1-Cyclohexylcyclohexene (30). A. Sensitized Irradiation. A solution containing 3.28 g of olefin **30** and 3.0 g of *p*-xylene in 100 ml of methanol was irradiated through a Vycor filter for 16 hr. Gas chromatographic analysis revealed the formation of two principal products accompanied by a number of minor products. Isolation of the first principal component afforded bicyclohexylidene (**32**). Isolation of a second component afforded a specimen of the ether **33** which was identical in all respects with that described above. These products were formed in yields of 29 and 53%, respectively.

B. Direct Irradiation. A solution containing 3.00 g of olefin **30** and 0.5 ml of concentrated sulfuric acid in 100 ml of methanol was irradiated for 16 hr. Gas chromatographic analysis revealed the formation of ethers **33** and **34** (50 and 10% yields, respectively) along with an unresolved mixture of olefins **30** and **32** (33%).

Irradiation of 1,1′-Bicyclohexenyl (31). A 75-ml methanolic solution containing 1.5 g of olefin **31** and 1.5 g of acetophenone was irradiated for 6 hr through a Pyrex filter as described above. Gas chromatographic analysis revealed the formation of a single principal product. Isolation by preparative techniques afforded a specimen of ether **34** which was identical in every respect with that described above.

Irradiation of 2-Methyl-2-butene (36). A solution containing 3.01 g of olefin **36** in 200 ml of methanol was irradiated as described above for 72 hr. Gas chromatographic analysis revealed a 20% recovery of olefin **36** and the formation of three hydrocarbon products having retention times corresponding to **2-methylbutane (41)**, **3-methyl-1-butene (42)**, and **2-methyl-1-butene (43)** in yields of 4, 17, and 21%, respectively. In addition, the presence of four ether products was indicated. Isolation of the first component by preparative techniques (A) afforded **1,2-dimethylpropyl methyl ether (37)**[27] as a colorless liquid: ν_{max} 1386, 1372, and 1100 cm^{-1}; nmr τ 6.77 (s, 3, CH_3O), 7.05 (t, 1, J = 7.5 Hz, CH-1), 8.98 (d, 3, J = 6 Hz, CH_3-1), and 9.12 (d, 6, J = 7.5 Hz, 2 CH_3-2). This material was identical in all respects with a specimen prepared independently by the treatment of 8.8 g of 3-methyl-2-butanol with 4.8 g of a 50% suspension of sodium hydride in 30 ml of ether for 5 hr at 25°, followed by the addition of 15 g of methyl iodide and continued stirring overnight. Decanting of the reaction mixture followed by distillation afforded 3.70 g of a colorless liquid, bp 70–74°.

Isolation of the second ether component afforded **1,2-dimethyl-2-propenyl methyl ether (38)** as a colorless liquid: ν_{max} 3080, 1650, 1371, 1115, 1095, 1078, and 901 cm^{-1}; nmr τ 5.16 (br s, 2, CH_2═), 6.40 (q, 1, J = 8 Hz, CH-1), 6.87 (s, 3, CH_3O), 8.37 (br s, 3, CH_3-2), and 8.82 (d, 3, J = 8 Hz, CH_3-1); *m/e* 100.0886 (calcd for $C_{16}H_{12}O$, 100.0888), 85, 69, 59, and 55. This material was identical in all respects with a specimen prepared independently by the treatment of 8.6 g of 3-methyl-3-buten-2-ol with 4.8 g of 50% sodium hydride suspension and 15 g of methyl iodide as described above. Decanting and distillation afforded 3.70 g of a colorless liquid, bp 60–68°.

Evidence for the presence of the isomeric tertiary ethers **39** and **40** was obtained by comparison of the retention times of authentic specimens and the irradiation products on three (A–C) gas chromatographic columns. **1,1-Dimethylpropyl methyl ether (39)**[28] was prepared by the treatment of 4 ml of olefin **36** with 10 ml of methanol containing 7 drops of concentrated sulfuric acid for 1 month at 25°. Quenching of the reaction with an excess of sodium bicarbonate followed by filtration and distillation afforded a colorless liquid, bp 60–64°. Final purification by preparative gas chromatography afforded ether **39** as a colorless liquid: ν_{max} 1380, 1365, 1189, and 1087 cm^{-1}; nmr τ 6.92 (s, 3, CH_3O), 8.55 (q, 2, J = 5 Hz, CH_2-2), 8.91 (s, 6, 2 CH_3-1), and 9.17 (t, 3, J = 5 Hz, CH_3).

1,1-Dimethyl-2-propenyl methyl ether (40)[29] was prepared by treatment of 8.6 g of 1,1-dimethyl-2-propen-1-ol with 4.8 g of 50% sodium hydride and 15 g of methyl iodide as described above. Decanting and distillation afforded 4.6 g of a colorless liquid: bp 70–75°; ν_{max} 3091, 3068, 1648, 1412, 1375, 1360, 1173, 1145, 1075, 1000, and 922 cm^{-1}; nmr τ 4.2, 4.8, and 5.05 (3 m, 3, vinyl H), 6.93 (s, 3, CH_3O), and 8.75 (s, 2 CH_3-1).

Gas chromatographic analysis revealed that ethers **37–40** were obtained in yields of 3, 10, 1, and 0.5%, respectively.

Acknowledgments. Support of this work by the U. S. Army Research Office in Durham is gratefully acknowledged, as is support (for the Research Triangle Center for Mass Spectrometry) from the Biotechnology Resources Branch of the Division of Research Resources of the National Institutes of Health under Grant No. PR-330.

Photochemical Transformations. VIII. Photosensitized Rearrangements of Some Acyclic Allylic Halides[1]

Stanley J. Cristol,* George A. Lee,[2a] and Allen L. Noreen[2b]

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received February 5, 1973*

Abstract: Photosensitizer-mediated irradiations of a number of acyclic allylic chlorides (and of allyl bromide) have been conducted. In addition to the cis–trans isomerization anticipated for appropriate olefins, allylic (1,3-sigmatropic) rearrangements and rearrangements of allylic halides to halocyclopropanes (1,2-sigmatropic photocyclizations) were observed. Solvent effects on these rearrangements and upon the competing free-radical processes have been studied. Evidence for triplet photosensitization has been adduced and some quantum yield and quenching studies have been conducted. Possible reaction paths are considered for the photorearrangements.

As reported earlier,[3] our interest in the preparation of bridged polycyclic compounds by the photoinduced di-π-methane rearrangement[4,5] led us to the irradiation of an acetone solution of **1**, anticipating the formation of **2**. Irradiation instead led to a mixture of the exo and endo epimers of **3**, a result which appeared to have no precedent in the photochemical literature, involving a process formally analogous to a Wagner–Meerwein rearrangement. As we had previously shown[6] that **3** is substantially less stable than **1**,

---

(1) (a) Previous paper in series: S. J. Cristol and G. C. Schloemer, *J. Amer. Chem. Soc.*, **94**, 5916 (1972). (b) Portions of this work were presented in the James Flack Norris Award address at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972. (c) Other portions were described in a preliminary communication: S. J. Cristol and G. A. Lee, *J. Amer. Chem. Soc.*, **91**, 7554 (1969).

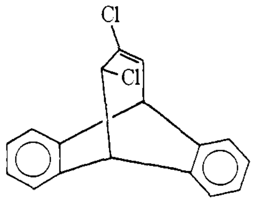
(2) (a) From the Ph.D. Thesis of G. A. L., 1971, NDEA Fellow; (b) from the Ph.D. Thesis of A. L. N., 1970.

(3) S. J. Cristol, G. O. Mayo, and G. A. Lee, *J. Amer. Chem. Soc.*, **91**, 214 (1969).

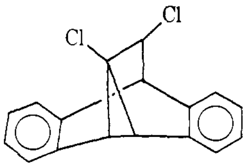
(4) E. Ciganek, *ibid.*, **88**, 2882 (1966).

(5) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967).

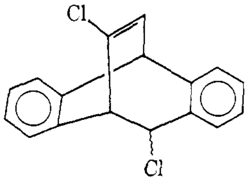
(6) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *ibid.*, **90**, 5564 (1968).



