

not rearrange in refluxing cyclohexane or in refluxing xylene in the presence of azobisisobutyronitrile and benzoyl peroxide. These results are consistent with the proposed mechanism for, in contrast to cationic species, 1,2 alkyl shifts in radical species are not generally observed.⁵

The facility of 1,2 shifts has been usefully discussed within a molecular orbital framework.^{5,15} The transition state (or metastable intermediate) is regarded to be a bridged or cyclic structure, which consequently has one bonding and two antibonding molecular orbitals. Using this model the cationic migration of an alkyl group is energetically permissible, the two electrons involved in the rearrangement being placed in the bonding orbital. However, the extra electron of the radical species must be placed in an antibonding orbital and the energy of the transition state then becomes prohibitive. This restriction need not apply in the case of silicon and other second-row elements¹⁶ because of their ability to use energetically accessible d orbitals to accommodate the extra electron.¹⁷

Apart from its theoretical significance, the rearrangement of polysilanethiols provides the first synthetic method of stepwise degradation of a polydimethylsilane chain and, as demonstrated above, may also prove valuable in determining the position of substituents and the structure of isomeric polysilanes.

(15) H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961); A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 380.

(16) For a recent summary, see P. S. Skell, "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 131; R. Kh. Freidlina, *Advan. Free Radical Chem.*, **1**, 211 (1965).

(17) Examples of anionic 1,2 shifts of trialkylsilyl groups are already well documented in the rearrangement of silylhydrazines¹⁸ and α -silyl-carbinols.¹⁹

(18) R. West and M. Ishikawa, *J. Am. Chem. Soc.*, **89**, 4981 (1967), and references therein.

(19) A. G. Brook, *Pure Appl. Chem.*, **13**, 215 (1966), and references therein.

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The Formation and Reactions of Monovalent Carbon Intermediates. II. Further Studies on the Decomposition of Diethyl Mercurybisdiazoacetate

Sir:

We have recently reported the photolysis of diazomercurials¹ as a source of the novel carbyne radicals. Further studies on the photolysis and thermolysis of diethyl mercurybisdiazoacetate (I) have led to important findings that we wish to outline briefly.

A. Effect of Wavelength. Like diazoalkanes, I exhibits two absorptions above 2200 Å ($\lambda_{\text{max}}^{\text{EtOH}}$ 3800 Å (ϵ 107) and 2640 Å (ϵ 24,900)).^{1,2} Photolysis in these bands may conceivably lead to different primary steps. In the earlier study¹ irradiations were conducted in Vycor 7910 vessels with a medium-pressure mercury arc. Under these conditions excitation is predominantly

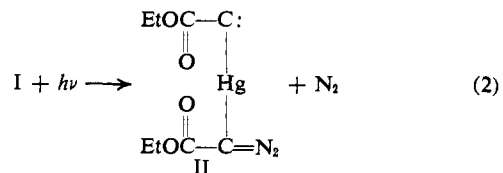
(1) T. DoMinh, H. E. Gunning, and O. P. Strausz, *J. Am. Chem. Soc.*, **89**, 6785 (1967).

(2) The analogous absorptions of diazoalkanes correspond to $\sigma^* \leftarrow \pi$ and $\pi^* \leftarrow \pi$ transitions: R. Hoffmann, *Tetrahedron*, **22**, 539 (1966), and references therein.

(>90%) in the higher energy band, resulting most likely in

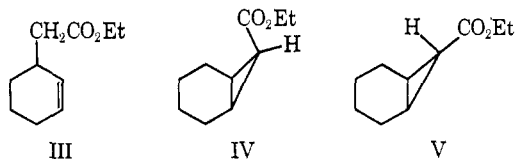


We now find that photolysis with Pyrex-filtered light ($\lambda > 2800$ Å) leads to an additional primary step



