Polar Radicals. IV. On the Photobromination of Several Optically Active 1-Substituted 2-Methylbutanes[1]

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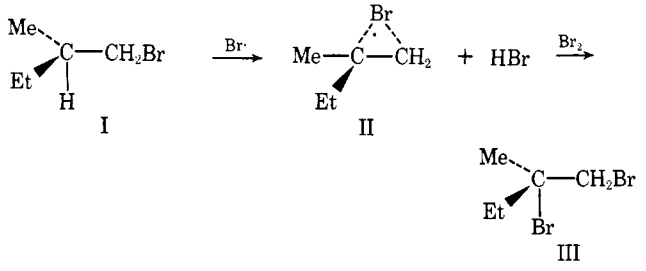
Abstract: The photobrominations of (+)-2-methylbutyl acetate, (−)-1-fluoro-2-methylbutane, and (+)-1-bromo-2-methylbutane were carried out with molecular bromine. The recovered nonbrominated fluoride and acetate had racemized to a large extent during the bromination reaction, while the bromide underwent only a small amount of racemization. The brominated fluoride, 2-bromo-1-fluoro-2-methylbutane, was found to be optically inactive while the 1,2-dibromide obtained as a product from the bromination of (+)-1-bromo-2-methylbutane, as was previously reported by Skell, Tuleen, and Readio, was found to be optically active. These results are discussed in relation to the general problem of bridged radical intermediates.

The photobromination of a large number of bromoalkanes have been found to give remarkably high yields of the corresponding 1,2-dibrominated hydrocarbons.[1,4–8] Contrary to the observed result, a consideration of the polar effects operative in radical substitution reactions would predict a deactivation of the carbon–hydrogen bonds adjacent to the bromine. These seemingly abnormal results have been explained in terms of anchimeric assistance by the neighboring bromine atom during the hydrogen abstraction reaction.[4–7]

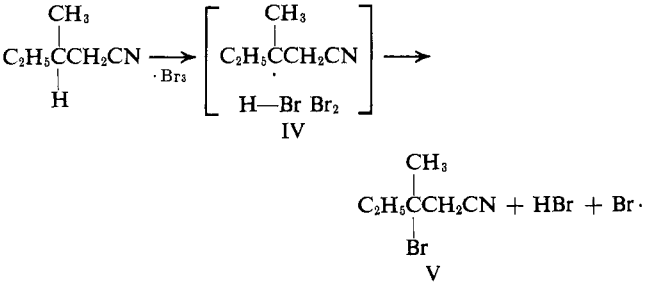
The liquid phase photobromination of (+)-1-bromo-2-methylbutane (I) to give (−)-1,2-dibromo-2-methylbutane (III) of high optical activity has been cited as good evidence in support of this concept.[4] However, as neither the absolute configuration of the dibromide nor its optical purity had been determined, it was not completely certain that the reaction proceeded with retention of configuration. Skell, Tuleen, and Readio rationalized their results on the basis of anchimeric assistance by bromine to form a bridged bromine radical (II), followed by transfer with molecular bromine to give the brominated product (III) with retained configuration.



Retention of activity was also observed in the product from the photobromination of (+)-1-chloro-2-methylbutane and a bridged chlorine radical was postulated to account for this result.

We have utilized the rather oversimplified, but empirically useful, Brewster's rules[9] to predict the sign and magnitude of rotation of the brominated compounds. The configuration about the active center has been assumed to have been retained on bromination[4,10] and this assumption has been made in our calculations. The calculations indicated that the β-brominated product should have a rotation of approximately the same magnitude but of opposite sign to the starting material. This is in fact observed in the case of the photobromination of 1-chloro- and 1-bromo-2-methylbutane.[4]

Haag and Heiba have examined the liquid phase photobromination of (+)-3-methylvaleronitrile (IV).[10] The reaction proceeded with high selectivity at the tertiary carbon to yield (+)-3-bromo-3-methylvaleronitrile (V).[11] An alternative explanation was offered by these authors to account for the stereoselective brominations. Since they believed that neighboring group participation leading to a cyano bridged radical is most unlikely, it was suggested that the abstracting species is $Br_3\cdot$, and that the resulting radical undergoes a cage reaction with bromine before rotation can occur. No data were presented concerning the degree of optical purity or configuration of the product.



The stereochemistry of the making and breaking of bonds to an asymmetric carbon atom by a free radical mechanism was first investigated by Brown, Kharasch, and Chao.[12] These workers generated a radical at an

(1) Part III: D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Amer. Chem. Soc.*, **91**, 7398 (1969).
(2) Visiting Scientist on leave from Sumitomo Chemical Co., Osaka, Japan.
(3) University of Alberta, Postdoctoral Fellow, 1969–1971.
(4) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, **85**, 2849 (1963).
(5) P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964).
(6) W. Thaler, *ibid.*, **85**, 2607 (1963).
(7) J. G. Traynham and W. H. Hines, *ibid.*, **90**, 5208 (1968).
(8) M. S. Kharasch, W. S. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **20**, 1432 (1955).
(9) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).
(10) W. O. Haag and E. I. Heiba, *Tetrahedron Lett.*, 3679 (1965).
(11) It is disturbing that no change in sign was observed by Haag and Heiba[10] on going from the (+)-3-methylvaleronitrile to the β-brominated product, since Brewster's rules calculations would predict an inversion of sign. However, in compounds with two polar groups on adjacent carbon atoms, the solvent may have a strong influence in favoring or disfavoring particular conformations because of their dipole properties. These conformations may well be ones with large individual rotatory contributions. Particularly when rotations are small because of cancellation of contribution by different conformations, there is a possibility that the magnitude and even the sign of rotation could be influenced by the solvent.

asymmetric center by the photochlorination of optically active 1-chloro-2-methylbutane. The 1,2-dichloro-2-methylbutane formed was found to be completely racemized. Further investigations have led to the conclusion that generation of a radical at an asymmetric center in optically active compounds generally yields inactive products.[13] This phenomenon has been attributed to either a planar structure of the radical or to a pyramidal structure which inverts at a greater rate than the rate of the transfer step. The interpretation of spectral evidence indicates that the planar configuration is the more stable conformation of the simple alkyl radical.[14] Chemical evidence would seem to indicate that both types of conformations are compatible with the generation of a free radical center.[15]

