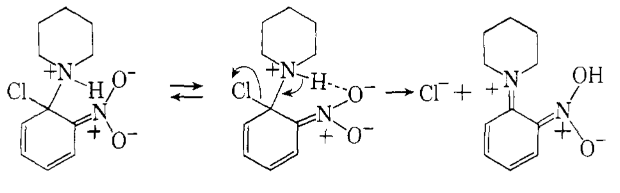
of hydrogen bonding.[16] The replacement of deuterium for hydrogen in even the strongest hydrogen bond, the F· · · H—F bond, changes the heat of formation by only 50 cal. mole^{-1}.[17]

Still another explanation lies in the possibility that the rate-determining step is a concerted process including breaking or partial breaking of the N–H bond together with breaking of the C–Cl bond. In this case, of course, the isotope effect would be masked. One such possible concerted process is illustrated below. The



hydrogen bonding increases the mobility of an electron pair in the N—H · · · O bond and facilitates the changes indicated by the arrows. A process of the type shown is fully consistent with the observed *ortho:para* ratio and the absence of a deuterium isotope effect.

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[16] P. B. D. De La Mare, in "Progress in Stereochemistry," Vol. II, W. Klyne and P. B. D. de la Mare, Ed., Academic Press, Inc., New York, N. Y., 1958, p. 85.

[17] R. W. Long, J. H. Hildebrand, and W. E. Morell, *J. Am. Chem. Soc.*, **65**, 182 (1943).

[CONTRIBUTION FROM THE CENTRAL BASIC RESEARCH LABORATORY, ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

Photobromination of Alkyl Halides, an Unusual Orienting Effect in the Bromination of Alkyl Bromides

BY WARREN THALER

RECEIVED FEBRUARY 16, 1963

An investigation of the halogenation of several alkyl and cycloalkyl halides revealed that the photobromination of alkyl bromides is quite different from the bromination of other alkyl halides, and from alkyl halide halogenations in general. The chlorination of alkyl bromide gave the expected isomer distribution; preferential attack occurred at positions remote from the bromine substituent. Bromination of alkyl chloride also showed the usual polar orienting effect; however, this higher activation energy reaction also gave a large amount of bromination on the substituent bearing carbon while primary hydrogens were essentially unreactive. Unlike other free radical halogenations of alkyl halides, which frequently give a multitude of products, the bromination of alkyl bromides was highly selective, giving 84–94% of the vicinal dibromide isomer. The influence of the bromine substituent directing the attack of a halogen atom to the adjacent carbon is contrary to other radical halogenations of substituted alkanes, in which this position has been demonstrated, generally, to be one of the least reactive positions in the molecule. A neighboring group effect has been postulated to explain the observed results.

The directive influence of polar substituents in free radical halogenation reactions has received considerable attention.[1–5] These studies have demonstrated that halogenations occur preferentially at positions removed from the electron-withdrawing substituent. The results are consistent with the theory that the electronegative attacking radicals prefer positions of high electron density and (with the possible exception of the α-position, which can give resonance-stabilized radicals) preferentially abstract hydrogens from carbon atoms, which are furthest from the electron-withdrawing substituents.

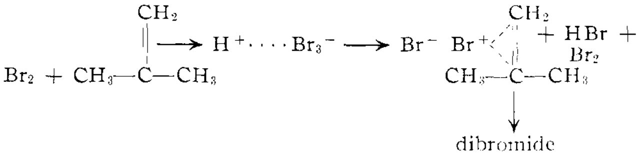
Some experiments which were carried out in this Laboratory involving the free radical bromination of alkyl halides revealed some unusual isomer distributions, which appeared to be inconsistent with predictions that can be made from the existing theories regarding polar orientations. This paper concerns itself with these apparent anomalies.

Results

Bromination of Bromocyclohexane.—Examination by vapor phase chromatography (v.p.c.) of reaction mixtures from some preliminary experiments involving the photobromination of bromocyclohexane revealed essentially one peak in addition to that of unreacted excess bromocyclohexane. The material corresponding to this peak was fractionated by v.p.c. Its elemental analysis was consistent with that of a dibromocyclohexane. The infrared spectrum was identical with that reported for *trans*-1,2-dibromocyclohexane.[6] Comparison of the v.p.c. and refractive index of this material with that of an authentic sample prepared by the addition of bromine to cyclohexene[7] confirmed the identity of this material as *trans*-1,2-dibromocyclohexane. Similar brominations involving random temperatures ranging from 20–80° showed no difference in the v.p.c. of the reaction mixtures.

Standard conditions were then chosen, and a fivefold molar excess of alkyl halide was used for all subsequent brominations which were conducted in the liquid phase at 60° in sealed Pyrex tubes.