1



2

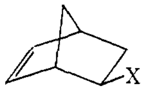


3

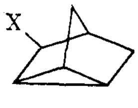
the process was clearly photochemical (that is, *not* the result of a photoinduced chain reaction). The process was shown[3] to be sensitized by benzene, acetone, and benzonitrile, but not by acetophenone or benzophenone. These results were interpreted as suggesting that a triplet state (of minimum energy 74–77 kcal/mol) intervened (although not necessarily as the product-forming intermediate), and this interpretation was strengthened by noting that **3** was not formed by direct irradiation of **1** in cyclohexane.

As the "ground-state" isomerization of **3** to **1** and analogous reactions had been studied in detail in our laboratory,[6] and various cationic intermediates had been demonstrated, we were naturally attracted to the idea that the chemistry done in the reverse photo process (**1** → **3**) might occur from a vibrationally excited cationic species rather than from some electronically excited one. Although, as will be seen below, this question remains unresolved, this idea suggested that other systems which (a) are capable of accepting energy from photosensitizers and (b) may have reaction paths available to them with formal analogy to carbenium ion rearrangements might be amenable to rearrangement.

Two systems immediately came to mind. These were the allylic system, which represents such an important part of the background of our knowledge of anionotropic rearrangements,[7] and the homoallyl-cyclopropylcarbinyl system, exemplified in the norbornenyl (**4**)–nortricyclyl (**5**) system, also studied[8] in great detail in ground-state chemistry and contributing much to our understanding of this area. The latter system was not fruitful for the purposes we had in mind, as rearrangements were not observed,[9] but our preliminary results on photorearrangements and other photoreactions of acyclic allylic halides are the basis of this paper.



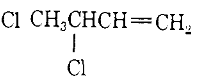
4



5

$CH_3CH{=}CHCH_2Cl$

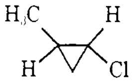
6



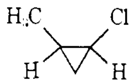
$CH_3\underset{\underset{Cl}{|}}{C}HCH{=}CH_2$

7

Irradiation with an Hanovia 450-W high-pressure mercury lamp of an acetone solution of crotyl chloride (**6**) in a thin-walled Pyrex tube for 8 hr led to the predicted formation of the allylic isomer, α-methylallyl chloride (**7**). In addition, it became clear that, as irradiation was continued, two new and unexpected isomeric products were formed. After 56 hr, the reaction mixture yielded 25% **6**,[10] 13% **7**, 15% of *trans*-2-chloro-1-methylcyclopropane (**8**), and 14% of the cis isomer **9**.[11] When a solution of **7** in acetone was irradiated for 30 hr, analysis revealed the recovery of 20% **7** as well as a 33% yield of **6**, 10% of **8**, and 5% of **9**. It should be noted that the irradiated solutions had a substantially higher ratio of **7**:**6** than that which results from thermodynamic equilibration,[12] so that we were dealing with a photochemical process in the transformation of **6** to **7**, and presumably in the reverse transformation as well, and not merely some photoinduced chain process. The formation of chlorocyclopropanes **8** and **9** from allylic chlorides **6** and **7** is also clearly the reverse of the ground-state thermodynamic result.[13] The cyclopropanes appeared to be photostable to light of λ >270 nm.



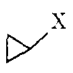
8



9

$CH_2{=}CHCH_2X$

10



11

Sensitization of allylic rearrangement and of cyclopropane formation was also noted with benzene and *m*-xylene, but these reactions were attended by substantial side reactions,[14] so that yields of C_4H_7Cl isomers were relatively small. For example, irradiation of **6** in *m*-xylene for 38 hr gave 3.7% **6**, 9.0% **7**, 7.1% **8**, and 4.5% **9** (76% loss), while that of **7** gave 4.9% **6**, 17.6% **7**, 6.2% **8**, and 5.3% **9** (66% loss) in a like time. Direct irradiation of **6** in pentane (λ >270 nm) gave no isomerization, and most of the **6** was recovered.[15]

Allyl chloride (**10**-Cl) and allyl bromide (**10**-Br) were then scrutinized briefly. Irradiation of **10**-Cl in methyl ethyl ketone for 12 hr gave 16% **10**-Cl and 17% of chlorocyclopropane (**11**-Cl), while in benzene, irradiation for 35 hr gave 24% of **10**-Cl and only 2.9% of **11**-Cl. Allyl bromide (**10**-Br) in acetone (16 hr) gave 25% of recovered **10**-Br and 10% conversion to bromocyclopropane (**11**-Br).

Volman and Phillips[16] have noted that at least 18

---

(7) For reviews, see (a) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956); (b) P. B. D. de la Mare in "Molecular Rearrangements," P. de Mayo, Ed., Wiley-Interscience, New York, N. Y., 1963, p 27 ff.

(8) See, for example, (a) J. D. Roberts, W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, **72**, 3329 (1950); J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954); J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **77**, 3034 (1955); (b) S. Winstein, H. M. Walborsky, and K. Schreiber, *ibid.*, **72**, 5795 (1950); S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); (c) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962); S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **88**, 3087 (1966).

(9) The photochemistry of a variety of norbornenyl systems, studied by G. A. Lee and J. E. Rodgers, will be published later.

(10) Our early gc analyses did not separate *cis*- and *trans*-crotyl chlorides.

(11) The spectroscopic data (ir, pmr, and ms) leading to the assignment of structures to **8** and **9** are given in the preliminary communication,[1c] and will not be repeated here.

(12) (a) J. F. Lane, J. Fentress, and L. T. Sherwood, Jr., *J. Amer. Chem. Soc.*, **66**, 545 (1944); (b) D. C. Dittmer and A. F. Marcantonio, *J. Org. Chem.*, **29**, 3473 (1964).

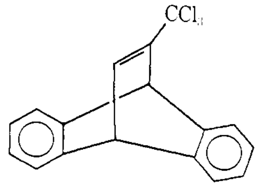
(13) J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951).

(14) These are the result of free-radical reactions. A detailed study is being carried out and will be reported later: R. Daughenbaugh, unpublished results.

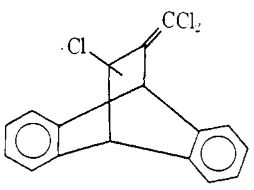
(15) It seems reasonable to assume that no light was absorbed in this system, and that the losses were due to adventitious polymerization of **6**.

(16) (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).

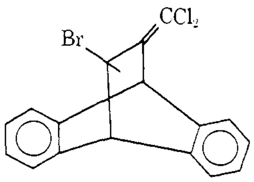
volatile compounds were formed by the unsensitized irradiation of allyl chloride with 254-nm light (chlorocyclopropane was not observed). They suggest that the (unsensitized) primary photochemical process was homolytic cleavage of the carbon–chlorine bond. Similarly, the allylic photochemical rearrangement of **12** to **13** noted by Jarvis,[17] which when carried out in bromotrichloromethane led[17b] to **14** as well as **13**, may be the result of homolytic reactions.



12



13



14

Our results, which were so different from Volman's (but see ref 14), again attracted us to the idea of a vibrationally excited cationic intermediate and to a study of solvent effects upon these photoisomerizations. It seemed reasonable to assume that, with competitive homolytic and heterolytic processes possible, the ionic processes might compete better in more polar solvents, or might be diverted to solvolysis in protic solvents. Attempts to test this idea with **6**, **7**, or **10**-Cl in an 80:20 methanol–acetone solvent–sensitizer combination were thwarted when side reactions occurred.[18] To reduce the possibility of radical-chain processes involving solvent, we decided to try acetonitrile as solvent. Irradiation of α-methylallyl chloride (**7**) in 80:20 (v/v) acetonitrile–acetone[20] solvent–sensitizer mixture for 31 hr produced a mixture containing 63% **7**, 16% *trans*-**6**, 3% *cis*- **6**, 11% **8**, and 7% **9** and 43-hr irradiation of a solution containing 75% *trans*-**6**, 23% *cis*-**6**, and 2% **7** gave 18% *trans*-**6**, 4% *cis*-**6**, 44% **7**, 18% **8**, and 16% **9**. Recovery of C_4H_7Cl isomers was close to quantitative in these and in subsequent experiments with acetonitrile–acetone, so that continued irradiation leads to high (often close to quantitative) yields of chlorocyclopropanes, suggesting a potentially useful synthetic procedure. Use of impure starting materials or solvents, or lack of careful deaeration procedures, greatly diminished the yield of chlorocyclopropanes.

