Photobromination of (−)-(2*R*)-2-Bromobutane with Bromine-81

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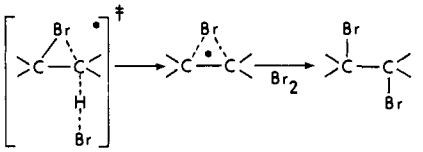
Abstract: The photobromination of 2-bromobutane with molecular bromine yields 2,2-dibromobutane, *meso*-2,3-dibromobutane, *dl*-2,3-dibromobutane, and small amounts of 1,2-dibromobutane and 2,2,3-tribromobutane. When (−)-(2*R*)-2-bromobutane was used in the bromination both the *dl*-2,3-dibromobutane and the 2,2,3-tribromobutane fractions had significant optical activity (~5%). The observation that the intermediate β-bromoalkyl radical can yield optically active bromination products established that the structure of the intermediate is not, as has been claimed, a symmetrical or very rapidly ($k_{eq} > 10^{11}$ s^{-1}) equilibrating radical. Brominations carried out with molecular bromine highly enriched in bromine-81 established that a major fraction of the *dl*-2,3-dibromobutane (36%) was formed by the elimination of a bromine atom from the β-bromoalkyl radical to form 2-butene. Addition of bromine to the olefin forms, of necessity, only achiral products. Other pathways were established or suggested to explain the formation of the remaining racemic *dl*-2,3-dibromobutane. Several of these pathways involve reaction with the hydrogen bromide produced in the reaction. When the bromination was carried out with molecular bromine and added NBS (to limit the reactions with hydrogen bromide), the *dl* fraction of the 2,3-dibromobutane showed an even higher degree of optical activity (~9%).

A great deal of attention has been given to the investigation of the structure and reactivity of the β-bromoalkyl radical[4-7] since a bridged radical intermediate was first proposed by Thaler[8] to rationalize the high yields of 1,2-dibrominated products produced in the photobromination of bromoalkanes.



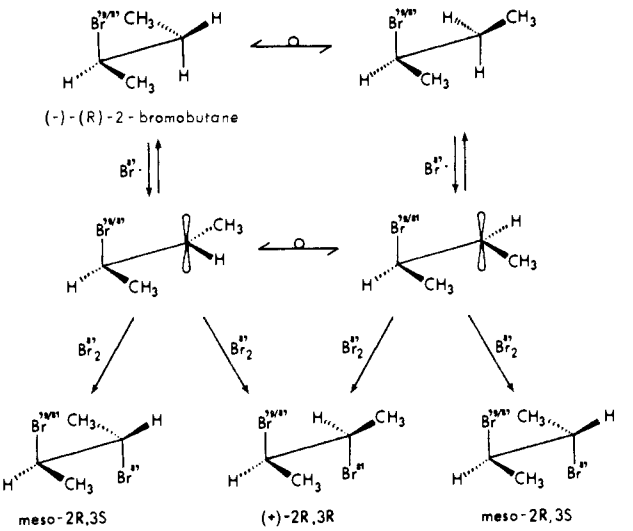
The concept of a bridged bromine radical formed by an atom transfer reaction implies the possibility of not only an accelerated rate of formation of the radical, but the possible observation of stereochemical control of its products. The mechanism of a larger number of reactions has been rationalized by invoking the intermediacy of a bridged species; however, a number of alternative explanations have been proposed, which for the cases in question may be equally well or better suited to rationalize the results.[4,9-15]

Recently direct information concerning the structure of the β-bromoalkyl radical has been reported. The generation of the 2-bromoethyl radical from the thermolysis of benzoyl-β-bromopropionyl peroxide yields, among others, the cage recombination product β-bromoethyl benzoate. The NMR spectrum of this ester shows a CIDNP effect, which demonstrates that at the time the 2-bromoethyl radical becomes polarized its methylene positions are nonequivalent.[16] The ESR spectrum of the matrix-isolated (adamantane matrix) 1,1-dimethyl-2-bromoethyl radical has been interpreted as showing that the tertiary radical is pyramidal and that its neighboring bromine substituent takes a gauche conformation to the orbital containing the lone electron,[11] a geometry which is inconsistent with a bridged species.

It is now proposed that the bridged intermediate is not symmetrically bridged when the two carbon atoms are nonidentically substituted;[7] however, it is inferred that when the carbon atoms involved in the bridge are identical then a symmetrically bridged species is formed.[7,17] The 2-bromo-1-ethyl radical fits this geometric criteria for symmetric bridging, and fails to show symmetry.[16]

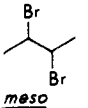
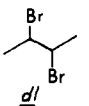
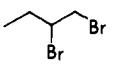
A chemical means for investigating the symmetry of the bridged intermediate is available by a study of the products of bromination of optically active 2-bromobutane with molecular bromine enriched in bromine-81. A consideration of the intermediate leading to the production of 2,3-dibromobutane produces the following predictions. The intermediacy of the classical 2-bromo-1-methylpropyl radical produced from hydrogen abstraction of either of the two methylene hydrogens in (−)-(2*R*)-2-bromobutane[18] will yield upon substitution two diastereomeric products, active (2*R*,3*R*)-2,3-dibromobutane and *meso*-(2*R*,3*S*)-2,3-dibromobutane. An analysis of the isotopic distribution of bromine would show one atom (the original one) to have the natural abundance of bromine-79/81 and one atom would have the isotopic distribution found in the enriched molecular bromine (see Scheme I).

Scheme I. Classical Radical Mechanism



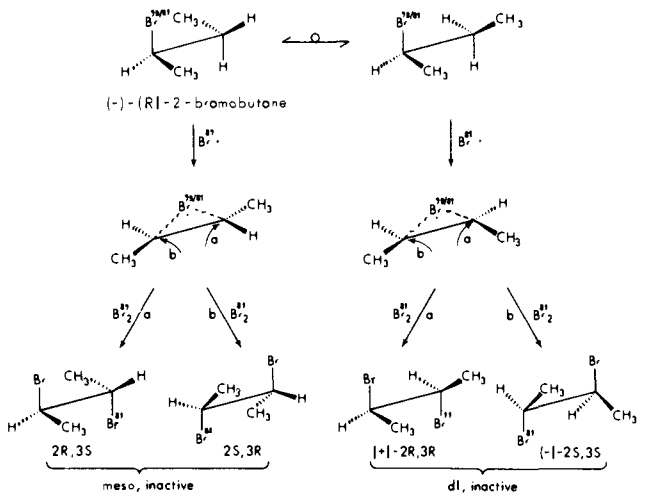
The formation of 2,3-dibromobutane via the intermediacy of a bridged radical, however, cannot as in the case of the mechanism involving the classical radical, lead to optically active dibromide. The isotopic distribution of bromine should be the same as that predicted for the reaction which proceeds via the classical radical (see Scheme II). A mechanism involving the formation of a bridge will produce two bridged intermediates, an asymmetric bridge and a symmetric bridge. Subsequent reaction of the symmetric radical must yield a racemic mixture of *dl*-2,3-dibromobutane, while transfer of the asymmetric bridged radical with the molecular bromine will yield *meso*-2,3-dibromobutane.