The appearance of only one out of seven isomeric dibromocyclohexanes suggested that perhaps this was not a free radical process but instead involved the elimination of HBr from bromocyclohexane, followed by the ionic addition of bromine to cyclohexene to give *trans*-1,2-dibromocyclohexane. Similar reactions are known to occur with *tertiary bromides*, particularly when the adjacent hydrogen is tertiary.[8] This "dark reaction" was postulated to occur by a mechanism in which a bromine molecule brings about the ionization of the tertiary bromide, followed by a reaction of a second bromine molecule with the high energy π-complexed form of the carbonium ion.



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[1] For a summary of some of the pertinent literature through 1955 see C. Walling, "Free Radical in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp. 356–376.

[2] M. S. Kharasch, W. S. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **20**, 1432 (1955).

[3] (a) C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959); (b) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960).

[4] L. Horner and L. Schaläfer, *Ann.*, **635**, 31 (1960).

[5] (a) P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960); (b) *ibid.*, 3520 (1961).

[6] M. S. Kharasch, J. S. Sallo, and W. Nudenberg, *J. Org. Chem.*, **21**, 129 (1956).

[7] H. Greengard, *Org. Syntheses*, **12**, 126 (1932).

[8] G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4025 (1955).

Dark reactions of this sort have, however, never been observed with secondary bromides. It was, therefore, of interest to determine the nature and scope of the bromination reactions of primary and secondary alkyl bromides.

To test this possibility of an ionic "dark reaction," several brominations were attempted at 60° using standard reaction mixtures, both with and without CCl_4 as a diluent. Each reaction was run in duplicate, one run was irradiated while the other was wrapped in aluminum foil and allowed to remain in the dark. The irradiated reactions were complete within a few hours, while the dark reaction mixtures still contained large amounts of unreacted bromine after seven days. The inclusion of HBr in these dark reaction mixtures did not alter the situation. These results appear to preclude the ionic addition of bromine to cyclohexene as a significant contributing path to this reaction.

The photobromination of bromocyclohexane was run on a somewhat larger scale in order to isolate the dibromide product(s) and determine the yield of this reaction. The excess bromocyclohexane was removed by distillation and the remaining liquid was distilled and cut into arbitratry fractions. These fractions were then analyzed by v.p.c. The v.p.c. of the higher boiling fraction showed that four very small peaks appeared after the *trans*-1,2-dibromocyclohexane peak. The lower boiling fraction showed one small peak, which was eluted prior to that of the *trans*-1,2-dibromide. This peak had previously been obscured by the tailing of the large quantity of excess bromocyclohexane. The four higher boiling peaks were identified as the *cis*- and *trans*-1,3- and 1,4-dibromocyclohexanes by comparison with the v.p.c. of samples obtained from Dr. B. Franzus.[9] The lower boiling peak was assumed to be 1,1- and/or *cis*-1,2-dibromocyclohexane. The total yield of dibromide isolated was 83% based on bromine; 94% of this dibromide was *trans*-1,2-dibromocyclohexane. The distribution of isomeric dibromocyclohexanes is presented in Table I.

TABLE I

ISOMER DISTRIBUTION OF DIBROMIDES FROM THE BROMINATION OF BROMOCYCLOHEXANE

Dibromocyclohexanes	% of total dibromide	Dibromocyclohexanes	% of total dibromide
1,1- and/or *cis*-1,2-	3.53	*trans*-1,4-	0.50
trans-1,2-	94.0	*cis*-1,3-	.52
trans-1,3-	0.92	*cis*-1,4-	.53

Bromination of Bromocyclopentane.—Vapor phase chromatographic analysis of these reaction mixtures showed five peaks, presumably corresponding to the five possible isomeric dibromocyclopentanes. The *trans*-1,2-dibromide was isolated by fractionation of the second peak, which made up 90% of the product. Elemental analysis indicated that it was a dibromocyclopentane. The infrared spectrum, refractive index, and v.p.c. retention time of this material were identical with that of *trans*-1,2-dibromocyclopentane, prepared by the ionic addition of bromine to cyclopentene. A prep-scale photobromination gave a 93% yield of dibromides. No attempt was made to designate structural assignments to the remaining isomers. The distribution of isomers in the order of their elution from the v.p.c. column, for three runs, is: P_1, 4.71 ± 0.76%; P_2 (*trans*-1,2-dibromocyclopentane), 89.9 ± 1.1%; P_3, 2.67 ± 0.32%; P_4, 1.80 ± 0.20%; P_5, 0.92 ± 0.07%.