Solvent effects were also looked at with allyl chloride (**10**-Cl) ring closure to cyclopropyl chloride (**11**-Cl). Table I gives the results observed when an 0.2 *M* solution of allyl chloride in a mixture (v/v) of 20% acetone–80% cosolvent was irradiated in Pyrex. As with the butenyl chlorides, solvent effects upon yields of chlorocyclopropanes were large, with chemical yields varying from about 3% in cyclohexane–acetone and methanol–acetone to about 90% in acetonitrile–acetone. The results in methanol have already been discussed.[18]

Table I. Solvent Effects on Allyl Chloride (**10**-Cl) Photocyclization to **11**-Cl Yields[a]

	% **10**-Cl		% **11**-Cl	
Cosolvent	Recovered	Consumed	Found	Yield[b]
Acetone	75.4	24.6	8.7	35
Methanol	10.4	89.6	3.3	4
Benzene	53.1	46.9	4.6	10
Cyclohexane	12.4[c]	87.6	2.6[c]	3[c]
Acetonitrile	87.5	12.5	10.8	86

[a] Irradiation of 0.2 *M* allyl chloride in 20% acetone–80% cosolvent for 6 hr at 8°. [b] Ratio of % **11**-Cl formed to **10**-Cl consumed. [c] Maximum value, standard obscured by solvent.

When the reaction in cyclohexane–acetone was scrutinized further, it was noted that a principal product was allylcyclohexane. It seems reasonable to assume that this is the result of the reactions in eq 1–3,

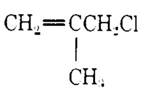
$$[CH_2{=}CHCH_2Cl]^* \longrightarrow [CH_2\!\cdots\!CH\!\cdots\!CH_2]\cdot + Cl\cdot \qquad (1)$$

$$Cl\cdot + C_6H_{12} \longrightarrow HCl + C_6H_{11}\cdot \qquad (2)$$

$$C_6H_{11}\cdot + C_3H_5\cdot \longrightarrow C_6H_{11}CH_2CH{=}CH_2 \qquad (3)$$

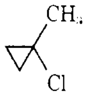
and is a consequence of the fact that homolysis of the carbon–chlorine bond in the photosensitized allyl chloride molecule is favored over the ring-closing path in this nonpolar hydrogen-donating solvent. Results in the other solvents will be discussed below in the section on mechanistic considerations.

A brief study was then undertaken as to the generality of these rearrangement reactions in the acetonitrile–acetone solvent sensitizer system. β-Methylallyl chloride (**15**) was converted to 1-chloro-1-methylcyclopropane (**16**) in high yield. *cis*- and *trans*-1,3-dichloropropene (**17**) were interconverted and were transformed to allylidene chloride (**18**) and to *cis*- and *trans*-1,2-dichlorocyclopropane (**19** and **20**, respectively), thus showing both allylic rearrangement and allyl to cyclopropyl rearrangement. Interestingly and importantly, *cis*-**17** gave more *cis*-cyclopropane (**19**) than *trans*- (**20**), while the reverse was true for *trans*-**17**.



$CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}CH_2Cl$

15



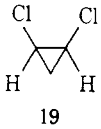
16

$CH_2ClCH{=}CHCl$

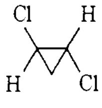
17

$CH_2{=}CHCHCl_2$

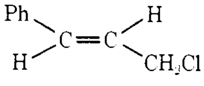
18



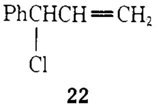
19



20

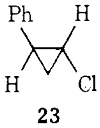


21

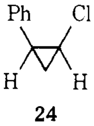


$Ph\underset{\underset{\displaystyle Cl}{|}}{CH}CH{=}CH_2$

22



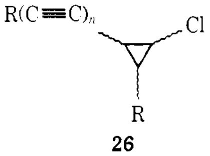
23



24

$R(C{\equiv}C)_nCH{=}CHCHR'Cl$

25



26

---

[17] (a) B. B. Jarvis, *J. Org. Chem.*, 33, 4075 (1968); (b) B. B. Jarvis and R. O. Fitch, *Chem. Commun.*, 408 (1970).

[18] The nature of these reactions remains to be investigated; no butenyl methyl ether, allyl methyl ether, or cyclopropyl methyl ether was observed and the recoveries of C_4H_7Cl or C_3H_5Cl species were substantially reduced compared with those of the acetone experiments. Presumably radical-chain reactions[19] involving methanol intervened.

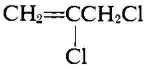
[19] W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *J. Amer. Chem. Soc.*, 76, 450 (1954).

[20] This concentration of acetone is sufficient to absorb 99% of the light passing through Pyrex glass and in the 300-nm region.

trans-Cinnamyl chloride (**21**) was transformed rapidly to its allylic isomer, α-phenylallyl chloride (**22**), and, at about one-half this rate, to *trans*-2-chloro-1-phenylcyclopropane (**23**). A small amount of *cis*-cinnamyl chloride was also formed. While the initial photocyclization gave only trans isomer **23**, extended irradiation gave a photostationary state containing approximately equal amounts of **23** and **24**, a result perhaps to be anticipated from the previously observed photoisomerizations of diphenylcyclopropanes.[21] As with other cases, the formation of **23** from **21** (and **22**) is close to quantitative.

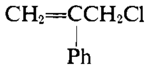
Bohlmann and coworkers[22] have recently described a number of apparently similar ring-closure reactions, in which a variety of allylic halides conjugated with alkynyl groups (**25**) were transformed to cyclopropanes (**26**). The reactions proceeded well (with direct irradiation at 254, 300, and 313 nm) in petroleum ether, somewhat less well in ether and benzene and not at all in acetone, methanol, or dimethyl sulfoxide. Allylic rearrangements were not observed, and reaction was said not to occur in the absence of alkynyl conjugation. Most of the reactions studied were not stereospecific, and the lack of stereoselection was demonstrated to be the result of the ring-closure reaction process and not that of prior cis–trans olefin isomerization or of subsequent cyclopropane isomerization. So many of these results are in sharp contrast to ours, and it remains for future work to rationalize these interesting differences.

While β-methylallyl chloride (**15**) readily underwent the photocyclization reaction to give **16**, irradiation of β-chloroallyl chloride (2,3-dichloropropene, **27**) and of β-phenylallyl chloride (**28**) failed to give observable amounts of cyclopropanes in the acetonitrile–acetone solvent.[23] Allyl fluoride (**10**-F) does not photocyclize,



$CH_2{=}C(Cl)CH_2Cl$

27



$CH_2{=}C(Ph)CH_2Cl$

28

but disappears by polymerization reactions. As reported earlier,[24] *trans*-crotyl alcohol, its methyl ether, and its acetate all failed to undergo photosensitized isomerization in acetone or benzene, except for cis–trans isomerization.

Cookson and coworkers[25] have reported that *trans*-cinnamyl benzoate is rearranged to α-phenylallyl benzoate in acetone or in benzene with cinchonidine as sensitizer. We saw a similar result in acetone–acetonitrile, observing cis–trans isomerization and allylic rearrangement, but even extended irradiation did not lead to the formation of cyclopropanes.

Mechanistic Studies. Although, as indicated above, our preliminary work[1c] seemed to implicate triplet photosensitization in these rearrangements, we have now carried out a number of quantum yield studies which clearly require that the first intermediate in the allylic halide isomerization and in the allyl to cyclopropyl rearrangement are triplet states of the allyl halides obtained by triplet–triplet energy transfer.

