Photobromination of Alkylcyclopropanes. Stereochemistry of Homolytic Substitution at a Saturated Carbon Atom

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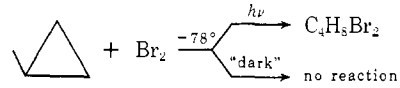
Abstract: Photobrominations of alkylcyclopropanes are rapid and produce 1,3-dibromoalkanes; at −78° the reaction is free of ionic complications. Orientation is Markovnikov type, the attacking Br atom going to the least substituted carbon, the second Br preferring the most substituted. The first step has been shown to occur by inversion at the reaction site, producing a classical γ-bromoalkyl radical, uncomplicated by bridging. Rates of reaction are greatly enhanced by progressive alkyl substitution, but these rates are not simply correlated to the stability of the γ-bromoalkyl radical produced.

There is only a sparse literature concerned with directive effects in ring-opening radical reactions of cyclopropanes. Under radical-chain conditions, cyclopropane is cleaved to 1,3-dihalopropanes.[1] Chlorination (Cl_2) of methylcyclopropane leads to 1,3-dichlorobutane and 1,3-dichloro-2-methylpropane, in addition to C–H substitution products;[2] ring-cleavage products are not obtained with *tert*-butyl hypochlorite. Chlorinations of spiropentane in gas and liquid phase lead to a variety of products,[3] among them 1,1-bischloromethylcyclopropane and $ClCH_2CH_2CCl(CH_2Cl)_2$; the former is the result of cleavage of the least substituted carbon bond, the origin of the latter is ambiguous since it may be the result of cleavage of the remaining cyclopropane ring (more substituted bond reacting), or it may be formed *via* a cyclopropyl–carbinyl radical intermediate which undergoes ring cleavage, etc.[3] Incremona and Upton[4] reported that the liquid phase chlorination of 1,1-dichlorocyclopropane occurs with cleavage of a ring bond to the substituted carbon atom to produce $ClCH_2CH_2CCl_3$ rather than $CH_2ClCCl_2CH_2Cl$. They also showed that inversion occurred at the methylene center, a result which can be interpreted to imply inversion attack by Cl· to produce $ClCH_2CH_2CCl_2$, or formation of a complex of cyclopropane and chlorine atom which reacts with Cl_2, inverting one of the methylenes.

Photobrominations of Alkylcyclopropanes

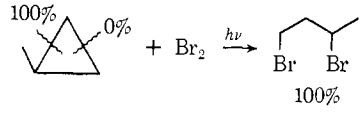
Radical-chain brominations of cyclopropanes follow a simpler course, although complicated by questions about competing ionic rections.[5] Fortunately, the latter do not present an insurmountable problem; it could be shown in each instance reported below that under the conditions employed for photobromination the dark reaction did not make a significant contribution. For example, a solution of methylcyclopropane and bromine in methylene chloride solvent does not react in the dark at −78° during the time required for complete discharge of bromine color in an identical experiment except for irradiation (1000-W Hg lamp, soft glass filter, cut off *ca.* 3500 Å). Conditions for photobromination without ionic contamination were found



even with the more highly substituted alkylcyclopropanes; in no case did dark reactions contribute as much as 10% to the products.

Photobrominations of alkylcyclopropanes are rapid clean reactions at −78°, yielding only 1,3-dibromoalkanes; no bromocyclopropanes were obtained.

Methylcyclopropane. Irradiation of a methylene chloride solution of methylcyclopropane (0.5 mmol) and bromine (0.2 mmol) at −78° for 8 min[6] gives 1,3-dibromobutane (0.2 mmol); glc analysis showed that 1,3-dibromobutane was the only product present. Tri-*n*-butyltin hydride reduction of the crude product yields butane uncontaminated by isomeric C_4 alkanes. Starting materials were recovered unchanged after 0.5 hr when light was excluded from the reaction.



It is interesting to compare these results with chlorination studies. The chlorination of methylcyclopropane has been studied by several groups. In the gas phase at elevated temperatures, attack occurs chiefly on the methyl group of methylcyclopropane to yield cyclopropylcarbinyl chloride and allylcarbinyl chloride in roughly equal quantities, together with some ring chlorinated material.[2b]

Liquid phase chlorination (CCl_4, 0–60°) of methylcyclopropane produces cyclopropylcarbinyl chloride (56%) as the major product, 1,3-dichlorobutane (7.3%), and 1,3-dichloro-2-methylpropane (5.5%).[2a] The 1,2 and 2,3 cleavages of the ring occur with nearly equal frequency, a behavior strikingly different than that observed in photobrominations.

(1) (a) G. Gustavson, *J. Prakt. Chem.*, [2] **62**, 273 (1900); (b) R. A. Ogg, Jr., and W. J. Priest, *J. Amer. Chem. Soc.*, **60**, 217 (1938); (c) *J. Chem. Phys.*, **7**, 736 (1939); (d) M. S. Kharasch, M. Z. Fineman, and F. R. Mayo, *J. Amer. Chem. Soc.*, **61**, 2139 (1939); (e) J. D. Roberts and P. H. Dirstine, *ibid.*, **67**, 1281 (1945); (f) P. G. Stevens, *ibid.*, **68**, 620 (1946); (g) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

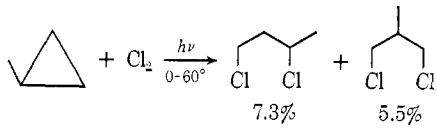
(2) (a) C. Walling and P. S. Fredericks, *J. Amer. Chem. Soc.*, **84**, 3326 (1962); (b) E. Renk, P. R. Shafer, W. H. Grahm, R. H. Mazur, and J. D. Roberts, *ibid.*, **83**, 1987 (1961).

(3) D. E. Applequist, G. P. Fanta, and B. Henrikson, *ibid.*, **82**. 2368 (1960).

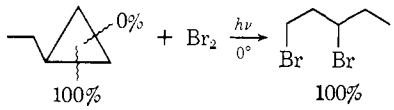
(4) J. H. Incremona and C. J. Upton, *ibid.*, **94**, 301 (1972).