Bromination of Chlorocyclohexane.—In order to determine the importance of the bromine substituent in directing the substitution of bromine to carbon two, the photobromination of chlorocyclohexane was investigated. Vapor phase chromatographic analysis of the reaction mixtures showed six peaks, in addition to excess chlorocyclohexane. Several small peaks due to high-boiling material were also apparent. The six peaks were collected as a unit by means of preparative v.p.c. The elemental analysis was consistent with that of isomeric bromochlorocyclohexanes.

trans-1-Bromo-2-chlorocyclohexane was prepared by the action of N-bromosuccinimide and HCl on cyclohexene.[10] Comparison of the v.p.c. of this material with that of the reaction mixture showed that the second peak, which was present as only 9.4% of the total product, corresponded to *trans*-1-bromo-2-chlorocyclohexane. The remaining dihalides were not identified, but the percentages of the various peaks in the order of increasing retention time are: P_1, 70.32 ± 0.19%; P_2 (1-bromo-2-chlorocyclohexane), 9.40 ± 0.40%; P_3, 5.50 ± 0.15%; P_4, 4.45 ± 0.02%; P_5, 5.90 ± 0.12%; P_6, 4.43 ± 0.02%.

The principal product was eluted first and comprised 70% of the total dihalide. We suspect this material was the 1,1-dihalide because of the low retention time, and by analogy with the isomer distribution observed in the bromination of 2-chlorobutane.

Bromination of 1-Bromobutane.—The vapor phase bromination of some alkyl halides was investigated by Kharasch[2]; the halogenation of butyl halides in general, more recently by Tedder and Fredricks.[5] Kharasch reported that the bromination of alkyl bromides in general led to the formation of large amounts of tri- and tetrasubstituted bromides. For example: 1-bromobutane was reported to yield 30% 1,2-dibromobutane, 13% 1,3-dibromobutane, 30% tribromobutane, and 10% tetrabromobutane. On the other hand, Tedder reported that this bromination did not proceed well; large portions of the bromine remained unreacted and a brown coating formed on the surface of the reaction vessel.

The liquid phase bromination which was carried out in this investigation, in the previously described manner, proceeded smoothly. The bromine color was absent after several hours of irradiation. An 84% yield of dibromobutanes was isolated by distillation from a large scale run, indicating that higher bromides are not the major products of this reaction. The v.p.c. of these reaction mixtures showed three peaks, tentatively identified by comparison with the v.p.c. of authentic samples of the other possible isomers of dibromobutane (with the exception of 1,1-dibromobutane which was not readily available). The two major peaks were fractionated by v.p.c. and their physical properties (infrared spectrum and refractive index) showed them to be the 1,2- and the 1,3-dibromobutanes. The average values of the isomer distribution for six runs is presented in Table II.

The findings here establish that 1,2-dibromide is the principal product from the bromination of a straight-chain alkyl bromide, as well as from cyclic alkyl bromides. To check the possibility of a dark reaction occurring, one run was kept in the dark for seven days, at the end of which time most of the bromine remained unreacted. The irradiated reactions were complete in several hours. The subsequent irradiation of this dark run and analysis by v.p.c. showed that the isomer distribution was identical with that of the other runs. If some preferential formation of 1,2-product had oc-

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[9] B. Franzus and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 2238 (1963).

[10] H. L. Goering and L. L. Sims, *J. Am. Chem. Soc.*, **77**, 3465 (1955).

Table II

Halogenation of 1-Halobutanes

Reagent	Substrate	Distribution of dihalide isomers (%) 1,1	1,2	1,3	1,4
Br_2	1-Bromobutane	0.9 ± 0.1	84.5 ± 0.6	14.6 ± 0.5	...
Br_2	1-Chlorobutane	22.8 ± .3	25.3 ± .3	51.9 ± .3	...
Cl_2	1-Bromobutane	5.0 ± .3	21.8 ± .4[a]	50.3 ± .5	22.9 ± 0.9

[a] Approximately 5% 1,2-dichlorobutane is also produced.

curred by a "dark reaction," then this isomer should have been present in greater concentration in this reaction since it had been in the dark for such a long period.

Kharasch[2] has pointed out that the presence of metals such as iron can influence the course of bromination reactions. For example, the bromination of 2-bromopropane normally gave exclusively 2,2-dibromopropane (80% yield), while bromine containing iron gave 1,2-dibromopropane. This reaction could therefore be used to check our reagents. Vapor phase chromatographic analysis of this reaction mixture showed 96% 2,2-dibromopropane and 4% 1,2-dibromopropane.

This result appears to rule out such metal-catalyzed ionic reactions and indicates that the preferential point of attack of a bromine atom is adjacent to the carbon containing the bromine substituent, when these hydrogens are not primary.

Bromination of 1-Chlorobutane.—The bromination of 1-chlorobutane was examined to compare the directing influence of chlorine to that of bromine. The v.p.c. analysis of the reaction mixture showed the formation of three major products, isolated and purified by a combination of fractional distillation and v.p.c. fractionation. The refractive indices of these highly purified products differed somewhat from those isolated by Kharasch from the vapor phase bromination of 1-chlorobutane.[2] His values followed the same pattern as ours; however, they were consistently 0.001 unit lower. The refractive index of the product which was presumed to be 1-chloro-2-bromobutane was identical with that reported in Beilstein.