Table I. Photobromination of (−)-2-Bromobutane with Molecular Bromine

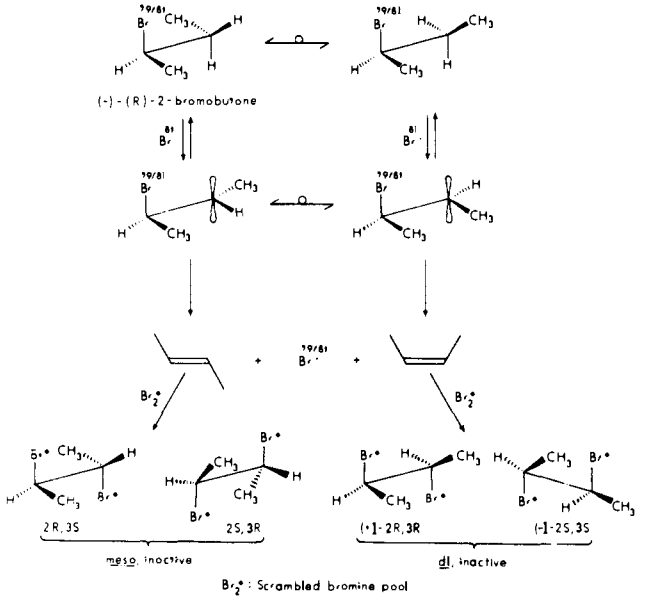
Reaction	RBr/Br_2	($[Br_2]$, M)	Temp, °C	% Yield [a,b]				
					 meso	 dl		
1	15:1	(0.6)	30	10.7	61.5	25.3		tr
2	6:1	(1.4)	30	10.2	60.0	26.1		3.4
3	4:1	(2.0)	30	10.7	57.6	24.7		7.0
4	3.9:1	(2.0)	20	9.8 ± 0.1	58.0 ± 0.2	26.1 ± 0.3	tr	6.1 ± 1.2
5	3.6:1	(2.2)	20	9.4 ± 0.2	54.8 ± 0.5	25.4 ± 0.1	tr	10.4 ± 0.3
6–8[c]	3:1	(2.6)	17	7.3 ± 0.3	55.9 ± 2.3	25.5 ± 0.8	1.9 ± 0.4	9.5 ± 2.5
9	2:1	(3.6)	17	9.0 ± 0.3	57.2 ± 0.3	27.1 ± 0.3	2.0 ± 0.2	4.7 ± 0.3
10	2:1	(3.6)	5	5.6 ± 0.2	61.2 ± 0.1	29.3 ± 0.1	1.5 ± 0.1	2.4 ± 0.2
11	1:1	(5.7)	−20	3.0 ± 0.1	57.7 ± 0.3	24.5 ± .2	2.2 ± 0.1	12.7 ± 0.3

[a] The errors indicated are average deviations from the mean for three or more analyses. [b] Reactions 1–8 were carried out to the complete consumption of bromine. Reaction 9 was carried out to 30% conversion of 2-bromobutane, reaction 10 to 10% conversion, and reaction 11 to 46% conversion. [c] Average of three independent experiments.

Scheme II. Bromine-Bridged Radical Mechanism



Scheme III. Elimination–Readdition Mechanism

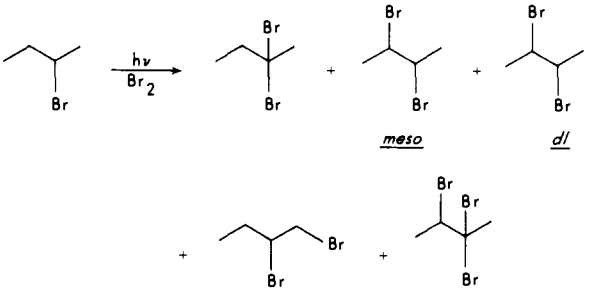


A third mechanism must be considered for the formation of 2,3-dibromobutane, which, although an intermediate classical radical is formed, yields only inactive material (see Scheme III). The extent of the involvement of this pathway for the formation of *meso*- and inactive *dl*-2,3-dibromobutane can be determined from an analysis of the isotopic distribution of bromine in each of the individual bromine atoms.[13,22,23]

During the course of this work a report was published of the study of the bromination of (+)-(2*S*)-2-bromobutane with mixtures of bromine and *N*-bromosuccinimide.[17] Skell and his co-workers concluded from this study that: "*The 2,3-bromobutyl radical exists in two bridged forms, one optically active, the other inactive; they are produced in kinetically controlled hydrogen abstraction steps from (+)-(S)-2-bromobutane. Either these intermediates have the bromine atom centered between C_2–C_3, or the bromine is not symmetrically disposed and moves between the extreme with a frequency in excess of 10^{11} sec^{-1}.*" Since our work was done in considerably more detail, and since the conclusions reached in our study differ qualitatively from those reported by Skell, we would like to report the results of our study at this time.

Discussion and Results

The Photobromination of (−)-(2*R*)-2-Bromobutane. The photobromination of (−)-(2*R*)-2-bromobutane with molecular bromine was carried out under a variety of conditions. An analysis of the reaction mixtures showed the presence of five products as well as unbrominated 2-bromobutane (see Table I). The products were isolated by preparative GLC and identified as 2,2-dibromobutane, *meso*-2,3-dibromobutane, *dl*-



2,3-dibromobutane, 1,2-dibromobutane, and 2,2,3-tribromobutane. The product distributions are listed in Table I. In all cases, the material balance for the reactions ranged from 97–103% based on starting material and on bromine consumed. The unbrominated 2-bromobutane and the products 2,3-dibromobutane (*dl* fraction) and 2,2,3-tribromobutane were subjected to polarimetric measurement in order to determine their optical rotations. The results are given in Table II.

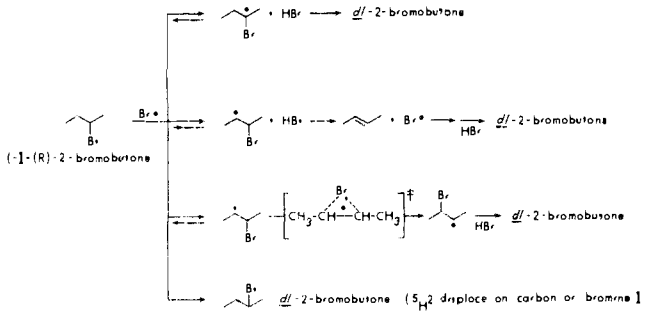
The product distributions listed in Table I are similar to that previously reported for the liquid-phase bromination of 2-bromobutane.[8] In that investigation, carried out under slightly

Table II. Optical Rotation of Products from the Molecular Bromine Bromination of (−)-(2*R*)-2-Bromobutane[a]

Reaction	RBr/Br_2 mole ratio	$([Br_2], M)$	$[\alpha]^{25}_{365}$ 2-Br before, deg	(% OP)[b]	$[\alpha]^{25}_{365}$ 2-Br after, deg	% racemized	$[\alpha]^{25}_{365}$ 2,2-Br Obsd	2,2-Br Corr[c]	$[\alpha]^{25}_{365}$ 2,2,3-Br Obsd
6	3:1	(2.6)	−69.16	(53.6)	−60.44	12.6	2.83	5.28	1.65
7	3:1	(2.6)	−68.91	(53.4)	−62.70	9.0	2.83	5.30	1.91
8	3:1	(2.6)	−76.00	(58.9)	−68.36	10.1	3.49	5.93	1.79
9	2:1	(3.6)	−68.91	(53.4)	−67.92	1.5	2.74	5.13	1.15
10	2:1	(3.6)	−76.00	(58.9)	−73.71	3.0	2.96	5.02	
11	1:1	(5.6)	−76.00	(58.9)	−62.31	18.0	1.75	2.97	
12[d]	3:1	(2.6)	−76.00	(58.9)	−76.01	0			
13[e]	3:1	(2.6)	−76.00	(58.9)	−75.73	0.4			

[a] All the rotations are measured in CCl_4 solvent except for starting material (measured as neat liquid). [α] listed at 365 for maximum rotation (see Experimental Section). [b] Optical purity (OP) based on maximum the reported value,[24] $[\alpha]^{25}_D$ 39.4°. [c] Corrected for optical purity of starting material. [d] Dark reaction under photoinitiated reaction conditions. [e] Dark reaction with added hydrogen bromide ($RBr/Br_2/HBr$ = 3:1:1) under photoinitiated reaction conditions.

Scheme IV



different conditions (RBr/Br_2, 5:1, 60 °C), three products were reported: 2,2-dibromobutane (16.3%), *meso*-2,3-dibromobutane (58.3%), and *dl*-2,3-dibromobutane (25.4%). In addition to the three dibromides found previously, 2,2,3-tribromobutane was always detected, and at higher concentrations of molecular bromine and lower temperatures, small amounts of 1,2-dibromobutane were also produced.