In the case of the recombination of geminately caged radicals, the loss of optical activity need not occur, and some degree of retention of configuration has been observed. Bartlett and McBride have reported the decomposition of *meso*- and *dl*-azobis-3-methyl-2-phenyl-2-butane in a glass matrix at 77°K and they observed 100% stereospecificity in the products.[16] Greene has observed some retention of configuration during the decomposition of optically active hydratropyl peroxide.[17] The cage coupling products obtained from the decomposition of some optically active 1,1′-diphenyl-1-methylazomethanes have been shown to be formed with net retention of configuration.[18]

We have recently observed that the abnormal product distribution in the photobromination of 1-bromobutane[1] and in the *N*-bromosuccinimide bromination of cyclohexyl bromide[19] and 1-bromobutane[1] is not observed at all stages in the reaction, but rather that at low conversion the distribution is very similar to that expected for a normal polar effect. We proposed that the initially formed radicals react with hydrogen bromide, a reaction which is well documented in free-radical brominations.[20] Consequently the distribution of the products is different from that of the initial kinetically formed radicals, and the extent of this difference should depend upon the concentration of the hydrogen bromide in the system. Evidence was presented in support of this concept.[1]

In the light of these results which have eliminated the possibility of anchimeric assistance by bromine in the formation of a secondary radical, it seems extremely doubtful if any assistance would be present during the formation of a tertiary radical. However, no distinction has been made between a mechanism which involves bridging after abstraction and a cage reaction. We have therefore reinvestigated the photobromination of (+)-1-bromo-2-methylbutane and looked at the photobromination of (−)-1-fluoro-2-methylbutane. A fluorine bridged radical is not possible as first row elements cannot expand their octets. We have also investigated the photobromination of (+)-2-methylbutyl acetate as we have previously shown that the acetate group does not form a bridged radical.[21]

Results and Discussion

The Bromination of (+)-1-Bromo-2-methylbutane. The photobrominations were investigated using essentially the same reaction conditions as were used by Readio in his study of the bromination of (+)-1-bromo-2-methylbutane.[22] A mixture (1:2 mole ratio) of molecular bromine and (+)-1-bromo-2-methylbutane was irradiated, under a positive pressure of helium, with an incandescent lamp until the reaction mixture was colorless (approximately 14 min). The dibromide was isolated by distillation under reduced pressure. The unreacted monobromide was isolated by glpc as described in the Experimental Section. The rotation of carbon tetrachloride solutions of the starting material and recovered monobromide and dibromide were determined. The results are summarized in Table I.

Table I. Specific Rotation of the Products from the Photobromination of (+)-1-Bromo-2-methylbutane. Specific Rotation at 27° (in Carbon Tetrachloride Solution)

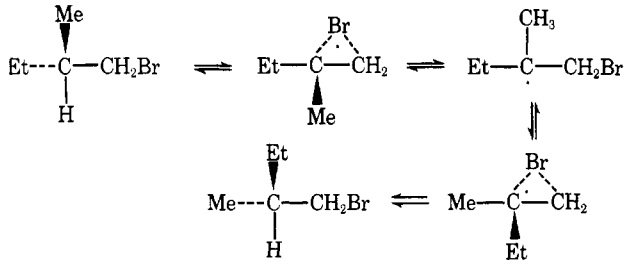
	[α], deg		
λ, mμ	Dibromide	Recovered monobromide	Starting material
589	−3.23	+4.04	+4.21
587	−3.37	+4.11	+4.28
546	−3.89	+4.45	+4.71
436	−7.99	+6.85	+7.43
365	−15.25	+9.60	+10.35

The rotation of the (−)-1,2-dibromo-2-methylbutane is essentially the same as that reported by Skell and his coworkers.[4,22] A slight racemization (3–7%) of the starting material was observed. The validity of this observation was verified by subjecting the starting material to the reaction conditions and isolation procedures in the absence of photoinitiation, thereby confirming that the racemization takes place during the reaction.

The retained activity of the dibromide was rationalized by Skell on the basis of the concomitant formation of a bridged bromine radical during the abstraction reaction. The activity of the product, dibromide, was found to be dependent upon the concentration of bromine in the solution,[4] and a competitive first-order racemization (ring opening to a classical radical) and a second-order stereospecific bromination were invoked to explain these observations.

(12) H. C. Brown, M. S. Kharasch, and T. H. Chao, *J. Amer. Chem. Soc.*, **62**, 3435 (1940).
(13) J. T. Gruver and J. G. Calvert, *ibid.*, **80**, 3524 (1958); W. von E. Doering, M. Forber, M. Sprecher, and K. B. Wiberg, *ibid.*, **74**, 3000 (1952); F. D. Greene, *ibid.*, **81**, 2688 (1959); H. J. Dauben, Jr., and H. H. McCoy, *ibid.*, **81**, 5404 (1959).
(14) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956); M. Karplus, *J. Chem. Phys.*, **30**, 15 (1959); M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961); D. Schrader and M. Karplus, *ibid.*, **40**, 1593 (1964).
(15) J. Thiele and K. Henser, *Justus Liebigs Ann. Chem.*, **290**, 1 (1896); M. S. Kharasch, F. Engelmann, and W. H. Urry, *J. Amer. Chem. Soc.*, **65**, 2428 (1943); P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954); O. Neunhoffer and H. Haase, *Chem. Ber.*, **91**, 1801 (1958); D. E. Applequist and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 2194 (1965); S. Seltzer and E. J. Hamilton, Jr., *ibid.*, **88**, 3775 (1966).
(16) P. D. Bartlett and J. O. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).
(17) F. D. Greene, *J. Amer. Chem. Soc.*, **77**, 4869 (1955).
(18) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969).
(19) D. D. Tanner, M. W. Mosher, N. C. Das, and E. V. Blackburn, unpublished results from this laboratory.
(20) K. B. Wiberg and L. H. Slaugh, *J. Amer. Chem. Soc.*, **80**, 3033 (1958); C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963); R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963); H. R. Anderson, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **21**, 1258 (1953); J. H. Sullivan and N. Davidson, *ibid.*, **19**, 143 (1951).
(21) D. D. Tanner and F. C. P. Law, *J. Amer. Chem. Soc.*, **91**, 7535 (1969).
(22) P. D. Readio, Ph.D. Thesis, The Pennsylvania State University, 1964.