(5) (a) N. C. Deno and D. N. Lincoln, *ibid.*, **88**, 5357 (1966); (b) D. N. Lincoln, Ph.D. Dissertation, The Pennsylvania State University, 1969.

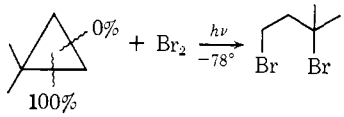
(6) The photolysis times given are only a rough indication of the rates of reaction. The relative rates of reaction are discussed in a subsequent section.



Ethylcyclopropane. Photolysis of a methylene chloride solution of ethylcyclopropane (1.0 mmol) and bromine (0.5 mmol) at 0° gave 1,3-dibromopentane (0.5 mmol). The photolysis was complete after 2 min and no reaction had occurred after 5 min in the absence of light.

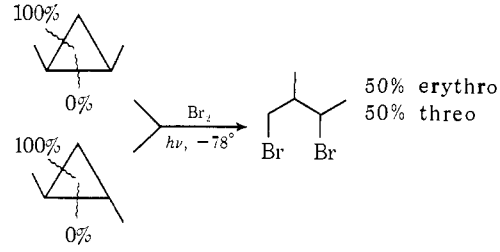


1,1-Dimethylcyclopropane. The product from the photobromination of 1,1-dimethylcyclopropane (2.5 equiv) and bromine (1 equiv) at −78° exhibited nmr absorptions at τ 8.25 (s), 7.58–7.23 (multiplet), and 6.31 (complex triplet), consistent with the structure 1,3-dibromo-3-methylbutane. Minor absorptions were also observed at τ 8.95 and 6.16 which amounted to approximately 4% of the total peak area. Glc analysis of the reaction mixture was not possible; extensive decomposition occurred. Reduction of the reaction products with $(n\text{-Bu})_3\text{SnH}$ gives isopentane (90%) together with 2-methyl-1-butene (7.8%) and 2-methyl-2-butene (2.2%). Isopentane is the product expected from reduction of 1,3-dibromo-3-methylbutane. The origin of the olefin product is not yet certain; however, since tri-*n*-butyltin hydride reduction of vicinal dibromides has been shown to give olefins,[7] the olefin precursors are tentatively assigned to 1,2-dibromo-2-methylbutane and 2,3-dibromo-2-methylbutane, respectively. These vicinal dibromides presumably arise from electrophilic attack by hydrogen bromide and bromine on 1,1-dimethylcyclopropane, with accompanying carbonium ion rearrangement.[1a] Additional evidence for this suggestion is obtained from the dark control reaction where as much as 8% of the cyclopropane had reacted in 5 min,[8] the amount of time necessary for the photolysis.



***cis*- and *trans*-1,2-Dimethylcyclopropane.** Photobromination of either *cis*- or *trans*-1,2-dimethylcyclopropane at −78° yields a 50:50 mixture of the two diastereomers of 1,3-dibromo-2-methylbutane. The photobrominations are quantitative and are not complicated by electrophilic cleavage. Tri-*n*-butyltin hydride reduction of the photobromination product yields isopentane uncontaminated with isomeric alkanes or olefins. Thus, it is clear that products resulting from 1,2-bond cleavage were not obtained.

The diastereomers were poorly resolved on a 50 ft capillary glc column. The ratios of diastereomers were

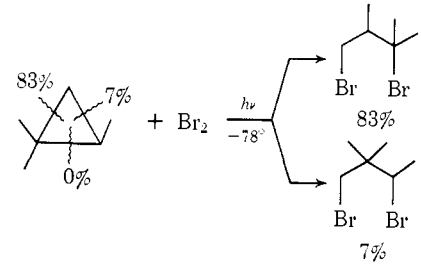


best obtained by integrating the cleanly separated nmr doublets of the 2-methyl substituents.

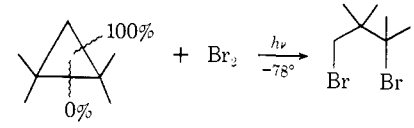
Two experiments were used to demonstrate the nonreactivity of the diastereomeric centers under the reaction conditions. *trans*-1,2-Dimethylcyclopropane was photobrominated in the presence of (+)-1-bromo-2-methylbutane; after complete reaction, the unreacted alkyl bromide was recovered; it had suffered no appreciable racemization. A similar experiment was carried out in the presence of *d,l*-2,3-dibromobutane without detectable conversion to the meso isomer.

Since the analogs of the asymmetric centers of 1,3-dibromo-2-methylbutane are stable to the reaction conditions, it follows that the 50:50 mixture of diastereomers obtained in the photobromination of the 1,2-dimethylcyclopropanes are not an equilibrated mixture; they are produced under kinetic control.

1,1,2-Trimethylcyclopropane. After 5 min of photolysis, a methylene chloride solution of 1,1,2-trimethylcyclopropane (5.0 mmol) and bromine (1.75 mmol) at −78° was colorless. Tri-*n*-butyltin hydride reduction of the residue gave a mixture of hydrocarbons: 2,3-dimethylbutane (83%), 2,2-dimethylbutane (7%), and two unidentified olefins (10%). 2-Methylpentane, the reduction product expected if 1,2-bond cleavage had occurred in bromination, was not present. The dark reaction resulted in the recovery of 92% of the starting material after 7 min reaction at −78°.[9]



1,1,2,2-Tetramethylcyclopropane. A methylene chloride solution of 1,1,2,2-tetramethylcyclopropane (1.0 mmol) and bromine (0.5 mmol) was photolyzed at −78° for 3 min. The nmr spectrum is consistent with the assignment of 1,3-dibromo-2,2,3-trimethylbutane as the product structure. Tin hydride reduction gave a 61% yield of hydrocarbon: 2,2,3-trimethylbutane (94%) and two unidentified peaks (6%). The absence of 2,4-dimethylpentane (1,2-bond cleavage) was established by peak enrichment techniques. From the 3-min dark reaction, 94% of the starting material was recovered.



(7) R. J. Strunk, P. M. DiGiacomo, K. Aso, and H. G. Kuivila, *J. Amer. Chem. Soc.*, **92**, 2849 (1970).

(8) Photolyses that took an unusually long time to run to completion (*ca.* 10 min) resulted in as much as 20% rearranged products. 1,1-Dimethylcyclopropane proved to be the most susceptible to electrophilic attack by bromine.