The unbrominated starting (−)-(2*R*)-2-bromobutane that was recovered after the reaction was found to have undergone appreciable racemization (see Table II). Control experiments (reactions 12 and 13, Table II) demonstrated that the racemization of the starting material was a result of the photolysis reaction and was not the result of a dark reaction catalyzed by molecular bromine or molecular bromine and hydrogen bromide. Several free radical processes are available for consideration and the four most plausible ones are given in Scheme IV. The racemization pathways with the exception of the S_H2 reaction all depend upon the reaction of an intermediate, be it a radical or an olefin, with hydrogen bromide. The dependence of the racemization reaction upon hydrogen bromide concentration suggested that at low concentration of hydrogen bromide little racemization will be observed. An indication that the prediction is correct can be seen from the results of reactions 9 and 10, Table II. At low final concentrations of hydrogen bromide (1.1 and 0.36 M), although the reactions were carried out under different conditions, the amount of racemization of the starting material was found to be minimized.

In all of the reactions carried out (see Table II) the isolated *dl*-2,3-dibromobutane was found to be optically active. Furthermore, the tribromide, 2,2,3-tribromobutane, which can be produced from the subsequent bromination of either 2,2-dibromobutane or 2,3-dibromobutane, was also found to be optically active (see Table II). The activity found in the tribromide, however, must come from the bromination of the chiral 2,3-dibromobutane (i.e., bromination of achiral 2,2-dibromobutane or *meso*-2,3-dibromobutane leads to achiral tribromide).

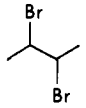
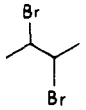
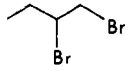
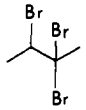
The observation that chirality was maintained in both the 2,3-dibromobutane (*dl* fraction) and its bromination product 2,2,3-tribromobutane clearly demonstrated that *the radical intermediate initially formed in the reaction was the classical 1-methyl-2-bromopropyl radical, which can be trapped by molecular bromine in its open unsymmetrical structure to yield optically active dibromide.* The active dibromide may, therefore, be assigned the (2*R*,3*R*) configuration according to this mechanism, since the asymmetric center of (−)-(2*R*)-2-bromobutane remains untouched during the bromination process. Similarly, the active tribromide is assigned the structure (+)-(3*R*)-2,2,3-tribromobutane. The optical purity of these two products is not known, since the preparations of these two compounds (optically pure) have not been reported. The optical purity of (+)-2,3-dibromobutane has, however, been estimated as $[\alpha]_{365} = +100°$ by differential scanning calorimetry[17] and its configuration can be assigned as (2*R*,3*R*), since (−)-2,3-dibromobutane has been synthesized from the reaction of (+)-(2*R*,3*S*)-3-bromobutan-2-ol with triphenylphosphine and bromine. In agreement with this assignment a calculation based on Brewsters' method, but assigning the rotational populations by means of NMR spectroscopy, assigned the (2*R*,3*R*) enantiomer a molar rotation of $[M]_D = +110°$.[25]

If the value $[\alpha]_{365} = +100°$ is accepted,[26] then *the optical purity of the 2,3-dibromobutane (5-6%, (+)-(2R,3R)-2,3-dibromobutane) obtained from the bromination reaction is not high. Since direct substitution of (−)-(2R)-2-bromobutane via an open radical predicts 100% optical purity for the 2,3-dibromobutane formed, then other pathways leading to racemization must be considered.*

Resolution and Racemization of (−)-2,3-Dibromobutane. Racemic 2,3-dibromobutane was partially resolved by the selective destruction of one enantiomer by brucine to yield (−)-2,3-dibromobutane[27] (see Experimental Section for discussion).

The partially resolved (−)-(2*S*,3*S*)-2,3-dibromobutane was found to racemize under the reaction conditions, in the absence of light. When a mixture of (−)-2,3-dibromobutane, molecular bromine, and hydrogen bromide ($RBr/Br_2/HBr$, 1.2:0.9:1) was allowed to stand for 22 h at 17 °C (the condition used for reactions 6-8, Table IV) the recovered dibromide was appreciably racemized (12%). The mechanism of this ionic racemization process undoubtedly involves a bromonium ion intermediate and is similar to that of the displacement and solvolysis reactions of vicinal dibromides which have been studied by other workers.[28] The racemization appeared to be com-

Table III. Photobromination of 2-Bromobutane with Bromine-81

Compd	M/e	Peak ratio	Total bromine content[a] $^{79}Br/^{81}Br$	Average isotopic abundance[a] % $^{79}Br/^{81}Br$	
				Br-1	Br-2
	P[b] P − 29[c]	0.970:1	49.23 ± 0.26/50.77 ± 0.26		
 (HBr)	P[d]	0.207:1	17.15 ± 0.10/82.85 ± 0.10		
	P − 29[e] P − Br[f]	1:10.29:9.57 0.419:1	29.49 ± 0.15/70.51 ± 0.15	49.17/50.83	9.75/90.25
 (meso)	P[g] P − Br[f]	1:11.46:17.87 0.288:1	22.28 ± 0.20/77.72 ± 0.20	34.94/65.06	9.44/90.56
 (dl)	P[g] P − Br[f]	1:10.90:18.05 0.277:1	21.61 ± 0.09/78.39 ± 0.09	32.93/67.07	10.14/89.86
	P[g]	1:13.4:47.8[h] (1:14.7:52.4)[i]	12.4 ± 0.1/87.6 ± 0.1 (12.3/87.7)	(14.1/85.9)	(10.4/89.6)
	P[j]	0.5:12.6:82.9:122.7 ± 0.2 ± 0.3 ± 0.4 ± 0.4	16.7 ± 0.1/83.3 ± 0.1	*k*	*k*

[a] Calculated from the observed peak ratio. The errors indicated are the average deviations from the mean for three or more analyses. [b] P 136, 138. [c] P − 29, 107, 109. [d] P 162, 164. [e] P − 29, 185, 187, 189. [f] P − Br, 135, 137. [g] P 214, 216, 218. [h] Measured peak intensities are 2.3 ± 0.2:30.8 ± 0.3:110.0 ± 0.4 (in mm). [i] Calculated using the peak intensities of 2.1:30.8:110.0. [j] P 292, 294, 296, 298. Reported as actual peak intensities (in mm). [k] The average isotopic abundances of each of the three bromine atoms in this tribromide are 32.4/67.6, 11.7/88.3, and 6.0/94.0, respectively.

pletely stereospecific, since no indication of isomerization of the active dibromide to *meso*-2,3-dibromobutane was observed. Although the concentrations used in the racemization experiment were approximately those at 50% of the photochemical reaction, the amount of racemization could be approximated under these conditions by allowing the reaction to proceed for the entire length of time required for the photochemical reaction, 22 h.

Since all the reaction products were isolated by preparative GLC using 10% Carbowax 20M TPA on Chromosorb PAW column, the optically active dibromide was subjected to these isolation conditions. It was found that the optically active 2,3-dibromobutane, collected by preparative GLC, had racemized substantially (15–16%) on a 10 ft × ¼ in. glass column (75–110 °C) and 5–6% on a 6 ft × ¼ in. glass column (75–110 °C). This racemization process is presumably analogous to those of the thermal isomerization of 5α,6β-dibromocholestereoids,[28c,29] and as were those reactions, it appears to be stereospecific, since no *meso*-2,3-dibromobutane was detected.

Photobromination of 2-Bromobutane with Isotopically Enriched Bromine-81. In order to determine the importance of the contribution of the elimination–readdition mechanism (Scheme IV) in the bromination of optically active (−)-(2*R*)-2-bromobutane, the photobromination of 2-bromobutane with isotopically enriched bromine (bromine-81) was studied. The bromination was carried out under the same conditions as were used for reactions 6–8, Table I, except that isotopically enriched molecular bromine ($^{79}Br/^{81}Br$, 2.19:97.81) was used instead of molecular bromine of natural isotopic abundance. At the completion of the reaction the hydrogen bromide produced during the reaction was distilled from the reaction mixture into a trap containing cyclohexene. The cyclohexyl bromide obtained from this reaction as well as the products produced in the bromination reaction were isolated by GLC and were in turn analyzed by high resolution mass spectrometry to determine their bromine-79 and bromine-81 content (see Table III).

A material balance determined for the bromine-79 and bromine-81 content of the product mixture was found to be in excellent quantitative agreement with that of the starting materials (see Table IV).