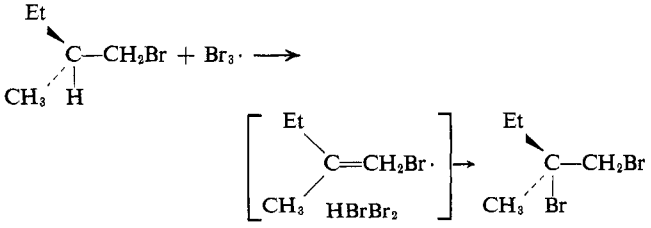
The small amount of racemization observed by us in the starting material, however, cannot be explained by transfer of the open radical with hydrogen bromide, but, if one adheres to the principle of microscopic reversibility, must be explained by transfer with the bridged radical to give back starting material. However, in



view of our earlier work which clearly ruled out participation by a neighboring bromine atom in the rate determining abstraction step of the bromination of butyl bromide[1] and cyclohexyl bromide,[19] one would have to propose that if bridging is to be invoked to explain the stereospecificity of the bromination it must occur after the abstraction reaction, and faster than a molecular rotation. A concomitant competing hydrogen transfer reaction with a first-formed open radical can easily accommodate the racemization observed.

The mechanism proposed by Haag and Heiba,[10] to explain the retention of activity found in the bromination of active 1-substituted 2-methylbutanes, could equally well accommodate the results observed. If atom transfer of the tertiary radical with hydrogen bromide occurred more slowly than molecular rotation, either within or outside of the solvent cage, then racemized starting material would be produced. If transfer with bromine, within the solvent cage, takes place at a rate faster than molecular rotation, then active dibromide would be the product formed.

In our previous paper[1] we had proposed that the production of 1,2-dibromides upon the bromination of bromoalkanes could possibly be explained by the facile elimination of a bromine radical from the intermediate β-bromoalkyl radical to give an olefin, which would subsequently add bromine. In the case of the bromination of the active bromide the elimination–readdition mechanism would necessarily take place within the solvent cage, if it were to be operative in a reaction producing an active dibromide. The bromination of the bromide was



carried out using isotopically enriched bromine (3.97% bromine-79, 96.03% bromine-81). It was anticipated that if olefin formation takes place some enrichment of the dibromide obtained would be observed, since similar experiments have shown enrichment in the bromination of 1-bromobutane at more elevated temperatures.[23]

If the mechanism involved a bridge or a direct substitution reaction within the solvent cage, the product must contain 27.3% bromine-79 and 72.7% bromine-81. Mass spectral analysis of the recovered dibromide showed a ratio of 27.4/72.6 for $^{79}Br/^{81}Br$. Thus if an elimination–readdition process was operative the original bromine never became free to mix with the bulk bromine in solution.

The Bromination of (−)-1-fluoro-2-methylbutane (VI). A mixture (2:1 mole ratio) of VI and bromine was irradiated in a fashion identical with that of the bromination of (+)-1-bromo-2-methylbutane (approximately 12 hr). Glpc analysis of the reaction mixture showed a number of products other than the starting material. Distillation of the reaction mixture gave the starting monofluoride (VI) and 1-fluoro-2-bromo-2-methylbutane (VII), 73%. A carbon tetrachloride solution of the bromo fluoride VII did not rotate plane polarized light. The recovered monofluoride (VI) was racemized to a much greater extent (86–88%) than the monobromide from the previous experiment as can be seen from Table II.

Table II. Specific Rotation of the Products from the Photobromination of (−)-1-Fluoro-2-methylbutane.
Specific Rotation at 27° (in Carbon Tetrachloride Solution)

	[α], deg		
λ, mμ	Bromo fluoride	Recovered monofluoride	Starting material
589	0	−1.18	−8.94
578	0	−1.18	−9.18
546	0	−1.35	−10.39
436	0	−2.15	−17.49
365	0	−3.33	−27.11

A similar mixture of the (−)-fluoride and molecular bromine was degassed and sealed in a Pyrex ampoule. The tube was irradiated with two 200-W incandescent lamps for 60 hr. The solution was brown and contained no molecular bromine. A very small amount of insoluble material was formed. Glpc analysis indicated the presence of 13 compounds present in the ratio 3.02:0.22:0.25:1.00:0.065:0.10:0.31:1.58:0.45:0.28:0.08:0.10:0.01 and a 95% material balance was obtained. The first compound was unreacted starting material.

The reaction mixture was subjected to glpc–mass spectral analysis. On the basis of their mass spectral cracking patterns the products could be assigned the following molecular formulas. Compounds 2–3, $C_5H_{11}Br$; compounds 4–6, $C_5H_{10}FBr$; compounds 7–8, $C_5H_{10}Br_2$; compounds 9–12, $C_5H_9FBr_2$; and compound 13, $C_5H_9Br_3$.

Compound 4 corresponded to 1-fluoro-2-bromo-2-methylbutane (VII). Its structure was assigned on the basis of its (^1H and ^{19}F) nmr spectra and elemental analysis. This product was also isolated by distillation and was optically inactive.

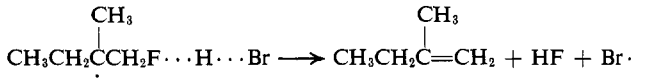
Compound 7 was 2,3-dibromo-2-methylbutane (VIII). It was identified by comparison of its infrared spectrum and its glpc retention time with those of an authentic sample prepared by the action of molecular bromine on 2-methyl-2-butene. The structure 1,2-dibromo-2-methylbutane (IX) was assigned to compound 8 by comparison of its infrared spectrum and its glpc retention time with those of an authentic sample prepared by the photobromination of 1-bromo-2-methylbutane.