The product thought to be the 1,1-dihalide was hydrolyzed with lead oxide and the 2,4-dinitrophenylhydrazone (DNP) derivative was prepared and shown to be butyraldehyde-DNP by melting point and mixed melting point. The bis-(S-alkyl)-isothiourea picrates were prepared from the isolated products presumed to be the 1,2- and 1,3-chlorobromobutanes and compared to those derived from 1,2- and 1,3-dibromobutanes. The infrared spectrum showed that 1-chloro-2-bromobutane and 1-chloro-3-bromobutane gave the same bis-(S-alkyl)-isothiourea picrates as the 1,2- and 1,3-dibromobutanes, respectively.

The boiling points and the v.p.c. elutions were in the order: 1-chloro-1-bromo-, 1-chloro-2-bromo-, and 1-chloro-3-bromobutane, which is the same order as that of the corresponding dibromobutanes. No 1-chloro-4-bromobutane could be detected (comparison with v.p.c. of authentic sample).

The isomer distributions which were observed (Table II) were essentially the same as those found by Kharasch[2] and Tedder.[5] The 1,1- 1,2-, and 1,3-chlorobromobutanes being approximately 1:1:2. It is, therefore, apparent that the course of the bromination of *n*-butyl chloride and cyclohexyl chloride is quite different from that of the corresponding bromides and does not occur preferentially at carbon two.

Chlorination of 1-Bromobutane.—The question arose as to whether the bromine substituent would also direct the attack of a chlorine atom to carbon two. Examination of the v.p.c. of the products from this reaction, using analytical conditions identical with those used for the determination of the products from the bromination of 1-chlorobutane, showed four peaks which could be attributed to bromochlorobutanes. The first peak had a retention time identical with that of 1-bromo-1-chlorobutane, and the fourth peak was identical with that of a sample of 1-bromo-4-chlorobutane. The second and third peaks had retention times only slightly different from those of 1-chloro-2-bromobutane and 1-chloro-3-bromobutane, respectively. They were therefore considered to be 1-bromo-2-chlorobutane and 1-bromo-3-chlorobutane by analogy.

In addition, there was one small peak due to a low boiling material which had a retention time identical with that of 1,2-dichlorobutane, accounting for about 5% of the total product. This prompted us to reexamine the products from the bromination of 1-chlorobutane; however, no 1,2-dibromobutane could be detected. This finding is consistent with observations concerning the stability of radicals of the type $XCH_2\text{-}\dot{C}HR$, which are reported to dissociate into an olefin and a halogen atom (vicinal effect.)[11] The dissociation of β-chloroalkyl radical into an olefin and a chlorine atom requires high temperatures (200–300°), while the dissociation of a β-bromoalkyl radical into olefin and bromine atom appears to occur much more readily. Tedder[5] has reported that 1,2-dichlorobutane was also produced in the gas phase chlorination of 1-bromobutane at 35°. The essentially complete absence of 1-bromo-2-chlorobutane was reported by Tedder for the gas phase reaction, even at temperatures as low as 35°. The formation of over 20% 1-bromo-2-chlorobutane in our liquid phase reactions at 60° can be attributed to the fact that the vicinal effect is not as enhanced here as it is in the gas phase where lower concentrations result in fewer collisions with chlorine molecules and, consequently, greater lifetimes for the β-bromoalkyl radicals. Although evidence of a small influence of a vicinal effect was observed in the liquid phase chlorination of 1-bromobutane, this effect appears to be much more significant in the gas phase and perhaps accounts for some of the differences between the products which have been reported in vapor phase brominations, and those observed in this investigation, from the liquid phase reactions.

The isomer distribution of the products from the chlorination of 1-bromobutane are presented in Table II. The results clearly indicate that attack on carbon two by chlorine atoms is not enhanced by the presence of a bromine substituent, and as such is quite different from the comparable bromination.

Bromination of 2-Bromobutane.—The reaction mixtures containing the bromination products were analyzed by v.p.c. and showed three peaks. The two latter peaks were not quite completely resolved. Comparison with samples of all the possible isomeric dibromide products showed these three peaks to be the 2,2-dibromobutane, *meso*-2,3-dibromobutane, and *dl*-2,3-dibromobutane, respectively.

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(11) The limited or reduced halogen substitution at the vicinal carbon atom ("vicinal effect") has been attributed to the instability of the β-haloalkyl radical intermediates: (a) F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, **6**, 479 (1941); (b) A. B. Ash and H. C. Brown, *Rec. Chem. Progr.*, **9**, 81 (1948); (c) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955).

The 2,3-dibromobutanes comprised over 83% of the products (Table III), again demonstrating the strong orienting influence toward the α-carbon atom which the bromine substituent exerts.

This result is quite different from that of Tedder,[5] who reported almost 100% 2,2-dibromobutane from the gas phase reaction.