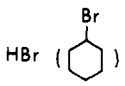
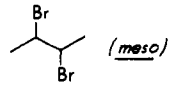
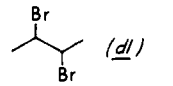
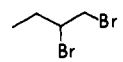
An analysis of the mass spectrum of the cyclohexyl bromide showed that the hydrogen bromide produced during the photobromination of 2-bromobutane was highly enriched in bromine-79 ($^{79}Br/^{81}Br$, 17.15:82.85). For a mechanism involving only direct substitution, the isotopic content of the hydrogen bromide should be the same as that initially present in the starting molecular bromine ($^{79}Br/^{81}Br$, 2.19:97.81). Since the only source of bromine-79 is from the original 2-bromobutane (natural abundance $^{79}Br/^{81}Br$, 50.57:49.43), and recognizing that the bromine atoms in the system, either as hydrogen bromide or molecular bromine, are in rapid equilibrium,[30,31] then the bromine-79 enrichment present in the hydrogen

$$^{81}Br_2 + {}^{79/81}Br\cdot \rightleftharpoons {}^{81}Br^{79/81}Br + {}^{81}Br\cdot$$

$$H^{81}Br + {}^{81}Br^{79/81}Br \rightleftharpoons H^{79/81}Br_3 \rightleftharpoons H^{79/81}Br + {}^{81}Br_2$$

bromide must either have come from atom exchange with 2-bromobutane or 2,3-dibromobutane, or from an atom elimination reaction from the intermediate β-bromoalkyl radical to form 2-butene. The olefin will ultimately lead to 2,3-dibromobutane by the addition of molecular bromine or return

Table IV. Material Balance on Bromine-79 and Bromine-81 of 2-Bromobutane Bromination with Isotopically Enriched Bromine-81

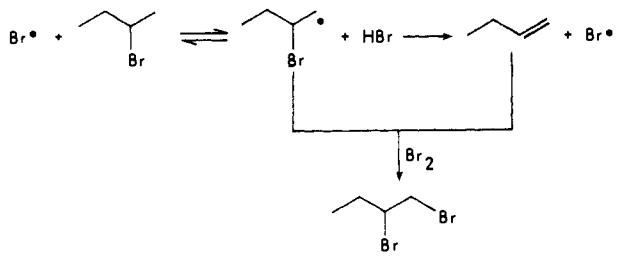
	(mol × atom %)(atoms/molecule) × 10^4	
	^{79}Br	^{81}Br
Reactants		
	795.5	777.5
Br_2	23.3	1038.7
	818.8	1816.2
Products		
	535.6	552.4
HBr 	91.1	439.9
	20.9	49.9
 (meso)	120.8	421.4
 (dl)	53.5	193.9
	2.3	16.1
	23.1	115.2
	847.3 (103.5%)	1788.8 (98.5%)

to starting material by the addition of hydrogen bromide. All atom exchange reactions which regenerated 2-bromobutane or 2,3-dibromobutane, be they S_H2 displacements on carbon or bromine or ionic S_N2 or S_N1 substitution reactions of 2-bromobutane or 2,3-dibromobutane catalyzed by bromine and/or hydrogen bromide, will result in both racemization and isotopic exchange of the 2-bromobutane and the 2,3-dibromobutane. Although the starting material was not racemized in the absence of light, when subjected to molecule bromine and hydrogen bromide (thus eliminating the possibility that the ionic reactions were responsible for its racemization) the starting material was racemized (9–13%) during photochemical bromination (reactions 6–8, Table II). This racemization, however, cannot be attributed to S_H2 displacement on carbon or bromine, since the unbrominated 2-bromobutane was found to be only slightly enriched in bromine-81 ($^{79}Br/^{81}Br$, 49.23:50.77 (±0.26)). The maximum degree of racemization allowable for this level of incorporation, if the reaction went entirely by S_H2 displacement on carbon (racemization equal to two times the exchange) would be 5%. However, since the racemization of the starting material was subsequently shown to involve hydrogen bromide (see brominations with molecule bromine and NBS), even this small degree of racemization was not attributable to S_H2 displacement, as the amount of radical displacement should not be controlled by the concentration of the acid.

During the course of the reaction, the isotopic distribution of the bromine pool changes as the bromine-79 isotope is released to the pool from the starting 2-bromobutane and the product 2,3-dibromobutane. The average isotopic distribution of the bromine pool ($^{79}Br/^{81}Br$, 9.67:90.33) can be calculated as the average of the starting molecular bromine ($^{79}Br/^{81}Br$, 2.19:97.81) and the final hydrogen bromide ($^{79}Br/^{81}Br$, 17.15:82.85).

The formation of 2,2-dibromobutane proceeds by α-hydrogen abstraction and yields dibromide by a mechanism, unlike those responsible for the formation of the other products, which precludes the elimination of a bromine atom. The isotopic distribution for this geminal dibromide is predictable: one atom of bromine should be the bromine for the average bromine pool ($^{79}Br/^{81}Br$, 9.67:90.33) and the second bromine atom should contain the average distribution of isotopic bromine from the starting 2-bromobutane and the final, reisolated, and slightly enriched in bromine-81, starting material ($^{79}Br/^{81}Br$, 49.90:50.10). An analysis of the relative intensities of the parent ions in the mass spectrum of the geminal dibromide allows the assignment of the individual isotopic distribution of each bromine atom.[3,13,22,23,32] The isotopic distribution predicted for the product, 2,2-dibromobutane, agreed extremely well with the experimentally obtained results (atom 1, $^{79}Br/^{81}Br$, 49.17:50.83; atom 2, $^{79}Br/^{81}Br$, 9.75:90.25).

The isotopic distribution of the 1,2-dibromobutane suggested that it is produced by a pathway involving a large amount of elimination, since the isomer distribution calculated for each atom is similar and quite close to that of the average bromine pool.



The isotopic distribution found for the bromine in either diastereomer of 2,3-dibromobutane cannot be accounted for solely by the direct substitution (or bridged mechanism) or the elimination-readdition pathway (see Table III); the former pathway predicts the retention of the original bromine ($^{79}Br/^{81}Br$, 50.57:49.43) and the introduction of a second bromine atom from the bromine pool ($^{79}Br/^{81}Br$, 2.19:97.81), while the latter pathway predicts that both of the bromine atoms that arise from the addition have the same distribution and that they will contain a statistical distribution of the bromine-79 and bromine-81 content of the original bromine in the starting material and in the bromine atom pool. Since the isotopic distributions observed for both 2,3-dibromobutanes (see Table III) are not in accord with either set of predictions, and since an ionic reaction which is mechanistically equivalent to the elimination-readdition pathway (effecting both racemization and exchange) must be considered for a fraction of the isotopic exchange, a mixture of these two limiting cases (or their mechanistic equivalents) must be considered.

The amounts of the 2,3-dibromobutane formed by each of the three pathways, ionic racemization, elimination-readdition, and direct substitution, can be calculated from the results of an analysis of the isotopic distribution of bromine in the products of bromination. The fraction of the 2,3-dibromobutane formed by direct substitution, S, will contain two bromine atoms each having the same distribution as the bromine atoms found in 2,2-dibromobutane (see Table III), a product also formed by direct substitution from the same reaction mixture.

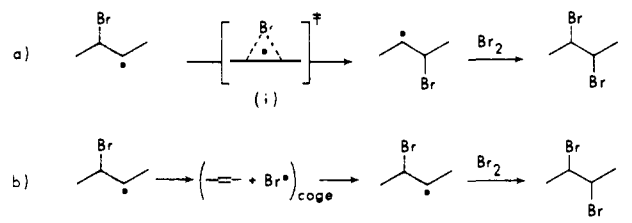
The fraction, E, of the 2,3-dibromobutane formed by elimination-readdition will contain two identical bromine atoms which have the same isotopic ratio as the second bromine atom introduced into 2,2-dibromobutane from the bromine pool ($^{79}Br/^{81}Br$, 9.75:90.25). The fraction of the 2,3-dibromobutane that is formed by ionic racemization, R, will effect the isotopic distribution of bromine observed in the isolated 2,3-dibromobutane. Since only one-half of the acts of racemization (12%) will lead to exchange, R can be equated to $0.06S$. The sum of each of the three fractions times its isotopic content (of either isotope) will equal the isotopic content of the 2,3-dibromobutane isolated from the reaction mixture. If the bromine-79 content of the 2,3-dibromobutane is considered, then ionic exchange of bromine with the bromine pool only changes the bromine-79 content of the pool by exchange with the original bromine atom in the 2,3-dibromobutane, since the other bromine atoms already reflect the composition of the pool. The original bromine that exchanges in this fraction will lead to an isotopic composition of bromine-79 (for the average of both bromines) of 9.67. The fraction of 2,3-dibromobutane formed by each process can be evaluated

$$S(29.49) + E(9.67) + R(9.67) = 21.61$$

and since $S + E + R = 1$ and R is equal to $0.06S$, then E, S, and R will be equal to 0.36, 0.60, and 0.04, respectively. Since both pathways E and R are mechanistically equivalent, both leading to exchange and racemization, then 40% of the bromination that yields 2,3-dibromobutane must produce racemic product by these two pathways alone.