With allyl chloride, where only the ring closure rearrangement can be observed, initial quantum yield measurements for chlorocyclopropane formation in the acetone–acetonitrile system gave values of ϕ ranging from 0.059 at [RCl] = 0.066 M to 0.071 at [RCl] = 0.550 M. A plot of $1/\phi$ *vs.* 1/[RCl] was linear with a slope of 0.211 and an intercept of 13.7 (lim ϕ = 0.073). The reaction was efficiently quenched (50% at 0.002 M) by *cis*-piperylene. Although the quantum yield for chlorocyclopropane formation was only 0.07, the chemical yield, as described above, was close to quantitative. This means that excited allyl chloride must have very efficient decay paths of $\phi \sim 0.9$ for deactivation without apparent reaction. The "hidden" allylic rearrangement, "hidden" cis–trans isomerization and return to itself must make up the sum of these paths. Following the normal treatment for photosensitized reactions,[26] one may calculate the rate constant for transfer of triplet excitation from acetone to allyl chloride as $1.6 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. This value is identical with that ($2 \times 10^7\ M^{-1}\ \text{sec}^{-1}$) reported[27] for transfer from acetone to 2-pentene, and is substantially lower than that of a diffusion-controlled reaction.

The photochemistry of allyl bromide (**10**-Br) was much less clean. Irradiation of a 0.117 M acetone solution of allyl bromide for 16.3 hr gave only 9.9% conversion to bromocyclopropane with 24.7% of the starting material remaining. Benzene sensitized the conversion to cyclopropyl bromide but with notably less efficiency. Quantum yields were determined for this system in acetonitrile–acetone to be 0.01 for bromocyclopropane (**11**-Br) formation and 0.08 for disappearance of allyl bromide.

The photochemical conversion of β-methylallyl chloride (**15**) to 1-chloro-1-methylcyclopropane (**16**) was particularly facile and gave very clean reaction mixtures. An 0.18 M solution of **15** in acetonitrile–acetone was converted quantitatively to **16** with ϕ = 0.13. Again quenching was observed with piperylene (linear Stern–Volmer data were obtained).

Preliminary quantum yield studies were conducted with *trans*-crotyl chloride (**6**) and α-methylallyl chloride (**7**), 0.3 M, in acetonitrile–acetone for each of the processes observable, but we are deferring the reports on these until more precise data are available. For the time being, one may note that allylic rearrangement occurs more readily than ring closure, and cis–trans isomerization occurs at about the same rate as closure. Again quenching experiments demonstrated the triplet nature of the sensitization reaction.

While it is clear that the first intermediate in these reactions is the first excited triplet state, the remainder of the reaction path remains obscure. Originally,[1c,3] we considered three reaction paths from the triplet. One of these assumed that intersystem crossing led to a vibrationally excited ground state, which would clearly have enough energy to permit heterolytic cleavage to

---

(21) (a) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964); (b) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965).

(22) (a) F. Bohlmann and W. Skuballa, *Tetrahedron Lett.*, 2109 (1970); (b) F. Bohlmann, W. Skuballa, C. Zdero, T. Kükle, and P. Stevil, *Justus Liebigs Ann. Chem.*, **745**, 176 (1971).

(23) While studies on **27** and **28** cannot be used to determine whether or not allylic rearrangements occurred, work done on similar systems by R. Micheli suggest that they do occur.

(24) S. J. Cristol, G. A. Lee, and A. L. Noreen, *Tetrahedron Lett.*, 4175 (1971).

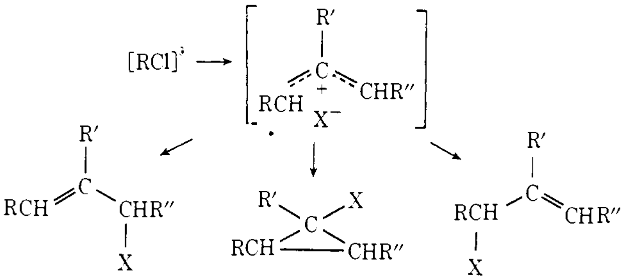
(25) R. C. Cookson, V. N. Gogte, J. Hudec, and N. A. Mirza, *ibid.*, 3955 (1965).

(26) See, for example, N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, **90**, 3274 (1968).

(27) R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).

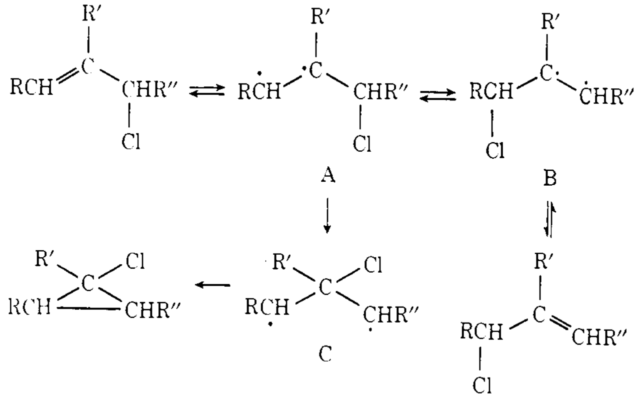
an allylic cation–halide ion ion pair (also vibrationally excited), which could then recombine to give thermodynamically unstable (or stable) covalent compounds (Scheme I).

Scheme I



A second process rationalizing our results includes triplet diradical intermediates as outlined in Scheme II,

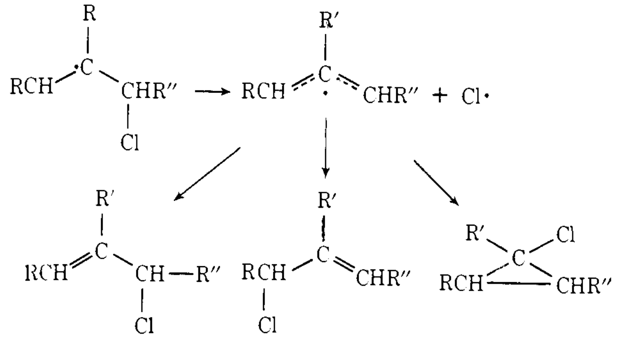
Scheme II



with triplet-ground-state interconversion occurring at the time of formation of the double bond or cyclopropane ring (but see below).

A third path, involving radical intermediates, is shown in Scheme III.

Scheme III



The triplet energy of the photosensitizers we have used[28] are somewhat higher than bond dissociation energies[29] of carbon–chlorine bonds in allyl chlorides and well in excess of energies required for homolytic cleavage of carbon–bromine bonds in allylic bromides. Indeed (see above) we have already concluded that this type of cleavage is responsible for the side reaction products in cyclohexane and in benzene,[14] but it seems less likely that radical cage-recombination reactions could be involved in the isomerizations. Thermochemical data suggest that the allyl radical produced in the homolysis should be approximately thermoneutral, so that its isomerization to a cyclopropyl radical would be endergonic. However, the recombination reaction is, of course, highly exergonic and would therefore allow thermodynamically for the formation of the chlorocyclopropane. We know of no case, however, where allyl radicals combine with other radicals to give cyclopropanes. For example, except for cyclopropane itself, Volman and Phillips[16] observed no cyclopropane products in their work, and none have been observed in work in our laboratory,[14] where allylic radicals are clearly implicated in combination reactions with other radicals. We therefore do not favor the paths suggested in Scheme III.

The paths outlined in Scheme II are attractive in that they suggest analogy to similar photochemical rearrangements involving unsaturated systems. Thus, the di-π-methane rearrangements[5,21b,30] of 1,4-dienes or of substituted allylbenzenes to vinylcyclopropanes and to phenylcyclopropanes, respectively, are assumed to involve diradical intermediates and 1,2-vinyl or 1,2-phenyl shifts analogous to our 1,2-halogen shift. The di-π-methane rearrangements differ in that acyclic and some monocyclic systems require singlet conditions,[31] although bicyclic systems proceed *via* triplet intermediates.[5] In addition to their observation of 1,2 shifts, Griffin and his students[30] have shown that highly substituted allylbenzenes undergo 1,3 shifts. Even benzyl and alkyl groups, as well as hydrogen atoms, undergo 1,2 or 1,3 shifts, although these appear to require the higher energy of singlet states[32] or of mercury photosensitization.[33] The stereochemistry of certain of these allylic rearrangements may involve suprafacial reaction.[34]

Similarly, β,γ-unsaturated ketones undergo 1,2 and 1,3 shifts of the acyl group.[35a] It has been suggested[35b] that 1,3 shifts occur from electronically excited singlet states while 1,2 shifts occur from triplet states. The 1,2 shift accompanied by ring closure has been formalized as an "oxa-di-π-methane" rearrangement.[36]

A difficulty with the diradical mechanism proposed in Scheme II is that the triplet biradical C might not be anticipated to maintain configuration during its lifetime before intersystem crossing and ring closure. Thus cis and trans compounds might be anticipated to give identical mixtures of cyclopropanes. As noted above, this is not true for *cis*- and *trans*-**17**.[37] Bohl-

---

(28) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 132.