TABLE III

BROMINATION OF 2-HALOBUTANES

	Distribution of dihalide isomers (%)[a]		
Substrate	2,2	2,3	
		meso	*racemic*
2-Bromobutane	16.3 ± 0.0	58.3 ± 0.1	25.4 ± 0.1
		erythro	*threo*
2-Chlorobutane	92.1 ± 0.3	4.8 ± 0.1	3.1 ± 0.3

[a] No substitution was observed at the one and four positions.

Bromination of 2-Chlorobutane.—Vapor phase chromatographic analysis of the reaction mixtures revealed a three-peak pattern similar to that observed from the 2-bromobutane bromination. The first peak, assumed to be the 2,2-chlorobromobutane, was collected and hydrolyzed using lead oxide. The DNP derivative was identical with that of methyl ethyl ketone. The other two small peaks were tentatively considered to be the *erythro*- and *threo*-2,3-dihalobutanes by analogy with the 2-bromobutane reaction.

In contrast to the bromination of the 2-bromo compound, 2,2-bromochlorobutane accounts for over 92% of the dihalide formed from 2-chlorobutane (Table III). The formation of *gem*-dihalides as principal products was reported by Kharasch and Tedder for the gas phase bromination of 2-chlorobutane[2,5] and 2-fluorobutane.[5]

Discussion

The large body of available data concerning free radical halogenation of hydrocarbons and derivatives indicates that there are two major factors influencing the distribution of possible isomers.

These factors are C–H bond energies and electronegative inductive effects. The halogenation of paraffins provides an example of the former. Hydrogens are substituted in the order tertiary > secondary > primary, which is the order of increasing bond energy. Furthermore, the selectivity between these hydrogens becomes increasingly greater as the activation energy of the abstracting process increases. This large difference in activation energy is the determining factor for the marked selectivity of brominations and the relatively poor selectivity of chlorinations.

The presence of electronegative groups on a molecule introduces an additional consideration. Halogen atoms are electronegative and prefer to attack positions of higher electron density, which are removed from the inductive influence of the substituent. However, the substituent also lowers the C–H bond energy of the carbon to which it is attached. In free radical chlorinations, and even more so in fluorinations, the polar effect predominates and the reactivity at the substituent bearing carbon is low. In the higher activation energy bromination process, the influence of bond energy is much more important, and the substituent bearing carbon is considerably more reactive than in chlorination.

With the exception noted for the substituent bearing carbon, the remaining carbons show increasing reactivity, as one proceeds to sites further removed from the electronegative substituent.

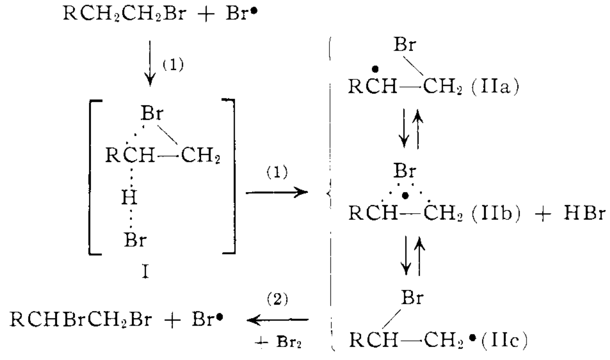
On the basis of the existing information, halogenations of alkyl halides would be expected to give very little vicinal dihalide. The C–H bonds on the carbon adjacent to the substituent bearing carbon are strongly deactivated by the electronegative substituent and receive none of the benefits of resonance stabilization, as do substitutions on the substituent bearing carbon.

A comparison of the chlorination and bromination of *n*-butyl chloride (Table IV) shows that bromination, because of its greater activation energy, gives more 1,1-dihalide and less 1,4-dihalide than chlorination. The reactivity of carbon-2 is about 0.5 that of carbon-3 for both the bromination and chlorination. The chlorination of *n*-butyl bromide reveals the similar deactivation of carbon-2 relative to carbon-3 (about 0.5) due to the inductive influence of the substituent. Bromination of *n*-butyl bromide, however, resulted in the formation of 1,2-dibromide as the principal product. The reactivity of carbon-2 was 5.78 times that of carbon-3, representing a greater than tenfold increase over that observed with the other *n*-butyl halides.

The preferential formation of vicinal dihalides was not apparent for any brominations (or halogenations in general) other than alkyl bromide brominations. This unusual behavior of alkyl bromides toward bromine atoms was observed throughout this investigation.

A comparison of the bromination of 2-halobutanes (Table V) shows that 2-chlorobutane is attacked at the weakest C–H bond to give geminal dihalide as the principal product, while 2-bromobutane gives predominantly the vicinal dihalide. Similarly, cyclopentyl and cyclohexyl bromide, which are capable of producing five and seven dibromo isomers, respectively, gave about 90% *trans*-1,2-dibromide product, while cyclohexyl chloride gave only about 10% of this vicinal dihalide isomer.