A Mechanism for the Bromination. The production of active (+)-(2*R*,3*R*)-2,3-dibromobutane and (+)-(3*R*)-2,2,3-tribromobutane from the bromination of (−)-(2*R*)-2-bromobutane demonstrates that the structure of the β-bromoalkyl radical is best represented as an open classical radical, Schemes I and III. Since active product is formed a symmetric intermediate cannot be formed at any stage of the reaction prior to product formation. As the activity of the resultant dibromide was low (5-6%), alternative pathways which lead to racemization (other than bridging) were investigated. The major portion of the racemization could be assigned as arising from elimination of the β-bromoalkyl radical (36%), ionic racemization of the resultant active 2,3-dibromobutane (12%), racemization of the 2,3-dibromobutane during GLC isolation (5-6%), and racemization of the starting material (9-13%). In order for the labeling experiments to be consistent with the optical results a pathway (or pathways) must be available which will account for the remaining 27-33% of the racemization that was observed. These pathways must lead to racemization without isotopic exchange of the bromine-79 remaining in the 2,3-dibromobutane. Several mechanisms are available (Scheme V) which meet these requirements. Path

Scheme V



a, a 1,2-homolytic halogen migration, becomes symmetric during its rearrangement. Species i is depicted as a transition state; however, it can also represent an intermediate bridged radical which is formed, after abstraction, competitively with the transfer products from the reactions of the open radical with bromine or hydrogen bromide. Path b depicts an elimination-readdition mechanism within the solvent cage. Since the cage concentration can be approximated as bulk concentration, the probability of readdition within the solvent cage at such high concentration cannot be ruled out. This mechanism was included for consideration by analogy, since cage reversal reactions of cyclohexyl radicals with hydrogen bromide were found to play an important part in the mechanism of the bromination of cyclohexane.[33] Although the occurrence of this reaction is consistent with these results, it cannot be differentiated from the rearrangement process.

Bromination of (−)-(2*R*)-2-Bromobutane with Molecular Bromine and NBS. Since a number of the racemization processes that take place during the bromination of active 2-bromobutane were found to involve reaction with hydrogen bromide, it was desirable to run the reaction under conditions where the concentration of hydrogen bromide could be kept minimal. When a mixture of molecular bromine and NBS was used as the brominating reagent the bromination of (−)-(2*R*)-2-bromobutane could be carried out without the interference of appreciable amounts of hydrogen bromide, since the hydrogen bromide produced in the reaction reacts with the NBS to form succinimide and a steady concentration of molecular bromine.

$$RH + Br\cdot \rightleftharpoons R\cdot + HBr$$
$$R\cdot + Br_2 \rightarrow RBr + Br\cdot$$
$$HBr + NBS \rightarrow NSH + Br_2$$

Mixtures of (−)-(2*R*)-2-bromobutane, NBS, molecular bromine, and solvent Freon 11 sealed in degassed Pyrex reaction flasks were thermostated at the desired temperature and irradiated with an incandescent lamp. The reaction mixtures were freed from active halogen, isolated, and analyzed by the procedure used for the molecular bromine brominations. The products formed were found to be identical with those found in the bromination reactions using molecular bromine and the product composition was almost the same (see Table V).

A comparison of the reactions run under similar conditions, one with molecular bromine and one with added NBS (see reactions 6-8 in Table I and reactions 2 and 3 in Table V) shows that the only major difference in the product distribution was a decrease of ~1% in the amount of 1,2-dibromobutane found in the reactions run with added NBS.

The desired products, (+)-2,3-dibromobutane and (+)-2,2,3-tribromobutane, as well as the unbrominated starting material were collected by preparative GLC and their optical rotations were measured (see Table VI). The unbrominated starting material was found to be only slightly racemized (1-2%, reactions 1-3, 5, Table VI). This amount of racemization of the recovered starting material, as expected, was smaller than that found in the corresponding reactions run with molecular bromine (reactions 6-8, Table II). This observation strongly supports the proposed reactions involving reversible abstraction processes that were suggested in Scheme IV.

Since hydrogen bromide affects the optical properties of the starting substrate as well as the product 2,3-dibromobutane, as expected, the optical purity of the recovered (+)-(2*R*,3*R*)-2,3-dibromobutane was greater than that obtained from the reactions carried out in the absence of NBS. The observed rotation, $[\alpha]^{25}_{365}$ 8-9.4°, was not affected appreciably by changing the bromine concentration from 0.15 to 2 M. However, at higher or lower bromine concentrations the rotation of the (+)-2,3-dibromobutane was decreased (see Table VI). The decrease in rotation at high concentrations (5 M, reaction 5, Table VI) can be attributed to the racemization of the (+)-2,3-dibromobutane upon treatment with high concentrations of molecular bromine. At lower concentrations of bromine (0.015 M, reaction 7, Table VI), the decreased rotation of the dibromide can be attributed to the increased lifetime of the intermediate β-bromoalkyl radical prior to its

Table V. Photobromination of (−)-2-Bromobutane with Br_2–NBS in Freon 11

Reaction	RBr/NBS/Br_2 mol ratio	($[Br_2]$, M)	% Conversion[a]	Temp, °C	% Yield[b]				
					2,3-dibromobutane			2,3-dibromopentane	
						(meso)	(dl)		
1	3:2:1.5	(3.3)	15	2	8.3 ± 0.3	63.8 ± 0.2	27.8 ± 0.1	tr	tr
2	3:2:1	(2.1)	28	17	11.7 ± 0.1	55.5 ± 0.1	23.8 ± 0.1	tr	8.9 ± 0.1
3	3:2:1	(2.1)	30	17	11.5 ± 0.2	56.5 ± 0.5	23.9 ± 0,2	tr	7.7 ± 0.8
4	4:2:1	(2.0)	36	20	12.0 ± 0.1	56.0 ± 0.3	24.7 ± 0.2	tr	7.3 ± 0.8
5	3:2:3	(5.2)	36	17	8.2 ± 0.2	58.3 ± 0.8	25.5 ± 0.2	0.4 ± 0.1	7.6 ± 0.9
6	3.3:3.3:1	(0.17)	46	17	15.9 ± 0.4	51.6 ± 0.5	19.0 ± 0.2	tr	13.5 ± 0.8
7	38:38:1	(0.015)	62	17	15.7 ± 0.3	47.1 ± 0.6	14.8 ± 0.2	tr	22.3 ± 0.8
8	3.7:3.6:1	(0.15)	71	17	15.3 ± 0.2	42.1 ± 0.2	12.6 ± 0.2	tr	30.0 ± 0.2
9	1:1:1	(1.2)	72	20	13.3 ± 0.2	42.3 ± 0.2	12.7 ± 0.2	tr	31.7 ± 0.5

[a] Percentage conversion of starting 2-bromobutane. [b] In all cases, material balance was >97% based on starting material consumed.