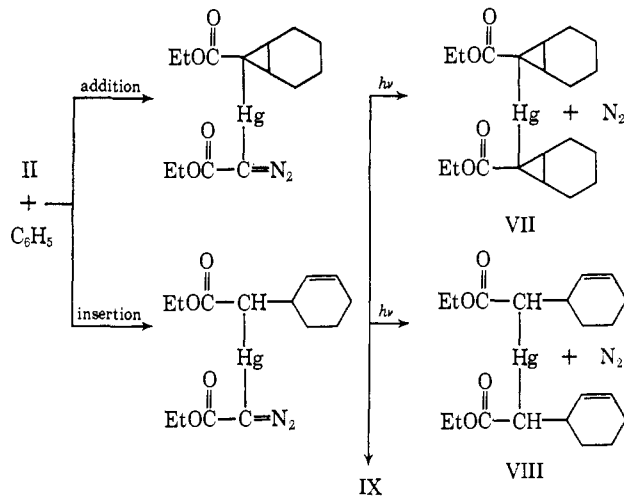
yielding the novel mercurycarbene^{3,3a} II. Above 3350 Å, step 1 diminishes (Table I) and the reaction becomes a relatively clean source of II. It is tentatively suggested that the photolysis of I in the first (π, σ^*) band proceeds *via* primary step 2 and in the second (π, π^*) band *via* step 1.

The carbyne formed in (1) reacts with cyclohexene¹ to give 3,3'-bicyclohexenyl (VI) and



and the mercurycarbene in (2) to give VII (stereostructure undetermined) along with C-H insertion (VIII) and mixed insertion-addition products (IX).

The following sequence appears to apply.



Insertion is probably into allylic C-H, with relative rates as compared to addition of 0.63 ($\lambda > 2800$ Å) and 0.50 ($\lambda > 3350$ Å).

Secondary photolysis of these mercurials with Pyrex-filtered light is insignificant as demonstrated by auxiliary experiments, and may not be the source of III-VI. However, photolysis of VII at shorter wavelengths in cyclohexene gave III-VI.

(3) This is the first reported example of a metal carbene; the phosphorus analogs have been described recently. Cf. D. Seyforth, P. Hilbert, and R. S. Marmor, *J. Am. Chem. Soc.*, **89**, 4811 (1967).

(3a) NOTE ADDED IN PROOF. Schöllkopf and Rieber have postulated the photochemical formation of analogous Sn- and Si-containing structures in a recent communication: U. Schöllkopf and N. Rieber, *Angew. Chem.*, **79**, 906 (1967).

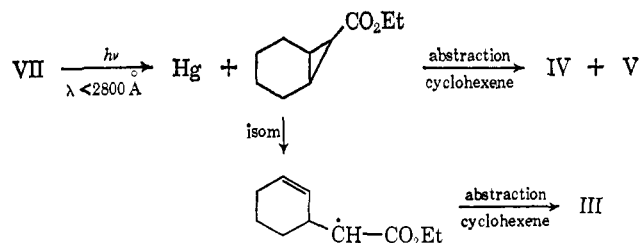


Table I shows product yield variations with experimental conditions. An increase in light energy causes a decrease in the apparent insertion to addition ratio,

Table I

Reaction	Filter	III	IV	V	III/ (IV + V)	IV/V	R(1)/ R(2)
VII $\xrightarrow{h\nu}$ C ₆ H ₁₀	Vycor 7910 $\lambda > 2150 \text{ \AA}$	11	73	16	0.12	4.6	
I $\xrightarrow{h\nu}$ C ₆ H ₁₀	Window glass $\lambda > 3350 \text{ \AA}$						<0.1
	Pyrex $\lambda > 2800 \text{ \AA}$	57	29	14	1.32	2.1	0.5
	Corex $\lambda > 2600 \text{ \AA}$	52	33	15	1.08	2.2	0.7
	Vycor 7910	44	36	20	0.79	1.8	
	Pyrex first followed by Vycor	41	44	15	0.69	2.9	
I $\xrightarrow{\Delta}$ C ₆ H ₁₀		52	29	19	1.07	1.5	

III/(IV + V). This trend is contrasted to what would be expected by inference from methylene⁴ and sulfur atom⁵ chemistry and seems to indicate the occurrence of an homoallylic rearrangement



with increasing probability in shorter wavelength photolysis. Such a rearrangement⁶ may well account for the observed *endo/exo* ratio (IV/V) which is considerably lower (1.5–2.2) than the value obtained from the photolysis of VII (4.6). To establish the occurrence of the insertion reaction among various possible isomerizations we examined the reaction with cyclohexane.