(29) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 50.

(30) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965); J. J. Brophy and G. W. Griffin, *ibid.*, 493 (1960).

(31) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969); H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 8971 (1967); **91**, 5307 (1969).

(32) E. C. Sanford and G. S. Hammond, *ibid.*, **92**, 3497 (1970); G. S. Hammond and H. Kristinsson, *ibid.*, **89**, 5968 (1967).

(33) W. A. Gibbons, W. F. Allen, and H. E. Gunning, *Can. J. Chem.*, **40**, 568 (1962); D. R. Arnold and V. Y. Abraitis, *Mol. Photochem.*, **2**, 27 (1970).

(34) R. C. Cookson and J. D. Kemp, *Chem. Commun.*, 385 (1971).

(35) (a) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1964); (b) J. Ipaktschi, *Tetrahedron Lett.*, 2153 (1969); 3179 (1970).

(36) (a) R. S. Givens and W. F. Oettle, *Chem. Commun.*, 1164 (1969); (b) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *ibid.*, **92**, 1786 (1970).

(37) It is to be noted that this result also places a restriction on the first triplet produced by the sensitization process. It is generally assumed[38] that triplets produced from cis–trans olefin pairs by sensitization in solution relax rapidly to more stable and identical "twist" triplets. This cannot be true for the allylic halides. Thus the formulation A in Scheme II must also be modified (presumably by involvement of

mann[22b] has accepted the diradical mechanism to rationalize his results; as described above, his reactions are nonstereospecific and show solvent effects opposite to ours.

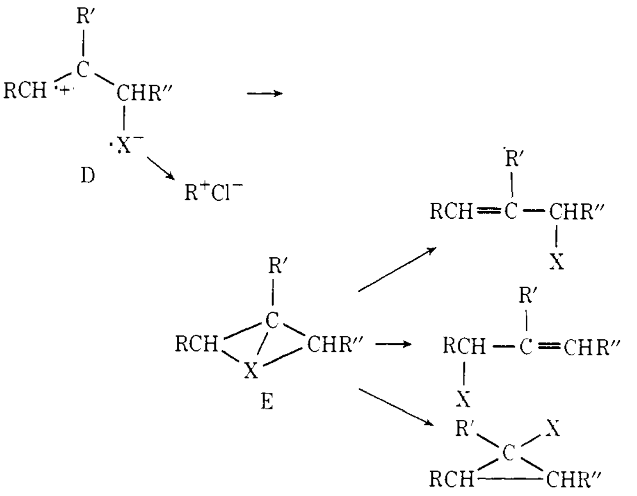
The carbenium ion process outlined in Scheme I seemed attractive in view of analogy to ground-state reactions. Carbenium ion intermediates have been postulated for certain photosolvolyses,[41] and now have been placed on a firmly demonstrated basis in one case[1a] of photosolvolysis and on a reasonable basis for a related photo-"Wagner–Meerwein" rearrangement.[1a] Stereochemical consequences can also be accommodated to such a process.[40]

Our use of acetonitrile as cosolvent was, as described above, predicated upon the idea that an ion pair was produced in competition with radical reactions and that introduction of a polar solvent would enhance the heterolytic process. At first glance, the considerable increases in chemical yield of the allylic and allyl to cyclopropane rearrangements seem to be a confirmation of this idea. However, closer inspection of the data of Table I shows that the great increase in yield of chlorocyclopropane from allyl chloride in acetonitrile–acetone *vs.* that in acetone or in benzene–acetone is only minimally that of quantum yield increase of the cyclopropane forming reaction. Instead it is largely the result of minimization of the "side-reaction" products which consume allyl chloride in the other solvents. Failure to observe photosolvolysis products in the methanol–acetone system also offers no support for Scheme I, although accommodation to tight ion-pair concepts seems possible. Failure of **27** and **28** to undergo photocyclization may be consistent with the carbenium ion concept, as it has been shown[42] that the cation to be anticipated from **27** does not have an allylic structure, but rather has a chloro-bridged structure, and an analogous situation should obtain with **28**.

It has recently been suggested[43] that certain photochemical reactions are best interpreted as involving charge-transfer or electron-transfer intermediates. Thus it has been proposed that ketone and aldehyde triplets are reduced by electron transfer (or partial electron transfer, *i.e.*, charge transfer) from amines (and other quenchers) to give ion-pair species. Interestingly, these reactions have only small solvent effects for acetonitrile *vs.* benzene.[43b]

An analogous possibility appears plausible in the allyl halide case, where electron transfer from the excited double bond to a halogen d orbital might lead to a structure such as D in Scheme IV, competitive with radical decomposition. Species D could decompose to an ion pair or give the halobicyclobutane[44,46] E (presumably E could also be formed without intervention of D, or from a zwitterion of charge direction opposite to that written). The halobicyclobutane E is an interesting intermediate to speculate on, as bond reorganization can lead from it to both allylic isomers and to the cyclopropane, presumably in concerted (and therefore stereospecific) processes.

Scheme IV



Clearly much work remains to determine the boundaries of these photoreactions from synthetic and mechanistic points of view. Experiments are presently in progress in this laboratory.

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with a Varian A-60A or a Varian HA-100 nmr spectrometer. Infrared spectra were run in carbon tetrachloride, using either Perkin-Elmer Model 337 or Model 137 infrared spectrophotometers. Mass spectra were obtained on a Varian MAT Model CH-7 mass spectrometer. Analyses of most experiments (except where otherwise noted) were performed by gas chromatography (gc) using a Varian Aerograph Model A-90 P-3 instrument. Preparative separations were carried out on an Aerograph Autoprep Model A-700 gas chromatograph. Irradiations were performed with a Hanovia 450-W mercury arc lamp (Engelhardt-Hanovia, Inc., Newark, N. J., Model L-679A-36) inserted into a water-cooled quartz immersion probe. The filters employed were Corex (cutoff at 270 nm) or Vycor (cutoff at 220 nm) glass sleeves which were inserted between the lamp and the probe. In quantitative experiments, samples were placed in preconstricted 13 × 100 mm Pyrex test tubes, degassed on a vacuum line with five or

---

the chlorine atom electrons and/or orbitals)[39] for the first triplet. This of course will be true for any of the reaction schemes utilized.[40]

[38] For a discussion, see N. J. Turro in "Technique of Organic Chemistry," Vol. XIV, P. A. Leermakers and A. Weissberger, Ed., Wiley-Interscience, New York, N. Y., 1969, p 133 ff.

[39] The absorption of 220-nm light by allyl chloride (ϵ 56) is much higher than that of *cis*-2-pentene (ϵ 4) or 2-propyl chloride (ϵ 1). Mixtures of pentene and *n*-propyl chloride show no evidence for interaction (no absorbance enhancement at 220 nm). Similarly the absorbance of allyl bromide (ϵ 54) at 260 nm is greater than can be attributed to additivity of the two isolated chromophores (double bond and halogen atom). It is of interest to note that allyl alcohol does not display any enhancement due to the oxygen allylic heteroatom. Based upon the absorption data, it seems reasonable to assume that the lowest excited singlet states (and perhaps also the lowest triplet states) of allylic chlorides (and bromides) are of lower energies than those ($\pi \rightarrow \pi^*$) states of simple olefins, due to orbital mixing of the double bond and halogen atoms. Interpretation of the spectroscopic data is thus consistent with that of the stereochemical data.

[40] The stereochemical consequences of ring closure have been scrutinized in several systems (L. Tenud and C. Ilenda, unpublished work) and will be reported later.