Table VI. Optical Rotation of Products from the Br_2–NBS Bromination of (−)-2-Bromobutane

Reaction	RBr/NBS/Br_2 mol ratio	($[Br_2]$, M)	% Conversion	$[\alpha]^{25}_{365}$				
				2-bromobutane		2,3-dibromobutane		2,3-dibromopentane
				recovered, deg	(% racemized)[a]	Obsd, deg	Corr,[b] deg	Obsd, deg
5	3:2:3	(5.2)	36	−74.37	(2.2)	3.52	5.98	2.36
1	3:2:1.5	(3.3)	15	−74.93	(1.4)	3.97	6.74	
3	3:2:1	(2.1)	30	−74.43	(2.1)	4.90	8.32	3.22
2	3:2:1	(2.1)	28	−75.21	(1.0)	4.72	8.01	
9	1:1:1	(1.2)	72	−71.28	(6.2)	4.68	7.95	3.02
6	3.3:3.3:1	(0.17)	46	−73.95	(2.7)	5.45	9.25	3.19
8	3.7:3.6:1	(0.15)	71			5.54	9.41	2.94
7	38:38:1	(0.015)	62	−72.06	(5.2)	2.10	3.57	0.40

[a] Starting material before reaction has a rotation of $[\alpha]^{25}_{365}$ −76.00° (58.9% optical purity). [b] Corrected for optical purity of starting material.

reaction with the low concentration of bromine. As the lifetime of the radical is increased the possibility of rearrangement as well as elimination to 2-butene becomes greater;[13] readdition to the butenes will lead, as does rearrangement, to inactive product (see Scheme III).

The results of these brominations with mixtures of molecular bromine and NBS can be compared with those previously reported.[17] Since the higher boiling tribromide was not detected by the previous authors, no absolute comparison of yields can be made; however, the ratio of *meso/dl*-2,3-dibromobutane reported (2.5) was very close to the values found in these reactions (see Table V). Residual activity in the product 2,3-dibromobutane, 5%, was also found by Skell and co-workers (approximately 50% of that found in this study); however, these authors chose to ignore this activity in their mechanistic conclusions and proposed to leave its explanation for further study.[17] The previous study reported the results of the bromination of the isotopically labeled model compound, 3-bromopentane-^{82}Br. The product 2,3-dibromopentane was found to have its label almost equally distributed between the 2 and 3 positions (0.49:0.51), while the unreacted bromine produced from the reaction of hydrogen bromide and NBS has acquired 8% of the activity that was accounted for after the reaction. The results reported previously are consistent with our proposed reaction scheme, since all of the racemization processes that were established for 2,3-dibromobutane, with the exception of the amount of racemization of the starting material that does not lead to exchange, will equally distribute the label between the 2 and 3 position in the 2,3-dibromopentane. In a process such as this a statistical treatment of the data predicts that if radioactive bromine atoms are released to the bromine pool a significant number of them will readd to the olefin as well as undergoing reaction with the β-bromoalkyl radicals that are produced, and the observation that 8% of the radioactivity found was in the molecular bromine, therefore, does not limit the percentage of elimination to 8%. Unfortunately, the data was not reported in sufficient detail for an accurate calculation to be carried out.

Mechanistic Conclusions. The observations made in this study have led to the conclusion that the optical activity found in the products 2,3-dibromobutane and 2,2,3-tribromobutane conclusively rules out a symmetrical intermediate as a structure for the intermediate β-bromoalkyl radical, which leads to dibrominated products. Since a number of alternate mechanistic pathways have been shown to lead to racemic products, the conclusions reached by previous workers[17] are neither sufficient nor necessary to explain the experimental results.

The question as to whether the β-bromoalkyl radical is unsymmetrically bridged or an open classical radical cannot be answered by this study and must be left to the readers evaluation and interpretation of the data referenced in the introduction.

Rearrangement of the classical radical, cage elimination–readdition, or the formation after abstraction of a nonclassical bridged radical can explain the portion of the racemization (27–33%) which could not be accounted for by other processes. Again a choice of one or more of these processes must be left to the discretion of the reader.

Experimental Section

Material. Bromine (McArthur Chemical Co., Ltd.) was washed with concentrated sulfuric acid and distilled from phosphorus pentoxide prior to use. Isotopically enriched bromine-81 (2.19 ± 0.5%

bromine-79 and 97.81 ± 0.5% bromine-81) was purchased from Isotope Development Center, Oak Ridge National Laboratory and was distilled twice prior to use.

(+)-2-Butanol (Norse Laboratories, Inc.), $[\alpha]^{25}_{589}$ 12.57° (lit.[34] $[\alpha]^{20}_{D} = +13.9°$), was used as purchased.

Hydrogen bromide (Matheson of Canada Ltd.) was passed over molecular sieve 4A, degassed, and distilled twice prior to use.

Brucine (Fisher Scientific Co.) was dried at room temperature by pumping in a high vacuum line for more than 2 days, and was stored in a vacuum desiccator in the presence of phosphorus pentoxide, mp 177.5 °C (lit.[35] mp 178.0 °C).

dl-2-Bromobutane (J. T. Baker Chemical Co.) was purified by washing with concentrated sulfuric acid, water, and saturated sodium bicarbonate, and drying over anhydrous sodium sulfate followed by subsequent fractional distillation. The middle fraction was collected, bp 88 °C (700 mm), n^{25}_{D} 1.4346 (lit.[36] bp 91.2 °C (760 mm), n^{20}_{D} 1.4366).

meso- and *dl*-2,3-dibromobutane were prepared in about 90% yields by the additon of a bromine/Freon 113 solution to *trans*- and *cis*-butene, respectively,[37] and were isolated by distillation under reduced pressure. *meso*-2,3-Dibromobutane had bp 66 °C (38 mm), n^{20}_{D} 1.5115 (lit.[38] bp 73.5-74 °C (50 mm), n^{25}_{D} 1.5093). *dl*-2,3-Dibromobutane had bp 74 °C (45 mm), n^{20}_{D} 1.5150 (lit.[38] bp 75.5-76.5 °C (50 mm), n^{25}_{D} 1.5126).

2-Bromo-2-butene (trans and cis mixture) (J. T. Baker Chemical Co.) was purified by fractional distillation prior to use, bp 83-85 °C (693 mm), n^{25}_{D} 1.4576 (lit.[38] bp 84.5-85.0 °C (740 mm), n^{25}_{D} 1.4565 for trans isomer).

2,2,3-Tribromobutane was prepared in a method similar to that for the preparation of *meso*- and *dl*-2,3-dibromobutanes, from 2-bromo-2-butene (trans and cis mixture). The colorless liquid had bp 50-51 °C (2.1 mm) (lit.[39] bp 83-84 °C (11.5 mm)) and n^{25}_{D} 1.5610 (lit.[40] n^{20}_{D} 1.5602): NMR (CCl_4) τ 7.89 (3 H, d, 3-H), 7.23 (3 H, s, 1-H), and 5.43 (1 H, q, 3-H). The mass spectrum of this tribromide gave parent peaks at *m/e* 292, 294, 296, and 298 (1:3:3:1 ratio).

(−)-(2*R*)-2-Bromobutane. The active halide was prepared by the reaction of (+)-2-butanol with anhydrous hydrogen bromide. A three-neck, 200-mL round-bottom flask was fitted with a magnetic stirring bar, a condenser with a gas outlet tube, a thermometer, and a gas inlet bubbler. (+)-2-Butanol (86.0 g, 1.16 mol) was placed in the flask and saturated with anhydrous hydrogen bromide for 1 h at −10 °C, the solution was stirred for an additional 1 h at room temperature (20 °C), and was finally heated at 60 °C for 4 h. The reaction mixture was washed with cold concentrated sulfuric acid, an ice-water mixture, a saturated sodium bicarbonate solution, and then dried over anhydrous sodium sulfate. Fractional distillation yielded 134.0 g (84%) of (−)-(2*R*)-2-bromobutane, bp 88 °C (700 mm), n^{20}_{D} 1.4370 (lit.[36] bp 90-91 °C (760 mm), $n^{19.5}_{D}$ 1.4359). GLC analysis (10 ft × ¼ in. 10% Carbowax 20M TPA, glass column) showed only a single compound. The NMR, IR, and mass spectra were identical with those of an authentic sample of *dl*-2-bromobutane. The specific rotation of the active bromide is listed in Table VII.

The active (−)-(2*R*)-2-bromobutane after reisolation by preparative GLC (10 ft × ¼ in. glass column packed with 10% Carbowax 20M TPA) gave the same rotation as was obtained after distillation, see Table VII.

Instruments. The optical rotations were recorded using a Perkin-Elmer Model 141 automatic polarimeter. Mass spectra were recorded on an AEI MS9 high resolution mass spectrometer.