(9) This dark reaction accounts for the formation of olefins on reduction of the crude product.

1-Halo-3-alkyl Radical Intermediates

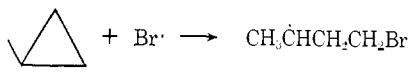
Photobrominations of alkyl cyclopropanes are characterized by the addition of bromines to the least substituted and the most substituted carbon atoms (Markovnikov addition) (Table I), a result to be contrasted with the less discriminate addition of chlorine which gives products that result from the three possible cleavages of the ring bonds.

Table I. Summary of Photobromination Products of Alkylcyclopropanes

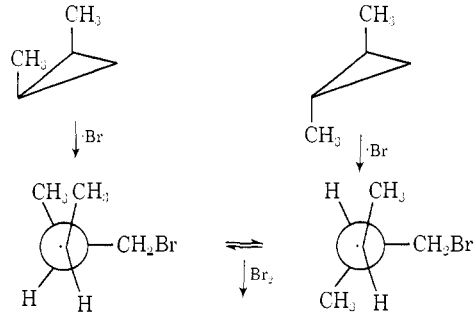
Compd	Product(s)
Cyclopropane	$CH_2BrCH_2CH_2Br$
Methylcyclopropane	$CH_3CHBrCH_2CH_2Br$
1,1-Dimethylcyclopropane	$CH_2BrCH_2CBr(CH_3)_2$
trans-1,2-Dimethylcyclopropane	$CH_3CHBrCH(CH_3)CH_2Br$[a]
cis-1,2-Dimethylcyclopropane	$CH_3CHBrCH(CH_3)CH_2Br$[a]
1,1,2-Trimethylcyclopropane	$CH_2BrC(CH_3)_2CHBrCH_3$ and $CH_2BrCH(CH_3)CBr(CH_3)_2$
1,1,2,2-Tetramethylcyclopropane	$CH_2BrC(CH_3)_2CBr(CH_3)_2$

[a] Equal mixture of diastereomers.

The most probable sequence of events leading to dibromide products is attack by bromine atom at methylene and cleavage to yield the most stable 1-bromo-3-alkyl radical, as illustrated for methylcyclopropane. Subsequent trapping of the intermediate by Br_2 yields dibromide product and generates a new bromine atom.



Evidence for a 1-bromo-3-alkyl radical intermediate is obtained from the photobromination of *cis*- and *trans*-1,2-dimethylcyclopropane. The 50:50 mixture of *erythro*- and *threo*-1,3-dibromo-2-methylbutane obtained can be explained if attack occurs at the methylene group accompanied by ring cleavage to a secondary alkyl radical which equilibrates by rotation before being trapped by Br_2. Loss of the stereochemical relationship



erythro- and *threo*-
1,3-dibromo-2-methylbutanes

between carbon atoms 1 and 2 in the parent cyclopropane is expected to occur if a classical 1-bromo-3-alkyl radical is the intermediate.

If the initial attack by Br· had occurred at the more substituted atom, 2,4-dibromopentane would have been the expected product; there is none produced.

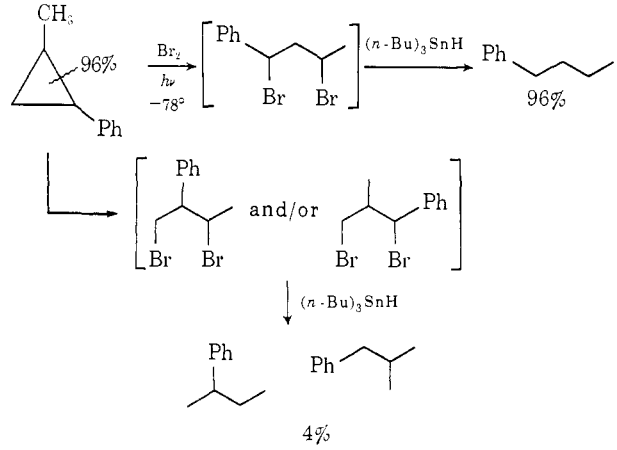
This result can be used to preclude a mechanism in which a complex of Br· and cyclopropane breaks a ring bond as it is attacked by Br_2, since this rationale would require the coincidence that the Br_2 attack 50% with inversion and 50% with retention for *both* the *cis*- and the *trans*-1,2-dimethylcyclopropanes.

Photobrominations of Arylcyclopropanes

Photobrominations of alkylcyclopropanes show a consistent pattern of behavior (Table I), cleavage of the ring between the least and most substituted ring atoms; for a 1,2-dialkylcyclopropane this is cleavage of the 1,3 bond.

A different pattern has been reported for radical brominations of 1,2-disubstituted arylcyclopropanes. Kuivila and coworkers[10] reported cleavage of the 1,2 bond of 1-isopropyl-2-phenylcyclopropane, and LaLonde and coworkers[11] report 1,2 cleavage of 1,2-diphenylcyclopropane. This markedly contrasting behavior forced us to reexamine the arylcyclopropane reactions; we confirm the pattern of 1,2-bond cleavage.

Free-radical bromination of 1-methyl-2-phenylcyclopropane followed by reduction of the products yields *n*-butylbenzene (96%) and small amounts of *sec*-butyl- and/or isobutylbenzene. The reaction does not proceed to an appreciable extent in the dark. The *n*-butylbenzene is probably the reduction product from 1,3-dibromo-1-phenylbutane, the 1,2-bond cleavage product. It is proposed below that the phenyl substituent causes a change of mechanism.

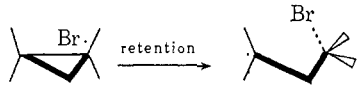


Stereochemistry of the Ring Cleavage

The formation of the same mixture of *erythro*- and *threo*-1,3-dibromo-2-methylbutane from either *cis*- or *trans*-1,2-dimethylcyclopropane indicates the initial formation of a γ-bromoalkyl radical which retains no steric memory of its progenitor; it must be a classical radical. This experiment leaves undefined the steric course of the attack of the bromine atom on the cyclopropane ring and the cleavage to the γ-bromoalkyl-radical.

