

reagent, although lithium aluminum hydride has been used to achieve similar results in some special cases.¹³

We have concluded, after examination of Dreiding molecular models, that the carbonyl of **3** is not reduced by lithium aluminum tri-*t*-butoxy hydride because it is sterically hindered by the four-membered ring; *i.e.*, the reagent is too bulky for *endo* approach to the carbonyl and the salt resulting from *exo* approach of the hydride donor cannot be accommodated in the *endo* position. Consequently, *exo* hydride donation in the β -position is favored, yielding the enolate anion which is subsequently hydrolyzed to the ketone (**8**).

The results of our studies with both the bicyclo[3.2.0]heptadienyl and bicyclo[3.2.0]heptenyl carbonium ions will be reported later.

Acknowledgment. We thank Professor S. Winstein for furnishing us with an infrared spectrum of authentic bicycloheptanone (**6**).

(13) O. L. Chapman, D. J. Pasto, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1213 (1962); N. G. Gaylord in "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 15.

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Formation of Monochlorocarbene by the Gas-Phase Decomposition of Dihalomethane Molecules Excited through Recoil Tritium Substitution Reactions¹

Sir:

We have formed monochlorocarbene in the gas phase through dehydrohalogenation of highly excited dihalomethane molecules and have detected the carbene through the formation of cyclopropyl chloride in the presence of ethylene. The observation of the cyclopropane-forming reaction with olefins has been an important feature of the earlier liquid-phase experiments on monochlorocarbene from various sources.^{2,3}

The dihalomethane molecules were excited in our system through the hot atom substitution of tritium for hydrogen, forming CHTClX* from CH₂ClX.^{4,5} The monochlorocarbene thus created, after the elimination of HX,⁶ is actually CTCl, and is detected through the radioactivity of cyclopropyl-*t* chloride. Reactions have thus far been carried out with CHTCl₂* and CHTClF*, representing the elimination of HCl and HF, respectively, in the dehydrohalogenation step.

Each system contained the dihalomethane parent compound, He³, and ethylene, while some contained O₂

(1) This research was supported by A.E.C. Contract No. AT-(11-1)-407 with the University of Kansas.

(2) See, for example, W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(3) G. L. Closs and G. M. Schwartz, *J. Am. Chem. Soc.*, **82**, 5729 (1960); G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960); G. L. Closs and J. J. Coyle, *ibid.*, **84**, 4350 (1962).

(4) E. K. C. Lee and F. S. Rowland, *ibid.*, **85**, 897 (1963).

(5) Y. N. Tang, E. K. C. Lee, and F. S. Rowland, *ibid.*, **86**, 1280 (1964).

(6) The dehydrohalogenation step also goes by the alternate path of elimination of TX, with the formation of CHCl. The carbene formed in this manner is not labeled and, since it is formed in the system in amounts of the order of 10⁻¹⁰ mole fraction, is not detectable with present analytical procedures.

in addition. The recoil tritium atoms are formed by thermal neutron reactions with He³, and are able to react chemically with both C₂H₄ and CH₂ClX in energetic atomic reactions.^{7,8} These irradiated systems are analyzed for their radioactive components by the usual techniques of radio-gas chromatography, utilizing a sufficient variety of separation columns to ensure isolation and identification of all of the radioactive components.⁹ Each of the compounds found from recoil tritium reactions with C₂H₄ and CH₂ClX separately is also observed in the irradiated mixtures. In addition cyclopropyl-*t* chloride is found both in the presence or absence of oxygen as a scavenger molecule.¹⁰ The yield of cyclopropyl-*t* chloride is given in Table I, relative to the yield of CHTClX as 1.0.¹¹ No activity was observed in the form of chloropropylene-*t*, and a particular search was made for the product expected from the insertion of CTCl into the C-H bond of ethylene. The maximum yield of CHTClCH=CH₂ was less than 0.02 times the yield of cyclo-C₃H₄TCl.