Gas Liquid Partition Chromatographic (GLC) Analysis. Throughout the course of this work, two types of GLC columns were used for both analytical and preparative purposes. They were either a 10% Carbowax 20M TPA on Chromosorb PAW or a 10% DEGS on Chromosorb PAW. Glass columns were used, since some of the products decomposed on metal columns. GLC responses were calibrated by the use of standard calibration curves constructed from mixtures of known composition.[41]

Photobromination of (−)-(2*R*)-2-Bromobutane with Molecular Bromine. The reaction mixtures, in the desired mole ratio of (−)-(2*R*)-2-bromobutane to molecular bromine, were degassed by the freeze-thaw method, sealed in 10-mL Pyrex reaction ampoules, and the ampules were thermostated in the absence of light at the desired temperature. The vapor space in the ampule was covered with aluminum foil and the liquid phase was irradiated with a 200-W incandescent lamp. The ampules were removed after complete reaction or prior to completion and cooled in liquid nitrogen. The reaction mixtures, kept at 0 °C, were diluted with Freon 11 and washed successively with ice-cold sodium bisulfite, water, saturated sodium bicarbonate, and water, and then dried over anhydrous sodium sulfate. The product composition was determined by GLC analysis (10 ft × ⅛ in. 10% Carbowax 20M TPA) of the reaction mixture with an added known amount of standard, chlorobenzene. The results are listed in Table I. The products were isolated by preparative GLC (6 ft × ¼ in. 10% Carbowax 20M TPA) of the concentrated reaction mixture. They were identified by the comparison of their GLC retention times, NMR, IR, and mass spectra with those of the authentic materials. 2,2-Dibromobutane was characterized by comparing its refractive index, n^{20}_{D} 1.5017 (lit.[42] n^{20}_{D} 1.5015), and spectral data: NMR (CCl_4) τ 8.76 (3 H, t, 4-H), 7.60 (2 H, q, 3-H), 7.43 (3H, s, 1-H); mass spectral, *m/e* (70 eV) 214, 216, 218 (parent peaks, 1:2:1 ratio), 185, 187, 189 (P − Et, 1:2:1 ratio), 135, 137 (P − Br, 1:1 ratio). The optical rotation of the GLC isolated (−)-(2*R*)-2-bromobutane, (+)-2,3-dibromobutane, and (+)-2,2,3-tribromobutane were measured and are listed in Table II.

Table VII. The Specific Rotation of (−)-(2*R*)-2-Bromobutane

λ, mμ	α^{25}_{obsd}, 1 dm,[a] deg	$[\alpha]^{25}$ [b]	Optical purity,[c] %
589	−29.08	−23.20	58.9
578	−30.38	−24.23	
546	−34.59	−47.58	
436	−59.55	−47.50	
365	−95.27	−76.00	

[a] The rotations measured with neat liquid. [b] Calculated by using $d^{25} = 1.2536$. [c] Based on maximum available value, $[\alpha]_D$ +39.4° (ref 24).

Control Reactions of (−)-(2*R*)-2-Bromobutane with Molecular Bromine and with Bromine and Hydrogen Bromide. Neat (−)-(2*R*)-2-bromobutane ($[\alpha]^{25}_{365}$ −76.00°) was placed, in the absence of light, in degassed reaction ampules at 17 °C for 22-24 h, admixed with either molecular bromine (19.2 mmol/57.5 mmol of alkyl halide) or with molecular bromine (8.3 mol) and hydrogen bromine (8.3 mol to 3.62 mmol of alkyl halide). The alkyl halide was recovered from the reaction mixtures in the manner described previously for the products arising from the photolysis reaction. The optical rotation of the recovered (−)-(2*R*)-2-bromobutane was $[\alpha]^{25}_{365}$ −76.01° (neat) for the dark reaction with bromine and $[\alpha]^{25}_{365}$ −75.73° (neat) for the reaction with bromine and hydrogen bromide.

Control Reactions of (−)-2,3-Dibromobutane with Molecular Bromine or Bromine and Hydrogen Bromide in the Absence of Light. Partially resolved (−)-2,3-dibromobutane (6.42 g, 29.7 mmol), α^{25}_{365} −29.61° (neat), n^{20}_{D} 1.5150, and molecular bromine (1.58 g, 9.88 mmol) were placed in a 10-mL Pyrex reaction ampule, degassed, and sealed. The ampule, protected from light with foil, was placed in a 17 °C thermostated water bath for 22 h. The reaction products were then isolated in the usual manner. GLC analysis of the reaction mixture showed only traces of a compound having the same retention time as 2,2,3-tribromobutane. Fractional distillation of this reaction mixture under reduced pressure yielded (−)-2,3-dibromobutane, α^{25}_{365} −28.81° (2.7% rac, neat) and n^{20}_{D} 1.5150.

A mixture of partially resolved (−)-2,3-dibromobutane (6.15 g, 28.5 mmol), α^{25}_{365} −29.03° (neat), n^{20}_{D} 1.5150, molecular bromine (3.33 g, 20.8 mmol), and hydrogen bromide (24.6 mmol) was placed in a reaction tube, degassed, and sealed under vacuum. The reaction mixture, which was protected from light, was allowed to warm to 17 °C and was kept at that temperature for 22 h. After isolation, GLC analysis of the reaction mixture showed that only traces of 2,2,3-tribromobutane were formed. No *meso*-2,3-dibromobutane was detected. The recovered (−)-2,3-dibromobutane (by fractional distillation) had a rotation α^{25}_{365} −25.46 (12.3% rac, neat) and n^{20}_{D} 1.5151.

Photobromination of (−)-(2*R*)-Bromobutane with Br_2-NBS Mixtures in Freon 11 as Solvent. All reactions were carried out in heterogeneous Freon 11 solution with continuous stirring. Reaction mixtures, consisting of a desired mole ratio of substrate to brominating agents as well as Freon 11 solvent, were degassed and sealed under vacuum in Pyrex reaction flasks. Photolyses were conducted at the desired temperature by irradiation with a 200-W incandescent lamp

Table VIII. The Observed Rotation of (−)-2,3-Dibromobutane Obtained from Partial Resolution of *dl*-2,3-Dibromobutane with Brucine[a]

λ, mμ	α^{25},[b] deg: Fraction I (48 h)[c]	Fraction II (76 h)[c]	Recovered from remaining solid (112 h)[c]
589	−11.35	−13.15	−17.01
578	−11.84	−13.68	−17.74
546	−13.42	−15.50	−20.11
436	−22.48	−25.96	−33.70
365	−35.04	−40.45	−52.60

[a] Using 2:1 ratio (RBr/brucine). [b] Observed rotations measured in neat liquid (1 dm). [c] Contact time after mixing.

for a time sufficient to produce approximately 30% conversion of the starting alkyl bromide. After reaction, the reaction mixtures were isolated as described for the molecular bromine brominations, and analyzed by GLC on a 10 ft × ⅛ in. 10% Carbowax 20M TPA glass column. The results and conditions used are listed in Table V. The unreacted starting material, 2,3-dibromobutane (*dl* fraction), and 2,2,3-tribromobutane were isolated by preparative GLC using a 6 ft × ¼ in. 10% Carbowax 20M TPA glass column. Their optical rotations were determined, and the results are listed in Table VI.

Photobromination of 2-Bromobutane (50.57% Bromine-79 and 49.43% Bromine-81) with Isotopically Enriched Molecular Bromine-81 (2.19% Bromine-79 and 97.81% Bromine-81). Degassed mixtures of 2-bromobutane (215.5 mg, 1.57 mmol) and isotopically enriched bromine-81 (86.0 mg, 0.537 mmol; $^{79}Br/^{81}Br$ 2.19:97.81) were thermostated at 16 °C in the absence of light. The vapor phase of the reaction vessel was shielded from light with foil while the liquid phase area of the reaction vessel was photolyzed (200-W incandescent lamp) until the bromine color had been discharged. The reaction vessel was opened to a vacuum line and the hydrogen bromide produced in the reaction was distilled into a reaction tube containing cyclohexene (200 μL). The cyclohexene and hydrogen bromide were allowed to react at room temperature, with constant shaking, for 12 h, and the cyclohexyl bromide formed was collected by preparative GLC on a 10% Carbowax 20M TPA, 10 ft × ¼ in. glass column.

