methanol. The white crystals (mp 109-110°) were identified as XIX. The residual high boiling fraction was subjected to mass spectra analysis and found to consist mainly of mercury adducts.

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