Scheme I results in net retention of stereochemistry at

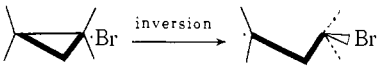
Scheme I



the carbon undergoing substitution and is the free-radical counterpart to bimolecular electrophilic substitutions (SE2). Scheme II results in a net inversion of

(10) H. G. Kuivila, S. C. Caywodd, W. F. Boyer, and F. L. Langrain, *J. Amer. Chem. Soc.*, 77, 5175 (1955).
(11) R. T. LaLonde, P. B. Ferrara, and A. D. Debboli, Jr., *J. Org. Chem.*, 37, 1094 (1972).

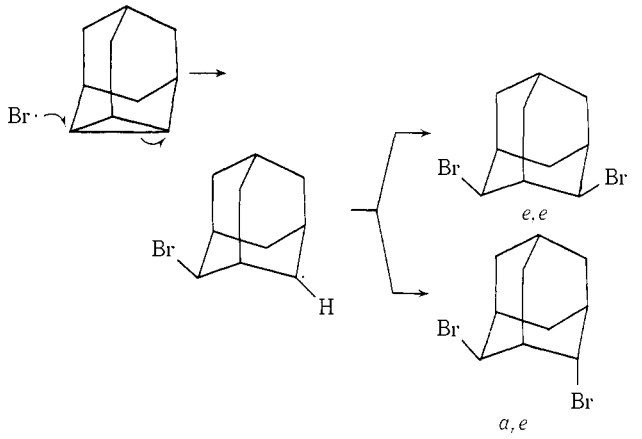
Scheme II



stereochemistry at carbon and is the free-radical counterpart to bimolecular nucleophilic substitution. To distinguish between the two types of bond cleavage, the carbon atom undergoing initial substitution must be a dissymmetric center in the dibromide product. Since, in all instances reported above, initial attacks occurred at the unsubstituted carbon atom (CH_2), it was necessary to examine a trisubstituted cyclopropane, 2,4-dehydroadamantane.

Photobromination of 2,4-dehydroadamantane at −78° yields a mixture: *a,e*-2,4-dibromoadamantane (66%) and *e,e*-2,4-dibromoadamantane.[12] Particular attention was given to the search for the diaxial isomer, but none was present (glc comparison with authentic sample).

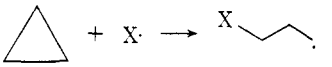
If the radical-chain bromination of 2,4-dehydroadamantane proceeds as do the brominations of alkylcyclopropanes, addition of a bromine atom produces a 4-bromo-2-adamantyl radical. This radical can react from either side with Br_2; the second bromine will be found in both axial and equatorial positions. Since no diaxial product was found, it follows that the first bromine must have entered an equatorial position, thus specifying the details of its attack on the three-membered ring *by inversion at the attacked center*.



These experiments also exclude an interpretation involving a 2,4-bridged radical since such bridging would have specified that the product be *a,e* exclusively.

Inversions have been demonstrated to be the modes of attack of radicals in cleavages of cyclopropane rings in a number of instances;[4,13-17] especially relevant is the report of inversion in the photobrominations of the isomeric 1,2,3-trimethylcyclopropanes.[13] Apparently there are no examples of radical displacements at saturated carbon centers except for those on derivatives of cyclopropane.

Attack with inversion dictates that the 1-halo-3-alkyl radicals be formed in the extended conformation.



The suggestion[18] that substitution by electrophilic radicals such as Cl· and Br· would occur with retention of configuration is contraindicated by these observations.

Relative Rates of Photobrominations

The results of a study of the relative rates of attack of bromine atoms on alkylcyclopropanes are shown in Table II. The relative reactivities were obtained by competing pairs of alkylcyclopropanes for a deficiency of bromine at −78°. Reaction mixtures were analyzed by the disappearance of starting materials relative to an inert internal standard (neopentane or carbon tetrachloride) or from product yields.

Table II. Relative Rates of Reaction of Alkylcyclopropanes at −78° with Bromine Atoms

Compd	k_{rel}[a]	k_{rel}/CH_2[b]
Bromocyclopropane	Very slow	
Cyclopropane	(1)	(1)
Methylcyclopropane	390	585
trans-1,2-Dimethylcyclopropane	8650	26,000
cis,cis-1,2,3-Trimethylcyclopropane	9100	
cis,trans-1,2,3-Trimethylcyclopropane	8900	
1,1-Dimethylcyclopropane	18,500	27,600
1,1,2-Trimethylcyclopropane	61,000	183,000

[a] Cyclopropane was arbitrarily chosen as unity. [b] Relative reactivity divided by the number of unsubstituted methylene groups.

An electronegative substituent decreases the rate of reaction relative to cyclopropane; no reaction occurs in 3 hr when solutions of bromine and bromocyclopropane were photolyzed at −78°. Alkyl substituents, on the other hand, increase reactivity toward bromine atoms; a 390-fold increase of rate results from introduction of one methyl substituent, an additional 20- to 40-fold by the introduction of a second methyl group; the introduction of a third methyl substituent (1,1,2-trimethylcyclopropane) results in a smaller increase in rate. This saturation effect on successive introduction of methyl substituents is reminiscent of similar effects, such as in the additions of bromine to olefins.[19]

The incremental increase of rate with alkyl substitution does not apply to the 1,2,3-trimethylcyclopropanes, for which one might have anticipated a rate similar to that of 1,1,2-trimethylcyclopropane. The retarding effect which is observed is the same one that explains the

(12) Ionic addition of bromine to dehydroadamantane was rapid enough, even at −78°, to require detailed examination. In the time required to do the photobromination (*vide infra*) the dark reaction (CH_2Cl_2 solvent, 0.30 *M* dehydroadamantane and 0.23 *M* bromine) used up 59% of the bromine in 3 min, producing a mixture of *a,e*- and *e,e*-2,4-dibromoadamantane (59 and 41%), respectively. This result is misleading since inclusion of 0.003 *M* isoamyl nitrite to the dark reaction resulted in 40% conversion of the bromine in 10 min. Apparently there is a spontaneous initiation of a radical chain in the dark, accounting for a substantial portion of the dark reaction (a similar occurrence has been reported for a Dewar anthracene). A 3-min photolysis of an identical reaction mixture at −78° resulted in 100% conversion of the bromine and produced the same mixture of isomers in 68 and 32% yields, respectively. Gas chromatography failed to reveal the presence of any other isomers. Particular attention was given to the search for the diaxial isomer, but none was present (glc comparison with authentic sample).

