(CO)$^+$ gave $C_6H_4D_2Fe^+$ (*m/e* 136). The mass spectra of both the nondeuterated and deuterated complexes exhibited bands at *m/e* 112 for $Fe(CO)_2^+$ and 84 for Fe(CO)$^+$ and the most intense band in both spectra was due to Fe^+ (*m/e* 56).

These results clearly indicate that the formation of conjugated diene–iron tricarbonyl complexes, by reaction of nonconjugated dienes with iron carbonyls, occurs *via* a π-allylhydroiron tricarbonyl intermediate. In addition it may be suggested that the mechanisms for complex formation and for catalytic isomerization of allylic alcohols are similar. An alternative mechanism involving hydrogen migration through a suprafacial pathway is also possible, but this alternative has been ruled out in the allylic alcohol–carbonyl isomerization reaction.[3]

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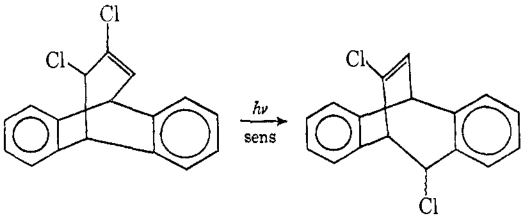
Photochemical Transformations. V. Allylic Rearrangements and Rearrangement of Allylic Halides to Cyclopropyl Halides[1]

Sir:

We recently reported[1c] the photosensitized rearrangement of 3,4-dichloro-6,7:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-triene (**1**) to a mixture of *exo* and *endo* epimers of 4,6-dichloro-2,3:8,9-dibenzobicyclo[3.2.2]-nona-2,6,8-triene (**2**). As the reaction **1** → **2** is formally related to a Wagner–Meerwein isomerization, we suggested that other systems, which (a) are capable of accepting triplet photosensitization and (b) may have formal analogy to carbonium ion rearrangements, may be amenable to rearrangement.



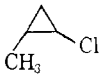
1 **2**

Preliminary work has suggested that a number of such processes do occur. These will be reported as data satisfactory for publication accumulate. The first experiments which we wish to report involve sensitized photorearrangements of α-methylallyl chloride (**3**), γ-methylallyl (crotyl) chloride (**4**), allyl chloride, and allyl bromide. Allylic systems represent reasonable choices to study, in view of the voluminous and important contributions which work on such compounds has led to in our understanding of anionotropic rearrangements.[2]

When crotyl chloride (**4**) was irradiated[3] in acetone, the expected isomerization to **3** occurred rapidly, with 16% of **3** formed in 8 hr. Continued irradiation slowly gave rise to two new and unexpected products. After 56 hr, the reaction mixture[4] consisted of 13% **3**, 25% **4**, 13% **5**, and 15% **6**.[5] Similarly, when a 75:25 mixture of **3**:**4** was irradiated in acetone for 30 hr, the product mixture contained 20% **3**, 33% **4**, 6% **5**, and 10% **6**; **5** and **6** do not appear to be photolabile (60-hr irradiation). Benzene and *m*-xylene were also found to be satisfactory solvent-sensitizers. Irradiation (λ >2700 Å) of **4** in pentane produced no **5** or **6** and only extremely slow conversion to **3**. **3** and **4** were stable in the dark when subjected to otherwise similar conditions. It should be noted that the irradiated solutions have a higher ratio of **3**:**4** than results from thermodynamic equilibration,[7] and the formation of **5** and **6** from **3** or **4** is also opposite to that observed in ground-state chemistry.[8]

$CH_2{=}CHCHClCH_3$ $CH_3CH{=}CHCH_2Cl$

3 **4**



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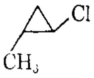

6

As the formation of the cyclopropanes was of substantial theoretical and practical interest, offering the possibility of a new synthetic procedure for cyclopropyl halides, we have looked briefly at photoreactions of allyl chloride and bromide. The chloride was irradiated in methyl ethyl ketone and gave 19% yield of chlorocyclopropane[9] in 24 hr, while the bromide in acetone gave 11% of bromocyclopropane[9] after 16 hr.