The unique ability of a bromine substituent to direct bromine atom attack to an adjacent carbon can be rationalized by invoking a neighboring group effect in these reactions.[12] Such a process could result in enhanced attack at carbons adjacent to those having a bromine substituent



We wish to emphasize that it is the site from which a hydrogen atom is abstracted that determines which dibromide isomer (1,2- 1,3-, etc.) will be formed. The *ultimate* structure of the intermediate bromoalkyl radical II and the mechanism of the subsequent reaction of this radical (reaction 2) to give dibromide is not relevant to the postulated neighboring group activation of the vicinal carbon (reaction 1). An enhanced attack by a bromine atom at the vicinal position is dependent on the stabilization of the transition state I by the bromine substituent, through delocalization of the unpaired electron, relative to other potential positions of attack on the alkyl bromide, which cannot be stabilized thusly. The question as to whether the intermediate bromoalkyl radical II exists as the three-

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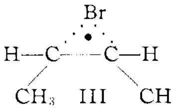
(12) We are indebted to Professor P. S. Skell for suggesting a "neighboring group" interpretation for our observations.

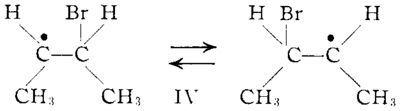
membered ring IIb, as a classical radical in which the bromine atom migrates rapidly between the two carbon atoms (IIa and c) (which must involve at least a transient three-membered ring structure), or is consumed by subsequent reaction before having an opportunity to migrate[13-15] is not resolved nor is the answer pertinent to the existence of a neighboring group effect in alkyl bromide brominations. However, the preponderence of the *trans*-1,2-dibromide product from bromination of bromocyclohexane and bromocyclopentane suggests that the intermediate bromoalkyl radical may exist as a three-membered ring species when it reacts with molecular bromine.

The influence of the nature of the abstracting radical on the course of this reaction can be rationalized by activation energy considerations. The abstraction of a hydrogen by a chlorine atom is a low energy process. Since the transition state resembles the reactants, there is little opportunity for a neighboring group effect to come into play. Stated more simply, abstractions made by the highly reactive chlorine atoms gain little or nothing from neighboring group assistance. On the other hand, the abstraction of a hydrogen by a bromine atom is a high activation energy process. The lowering of the activation energy for abstraction from the vicinal position by delocalizing the unpaired electron would be expected to increase the rate of attack at this position, thereby enhancing the formation of vicinal dibromide relative to other possible isomers.

The inability of halogen substituents such as chlorine to direct bromine atoms to an adjacent position requires that chlorine be unable to act as an effective neighboring group. The greater size and polarizability of a bromine substituent suggests that bromine might be able to form a three-membered ring, and sustain an unpaired electron, better than chlorine. It is difficult, however, to find any quantitative estimation as to the relative abilities of chlorine and bromine to delocalize an unpaired electron through bridging.

The credibility of a radical mechanism which involves neighboring group assistance by an adjacent bromine is enhanced by the observations made by Skell[13] and Abell.[14] Skell observed that the chlorination of some alkyl bromides resulted in the migration of the bromine to an adjacent carbon. This observation suggests that the bromine substituent of a β-bromoalkyl radical possess a good deal of mobility. Abell studied the electron resonance for the intermediate bromoalkyl radical formed in the addition of HBr to 2-butene. The observed spectra were consistent with an intermediate bromoalkyl radical in which the bromine resided equally on both carbon two and carbon three. These observations are consistent with a cyclic intermediate radical III and/or an intermediate in which the bromine migrated rapidly between the two carbon atoms (IV)


III


IV

The enhancement of free radical substitution on vicinal carbons due to neighboring group influences could be expected to occur as a rather general phenomenon, provided the abstraction is a high activation energy process and other substituents could be as effective as bromine in forming three-membered rings.

Unfortunately it is difficult to find another substituting agent as selective as bromine in radical reactions. Furthermore, the use of hydrocarbons with substituents other than halogen which would be expected to participate in neighboring group enhancement of bromination reactions is restricted because most of these groups undergo side reactions with bromine or hydrogen bromide.

N-Bromosuccinimide is a highly selective free radical brominating agent which has been postulated to involve the rather high activation energy abstraction of hydrogen atoms by succinimide radical. Attempts on our part to evaluate the ability of bromine substituents to direct attack by this radical to an adjacent carbon were abandoned when HBr was observed among the reaction products. HBr is known to react with NBS to give succinimide and bromine, making a distinction between the active chain-carrying species difficult.[16] Attempts to study the reaction between bromotrichloromethane and bromocyclohexane were unsuccessful owing to the intractability of the reaction products. Further demonstration of neighboring group interactions in free radical halogenations of alkyl bromides should be possible with some of the higher activation energy halogenating agents presently available; however, the further demonstration of neighboring group effects as dramatic as those observed using molecular bromine may possibly require the advent of different selective (high activation energy) chain carriers.