(13) G. G. Maynes and D. E. Applequist, *J. Amer. Chem. Soc.*, **95**, 856 (1973).

(14) D. E. Applequist and R. Searle, *ibid.*, **86**, 1389 (1964).

(15) M. Gartonde, P. A. Vatakencherry, and S. Dev, *Tetrahedron Lett.*, 2007 (1964).

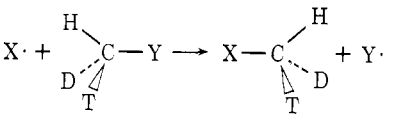
(16) M. L. Poutsma, *J. Amer. Chem. Soc.*, 87, 4293 (1965).

(17) B. Jarvis, *J. Org. Chem.*, **35**, 924 (1970).

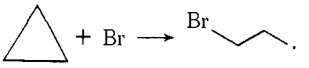
(18) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971, p 77.

(19) C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2354 (1931); S. V. Anatakrishnen and C. K. Ingold, *ibid.*, 984, 1396 (1935).

orientation of the initial attack on a methylene rather than on a more substituted position. Apparently these radical backside displacements show the same sensitivity to steric hindrance as is well known for SN2 displacements. This undoubtedly accounts for the failure to observe radical displacements on noncyclopropane asymmetric centers since these are usually hindered positions. Perhaps this type of displacement will be found to be important for an unhindered substrate.



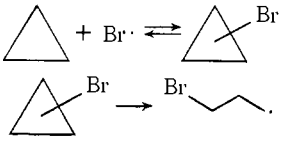
Since attack occurs on the methylene when one is available, the reactivities of cyclopropanes should be compared after a statistical correction for the number of methylenes, as shown in the last column of Table II. This comparison has a puzzling feature, the insensitivity of rates to the stability of the radical produced when the ring is opened. If the rates were dependent solely on the stability of the radical produced, then it would have been expected that methylcyclopropane and 1,2-dimethylcyclopropane would show the same rates because both go to secondary radicals, and that 1,1-dimethyl- and 1,1,2-trimethylcyclopropanes would also show the same rates, since both go to tertiary radicals. Clearly this is an incorrect picture, and it suggests the conclusion that the transition state for the ring cleavage step has very little radical character on carbon. This is not wholly unanticipated, for the reaction is exothermic even when a primary radical is produced; the reaction would be 4 and 8 kcal more exothermic for secondary



ΔH = −14 kcal/mol

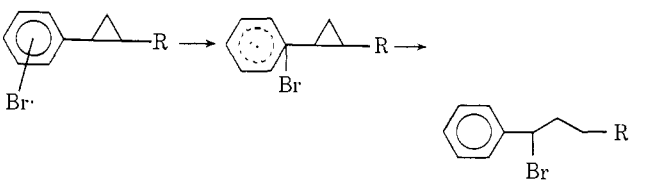
and tertiary radicals, respectively. However, even this explanation is not complete, for it fails to account for the increase in rate which accompanies alkyl substitution regardless of their distribution on the ring.

An hypothesis which can account for the observed rates includes a prior equilibrium in which complex formation is favored by increasing alkyl substitution, collapse of the complex to the 1-halo-3-alkyl radical being the slow step. The rate of the slow step is



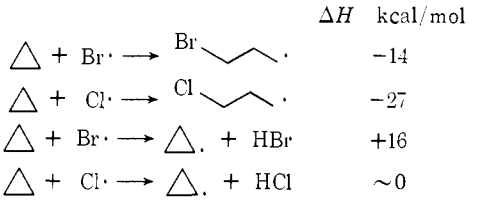
controlled by steric hindrance at the carbon receiving the bromine and the stability of the open chain radical. The low reactivity of bromocyclopropane is attributed to low stability of the complex.

The arylcyclopropane cleavages cannot be explained with the above rationale since initial attack does not occur at the least substituted ring atom. We propose that initial attack occurs on the aromatic nucleus, placing the bromine atom closest to the cyclopropane ring atom bearing the aryl group. With this hypothesis one predicts control of stereochemistry at the aryl bearing carbon rather than at the alkyl bearer.



Chlorination and Bromination

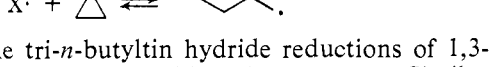
Photochlorination of alkylcyclopropanes occurs with little discrimination for the bonds broken, all possible ring cleavages competing with all possible hydrogen abstractions;[2a,b] chlorination of cyclopropane yields 1,3-dichloropropane and cyclopropyl chloride, the latter increasing with increasing temperature. Photobromination of cyclopropane and alkylcyclopropanes results in ring cleavage exclusively, with a strong preference for Markovnikov-type cleavage. The heats of reactions make these differences understandable. A low activation energy is reasonable for the ring-cleavage reactions.



Because it is smaller in size, the chlorine atom is less discriminating in its choice of ring atom attacked in an alkylcyclopropane. While the H abstraction from a ring atom (or side chain) by bromine atoms can be expected to have a large activation energy, making ring cleavage the exclusive reaction, the H abstractions by chlorine atoms should have much smaller activation energies, making all the reactions competitive. Hydrogen abstraction by chlorine atom must have a larger activation energy than ring cleavage to account for the preferred formation of cyclopropyl chloride at elevated temperatures.

1-Halo-3-alkyl Radicals → Δ + X·

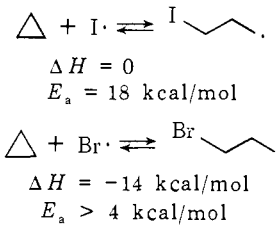
Kaplan has reported the free-radical reduction of 1,3-diiodopropane yields cyclopropane in high yields.[20] Similarly, reaction of methylene iodide with olefins in the presence of free-radical initiators is reported to yield cyclopropanes.[21] The author has suggested the results could be interpreted in terms of an internal homolytic displacement on carbon. These cyclization reactions are the reverse of cyclopropane cleavage by halogen atoms and undoubtedly occur with inversion.