Volman and Phillips[10] have noted that at least 18 volatile compounds are formed by the unsensitized irradiation with 2537-Å light of liquid allyl chloride; chlorocyclopropane was not found. They suggest that the (*unsensitized*) primary photochemical process is homolytic cleavage of the carbon–chlorine bond. Our results, which are so different from Volman's, are consistent with the idea suggested earlier[1c] that such photochemical processes proceed through vibrationally excited carbonium ion–halide ion ion pairs which combine to give thermodynamically unstable (or stable)

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[1] Previous papers in series: (a) S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.*, **76**, 5000 (1954); (b) *ibid.*, **80**, 1950 (1958); (c) S. J. Cristol, G. O. Mayo, and G. A. Lee, *ibid.*, **91**, 214 (1969); (d) S. J. Cristol and G. O. Mayo, *J. Org. Chem.*, **34**, 2363 (1969).

(2) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

(3) A Hanovia 450-W high-pressure mercury vapor lamp (type L) was used with a water-jacketed quartz immersion well. Approximately 0.1–0.3 *M* solutions of the allylic halide in solvent-sensitizer were degassed and irradiated in thin-wall Pyrex tubes.

(4) Reaction progress was monitored by gas chromatography (gc) using a Aerograph Model 90-P instrument. Product mixtures were satisfactorily analyzed using a 15-ft × 0.25 in. column packed with 25% SE-30 on 60–80 mesh Chromosorb W and a 10 ft × 0.25 in. column packed with 18% SE-30 on 60–80 mesh Chromosorb W.

(5) Compounds **5** and **6** were isolated from photoreaction mixtures by preparative gc and the assigned structures were consistent with the following spectral data: (**5**) pmr (CCl_4), H-1 τ 8.8 (m), H-2 6.96 (m), H-3_{syn} 9.64 (d, $J = 3.4$ Hz), H-3_{anti} 8.98 (m), 1-CH_3 8.8; ir (CCl_4)[6] 1032 cm^{-1} (w); *m/e* (70 eV) 90 (3), 92 (1); (**6**) pmr (CCl_4), H-1 τ 9.0 (m), H-2 7.4 (m), two H-3 9.38 and 9.14 (b-m), 1 CH_3 8.9 (d, $J = 1.1$ Hz); ir (CCl_4)[6] 1029 (m), 1060 cm^{-1} (w); *m/e* (70 eV) 90 (3), 92 (1).

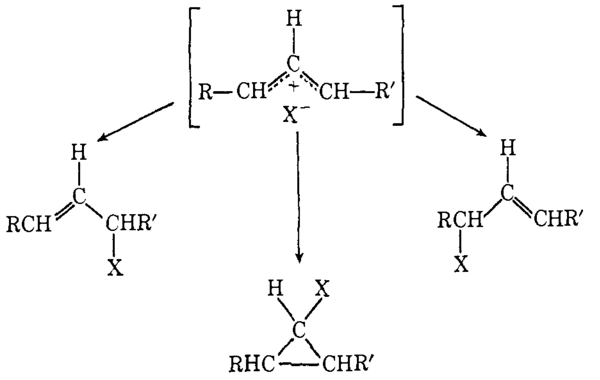
(6) Analogous to the corresponding bromides reported by H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).

(7) J. F. Lane, J. Fentress, and L. T. Sherwood, Jr., *J. Amer. Chem. Soc.*, **66**, 545 (1944).

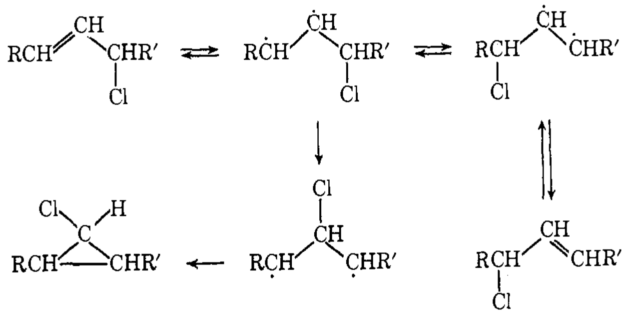
(8) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(9) These products were identified by comparison of retention volumes and ir spectra with authentic compounds.

(10) (a) D. H. Volman and R. W. Phillips, *Ber. Bunsenges Phys. Chem.*, 72, 242 (1968); (b) R. W. Phillips and D. H. Volman, *J. Amer. Chem. Soc.*, **91**, 3418 (1969).