(23) D. D. Tanner, M. W. Mosher, H. Yabuuchi, E. V. Blackburn, and Y. Kosugi, unpublished results from this laboratory.

Compound 9 corresponded to 2,3-dibromo-1-fluoro-2-methylbutane (X). The structure was assigned on the basis of elemental analysis and nmr spectra.

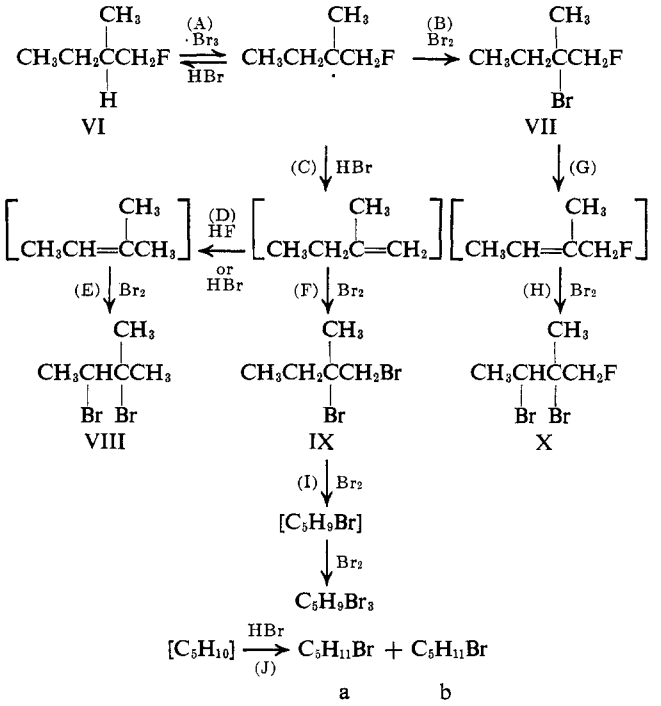
Glpc analysis of the reaction products from the bromination in the open system indicated the presence of 2-bromo-1-fluoro-2-methylbutane, 2,3-dibromo-2-methylbutane, 1,2-dibromo-2-methylbutane, 2,3-dibromo-1-fluoro-2-methylbutane. They were present in the ratio 1.00:0.016:0.11:0.09. The compounds corresponding to compounds 3, 5, 6, and 10 were also present in this reaction mixture (open system) in the ratio 0.025:0.017:0.09:0.02.

The differences observed between the reactions carried out in a closed system and those carried out in an open system presumably are due to the amounts of hydrogen bromide present during the reactions. Thus in the absence of large amounts of hydrogen bromide (open system) 2-bromo-1-fluoro-2-methylbutane is the major product from the photobromination of 1-fluoro-2-methylbutane whereas when hydrogen bromide is present in higher concentrations (closed systems), dibromides and other polyhalogenated compounds predominate. The hydrogen bromide probably complexes with the fluorine and upon formation of the β halo free radical lends itself to the elimination of the fluorine in the energetically favorable process of hydrogen fluoride formation. The proposed sequence of reactions for the



formation of these products is shown in Scheme I.

Scheme I



The reversibility of step A is shown by the partial racemization of the monofluoride during the reaction; this seems to be a general phenomenon in these brominations.[1] The transfer step (B) would then lead to the product bromo fluoride (VII). The tertiary radical can also lose fluorine by hydrogen bromide assisted abstraction; this seems reasonable, in view of the fact that the dibromide (IX) is the major product when the reaction is carried out in the presence of high concentrations of hydrogen bromide. The olefin formed in this step (C) can then either rearrange in step D, react with HBr in step J, or add bromine in step F. Acid-catalyzed olefinic rearrangements (step D) have been well documented,[24] and the olefin formed would then add bromine to give compound VIII. Dibromide IX could arise by step F or bromination of 1-bromo-2-methylbutane. Both paths are probably followed since some monobromide was detected by mass spectrometry in the reaction mixture (glpc peaks 2 and 3). Compounds VII and IX could both undergo bromine or acid-catalyzed eliminations of hydrogen bromide *via* steps G and I, respectively. This type of elimination has been observed in the ionic "dark" bromination of *tert*-butyl bromide.[25] The olefins formed would then react with molecular bromine to form X and the tribromide (glpc peak 13).

The Bromination of (+)-2-Methylbutyl Acetate (XI). Acetate XI and molecular bromine were irradiated under the conditions used in the bromination of 1-bromo-2-methylbutane. Glpc analysis of the products indicated the presence of eleven compounds in the ratio 0.23:0.12:1.00:0.037:0.23:0.015:0.014:0.007:0.004:0.015:0.19. The first compound was shown to be acetic acid by its characteristic odor and by comparison of its ir and ^{1}H nmr spectra with those of an authentic sample. The compound corresponding to peak three was unreacted 2-methylbutyl acetate which was isolated by distillation. The specific rotation of this compound is given in Table III. It was 44% racemized which again

Table III. Specific Rotations of 2-Methylbutyl Acetate. Specific Rotations at 27° (in Carbon Tetrachloride Solution)

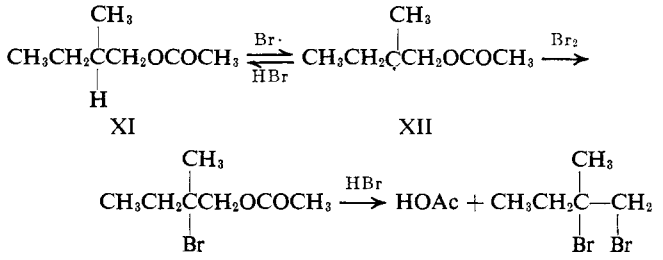
	[α], deg		
λ, mμ	Before bromination	Recovered after bromination	%
589	+3.61	+2.01	44
578	+3.78	+2.11	44
546	+4.29	+2.41	44
436	+7.36	+4.11	44
365	+11.61	+6.52	44

suggests that reversibility of the abstraction of the tertiary hydrogen occurred. Compound 5 was identical with 1,2-dibromo-2-methylbutane as shown by comparison of its ^{1}H nmr and ir spectra with those of authentic samples. The dibromide was isolated by distillation and was found to be racemic. MS9 spectra of the remaining compounds indicated that peak 2 could be assigned to 1-bromo-2-methylbutane, peaks 4–10 corresponded to dibromides or bromo acetates, and peak 11 corresponded to a tribromide.