[41] (a) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963); H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963); (b) A. L. Maycock and G. A. Berchtold, *J. Org. Chem.*, **35**, 2532 (1970); (c) M. A. Ratcliff and J. K. Kochi, *ibid.*, **36**, 3112 (1971).

[42] J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, 92, 4025 (1970).

[43] (a) S. G. Cohen, G. A. Davis, and W. D. K. Clark, *J. Amer. Chem. Soc.*, 94, 869 (1972), and previous papers; (b) J. B. Guttenplan and S. G. Cohen, *ibid.*, 94, 4040 (1972), and references therein; (c) I. Kochevar and P. J. Wagner, *ibid.*, 94, 3859 (1972).

[44] An analogy to the photochemical isomerization of transoid 1,3-dienes to bicyclobutanes[45] can be drawn, although these are all singlet (unsensitized) reactions.

[45] W. G. Dauben and F. G. Willey, *Tetrahedron Lett.*, 893 (1962); W. G. Dauben and C. D. Poulter, *Tetrahedron Lett.*, 3021 (1967); W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **90**, 802 (1968).

[46] It seems reasonable that there is enough energy in the photoexcited molecule to allow for the formation of D and/or E even though d orbitals on the halogen would be involved.

more freeze–pump–thaw cycles and sealed at pressures less than 10^{-5} Torr. The sealed tubes for any single experiment were irradiated in parallel with *cis*-2-pentene actinometer solutions[27] in a merry-go-round photolysis apparatus.

Solvents employed for irradiation experiments were Spectroquality grade and were used without further purification. Most of the allylic halides studied were commercially available (Aldrich) and were purified immediately prior to use by preparative gas chromatography.

Irradiation of Crotyl Chloride (6) in Acetone. A solution of 70 μl of gc purified crotyl chloride, 70 μl of *n*-heptane (added as internal standard), and 0.5 ml of acetone was deaerated with nitrogen in a stoppered Pyrex nmr tube. Initial gc analysis (10 ft × 0.25 in. aluminum tubing; 18% SE-30 (dimethyl silicone oil) on Chromosorb W (diatomaceous earth), 60–80 mesh) indicated the mixture contained 99.8% **6** and 0.2% **7**. The tube was clamped next to the immersion well of a 450-W Hanovia lamp and irradiated for 56 hr. The following product composition was obtained: 25.1% **6**, 13.3% **7**, 14.6% **8**, and 13.6% **9**. Products **8** and **9** were isolated by preparative gas chromatography and were assigned structures on the basis of spectral data.[1c]

Irradiation of Crotyl Chloride (6) in Pentane. When a solution of **6** in *n*-pentane was irradiated for 54 hr, over 85% of **6** could be recovered, with at most a few per cent of **7** being formed.

Irradiation of α-Methylallyl Chloride (7) in Acetone. A sample of **7** (50 μl), *n*-heptane (50 μl), and 0.5 ml of acetone was placed in an nmr tube and the contents degassed for 0.5 hr. The sample was analyzed by gc (10 ft × 0.25 in. aluminum column, 18% SE-30 on Chromosorb W, 60–80 mesh) and found initially to contain 74.4% **7** and 25.6% **6**. The tube was irradiated for 30 hr. The following product yields were determined: 32.7% **6**, 20.2% **7**, 10.3% **8**, and 6.3% **9** (relative to *n*-heptane as internal standard).

Irradiation of α-Methylallyl Chloride (7) and Crotyl Chloride (6) in Xylene. α-Methylallyl chloride (9.9 mg, 0.11 mmol) was diluted with 0.5 ml of xylene containing 15 μl of *n*-heptane and placed in an nmr tube. The tube was capped with a serum stopper, degassed, and irradiated. From a solution consisting initially of 100% **7**, irradiation for 39 hr produced a mixture containing 17.6% **7**, 5.0% **6**, 6.2% **8**, and 5.3% **9** (yields, based upon *n*-heptane standard). Similar treatment of crotyl chloride (**6**) gave 3.6% **6**, 9.0% **7**, 7.1% **8**, and 4.5% **9**.

Irradiation of α-Methylallyl Chloride (7) and Crotyl Chloride (6) in Acetonitrile–Acetone. Purified α-methylallyl chloride (20 μl, 18 mg, 0.2 mmol) was added to an nmr tube containing 0.8 ml of acetonitrile, 0.2 ml of acetone, and 5 μl of *n*-heptane. The tube was capped with a rubber serum stopper and degassed for 45 min. Irradiation of the sample, initially consisting of 100% **7**, for 31.5 hr produced a mixture containing 62.7% **7**, 16.1% *trans*-**6**, 3.1% *cis*-**6**, 10.7% **8**, and 7.5% **9** (determined by gc using a 5 ft × 0.125 in. aluminum column, 15% β,β-oxydipropionitrile on Chromosorb P (firebrick), 120–140 mesh).

Similar treatment of crotyl chloride (**6**, initially consisting of 2.6% **7**, 74.8% *trans*-**6**, and 22.7% *cis*-**6**) for 42.8 hr indicated the following composition: 43.7% **7**, 18.0% *trans*-**6**, 4.5% *cis*-**6**, 18.1% **8**, and 15.8% **9**.

Quantum Yield Determination for α-Methylallyl Chloride (7) and Crotyl Chloride (6) in Acetonitrile–Acetone. α-Methylallyl chloride (**7**) (846.4 mg, 9.34 mmol) was weighed into a 10-ml volumetric flask, 0.25 ml of cyclooctane was added as an internal standard, and sufficient acetonitrile–acetone was added to make 10 ml of solution. To several Pyrex test tubes were added 1.0 ml of the allyl chloride solution and 2.0 ml of acetonitrile–acetone solution ($[RCl]_0 = 0.312\ M$). The tubes were degassed and sealed on a vacuum line. Initially the tubes contained 94.9% **7** and 5.2% *trans*-**6**. After 240-min irradiation, one of the tubes contained 85% **7** ($\Phi_{-7} = 0.133$), 8.5% *trans*-**6** ($\Phi_{t-6} = 0.044$), 3.8% *cis*-**6** ($\Phi_{c-6} = 0.050$), 1.4% **8** ($\Phi_8 = 0.019$), and 1.5% **9** ($\Phi_9 = 0.020$). After 483 min irradiation two tubes contained 82% **7** ($\Phi_{-7} = 0.087$), 9.2% *trans*-**6** ($\Phi_{t-6} = 0.027$), 3.9% *cis*-**6** ($\Phi_{c-6} = 0.026$), 2.6% **8**, ($\Phi_8 = 0.017$), and 2.7% **9** ($\Phi_9 = 0.018$).

Enriched *trans*-crotyl chloride containing 2.9% **7**, 84.8% *trans*-**6**, and 12.3% *cis*-**6** was treated similarly. After 240-min irradiation, the mixture comprised 15.2% **7** ($\Phi_7 = 0.158$), 66.9% *trans*-**6** ($\Phi_{-(t-6)} = 0.229$), 15.3% *cis*-**6** ($\Phi_{c-6} = 0.0375$), 1.4% **8** ($\Phi_8 = 0.018$) and 1.3% **9** ($\Phi_9 = 0.016$). After 483-min irradiation the mixture comprised 21.6% **7** ($\Phi_7 = 0.119$), 57.9% *trans*-**6** ($\Phi_{-(t-6)} = 0.171$), 16.0% *cis*-**6** ($\Phi_{c-6} = 0.0229$), 2.2% **8** ($\Phi_8 = 0.014$), and 2.3% **9** ($\Phi_9 = 0.015$).