Table I. Relative Yields of Cyclopropyl-*t* Chloride from Recoil Tritium Reactions with Ethylene-Scavenged Dihalomethanes^a

Gas pressures, cm.				Rel. radioactivity c-C ₃ H ₄ TCl	
CH ₂ Cl ₂	25.0	C ₂ H ₄	9.5	O ₂	0.30 ± 0.01
	26.2		33.3		0.28 ± 0.01
	5.0	28.1	0.32 ± 0.03		
	23.6	9.1	0.20 ± 0.01		
CH ₂ ClF	27.8	C ₂ H ₄	29.8	O ₂	0.27 ± 0.02
	12.5		22.1		0.22 ± 0.02
	56.1	17.5	3.4	0.10 ± 0.01	
	47.3	17.7	3.4	0.11 ± 0.02	

^a Radioactivity of CHTClX = 1.0

The amount of cyclopropyl-*t* chloride observed among the products is relatively insensitive to the presence or absence of O₂, and to the ratio of CH₂Cl₂/C₂H₄. These observations indicate semiquantitatively that the CTCl formed in this decomposition reacts approximately as well with the double bond of ethylene as with O₂, and much better than with the C-H bond of CH₂Cl₂. By analogy with current CH₂ hypotheses, we conclude that the CTCl is largely in the singlet state.¹² Quantitative evaluation of the significance of the variations in the ratios of cyclo-C₃H₄TCl/CHTClX will require further experiments on the effects of pressure, mole fraction, oxygen, etc.

The absence of CHTClCH=CH₂ as an observed product in CH₂Cl₂-C₂H₄ mixtures indicates not only that no insertion occurs for CTCl into the C-H bond of ethylene but also that no isomerization of the cyclopropyl-*t* chloride occurs. The failure to insert into

(7) For example, see "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, 1961.

(8) Y. N. Tang, Ph.D. Thesis, University of Kansas, 1964.

(9) J. K. Lee, E. K. C. Lee, B. Musgrave, Y. N. Tang, J. W. Root, and F. S. Rowland, *Anal. Chem.*, **34**, 741 (1962).

(10) Other radioactive compounds, including *n*-propyl-*t* chloride, are found in the absence of O₂.

(11) The yield of CHTClX is not an absolute standard, since it is somewhat dependent upon the pressure and composition of the system, especially the former through collisional de-excitation competition with the dehydrohalogenation reaction.⁸

(12) See, however, P. O. Gaspar and G. Hammond, Chapter 12 in ref. 2, for a discussion of the validity of these presumptions for CH₂.

ethylene C-H bonds in competition with reaction at the double bond is consistent with the liquid phase experiments of Closs, *et al.*³ The isomerization of cyclopropane formed by the addition of CH₂ to C₂H₄ is readily observed, and, at these pressures, would account for more than half of the original cyclopropane formed. The kinetic parameters, including especially the energies of activation, are not very different for monohalocyclopropanes from those of the pure hydrocarbon. Consequently, the lack of isomerization following CCl addition to ethylene must result from a considerably lower excitation energy in the excited molecule, reflecting a lower heat of addition to the double bond for monochlorocarbene than in the corresponding CH₂.

An additional major radioactive product was observed from the CH₂ClF-C₂H₄-O₂ samples, with a relative yield compared to the parent of 0.36 ± 0.02. This compound corresponds to a monofluoro C₃ compound, and probably is cyclopropyl-*t* fluoride, from the reaction with ethylene of CTF formed by the expected elimination of HCl from CHTClF*. Further experiments are being carried out since monofluorocarbene has not yet been reported in the literature.

Pyrolytic decomposition of the molecules CH₂Cl₂ and CH₂ClF presumably will also result in the formation of monohalocarbenes. The recoil tritium method of excitation has the advantage that all of the other molecules in the system except those specifically excited by tritium reaction have a much lower state of excitation, determined by the ambient temperature of irradiation, and are not expected to undergo subsequent pyrolytic reactions. This is particularly useful and important when the observations are based on molecules (*e.g.*, monohalocyclopropane) whose kinetic parameters indicate comparable or more rapid rates of decomposition than the dihalomethane molecules themselves. The recoil tritium has in addition both the advantages and disadvantages of being a radioactive tracer method: the products have the asset of containing radioactive atoms, and hence can easily be traced; on the other hand, they are formed in negligible quantities unsuitable for further experiments (synthetic, spectroscopic, etc.) requiring macroscopic quantities of the compound.