This reaction resembles the bromination of 1-fluoro-2-methylbutane in that a multitude of products is formed. However, in this case, no bromo acetate could be positively identified or isolated. If any were present in the reaction mixture, it must have been in extremely low yield. The principal reaction is the elimination of acetic acid followed by bromination to give 1,2-dibromo-2-methylbutane (Scheme II).

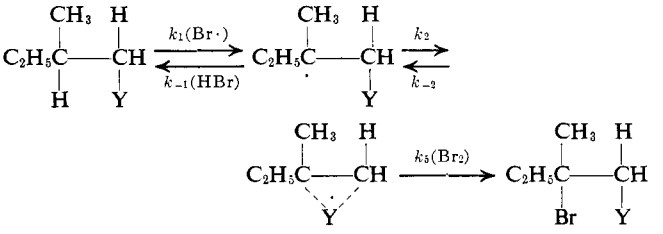
(24) D. H. Martin and F. Williams, *J. Amer. Chem. Soc.*, **92**, 769 (1970), and references therein.
(25) G. A. Russell and H. C. Brown, *ibid.*, 77, 4025 (1955).

Scheme II



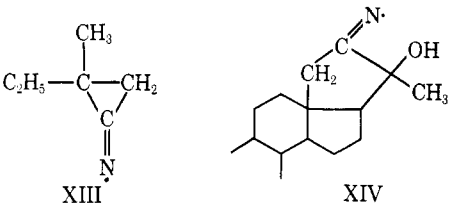
Since a radical is reversibly formed at the 2 position, as evidenced by racemization of the starting acetate, a competition for the radical between hydrogen bromide and molecular bromine is necessitated. The implied formation of the tertiary bromide, by the more facile transfer of a tertiary radical with bromine as opposed to hydrogen bromide, leads to the conclusion that the bromide when formed is rapidly destroyed, by an ionic mechanism, under the condition of the reaction (Scheme II). The radical fragmentation of XII would not be expected to yield acetic acid but rather carbon dioxide and the products derived from methyl radicals.[26]

Mechanistic Conclusions. Several mechanistic explanations can be proposed to account for our observations. Since anchimeric assistance by a neighboring bromine to form a bridged intermediate can be discounted for a secondary radical,[1] and since it is unlikely that it would then be more favorable in the formation of a tertiary radical, an explanation, where there is formation of a bridged species after the radical is formed, can be suggested to account for the retention of activity in the bromination of (+)-1-bromo-2-methylbutane.



If k_2 is faster than molecular rotation and the bridge always closes specifically from the side opposite the abstracted hydrogen, then transfer of the radical with bromine would give products with retained configuration and activity, while a competing transfer of hydrogen bromide with the open radical (k_{-1}) would lead to racemized starting material.

The results obtained in the bromination of the fluoride would be explained in the following manner: the inability of a first row element to expand its octet could explain the racemization of both the starting material and the product in the bromination of the active fluoride. In the case of the acetate, the results would confirm the observation that a single bridged intermediate acetoxy radical is not the sole intermediate in the formation of products from a β-acetoxy alkyl radical.[21] The results of Haag and Heiba[10] do not necessarily exclude the possibility of a bridged intermediate in these reactions as it is possible to envisage a bridge radical involving the nitrile. Such a radical would be an imidyl radical (XIII) and imidyl radicals have been proposed as intermediates by several groups of workers.[26,27] Participation of a bridged cyanide group has been proposed in the rearrangement which takes place in the hypoiodite reaction of 20-hydroxy-20-cyano steroids to give 18-cyano-20-keto steroids.[27] A bridging imidyl radical (XIV) is suggested as an intermediate.



An alternative explanation for the results obtained from the bromination of active 1-substituted 2-methylbutanes would be a modification of the mechanism proposed by Haag and Heiba.[10] Abstraction of hydrogen by $Br_3\cdot$ and rapid transfer of the radical with a geminate molecule of bromine or hydrogen bromide in a rapid cage reaction could give optically active products. The cage transfer reactions would compete with the speed of a molecular rotation, the rate of which will in turn be proportional to the size and polarity of the groups attached to the asymmetric carbon radical. Since both the cyanide and the bromide are effectively larger than the fluoride or acetate groups the rate of cage transfer will be faster than the rate of rotation and the products obtained from these brominations will retain optical activity, while those involving the smaller groups will rotate at a faster rate than they undergo cage transfer, or transfer outside the cage, and therefore will give racemic products.

Further work is now in progress on cyanide brominations, as well as brominations of other derivatives of this system and will be reported at a later date.

Experimental Section

Materials. Bromine was redistilled before use. We thank Professor H. S. Mosher for a gift of (−)-2-methylbutanol ($[\alpha]^{25}D$ (obsd) −4.75°). Bromine-81 (96.03%) was purchased from Isotope Development Center, Oak Ridge National Laboratory.

Instruments. Glpc analyses were carried out on an Aerograph 1520 instrument using isothermal conditions. A 20 ft × 0.25 in. glpc column packed with 15% diethylene glycol succinate on 60–80 mesh acid-washed Chromosorb W was used. Rotations were recorded on a Perkin-Elmer 141 polarimeter. Mass spectra were recorded on an A. E. I. MS12 instrument with an on-line connection to a glpc instrument. Nmr spectra were determined in carbon tetrachloride solution, with trimethylsilane as internal standard on a Varian Associates A-60 nuclear magnetic resonance spectrometer.