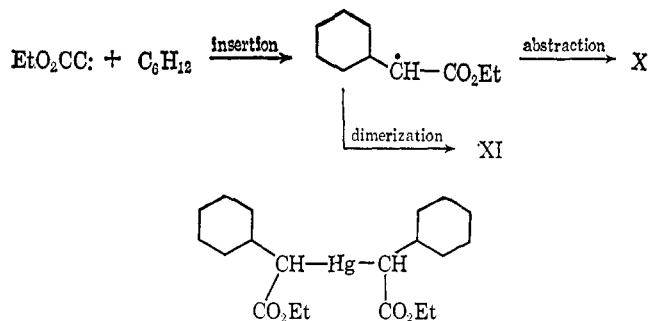
B. Photolysis in Cyclohexane. Irradiation ($\lambda > 2100 \text{ \AA}$) in cyclohexane afforded ethyl cyclohexylacetate (X) (23%), diethyl 2,3-dicyclohexylsuccinate (XI) (31%), and bicyclohexyl. Since photolysis of ethyl diazoacetate in cyclohexane⁷ has been reported to produce only X, the results suggest an efficient C–H insertion of the carbethoxymethylene. Cyclohexane was again selected as substrate to probe the insertive ability of the mercurycarbene. Photolysis using a Pyrex filter afforded high yield of essentially pure insertion product XII.

(4) See H. M. Frey in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, p 217.

(5) (a) A. R. Knight, O. P. Strausz, S. M. Malm, and H. E. Gunning, *J. Am. Chem. Soc.*, **86**, 4243 (1964); (b) K. S. Shidu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, *ibid.*, **88**, 2412 (1966).

(6) (a) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 934, 6556 (1967); (b) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, **89**, 3051 (1967).

(7) W. von E. Doering and L. H. Knox, *ibid.*, **78**, 4947 (1956).



C. Stereospecificity of Carbyne Addition. Photolysis in *cis*- and *trans*-Butenes. The mechanism of carbene addition reactions has been in the focus of attention for over a decade. The key to understanding lies in the stereochemical aspects of the reactions. Experimentally the majority of singlet carbene additions are stereospecific while triplets add nonspecifically. Two theories have been advanced. According to Skell,⁸ stereochemistry is governed by the spin conservation principle and thus the spin state of the reagents, while Hoffmann's extended Hückel MO calculation⁹ attributes stereochemical differences not to differences in spin, but the spatial part of the wave function.

The addition of carbethoxymethylene reported here is the first carbene addition reaction studied from the standpoint of stereochemistry. On a spin multiplicity basis, doublet ground-state carbene may be viewed as the analog of singlet carbene and quartet carbene as that of triplet carbene. Consequently, Skell's arguments would predict the possibility of stereospecific addition for doublet carbethoxymethylene, but MO calculations are not available. Experimentally, we find the addition to be highly stereospecific.

Irradiation of I in *trans*-butene ($\lambda > 2100 \text{ \AA}$) gave ethyl *trans*-1,2-dimethylcyclopropane-3-carboxylate with little insertion. With *cis*-butene the major products were the *cis,cis,trans* and all-*cis* isomers formed with the exclusion of the one found with *trans*-butene. Identification of the isomers was based on comparison with the products of the photolysis of ethyl diazoacetate in *trans*- and *cis*-butenes which was also found to be an entirely stereospecific reaction as reported by Doering for methyl diazoacetate.¹⁰

D. Thermolysis. At 160° in cyclohexene solution, I gave a complex reaction mixture of diethyl oxalate (III–VII) and an unidentified product. In cyclohexane, X and the same unknown compound were isolated. Thus the nature of the products indicates the intervention of similar intermediates as in photolysis. Catalytic decomposition by Cu in methylcyclohexane proceeded differently, giving (Hg(CCO₂Et)₂)₃ as the apparent major product.

Acknowledgment. We thank the National Research Council of Canada for financial support.

(8) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(9) R. Hoffmann, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstracts, K109.

(10) W. von E. Doering, *Tetrahedron*, **100**, 65 (1960).

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