We find the tri-*n*-butyltin hydride reductions of 1,3-dibromoalkanes do not yield cyclopropanes. Similar reduction of 1,3-diiodopropane by an equimolar quantity of the tin hydride results in a 3.4% yield of cyclopropane at high concentration of reactants and 6.8% at lower concentrations. The concentration effect is reasonable for a competition between reduction and cyclization of a 3-iodo-1-propyl radical intermediate. However, even at high dilution reductions of dibromides yield alkanes rather than cyclopropanes.

(20) L. Kaplan, *J. Amer. Chem. Soc.*, **89**, 1753 (1967).
(21) L. Kaplan, *ibid.*, **89**, 4566 (1967); *Chem. Commun.*, 754 (1968); 106 (1969); *J. Org. Chem.*, **32**, 4059 (1967).

Energetic considerations can explain this difference in behavior.[22] The E_a for the cyclization of the bromo-



propyl radical must be greater than 18 kcal/mol to account for reduction to the alkane being the sole reaction.

Experimental Section

Materials. Cyclopropanes. Most of the alkylcyclopropanes used in this study were obtained commercially. Purification was achieved by treatment with bromine at −78° to remove olefin impurities. The compounds were shown to be pure (>99%) by glc. The isomeric 1,2,3-trimethylcyclopropanes were made from the dibromide by ring closure with zinc;[23] the cis,cis and cis,trans isomers were separated by gas chromatography on a cyanoethyl silicone substrate. 2,4-Dehydroadamantane was prepared as described;[24] adamantane (15%) was the only impurity found and was not removed since it is unreactive under the reaction conditions.

A sample of *a,a*-2,4-dibromoadamantane was kindly provided by Professor M. A. McKervey, The Queens University, Belfast.

Alkyl Bromides. 1,3-Dibromobutane, 1,3-dibromopropane, and 1,3-dibromopentane were obtained commercially.

1,3-Dibromo-2-methylbutane. 2-Methyl-1,3-butanediol was prepared by the reduction of ethyl 2-methylacetoacetate (Aldrich) with lithium aluminum hydride.[25] Treatment of the diol with 2 equiv of triphenylphosphine dibromide in DMF yielded, after work-up, 1,3-dibromo-2-methylbutane (25%); bp 50–52° (4 mm); nmr (60 MHz, CCl_4) τ 8.917 (d, J = 6.5 Hz), 8.850 (d, J = 6.5 Hz), 3 H for sum of both, 8.29 (d, J = 7 Hz), 8.066 (m), 4 H for sum of both, 6.57 (m, 2 H), 5.66 (m, 1 H); at 100 MHz (benzene) the pair of doublets at τ 8.917 and 8.850 appeared to be a triplet, τ 9.07; ms (70 eV) 232, 230, 228 (M^-) (intensityr atio 1:2:1), 151, 148, 123, 121, 108, 106, 69, 68 (base), 54.

Partial separation of the two diastereomers was achieved on a 50 ft × 0.02 in. tricresyl phosphate capillary column. Two peaks of equal intensity were observed. The diastereomeric composition was found to coincide with peak heights of the two doublets at τ 8.917 and 8.890 in the nmr spectrum. The two doublets are assigned to the 2-methyl absorption in the diastereomeric 1,3-dibromo-2-methylbutanes. Preparation of 1,3-dibromo-2-methylbutane, employing phosphorus pentabromide, gave the same mixture of diastereomers in 2:1 ratio.

Tri-*n*-butyltin Hydride. This compound was prepared by the method of van der Kerk and Luijten.[26]

General Procedure for the Photobromination of Alkylcyclopropanes. A low temperature photobromination procedure was employed to minimize complications of ionic cleavage of cyclopropanes by bromine.

At least a twofold excess of degassed alkylcyclopropane was condensed into a frozen (liquid nitrogen) degassed solution of bromine in methylene chloride. The flask was sealed off and warmed rapidly to −78°. Solutions were then irradiated at −78° with a G. E. A-H6 high-pressure mercury arc (soft glass filter) until the disappearance of bromine color. Nmr and glc analyses were performed directly on the reaction mixtures. Additional evidence for the product structures was obtained by tri-*n*-butyltin hydride reduction.

Dark reactions, used to establish the contribution, if any, of ionic ring cleavage, were performed in an identical manner as described above, except light was carefully excluded. The dark reactions were run for a length of time that was sufficient for the light reaction to run to completion. After this time, the solution was cooled and propylene added to remove unreacted bromine. Work-up and analysis of products were carried out in a manner identical with that used for the work-up of the light-catalyzed reaction. In situations where products were unstable toward glc analysis, the ionic reaction of alkylcyclopropane was monitored by comparison of the amount of alkylcyclopropane (glc) and an inert internal standard, neopentane, before and after the dark reaction; reactions were terminated by quenching with propylene.

Photobrominations. Methylcyclopropane. Methylcyclopropane (0.5 mmol) and bromine (0.2 mmol) in methylene chloride (1 ml) were photolyzed at −78° until the solution was colorless (8 min). Glc analysis showed a single product, 1,3-dibromobutane (0.2 mmol, 100%), identified on the basis of glc retention time and by comparison of spectral properties with an authentic sample. A dark reaction, after 10 min, gave 1,2-dibromopropane (0.18 mmol), from the propylene as the only product. 1,3-Dibromobutane was not observed.

Ethylcyclopropane. Photobromination of ethylcyclopropane (0.5 mmol) with bromine (0.2 mmol) at 0° yields a single product, 1,3-dibromopentane (0.2 mmol, 100%), isolated by preparative glc; nmr (CCl_4) identical with authentic sample. No products were observed from the 10-min dark control reaction of bromine with ethylcyclopropane.