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Photosensitization by Ferrocene. Photochemistry of Higher Electronic Excited States

Sir:

We wish to report that ferrocene catalyzes the photochemical *cis-trans* isomerization of piperylene and the dimerization of isoprene. The evidence leads us to suggest that the mechanism for these reactions involves a complex of ferrocene and olefin which absorbs light and is excited to an electronic state considerably higher than the first excited singlet. This excited state disso-

ciates to ferrocene in a triplet state and to a triplet olefin which then isomerizes or adds to a ground-state olefin.

Much recent work has demonstrated the capacity of various substances, called photosensitizers, to promote the isomerization and dimerization of various olefins.¹⁻⁴ In many of these cases the mechanism of photosensitization has been shown to involve transfer of energy and multiplicity from the sensitizer to the olefin with resultant excitation of the olefin to its lowest triplet state. In some other cases, *e.g.*, the photoaddition of maleic anhydride to benzene, the reaction proceeds *via* the triplet state of the complex.⁵ The addition of maleic anhydride to cyclohexene has been reported to involve formation of an intermediate complex.⁶ Also, recent reports indicate that cuprous chloride and rhodium chloride catalyze photocyclization of 1,5-cyclooctadiene.⁷

We have observed that ferrocene accelerates the photoisomerization of *trans*-piperylene by a factor of at least five and catalyzes the photodimerization of both piperylene and isoprene. The photolyses were carried out in sealed, degassed Pyrex tubes. A Hanovia 450-watt medium-pressure mercury lamp in a quartz immersion well provided the necessary irradiation. The dimerization reactions were studied using neat olefin solutions; the isomerizations were accomplished using various concentrations of piperylene in solvents such as benzene, decalin, and *trans*-1,2-dimethylcyclohexane. In a typical isomerization experiment a solution of 1.0 *M* ferrocene and 0.2 *M trans*-piperylene in benzene was isomerized 9.3% (corrected for back reaction) in 3 hr. while a similar solution without ferrocene was isomerized 2.0% after 4 hr. The dimerization of isoprene was studied in neat solutions of isoprene that contained 0.05 *M* ferrocene. If a Pyrex immersion well housed the lamp (minimum wave length 2800 Å.) the reactions were markedly slowed. A uranyl glass filter (minimum wave length 3300 Å.) completely stopped the ferrocene-induced isomerization of piperylene. On the other hand, substitution of quartz for Pyrex tubes accelerated the isomerization reaction by increasing the intensity of the light in the 2800 Å. region.

The photostationary state observed in ferrocene-sensitized piperylene isomerization and the product distribution for the ferrocene-sensitized dimerization of isoprene are the same as those reported in cases where the energy of the triplet state of the sensitizer exceeds the triplet-state energy of the olefin so that olefin triplet states are easily generated from both isomers ("high energy" sensitizers).^{1, 2, 8} Thus, we find that ferrocene-

(1) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(2) J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515 (1963).

(3) R. S. H. Liu, Ph.D. Thesis, California Institute of Technology, 1964.

(4) G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963).

(5) G. S. Hammond and W. M. Hardham, *Proc. Chem. Soc.*, 63 (1963).

(6) R. Robson, P. W. Grubb, and J. A. Barltrop, *J. Chem. Soc.*, 2153 (1964).

(7) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963); **86**, 3318 (1964).

(8) The value for the percentage cyclobutanes and cyclooctadienes reported in ref. 5 is incorrect. The correct value of the dimer composition for a high-energy sensitizer is 92% cyclobutanes and cyclooctadienes (R. S. H. Liu, personal communication).