TABLE IV

RELATIVE REACTIVITIES IN LIQUID PHASE HALOGENATIONS OF 1-HALOBUTANES AT 60°[a]

	XCH_2—	—CH_2—	—CH_2—	—CH_3
n-Butyl chloride				
Cl_2[b]	0.158	0.478	1.00	0.397
Br_2	0.439	0.488	1.00	...
n-Butyl bromide				
Cl_2	0.093	0.434	1.00	0.455
Br_2	0.062	5.78	1.00	...

[a] Relative to carbon three which is taken arbitrarily as unity. [b] 68°; Walling and Mayahi.[3a]

TABLE V

RELATIVE REACTIVITIES IN LIQUID PHASE BROMINATION OF 2-HALOBUTANES AT 60°[a]

	CH_3—	—CHX—	—CH_2—	—CH_3
2-Chlorobutane	...	1.00	0.0858	...
2-Bromobutane	...	1.00	5.13	...

[a] Relative to carbon two which is taken arbitrarily as unity.

Experimental

Materials.—J. T. Baker bromine was used without further purification. All the alkyl halides used were purified by passage through silica gel followed by careful fractionation. Their purity was checked by v.p.c.

Authentic samples of dihalides were either purchased or prepared by established procedures.

Procedure.—Reaction mixtures consisted of a 1:5 mole ratio of bromine to alkyl halide. Reactions were carried out in Pyrex tubes degassed by alternately evacuating on a water pump and flushing with nitrogen three times while cooling in a trichloroethylene-Dry Ice bath. The sealed tubes were placed in a thermostated bath at 60° and irradiated with a 150-watt unfrosted incandescent bulb, which was also immersed in the bath about 10 cm. from the reaction tubes. The irradiations were continued until the color of bromine was absent, at which time the mixtures were either water-white or pale yellow in color.

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(13) P. S. Skell, R. G. Allen, and N. D. Gilmour, *J. Am. Chem. Soc.*, **83**, 504 (1961).

(14) P. I. Abell and L. H. Piette, *ibid.*, **84**, 916 (1962).

(15) D. E. Applequist and N. D. Werner, *J. Org. Chem.*, **28**, 48 (1963).

(16) At the time this experiment was attempted there was some suggestion that bromine atoms were the effective chain-carrying species in N-bromosuccinimide brominations. Since then most convincing evidence has been set forth by several workers confirming this. See R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354 (1963), and G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963), for references to earlier publications.

TABLE VI

PHYSICAL CONSTANTS OF ALKYL HALIDES USED IN THIS STUDY

Reactant	Source	B.p. °C.	B.p. mm.	n_D^{20}
Bromocyclohexane	Matheson	66–67	25	1.4953
Bromocyclopentane	Matheson	75.5	100	1.4892
Chlorocyclohexane	Eastman	48.5–50	25	1.4622
1-Bromobutane	Eastman	101.5	760	1.4400
1-Chlorobutane	Matheson	78.5	760	1.4022
2-Bromobutane	Eastman	91.5	760	1.4368
2-Chlorobutane	Matheson	68.5	760	1.3968

TABLE VII

REFRACTIVE INDICES OF AUTHENTIC DIHALIDE SAMPLES

Material	Source	Refractive index Found	Refractive index Reported
trans-1,2-Dibromocyclohexane[a]	[b]	$n^{25}\mathrm{D}$ 1.5505	$n^{25}\mathrm{D}$ 1.5507[d]
trans-1,2-Dibromocyclopentane	[b]	$n^{25}\mathrm{D}$ 1.5471	$n^{25}\mathrm{D}$ 1.5466[d]
trans-1-Bromo-2-chlorocyclohexane	[c]	$n^{25}\mathrm{D}$ 1.5170	$n^{25}\mathrm{D}$ 1.5173[c]
1,2-Dibromobutane	Eastman	$n^{16}\mathrm{D}$ 1.5160	$n^{16}\mathrm{D}$ 1.5161[f]
1,3-Dibromobutane	Matheson	$n^{20}\mathrm{D}$ 1.5092	$n^{16}\mathrm{D}$ 1.5090[e]
1,4-Dibromobutane	Eastman	$n^{20}\mathrm{D}$ 1.5188	. . .
meso-2,3-Dibromobutane	Eastman	$n^{20}\mathrm{D}$ 1.5115	$n^{20}\mathrm{D}$ 1.5116[f]
dl-2,3-Dibromobutane	[b]	$n^{20}\mathrm{D}$ 1.5136	$n^{20}\mathrm{D}$ 1.5147[f]
1-Bromo-4-chlorobutane	Aldrich	$n^{20}\mathrm{D}$ 1.4888	. . .

[a] A mixture of *cis*- and *trans*-1,3- and 1,4-dibromocyclohexanes was obtained from Dr. B. Franzus.[9] [b] Prepared from olefin and Br_2 by a procedure similar to that of Greengard.[7] [c] Prepared by the action of N-bromosuccinimide and HCl on cyclohexene according to the procedure of Goering and Sims.[10] [d] S. Winstein.[17] [e] M. S. Kharasch.[2] [f] Beilstein.