***trans*-1,2-Dimethylcyclopropane.** A solution of *trans*-1,2-dimethylcyclopropane (5 mmol) and bromine (2.0 mmol) in methylene chloride (5 ml) was irradiated at −78° for 10 min. Glc analysis revealed the presence of a single product (1.99 mmol, 99%) with a retention time identical with that of an authentic sample of 1,3-dibromo-2-methylbutane. The product was isolated by preparative glc. The mass spectrum and nmr were identical with that of an authentic sample of an equal mixture of diastereomers of 1,3-dibromo-2-methylbutane. The two doublets, τ 8.925 and 8.855, from the nmr spectrum, were of equal intensity. In three runs, one of the isomers was obtained in yields of 49.5, 50.3, and 50.4%.

(+)-1-Bromo-2-methylbutane (2.8 mmol, $[\alpha]^{27}D$ +3.99°) was added to reaction mixture (cyclopropane, 5 mmol; bromine, 2 mmol; methylene chloride, 3 ml). After photolysis the active amyl bromide was recovered by preparative glc, not racemized, $[\alpha]^{25}D$ +4.08°. Further, in an identical photobromination, a mixture of *d,l*-2,3-dibromobutane (96.4%) and *meso*-2,3-dibromobutane (4.1%) was added to the reaction. The 2,3-dibromobutanes were recovered unchanged in composition, 96.4% *d,l* and 3.6% *meso*.

To further verify the structure assignment, a tri-*n*-butyltin hydride reduction was carried out. Solvent and unreacted cyclopropane were removed and the residue (*ca.* 2 mmol) was treated with tri-*n*-butyltin hydride (6 mmol) in THF (1 ml) in a sealed tube at 100° for 1 hr. Distillation of the volatiles (1.6 mmol) and subsequent analysis by glc and ir showed the presence of a single product, isopentane, from the reduction.

***cis*-1,2-Dimethylcyclopropane.** Photobromination of *cis*-1,2-dimethylcyclopropane (5.0 mmol) with bromine (2.0 mmol) as above yields a single product (1.96–2.0 mmol, 98–100%), 1,3-dibromo-2-methylbutane. Nmr analysis of the isolated product showed it to be a mixture of diastereomers (50.0% each), identical with the photobromination product of *trans*-1,2-dimethylcyclopropane. No reaction occurred when the reactants were stored for 10 min at −78° in the dark.

1,1-Dimethylcyclopropane. 1,1-Dimethylcyclopropane (5.0 mmol) and bromine (2.5 mmol) in methylene chloride (2.5 ml) were irradiated at −78° until the disappearance of bromine color (5 min). Nmr analysis of the reaction solution showed new absorptions at τ 8.23 (s), 7.58–7.23 (m), 8.5 H for sum of both areas, and 6.41 (complex triplet, 2 H). Minor absorptions were also observed at τ 8.95 and 6.16, amounting to approximately 4% of the total peak area. The nmr spectrum is consistent with the structure assignment of 1,3-dibromo-3-methylbutane for the major reaction product. Extensive decomposition occurred when glc analysis was attempted. After removal of solvent and unreacted cyclopropane, reduction of the residue with tri-*n*-butyltin hydride yields isopentane (90%) together with 2-methyl-1-butane (7.8%) and 2-methyl-2-butane (2.2%). The yields of olefins varied between 3 and 20% of the reaction mixture, increasing with length of time required to achieve complete disappearance of bromine color.

When samples of 1,1-dimethylcyclopropane were treated with bromine in the dark at −78° for 7 min, starting material was recovered in 92–98% yield. Thus, as much as 8% ionic reaction took place in the time necessary for the photobromination to run to completion.

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(24) A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatmann, *Chem. Commun.*, 657 (1966).
(25) E. Buchta and H. Bayer, *Justus Liebigs Ann. Chem.*, 573, 227 (1951).
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1,1,2-Trimethylcyclopropane. A solution of 1,1,2-trimethylcyclopropane (5.0 mmol) and bromine (1.75 mmol) in methylene chloride (5 ml) required 6 min for the bromine color to disappear on irradiation at −78°. The volatiles were removed from the resulting solution yielding a pale yellow residue (0.43 g, 98%): nmr (neat) τ 9.10–8.66 (m), 8.27 (t), 8.16 (s), 8.0 (m), 6.825 ("t"), 6.91 (m).

The residue was treated with tri-*n*-butyltin hydride (1.9 g, 6.5 mmol) in a sealed tube at 100° for 1 hr. After work-up, glc analysis indicated the presence of two alkanes, 2,3-dimethylbutane (82.3%) and 2,2-dimethylbutane (7.1%), identified by comparison of glc retention times and ir spectra with authentic samples. In addition, two unknown products (5%) were observed. They are tentatively identified as C_6 olefins on the basis that they disappear from the hydrocarbon mixture after treatment with bromine, and they both exhibit much longer retention time than the two alkanes on a dioctyl phthalate glc column, characteristic of olefins. Dark control reactions run for 8 min resulted in recovery of *ca.* 90% of 1,1,2-trimethylcyclopropane.

1,1,2,2-Tetramethylcyclopropane. Methylene chloride (5 ml), bromine (0.50 mmol), and 1,1,2,2-tetramethylcyclopropane (1.0 mmol) were irradiated at −78° until the bromine color disappeared (3 min). After removal of solvent on the rotary evaporator, a pale yellow residue remained (*ca.* 1.2 g, 100%): nmr (neat) τ 8.80 (s, 6 H), 8.15 (s, 6 H), 6.317 (s, 2 H). Several smaller peaks were centered about the two high field absorptions. The nmr spectrum is consistent with the assignment of 1,3-dibromo-2,2,3-trimethylbutane as the major photobromination product. Reduction of the residue with tri-*n*-butyltin hydride (2.0 mmol) at 100° for 1 hr gave 0.30 g (61%) of a hydrocarbon mixture. The mixture consisted of 2,2,3-trimethylbutane (94%) and two unidentified higher boiling products (combined yields 6%). 2,4-Dimethylpentane was shown to be absent by peak enrichment techniques (limit of detection, 2%). A dark control reaction (3 min) resulted in the recovery of 92% of the starting material.