Irradiation of Allyl Chloride (10-Cl) in 2-Butanone. Allyl chloride (**10**-Cl) (50 μl) was dissolved in 2-butanone containing *n*-heptane as an internal standard. The mixture was deaerated and irradiated for 12 hr. Gc analysis (18% SE-30 on Chromosorb W) of the reaction mixture indicated 15.8% **10**-Cl and 16.6% chlorocyclopropane (**11**-Cl). Chlorocyclopropane was identified, after isolation from reaction mixtures by preparative gc, based on the following spectral data: pmr (CCl_4) δ 2.94 (m, 1 H, H-1), 0.82 (m, 4 H, H-2 and H-3); ir (CCl_4) 3100 cm^{-1}, 3020, 2965, 1444, 1410, 1289, 1065, 1020, and 920. The infrared spectrum corresponded exactly to that reported for chlorocyclopropane.[47]

Irradiation of Allyl Chloride in Benzene. Purified allyl chloride (20.5 mg, 0.268 mmol) was diluted with 0.6 ml of benzene (containing 40 μl of *n*-heptane) and deaerated. Irradiation of the sample for 35 hr gave a mixture containing 23.5% **10**-Cl and 2.9% **11**-Cl.

Solvent Effects on Allyl Chloride Photolysis. Allyl chloride (**10**-Cl, 780.1 mg, 10.18 mmol) was weighed into a 10-ml volumetric flask, 0.25 ml of *n*-heptane was added, and the contents of the flask was diluted to 10 ml with acetone. Five preconstricted Pyrex test tubes were each charged first with 0.6 ml of the allyl chloride–acetone solution, then respectively with 2.4 ml of the following solvents: acetone, benzene, cyclohexane, methanol, and acetonitrile. The samples ($[RCl]_0 = 0.204\ M$) were degassed with six freeze–pump–thaw cycles and sealed at 3×10^{-4} Torr. Irradiation of the samples in an 8° bath for 300 min gave the following results: acetone solvent (75.4% **10**-Cl, 8.7% **11**-Cl), benzene solvent (53.1% **10**-Cl, 4.6% **11**-Cl), cyclohexane solvent (12.4% **10**-Cl*, 2.6% **11**-Cl* (*standard masked by solvent in gc)), methanol solvent (10.4% **10**-Cl, 3.3% **11**-Cl), and acetonitrile solvent (87.5% **10**-Cl, 10.8% **11**-Cl).

Irradiation of Allyl Chloride in Cyclohexane–Acetone. Purified allyl chloride (332.0 mg, 4.33 mmol) was placed in a 13 × 100 mm Pyrex test tube and diluted with 2.0 ml of cyclohexane and 0.5 ml of acetone. After being deaerated, the sample was irradiated and analyzed periodically by gc (6 ft × 0.25 in. aluminum column, 25% Carbowax 20M on Chromosorb P, 60–80 mesh, column temperature 130°). After 4.5-hr irradiation, the sample contained a number of higher molecular weight components. The major product was isolated by preparative gc and gave the following spectral information: pmr (CCl_4) δ 5.62 (m, 1-H), 4.94 (m, 1-H), 4.80 (m, 1-H), 1.88 (t, J = 3.5 Hz, 2-H), 1.63 (m, 5-H), and 1.16 (m, 6-H); mass spectrum (15 eV) m/e 125 (2.98), 124 (31.59), 109 (28.36), 83 (77.25), 82 (62.05), 81 (69.80), 67 (67.09), 56 (8.63), 55 (100), 41 (66.44). These data are consistent with those anticipated for allylcyclohexane.[48]

Dependence of Quantum Yield of Cyclopropyl Chloride Formation on Initial Allyl Chloride Concentration. Tubes containing 0.066–0.550 *M* allyl chloride in 20% acetone in acetonitrile (with *n*-heptane as internal standard) were degassed, sealed at 5×10^{-6} Torr, and irradiated for 300 min. Analysis of the samples gave the following results: tube 1, $[RCl]_0 = 0.066\ M$, 59.6% **10**-Cl, 29.5% **11**-Cl, $\Phi_{11-Cl} = 0.059$; tube 2, $[RCl]_0 = 0.110\ M$, 69.1% **10**, 19.2% **11**, $\Phi_{11} = 0.064$; tube 3, $[RCl]_0 = 0.220\ M$, 87% **10**, 11.1% **11**, $\Phi_{11} = 0.074$; tube 4, $[RCl]_0 = 0.330\ M$, 89.4% **10**, 6.62% **11**, $\Phi_{11} = 0.066$; tube 5, $[RCl]_0 = 0.440\ M$, 89.2% **10**, 5.3% **11**, $\Phi_{11} = 0.070$; tube 6, $[RCl]_0 = 0.550\ M$, 94.3% **10**, 4.3% **11**, $\Phi_{11} = 0.071$. A plot of $1/\Phi_{11}$ *vs.* $1/[RCl]_0$ gave a reasonably linear plot with slope = 0.211 and an intercept of 13.7. Addition of 0.001 *M cis*-piperylene reduced the quantum yield ($[RCl]_0 = 0.22\ M$) to about 0.02.

Irradiation of Allyl Bromide (10-Br) in Acetone. Purified allyl bromide (7.9 mg, 0.065 mmol) was weighed into an nmr tube and diluted with 0.6 ml of acetone containing *n*-heptane, and the tube was capped and deaerated. Irradiation of the sample for 16.3 hr gave 24.7% **10**-Br and 9.9% **11**-Br. The compound corresponding to **11**-Br was isolated by preparative gc and found to be identical in all respects with an authentic sample.[49]

Quantum Yield Determination for Allyl Bromide (10-Br) Photolysis. Allyl bromide (392.6 mg, 3.246 mmol) was weighed into a 10-ml volumetric flask, 0.05 ml of *n*-nonane was added, and the contents of the flask was diluted to 10 ml with acetonitrile–acetone solution. Three preconstricted Pyrex test tubes were each charged with 1.0 ml of the allyl bromide solution and 2.0 ml of the acetonitrile–acetone diluent. The samples ($[RBr]_0 = 0.108\ M$) were degassed with five freeze–pump–thaw cycles and sealed at 6 ×

---

(47) V. A. Slabey, *J. Amer. Chem. Soc.*, 74, 4928 (1952).

(48) Compare pmr spectrum in Sadtler Research Laboratories, "Nuclear Magnetic Resonance Spectra," Philadelphia, Pa., 1967, No. 3949.

(49) We are grateful to Professor J. S. Meek for supplying us with authentic bromocyclopropane.

10^{-6} Torr. Irradiation of one sample on the "merry-go-round" for 240 min gave 17.9% loss of **10-Br** ($\Phi_{-10\text{-Br}} = 0.082$) and 2.21% **11-Br** formed ($\Phi_{11\text{-Br}} = 0.010$); irradiation of the other two samples in parallel with the first but for 360 min gave 20.04% loss of **10-Br** ($\Phi_{-10\text{-Br}} = 0.062$) and 2.6% **11-Br** formed ($\Phi_{11\text{-Br}} = 0.008$).

Quantum Yield Determination for β-Methylallyl Chloride (15). A solution of **15** (0.194 *M*) prepared and treated as described in the preceding paragraph was irradiated for 90 min on the "merry-go-round" apparatus and 89.9% **15** remaining and 6.8% **16** formed ($\Phi_{16} = 0.13$), and continued irradiation for an additional 90 min resulted in 85.5% **15** remaining and 12.0% **16** formed ($\Phi_{16} = 0.12$). Addition of 0.001 *M* *cis*-piperylene reduced the quantum yield of **16** to about 0.05. The structure of 1-chloro-1-methylcyclopropane was assigned on the basis of the following spectroscopic data: pmr ($CDCl_3$) δ 1.63 (t, *J* = 0.6 Hz, CH_3), 0.9 (m, 4 H, H-2 and H-3); ir (neat) 3060, 2990, 2880, 2800, 1440, 1375, 1195, 1100, 1025, 1013, 950, 860, and 810 cm^{-1}.

Irradiation of 1,3-Dichloropropene Isomers in Acetonitrile–Acetone. A solution of 16.3 mg (0.147 mmol) of *cis*-1,3-dichloropropene (*cis*-**17**) and 16 μl of *n*-nonane in 0.80 ml of acetonitrile and 0.20 ml of acetone in a Pyrex tube was degassed and then irradiated. After 2-hr irradiation, analysis by gc (5 ft × $^1/_8$ in. aluminum column packed with 15% SE-52 (methyl phenyl silicone oil) on Chromosorb W (100–120 mesh)) indicated a mixture containing 18.0% *cis*-**17**, 23.6% *trans*-**17**, 30.7% allylidene chloride (**18**), 12.8% *cis*-1,2-dichlorocyclopropane (**19**), and 8.6% *trans*-1,2-dichlorocyclopropane (**20**). After 6-hr irradiation, the mixture contained 3.5% *cis*-**17**, 3.5% *trans*-**17**, 19.4% **18**, 28.8% **19**, and 26.2% **20**.