(+)-1-Bromo-2-methylbutane (I). This was prepared by the method of Crombie and Harper,[28] and was purified by glpc on the 15% diethylene glycol column at 100°. The specific rotation was measured and is shown in Table I.

Bromination of (+)-1-Bromo-2-methylbutane. The bromide (5.01 g, 0.033 mol) and molecular bromine (2.83 g, 0.018 mol) were placed in a 50-ml flask equipped with a magnetic stirring bar and a reflux condenser. The system was connected *via* another condenser to a T tube, one junction of which was immersed in dioctyl phthalate while the other led to a helium source. The system was maintained under positive helium pressure and the flask immersed in a bath at 28°. The solution was irradiated with two 200-W incandescent lamps until the solution was colorless (approximately 15 min). Copious evolution of hydrogen bromide was observed which bubbled out through the dioctyl phthalate. Potassium carbonate was added to neutralize the dissolved hydrogen

(26) D. D. Tanner and N. J. Bunce, *J. Amer. Chem. Soc.*, **91**, 3028 (1969); M. L. Poutsma and P. A. Ibarbia, *J. Org. Chem.*, **34**, 2848 (1969).

(27) K. Heusler and J. Kalroda, *Angew. Chem., Int. Ed. Engl.*, **3**, 525 (1964).

(28) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 2685 (1950).

bromide and the product distilled. A fraction distilling at 50° (8 mm), $n^{25}D$ 1.5070 (lit.[22] $n^{25}D$ 1.5073), was collected and found to be the pure dibromide by glpc analysis. The optical rotation of this compound was determined in carbon tetrachloride solution. The unreacted monobromide was collected by glpc from another portion of the reaction mixture. It had $n^{25}D$ identical with that of the starting material. The dibromide was not collected by glpc as racemization was found to occur under the glpc conditions used.

A bromination mixture of I which had been saturated with hydrogen bromide was subjected to the same conditions of reaction used in the photobrominations with the exception that the mixture was not irradiated. The unreacted bromine was removed by washing with an aqueous mixture of sodium thiosulfate and the unreacted alkyl bromide was isolated as before. The rotation obtained was identical with that observed before the control was run.

1-Fluoro-2-methylbutane (VI). (−)-2-Methylbutanol ($[\alpha]^{25}D$ (obsd) −4.75°) (88 g, 1.00 mol) was added to a solution of *p*-toluenesulfonyl chloride (200 g, 1.05 mol) in pyridine (1 kg) and left at room temperature for 18 hr. Cold water was added to the solution followed by ether (30 ml). The ether layer was extracted with dilute sulfuric acid to remove the pyridine, washed with water, aqueous sodium bicarbonate, and water, and then dried over anhydrous magnesium sulfate. Removal of the ether under reduced pressure gave the tosylate which was used without further purification. The tosylate (23.1 g, 0.10 mol) was added to a suspension of anhydrous potassium fluoride (29.5 g, 0.51 mol) in diethylene glycol (29.5 g). A Hempel column fitted with a still head, Liebig condenser, and receiver flask cooled by a Dry Ice–acetone mixture was attached to the reaction flask. A slight vacuum was applied to the system and the mixture heated to 100° at which temperature the reaction proceeded without further heating. The fluoride distilled over and was collected in the cooled receiver flask. The yield of crude product was 5.78 g (67%). The crude material was treated with concentrated sulfuric acid to remove any olefin formed and was then washed with sodium bicarbonate solution and water. The fluoride was dried over anhydrous magnesium sulfate and further purified by fractionation using a 20 ft × 0.25 in. glpc column packed with 15% diethylene glycol succinate on 60–80 mesh acid-washed Chromosorb W at 75° and 30 ml/min flow rate. The purified fluoride (2.8 g, 31%) had $n^{20}D$ 1.3568 (lit.[29] 1.3570); $[\alpha]^{27}D$ −8.94° (lit.[29] −8.865°); τ (CCl_4) 9.12 (3 H, q, 4-H), 9.01 (3 H, d, 2-CH_3), 8.0–9.0 (3 H, m, 2- and 3-H), 5.44 and 6.25 (2 H, doublet of doublets, 1-H split by 1-F ($J_{H,F}$ = 47.0 Hz) and by 2-H ($J_{H,H}$ = 6.0 Hz)). The ^{19}F nmr spectrum showed a triplet of doublets ($J_{1\text{-}H,F}$ = 47.0 Hz, $J_{2\text{-}H,F}$ = 9.0 Hz).

Anal. Calcd for $C_5H_{11}F$: C, 66.62; H, 12.30. Found: C, 66.75; H, 12.34.

Bromination of (−)-1-Fluoro-2-methylbutane. (a) The reaction mixtures consisted of a 1:2 mole ratio of distilled bromine to the neat fluoride. Aliquots of the reaction mixtures were placed in Pyrex ampoules and degassed by the freeze–thaw method. One tube was irradiated in a sealed Pyrex ampoule with two 200-W incandescent lamps at 30° for 60 hr. Fractionation of the resulting solution using the 15% diethylene glycol succinate column described previously gave peaks corresponding to 13 compounds in a ratio of 3.02:0.22:0.25:1.00:0.065:0.10:0.31:1.58:0.45:0.28:0.08:0.10:3.01. Compound 1 was unreacted starting material. This was recovered and had $[\alpha]^{25}D$ (CCl_4 solution) −3.34° indicating that 62% racemization of the fluoride had occurred. The fluoride could be isolated unchanged when it was subjected to the reaction conditions (Br_2 and HBr) in the absence of light.

Mass spectral analysis indicated that compounds 2 and 3 were monobromides with molecular formula $C_5H_{11}Br$. Both of these compounds had cracking patterns indicative of this molecular formula. The parent peaks were at *m/e* 152 and 150 ($C_5H_{11}Br$).