1-Methyl-2-phenylcyclopropane. A solution of bromine (0.60 mmol) and 1-methyl-2-phenylcyclopropane (1.21 mmol) (a mixture of cis and trans in methylene chloride (5 ml)) was decolorized by photolysis at −78° (3 min). After removal of methylene chloride, the residue was treated with tri-*n*-butyltin hydride (0.51 g, 1.75 mmol) at 100° for 1 hr. Glc analysis showed, in addition to unreacted starting material (0.88 mmol), *n*-butylbenzene (0.40 mmol, 96% based upon hydrocarbon products) and *sec*-butylbenzene and/or isobutylbenzene (0.018 mmol, 4%) (these latter isomers could not be separated on the columns employed). Identities were established by comparison with glc retention times of authentic samples.[27] The yield of recovered alkyl benzenes (0.42 mmol) is 75% based upon bromine. The dark reaction, run for 4 min, resulted in recovery of 99% of the unreacted starting material, after reduction with tin hydride, together with small amounts of alkylbenzenes (<1 mol %).

Bromocyclopropane. Solutions of bromine (5 mmol) and bromocyclopropane (10 mmol) in methylene chloride (25 ml) were unchanged after irradiation at −78° for periods of up to 3 hr.

2,4-Dehydroadamantane. Solutions of methylene chloride (10 ml), 2,4-dehydroadamantane (3.3 mmol), and bromine (2.5 mmol) were decolorized by irradiation at −78° for 3 min. Removal of solvent afforded a residue (*ca.* 0.85 g) which exhibited absorptions in the nmr (CCl_4) at τ 5.52, 5.316, and 4.91 (broad singlets, intensity ratio 1:1:1), 7–9 (broad complex absorption). Glc analysis of the residue (6-ft silicone rubber, 180°) showed, in addition to starting material, two partially resolved peaks (2:1 ratio). The absence of *a,a*-2,4-dibromoadamantane was confirmed by failure to observe a peak at the retention time of an authentic sample (earlier than the other isomers) and the absence of an nmr absorption for the diaxial dibromide at τ 5.35. Tri-*n*-butyltin hydride reduction of a portion of the reaction products yields a hydrocarbon with glc retention time and mass spectrum identical with that of an authentic sample of adamantane.

The mixture of products was separated by liquid chromatography (30 × 1 cm column of neutral alumina), collecting fraction 1, 40 ml of hexane, and fraction 2, 25 ml of hexane–benzene (3:1). Fraction 2 was evaporated to dryness and recrystallized from hexane to yield 0.2 g of a colorless solid, *e,e*-2,4-dibromoadamantane: mp 114–115° (lit.[28] mp 115–117°); nmr (CCl_4) τ 7.2–8.6 (m, 12 H), 5.51 (broad s, 2 H (lit.[29] τ 5.51)); ms (70 eV) 296, 294, 292 (M^+, intensity ratio 1:2:1), 215, 213 (base), 133, 105, 91, 79; ir (μ, KBr) 3.42, 3.5 (sh), 6.87, 6.94, 7.46 (sh). 7.41, 7.46, 7.55, 7.64, 7.75, 7.83, 8.28, 8.35, 8.51, 9.23, 9.30, 9.54, 9.70, 10.22, 10.45, 10.86, 11.17, 11.46, 12.17, 12.35, 12.85, 13.10, 14.38, 14.45. Fraction 1 was rechromatographed on the alumina column to give fraction 3 (20 ml of hexane) and fraction 4 (30 ml of hexane–benzene). Fraction 3 contained largely unreacted starting material. The solvent was removed from fraction 4 and the resulting residue was vacuum sublimed (70° (1 mm)) yielding *ca.* 30 mg of a white crystalline material, *a,e*-2,4-dibromoadamantane: mp 110–113° (lit.[30] mp 119–121°); nmr (CCl_4) τ 7.3–8.6 (m, 12 H), 5.31 (broad s, 1 H (lit.[29] (τ 5.27)), 4.91 (broad s, 1 H (lit.[29] τ 4.85)); ms (70 eV) 296, 294, 292 (M^+, intensity ratio 1:2:1), 215, 213 (base), 133, 105, 91, 79; ir (μ, KBr) 3.46, 3.53 (sh), 6.87, 6.95, 7.46, 7.54, 7.70, 7.81, 8.10, 8.37, 8.45, 8.50, 8.65, 9.00, 9.14, 9.30, 9.44, 9.54, 9.72, 9.80, 10.30, 10.49, 10.59 (sh), 10.81, 11.05, 11.17, 12.20, 12.39, 12.90, 13.13, 14.16, 14.35 (sh). The ir spectrum of this product could be superimposed on an ir of an authentic sample of *a,e*-2,4-dibromoadamantane (provided by Professor M. A. McKervey, The Queens University, Belfast).

The dark reaction in the presence of 1 mol % isoamyl nitrite results in 40% reaction in 10 min. During the 3-min photobromination a 12% contribution is made by the ionic bromination. In the absence of isoamyl nitrite the dark reaction is 59% complete in 4 min, indicating a self-initiating chain.

Competition Photobrominations. Pairs of alkylcyclopropanes were permitted to compete for a deficiency of bromine under conditions described above. Relative rate constants were calculated by one of two methods: (a) disappearance of starting materials relative to an inert internal standard (neopentane or CCl_4), or (b) from ratios of starting materials and products. The results of the competition photobrominations are summarized in Table II.

Reduction of 1,3-Diiodopropane with Tri-*n*-butyltin Hydride. A 25-ml flask, equipped with magnetic stirring bar and rubber septum, was charged with 1,3-diiodopropane (0.296 g, 1.0 mmol) and benzene (1–10 ml). After purging with dry nitrogen for 1 min, tri-*n*-butyltin hydride (0.291 g, 1.0 mmol) was added by syringe to the stirred solution (50%) over a period of 10 min. After an additional 5 min of reaction, the reaction mixture was fractionated on the vacuum line, then analyzed by glc.

In 1 ml of benzene the reaction products consisted of starting material (0.28 mmol), 1-iodopropane (0.49 mmol), and C_3 hydrocarbons (0.22 mmol, 3.4% cyclopropane). In 10 ml of benzene the product distributions were: starting material (0.33 mmol), iodopropane (0.40 mmol), and C_3 hydrocarbons (0.24 mmol, 6.8% cyclopropane).

Acknowledgment. The financial assistance from the Air Force Office of Scientific Research (1983) is acknowledged with gratitude.

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