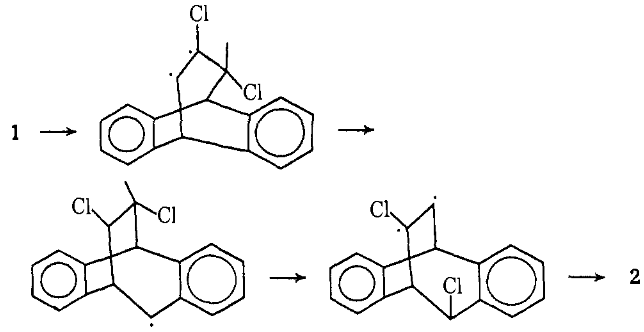


Scheme I



products. Support for such ideas may be found in the photochemical solvolysis experiments described by Zimmerman[11] and in the work of Beugelmans,[12] who has reported photochemical rearrangements, solvolyses, and eliminations, which also appear to involve carbonium ion intermediates.

On the other hand, our work on halides can be rationalized *via* triplet diradical intermediates, for example, as in Scheme I. A similar process can be imagined for the **1** → **2** conversion *via* triplet intermediates, but with a 1,4-chlorine shift, rather than a 1,2 or 1,3 shift.



Further exploratory and mechanistic work on such rearrangements is in process or planned.

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[11] H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963); H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963).

[12] (a) J. Pusset and R. Beugelmans, *Tetrahedron Lett.*, 3249 (1967); (b) H. C. de Marcheville and R. Beugelmans, *ibid.*, 6331 (1968); (c) R. Beugelmans and H. C. de Marcheville, *Chem. Commun.*, 241 (1969).

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Additions and Corrections

Radical Additions of Cl–CCl$_3$ to *cis*-Cyclooctane [*J. Am. Chem. Soc.*, **89**, 3205 (1967)]. By James G. Traynham and Thomas M. Couvillon, Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803.

The correct symmetry number for BrCCl$_3$ was used for the calculations summarized on page 3308, although the number itself is erroneously printed.

Addition of Electronegatively Substituted Azides to Allenes [*J. Am. Chem. Soc.*, **90**, 2131 (1968)]. By R. F. Bleiholder and H. Shechter, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

On page 2133, paragraphs 1 and 2, and page 2134, paragraphs 1 and 2, the unusual nmr spectra of N-(1,2-3-trimethyl-2-butenylidene)benzenesulfonamide (XVII) and N-(1,2,3-trimethyl-2-butenylidene)-*p*-toluenesulfonamide (XIX) were discussed on the basis of hindered rotation of their α-methyl groups or *syn–anti* isomerism of the arylsulfonimino groups. Reevaluation of the nmr spectra of XVII and XIX reveals that the absorptions of the methyl groups in the τ 7.8–7.9 and the 7.4 regions are singlets. The interpretation that the nmr results from a barrier to rotation of one of the methyl groups in XVII and XIX is untenable in that the nonequivalent protons should thus constitute an A$_2$X group with a minimum of 5 lines and J_{AX} quite large. The nmr spectra of XVII and XIX are interpretable however in that in solution the sulfonimines exist as equilibrium mixtures of *syn* and *anti* isomers. Confirmation of the latter conclusion is derived from observations that in various solvents the singlets for the α-methyl groups in XVII and XIX occur in ratios of less than 2:1. The long-range deshielding, the rapid *syn–anti* isomerization upon heating, and the crystallization of single geometric isomers from *syn* and *anti* mixtures of XVII and XIX, respectively, in solution parallel the behavior reported previously for N-(3b,4,-5,6,6,6a-hexachlorodecahydro-2,5,7-metheno-3H-cyclopenta[*a*]pentalen-3-ylidene)-*p*-toluenesulfonamide [R. J. Stedman, A. C. Swift, and J. R. E. Hoover, *Tetrahedron Lett.*, 2525 (1965); R. J. Stedman, private communication]. We wish also to acknowledge communication with M. Raban on this subject.

Temperature Effect on Sulfur Dioxide Vapor Luminescence [*J. Am. Chem. Soc.*, **90**, 2972 (1968)]. By H. D. Mettee, Department of Chemistry, University of Texas at Austin, Austin, Texas 78712.

Reactions 1, 2, and 3 between SO and O$_3$ do *not* require the third body M as shown. The bimolecular