Compound 4 was shown to be 1-fluoro-2-bromo-2-methylbutane and was racemic: τ (CCl_4) 8.92 (3 H, t, 4-H), 8.25 (3 H, d, 2-CH_3), 8.10 (2 H, q, 3-H), 5.60 (2 H, d, 1-H), $J_{H,F}$ = 48.0 Hz); ^{19}F nmr spectrum showed a quartet, $J_{H,F}$ = 47.5, 5 Hz.

Anal. Calcd for $C_5H_{10}BrF$: C, 35.50; H, 5.92. Found: C, 35.67; H, 6.04.

Compounds 5 and 6 were found to be bromofluorides by mass spectral analysis. The cracking patterns of these two compounds closely resembled that of 2-bromo-1-fluorobutane. The parent ions were at *m/e* 170 and 168 in each case. Mass measurement of the peak at *m/e* 148 in the spectrum of compound 6 showed that its mass was 147.9889 ($C_5H_9{}^{79}Br$ requires 147.9888). This ion is formed by loss of HF from the parent ion. This *m/e* ratio is observed in the mass spectra of glpc compounds 4, 5, and 6.

Compound 7 was 2,3-dibromo-2-methylbutane by comparison (glpc retention time ir and ^1H nmr) with a sample prepared from the action of bromine on 2-methyl-2-butene: τ (CCl_4) 5.3–5.8 (1 H, q, 3-H), 8.09 (3 H, d, 4-H), 8.00 and 8.18 (6 H, two singlets, 1-H and 2-CH_3).

Compound 8 was 1,2-dibromo-2-methylbutane by comparison (glpc retention time, ir and ^1H nmr) with an authentic sample prepared by the bromination of 1-bromo-2-methylbutane: τ (CCl_4) 6.16 (2 H, s, 1-H), 8.06 (2 H, q, 3-H), 8.15 (3 H, s, 2-CH_3), and 8.91 (3 H, 4-HO).

Compound 9 was 2,3-dibromo-1-fluoro-2-methylbutane: τ (CCl_4) 5.39 (2 H, d, 1-H, $J_{H,F}$ = 47.0 Hz), 5.48 (1 H, q, 3-H), 8.10 (3 H, d, 4-H), 8.20 (3 H, d, 2-CH_3); ^{19}F nmr spectrum showed a triplet, $J_{H,F}$ = 47.0 Hz.

Anal. Calcd for $C_5H_9Br_2F$: C, 24.20; H, 3.63. Found: C, 24.50; H, 3.88.

Compounds 10–12 were dibromo fluorides. Their mass spectra were very similar to that of 2,3-dibromo-1-fluoro-2-methylbutane. Parent ions occurred at *m/e* 250, 248, and 246 with abundance 1:2:1. These peaks are due to $C_5H_9{}^{81}Br_2{}^+$, $C_5H_9{}^{79}Br{}^{81}Br^+$, and $C_5H_9{}^{79}Br_2{}^+$. The signal at *m/e* 227 in the case of peak 12 had accurate mass of 226.9070 ($C_5H_9{}^{79}Br_2$ requires 226.9070). The spectra of compounds 9–12 all showed peaks at *m/e* 169 and 167 of relative abundance >25%. These peaks are due to $C_5H_9FBr^+$. Compound 13 showed no signals at *m/e* 250, 248, 246, 169, and 167. Its ^{19}F nmr spectrum showed the absence of any fluorine. The compound was a solid unlike compounds 9–12 which were liquids. The mass spectrum showed peaks at *m/e* 231, 229, and 227 ($C_5H_9Br_2$) with relative abundances in the ratio 1:2:1. This compound is therefore thought to have molecular formula $C_5H_9Br_3$.

(b) The bromination was repeated using the conditions used in the bromination of (+)-1-bromo-2-methylbutane. The reaction time was 18 hr. Glpc analysis of the reaction products indicated the presence of 2-bromo-1-fluoro-2-methylbutane, 2,3-dibromo-2-methylbutane, 1,2-dibromo-2-methylbutane, and 2,3-dibromo-1-fluoro-2-methylbutane in the ratio 1.00:0.016:0.12:0.09. Compounds 3, 5, 6, and 10 were also present in the ratio 0.025:0.017:0.09:0.02.

The bromo fluoride was isolated by distillation. The optical rotation of this compound was determined in carbon tetrachloride solution and was found to be zero. The recovered (−)-1-fluoro-2-methylbutane (by glpc) had a refractive index identical with that of the starting material. The optical rotation of this compound is recorded in Table II. Recollection of the same material gave the same rotation, hence racemization did not occur on the column.

(+)-2-Methylbutyl Acetate. Acetyl chloride (15.7 g, 0.20 mol) was added to a stirred solution of (−)-2-methylbutanol (17.6 g, 0.20 mol) and pyridine (30 g) over 30 min. The solution was left overnight and water was added. The organic layer was extracted, washed with dilute hydrochloric acid, water, aqueous sodium bicarbonate, and water, and dried over anhydrous magnesium sulfate. Distillation, 138° (690 mm), gave the (+)-2-methylbutyl acetate (23 g, 0.18 mol, 89%): $n^{25}D$ 1.4006 (lit.[30] $n^{20}D$ 1.4012), $[\alpha]^{27}D$ +3.61° (lit.[30] $[\alpha]^{20}D$ +3.30°).

Bromination of (+)-2-Methylbutyl Acetate. (+)-2-Methylbutyl acetate (12 g, 0.090 mol) and bromine (7.5 g, 0.047 mol) were irradiated under a helium atmosphere in the apparatus described in the bromination of 1-bromo-2-methylbutane, at 25°. After 5 days the solution was colorless. Glpc analysis of the solution, after removal of hydrogen bromide under reduced pressure, indicated the presence of several compounds. The major components

Table IV

m/e		$^{81}Br:{}^{79}Br$
232	54.8 ± 0.6	
230	34.4 ± 0.1	72.0:28.0
228	10.7 ± 1.5	
203	53.3 ± 0.3	
201	38.6 ± 0.8	72.6:27.4
199	8.1 ± 0.7	

(29) D. H. Brauns, *Recl. Trav. Chim. Pays-Bas*, **69**, 1175 (1950).