Similar treatment of enriched *trans*-1,3-dichloropropene (containing 78.5% *trans*-**17** and 21.5% *cis*-**17**) gave, upon irradiation for 1.5 hr, 28.4% *trans*-**17**, 24.3% *cis*-**17**, 29.0% **18**, 8.2% **19**, and 10.1% **20**. Six-hour irradiation gave 3.3% *trans*-**17**, 2.9% *cis*-**17**, 13.3% **18**, 31.2% **19**, and 34.8% **20**.

cis-**17** and *trans*-**17** were commercial samples. Allylidene chloride (3,3-dichloropropene, **18**) was identified by its pmr spectrum (CCl_4): δ 5.22 (d, d, d, *J* = 1.0, 1.5, and 9.0 Hz, H-3), 5.53 (m, H-1 anti), 6.10 (m, H-1 syn and H-2). **19** was identified on the basis of the following spectroscopic data: pmr (CCl_4) δ 3.12 (d, d, *J* = 5.5, 8.0 Hz, H-1 and H-2), 1.50 (d, t, *J* = 8.0 and 8.0 Hz, H-3 anti to Cl), 0.99 (d, t, *J* = 5.5 and 8.0 Hz, H-3 syn to Cl); ir (CCl_4), 3080, 3050, 2995, 1420, 1299, 1280, 1100, 1070, 1040, 1020, and 920 cm^{-1}. **20** was identified similarly: pmr (CCl_4) δ 1.38 (d, d, *J* = 6.5 Hz, 2 H-3), 3.17 (d, d, H-1 and H-2); ir[47] (CCl_4), 3100, 3070, 1980, 1430, 1424, 1405, 1095, 1070, 1040 (strong), 940, 935, 920, 915, and 880 cm^{-1}.

Irradiation of *trans*-Cinnamyl Chloride (21). A solution of 122 mg (0.8 mmol) of *trans*-cinnamyl chloride[50] (**21**, containing about 1% of the cis isomer) and 20 mg of *n*-decane in 1.8 ml of 20% acetone-d_6 in acetonitrile-d_3 was placed in a Pyrex nmr tube and deaerated. The solution was irradiated and subjected periodically to a combination of pmr and gc analysis. α-Phenylallyl chloride (**22**)[50] was determined by integration of the terminal vinyl protons and benzylic proton relative to the protons α to the chlorine in the cinnamyl chlorides (**21**). The gc column employed was a 10 ft × 0.25 in. aluminum column with 10% SE-52 on Chromosorb W (HMDS treated), 100–200 mesh, column temperature 140°; retention volumes: decane 260 ml, *trans*-2-phenylcyclopropyl chloride (**23**) 760 ml, and *cis*-cinnamyl chloride (*cis*-**21**) and *cis*-2-phenylcyclopropyl chloride (**24**) 965 ml. α-Phenylallyl chloride (**22**) rearranges to *trans*-cinnamyl chloride (**21**) on the injector so one peak is observed at 1250 ml. Based on the internal standard, the conversion to **23** and **24** was quantitative after 24 hr (92:8, respectively) and continued irradiation (~250 hr) gave a 57:43 ratio. The products were collected and compared to the products obtained from the addition of chlorocarbene to styrene[51] (which were isolated on the same column described above) and found to be identical. Another column was found later which separated *cis*-2-phenylcyclopropyl chloride (**24**) and *cis*-cinnamyl chloride (*cis*-**21**) and this was employed to gather the data for Table II. The column was a 6 ft × 0.25 in. stainless steel tube packed with 3% STAP on Aeropack 30, 100–200 mesh, column temperature 100°; retention volumes: *trans*-2-phenylcyclopropyl chloride (**23**) 346 ml, *cis*-cinnamyl chloride (*cis*-**21**) 485 ml, *cis*-2-phenylcyclopropyl chloride (**24**) 630 ml, and *trans*-cinnamyl chloride (**21**) 990 ml. The data obtained are given in Table II.

Table II. Product Distribution from the Irradiation of 0.4 *M* *trans*-Cinnamyl Chloride in 20% Acetone in Acetonitrile

	Per cent of compound present				
Time, hr	**21**[a]	**22**[a]	*cis*-**21**[b]	**23**[b]	**24**[b]
0	99	0	1	0	0
0.5	74	16	2	8	0
1.0	60	23	4	13	0
1.5	50	28	4	19	Trace
4.0	8	32	2	56	3
24.0	0	0	0	92	8
250	0	0	0	57	43

[a] Percentages determined by pmr and gas chromatography. [b] Determined by gas chromatography.

Irradiation of *trans*-Cinnamyl Chloride (21) without Sensitizer. A 1.3 *M* solution of *trans*-cinnamyl chloride (**21**) in acetonitrile-d_3 was prepared in a pmr tube and deaerated. The solution was irradiated and the reaction followed by pmr and gas chromatography. After 7 hr there was 9% *trans*-2-phenylcyclopropyl chloride (**23**) and 3% *cis*-cinnamyl chloride (*cis*-**21**). Loss of starting material was evident in the need for increased injection volumes to attain the same size peaks on the gc detector.

Irradiation of 2,3-Dichloropropene (27) and 2-Phenyl-3-chloropropene (28). Solutions of **27** in acetone, in acetonitrile–acetone, or in acetonitrile–*m*-xylene were irradiated. Although **27** disappeared slowly, no isomeric products were observed. No reaction seemed to occur when **28** was irradiated in acetone.

Photolysis of Allyl Fluoride (10-F). About 50 mg of allyl fluoride[52] (bp −3°) was distilled into a pmr tube and acetonitrile-d_3 (0.8 ml) with 10 vol % benzene-d_6 was added. A second tube was also prepared containing 20 mg of benzoyl peroxide in addition to allyl fluoride and solvent. The tubes were degassed by a freeze–pump–thaw cycle on a vacuum line (10^{-6} mm) and sealed under vacuum. The tube without benzoyl peroxide was irradiated. After 48 hr no cyclization was evident and the sharp peaks of the starting material were being replaced by broad peaks. The pmr spectrum of the broad peaks was identical with those seen when the second tube containing benzoyl peroxide was heated to 80° for 8 hr. A second run was made employing acetone-d_6 (10 vol %) in acetonitrile-d_3 as the solvent. Again there was a slow buildup of broad peaks and no cyclization was evident.

Irradiation of *trans*-Cinnamyl Benzoate. *trans*-Cinnamyl benzoate was prepared from benzoyl chloride and *trans*-cinnamyl alcohol in pyridine. The product was purified by distillation in a "Kugelrohrofen" (165–170° (0.5 mm)). The photolysis was run in 20% acetone-d_6 in acetonitrile-d_3 and followed by pmr and vapor phase chromatography analysis. The column employed was a 5 ft × 0.25 in. stainless steel column with 3% STAP on Aeropack-30, 100–200 mesh, column temperature 170°, flow rate ~60 ml/min. Allylic isomerization (30%) was observed after 3 hr of irradiation. Only trans–cis isomerization occurred during the next 70 hr (as determined by pmr). No peaks were visible which could be attributed to the formation of phenylcyclopropyl benzoate.

Acknowledgments. The authors are indebted to the National Science Foundation for support of this work, and to Dr. J. E. Rodgers for preliminary work on β-methylallyl chloride photorearrangement. One of us (G. A. L.) was also supported by an NDEA Fellowship.

---

(50) F. F. Caserio, G. E. Dennis, R. H. DeWolfe, and W. G. Young, *J. Amer. Chem. Soc.*, 77, 4182 (1955).

(51) R. M. Magid and J. G. Welch, *Tetrahedron Lett.*, 2619 (1967).

(52) E. T. McBee, C. G. Hsu, O. R. Pierce, and C. W. Roberts, *J. Amer. Chem. Soc.*, 77, 915 (1955).