A small amount of powdered sodium bicarbonate was added to the original reaction mixture to remove any undistilled hydrogen bromide, and the reaction mixture was then subjected to preparative GLC on a 10 ft × ¼ in. glass column packed with 10% Carbowax 20M TPA. The isolated 2-bromobutane, 2,2-, *meso*-2,3-, *dl*-2,3-, and 1,2-dibromobutanes, and 2,2,3-tribromobutane were analyzed by mass spectrometry (AEI MS-9 mass spectrometer) for their bromine contents. The mass spectra were taken by scanning at the appropriate peak region for at least five times at slow scanning speed (70 eV). The results are listed in Table III.

Resolution of *dl*-2,3-Dibromobutane with Brucine. The resolution of *dl*-2,3-dibromobutane with brucine using pentane or dioxane as solvent leads, as reported,[27] to the selective destruction of one enantiomer and the production of (−)-2,3-dibromobutane, but of low optical purity. Subsequent to these experiments the resolution was reported using a mixture of neat *dl*-2,3-dibromobutane and brucine.[17] After standing at room temperature, the active 2,3-dibromobutane could be distilled from the neat mixture; however, in opposition to the previously reported resolution[27] it was claimed[17] that, "Contrary to the earlier statements, this separation does not depend on preferential destruction of one of the enantiomers. Preferential entrapment of the (+)-dibromide in the brucine crystals is the basis of the separation." This claim was based on the observation that the dibromide isolated by distillation was (−)-2,3-dibromobutane, and that when the solid brucine was treated with acid, (+)-2,3-dibromobutane could be isolated. In our hands, contrary to these interesting claims, only *trans*-2-bromo-2-butene, the elimination product, and the active (−)-2,3-dibromobutane could be obtained from either the distillation or the brucine entrapped material.

A method, similar to that reported by Skell,[17] a one cycle resolution, was used and yielded (−)-2,3-dibromobutane of high optical purity. *dl*-2,3-Dibromobutane was mixed with brucine in approximately a 2:1 mol ratio. The resulting thick paste solidified and was allowed to stand for several days at room temperature. The solid was then broken up and subjected to vacuum distillation at room temperature. Two fractions were collected after 48 and 76 h standing. Analysis of the distillate showed that it contained only the dehydrobromination product, *trans*-2-bromo-2-butene, and 2,3-dibromobutane. The dibromide was found to be optically active with high levorotatory enrichment. Furthermore, the results showed that the optical rotation increased with increasing contact time between brucine and the dibromide (i.e., with increasing formation of the dehydrobromination product). After distillation, the remaining solid was dissolved in 1 M sulfuric acid and extracted with Freon 11. This fraction of the dibromide was isolated from the Freon 11 by fractional distillation. The obtained rotation of each fraction is listed in Table VIII.

When *dl*-2,3-dibromobutane and brucine (2:1) were stirred in pentane solvent at room temperature for 48 h, GLC analysis of the reaction mixture showed <1% of the dehydrobromination product. The recovered dibromide gave only a slightly negative rotation. If the resolution was carried out with no solvent for the same period, and pentane added to extract the products, GLC analysis showed that the pentane solution contained about 10% of the dehydrobromination product. A reaction was left to stand for 70 h, and the resulting solid was broken up and 150 mL of pentane was added and stirred for another 2 h. Analysis of this pentane solution showed that it contained 24.3% *trans*-2-bromo-2-butene. The observed rotation of the recovered 2,3-dibromobutene was α^{25}_{365} −37.05° (neat). The dehydrobromination product from this reaction was isolated by preparative GLC (6 ft × ¼ in. 10% Carbowax 20M TPA, glass column). Its structure was assigned as *trans*-2-bromo-2-butene by a comparison of its refractive index and NMR spectrum with those previously reported: n^{25}_D 1.4568 (lit.[38] n^{25}_D 1.4565); NMR[43] (CCl_4) τ 8.31 (3 H, q of d, 3-CH_3), 7.74 (3 H, quintet, 1-H), and 4.35 (1 H, q of q, 3-H).

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$$x^2 - \frac{p_2}{p_1}x + \frac{p_3}{p_1} = 0$$

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Photoisomerization of the Enol Form of 1,3-Dicarbonyl Compounds[1]

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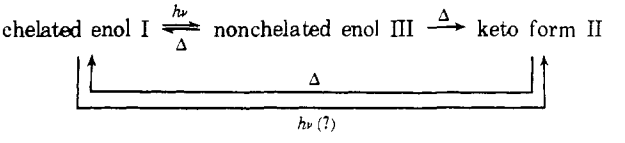
Abstract: 1,3-Dicarbonyl compounds II, which exist in hydrocarbon solvents predominantly in the chelated enol form I, are shown by flash photolysis to undergo facile photoisomerization to the corresponding nonchelated and short-lived enol form III (Scheme I), whose existence and UV absorption spectra are reported here for the first time. The III isomers are thermally unstable and revert spontaneously to either I (diketones), II (ethyl acetoacetate), or both (ethyl benzoylacetate). A UV-induced low-yield photoconversion I → II and the reverse thermal reaction are observed with stationary spectrophotometric methods.

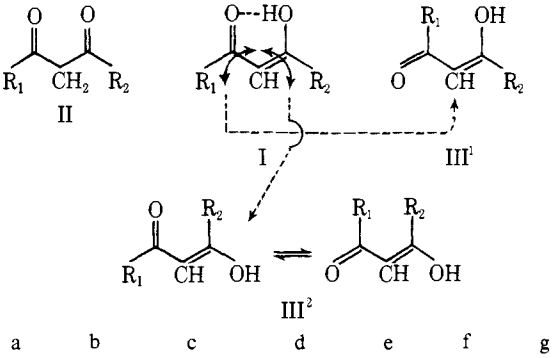
Open-chain β-dicarbonyl compounds can in principle exist in three forms: a chelated enol I, a keto form II, and several nonchelated enols III. However, in hydrocarbon solvents they usually exist as an equilibrium mixture of I and II (Scheme II). (For $R_1 \neq R_2$ either of the two acylic groups may undergo enolization, giving rise to a second set of enols derived from $R_1C(OH):CHCOR_2$.) An exception are several 2-formyl esters which exist[3] in solution as III. The chelated enolic form I with its "pseudoaromatic" ring was considered to be photochemically stable,[4] except compounds a and f which undergo photoketonization[5] I → II.

We now report[1] a photoisomerization I → III observed with eight compounds, I_a-I_h, with quantum yields of 5-20%. III reverts spontaneously to I and II.

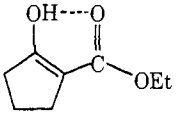
Scheme I



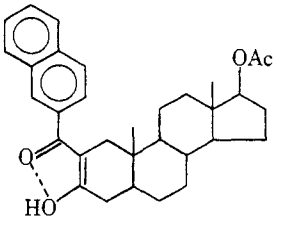
Scheme II



	a	b	c	d	e	f	g
R_1	methyl	methyl	methyl	methyl	phenyl	ethoxy	ethoxy
R_2	methyl	phenyl	2-naphthyl	2-anthryl	phenyl	methyl	phenyl



I_i



I_h

Experimental Section

Photochemical Methods. Ultraviolet (UV) irradiations and spectrophotometry were carried out in a Cary 14 recording spectrophotometer. Analysis was based on the changes in the UV absorption spectrum, as determined separately. Irradiations were at wavelengths where I_{a-i} absorb 50-100 times more than the corresponding II_{a-i}. In solutions of these compounds in aliphatic hydrocarbons, the thermal equilibrium is largely in favor of the I form. Light sources used for steady irradiations were: at 254 nm, a low-pressure mercury arc, combined with a chlorine filter (30-mm light path, at 1 atm) and a Co/Ni filter ($CoSO_4 \cdot 7H_2O$ (145 g) + $NiSO_4 \cdot 6H_2O$ (450 g) in 1 L of H_2O, placed in a 30-mm cell); a HBO-200 Osram mercury arc, combined with a Schott interference filter for 313 nm, or a Corning Glass filter combination 7-54 + 0-54 for 295-410 nm. Irradiations were carried out in regular 10-mm square cells in the Cary 14 cell compartment, unless stated otherwise. The light flux under these conditions was determined by ferrioxalate actinometry.[6] Representative values were 4.4×10^{-8} einsteins/min at 254 nm and 5.0×10^{-9} einsteins/min at 313 nm. Relative light intensities were determined