(30) "Dictionary of Organic Compounds," Vol. 4, Eyre and Spottiswode, London, 1965, p 2146.

(>80%) were acetic acid, unreacted acetate, and 1,2-dibromo-2-methylbutane by comparison (glpc retention time, ir, and ^{1}H nmr) with authentic samples. The unreacted acetate and 1,2-dibromide were isolated by distillation. The rotation of the acetate is recorded in Table III. The isolated dibromide was racemic.

Bromination of 1-Bromo-2-methylbutane with Bromine-81. 1-Bromo-2-methylbutane (0.11 g) and bromine-81 (60 mg) were degassed in a Pyrex ampoule and irradiated at 30° with two 200-W bulbs until the solution was colorless (0.5 hr). The unreacted 1-bromo-2-methylbutane and the 1,2-dibromo-2-methylbutane were isolated by glpc on the 20 ft × 0.25 in. glpc column packed with 15% diethylene glycol succinate at a temperature of 110°. The mass spectra of the compounds were recorded on an A.E.I. MS9 instrument. The 1-bromo-2-methylbutane had incorporated no additional bromine-81 and the dibromide had been formed by the incorporation of one atom of bromine-81 into each molecule of the bromobutane. The ratios of the parent peaks and M − 29 peaks averaged for three sets of spectra are given in Table IV.

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The Influence of Rotational Freedom on Excited Diene Reactivity. The Direct and Photosensitized Reactions of 5,5-Diphenyl-1,3-cyclohexadiene[1]

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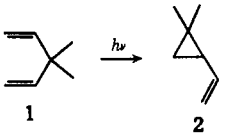
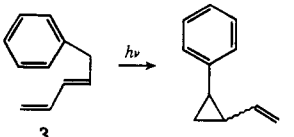
Abstract: The direct and sensitized photochemistry of 5,5-diphenyl-1,3-cyclohexadiene (**7**) has been studied in detail. Direct excitation of **7** at 2537 Å afforded 1,1-diphenyl-1,3,5-hexatriene (**8**) in 80% yield; the structure of the triene was established by hydrogenation to 1,1-diphenylhexane. Sensitized photolysis of **7** with Michler's ketone (E_t = 61 kcal/mol), 2-acetonaphthone (E_t = 59.5 kcal/mol), or fluorenone (E_t = 53.3 kcal/mol) afforded two products in a ratio of 91:9 (80–90% yield). The major product was identified as *trans*-5,6-diphenylbicyclo[3.1.0]-hex-2-ene (**10**) and the minor product as *trans*-4,5-diphenylbicyclo[3.1.0]hex-2-ene (**12**) by comparison with synthesized authentic samples. In contrast, preparative irradiations using the high-energy sensitizers acetone (E_t > 75 kcal/mol), *m*-methoxyacetophenone (E_t = 72.4 kcal/mol), and benzophenone (E_t = 68.5 kcal/mol) yielded in addition to **10** and **12** moderate amounts of *cis*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (**11**). Quantum yield studies indicated that both the singlet- and triplet-excited states of the diene have reactive processes of moderate efficiency, Φ_{dir} = 0.35 and Φ_{sens} = 0.26. The results reported here are discussed in relation to the triplet reactivity of the diene chromophore in the di-π-methane rearrangement.

The recognition of the di-π-methane to vinylcyclopropane transformation (eq 1) as a general photochemical transformation by Zimmerman[3] has been fol-



1 2 (1)

lowed by intense interest in this area. While numerous examples of this process now abound in the literature establishing its generality and synthetic usefulness, several mechanistic aspects of the reaction remain of general interest. One of these is the dependence of the multiplicity of the rearranging state on the structural character of the substrate.[4] Thus, molecules having the possibility of rotational freedom in the excited state (*i.e.*, acyclic olefins and dienes having exocyclic methylene groups) undergo rearrangement most efficiently in the excited singlet state.[5] The largest class of such compounds has conjugated diene and phenyl moieties as typified by **3**.[6,7] In contrast, rigid systems as exempli-



3 4 (2)

fied by benzonorbornene (**5**) undergo rearrangement most efficiently in the triplet state (eq 3).[8,9]

(1) (a) For a preliminary report see J. S. Swenton, A. L. Crumrine, and T. J. Walker, *J. Amer. Chem. Soc.*, **92**, 1406 (1970); (b) for a parallel study see H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970).

(2) (a) Ohio State University Fellow, 1970; (b) undergraduate research participant, 1969; (c) National Science Foundation undergraduate research participant, 1969.

(3) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **89**, 3932 (1967).

(4) H. E. Zimmerman and R. S. Mariano, *ibid.*, **91**, 1718 (1969).

(5) (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965); (b) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967); (c) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); **91**, 5307 (1969); (d) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967); (e) E. C. Sanford and G. S. Hammond, Paper 63, Western Regional American Chemical Society Meeting, Anaheim, Calif., Oct 6, 1969.

(6) Recently, examples of diphenylethylenes and styrenes as partners in the reaction have been reported. These species also react most efficiently in the singlet state: (a) ref 4; (b) H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970); (c) *ibid.*, **92**, 6267 (1970). See also (d) M. Comtet, *ibid.*, **91**, 7761 (1969); (e) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetrahedron Lett.*, 3895 (1970).

(7) The multiplicity of the rearranging state has not been completely established in several cases: R. C. Hahn and L. J. Rothman, *J. Amer. Chem. Soc.*, **91**, 2409 (1969); S. J. Cristol and G. O. Mayo, *J. Org. Chem.*, **34**, 2363 (1969); W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 5817 (1970). For these molecules either singlet and triplet give the same product, or intersystem crossing is facilitated by the aromatic ring, and both direct and sensitized reaction yield the triplet reactant.

(8) (a) E. Ciganek, *ibid.*, **88**, 2882 (1966); (b) J. R. Edman, *ibid.*, **88**, 3454 (1966); (c) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and