The small scale runs which were used for quantitative analysis of dihalide isomer distribution were worked up in the following manner. The tubes were cooled, cut open, and allowed to warm slowly while the excess HBr escaped. The mixture was then allowed to stand over a small quantity of solid K_2CO_3 until HBr fumes were no longer detectable. The reaction mixtures were then analyzed using a Perkin–Elmer 154D vapor fractometer.

The prep-scale runs, which were performed in order to isolate products and determine yields of dihalides, were treated in a somewhat similar manner. The HBr vapors were allowed to escape through a reflux condenser in series with two cold traps. When the bulk of the HBr had escaped the small amount of material in the traps was combined with the remaining reaction mixture. After treatment with a small quantity of carbonate, the unreacted excess alkyl halide was distilled off. The remaining dihalides were isolated by fractional distillation and were then separated by distillation and/or preparative v.p.c.

Bromination of Bromocyclohexane.—Distillation of a preparative scale run yielded a fraction, b.p. 116–118.5° (25 mm.), which was demonstrated by v.p.c. to contain dibromocyclohexanes in 83% yield based on bromine. *trans*-1,2-Dibromocyclohexane was isolated by fractionation, using a 6-m., 0.25-in. v.p.c. column packed with 20% ethylene glycol succinate on 60–80 mesh acid-washed Chromosorb W (obtained from Wilkens Instrument & Research, Inc.) at 136° and 144 ml./min. flow rate; $n^{25}\mathrm{D}$ 1.5500. *Anal.* Calcd. for $C_6H_{10}Br_2$: C, 29.75; H, 4.13; Br, 66.12. Found: C, 29.96; H, 4.09; Br, 65.36.

Quantitative analyses of the reaction mixtures to determine the composition of dibromocyclohexane isomers were performed using the same v.p.c. conditions and showed that 94% of the dibromocyclohexane was the *trans*-1,2 isomer.

Bromination of Bromocyclopentane.—Distillation of a preparative scale run gave a 93.2% yield of dibromides, b.p. 90–94° (30 mm.). This material was fractionated using a 3.8-m., 0.5-in. v.p.c. column at 136° packed with the polyester succinate material described above. *trans*-1,2-Dibromocyclopentane was isolated; $n^{25}\mathrm{D}$ 1.5471. *Anal.* Calcd. for $C_5H_8Br_2$: C, 26.34; H, 3.54; Br, 70.12. Found: C, 26.43; H, 3.58; Br, 70.42.

Quantitative analysis of reaction mixtures using the 6-m., 0.25-in. succinate polyester column described previously at 135° and 42 ml./min. flow rate revealed that the *trans*-1,2-dibromide comprised 89.9% of the dibromocyclopentane products.

Bromination of Chlorocyclohexane.—The six product peaks believed to be bromochlorocyclohexanes were collected in a single fraction using the 3.8-m., 0.5-in. preparative succinate polyester column described previously. *Anal.* Calcd. for $C_6H_{10}BrCl$: C, 36.49; H, 5.10; Br, 40.46; Cl, 17.95. Found: C, 36.53; H, 5.25; Br, 40.07; Cl, 18.10.

Quantitative analysis of reaction mixtures using the 6-m., 0.25-in. polyester column, described previously, at 136° and 146 ml./min. revealed that the *trans*-1,2-dihalide comprised 9.4% of the total dihalide.

Bromination of 1-Bromobutane.—Distillation of a preparative scale run gave an 85% yield of dibromide, b.p. 65–74° (24 mm.). This material was refractionated into two portions; fraction 1, b.p. 65.0–67.5° (24 mm.), containing about 90% 1,2-dibromobutane, and fraction 2, b.p. 68.9–72° (24 mm.), containing 29% 1,3-dibromobutane. Using a 6-m., 0.25-in. ethylene glycol succinate polyester column at 136° and 42 ml./min., 99.9% pure 1,2-dibromobutane $n^{20}\mathrm{D}$ 1.5148 was isolated from fraction 1 while 98.6% pure 1,3-dibromobutane, $n^{20}\mathrm{D}$ 1.5098, was isolated from fraction 2.

Quantitative analysis of reaction mixtures was accomplished using the same v.p.c. conditions. The isomer distribution of dibromobutane products is presented in Table II.

Bromination of 1-Chlorobutane.—A 72% yield of dihalide was isolated by distillation of the products of a preparative scale run, b.p. 69–84° (75 mm.). The fraction b.p. 82–82.9° (75 mm.) contained 97.5% pure 1-chloro-3-bromobutane, $n^{20}\mathrm{D}$ 1.4788. This material was purified by fractionation on a Perkin–Elmer 1-in., 3-m., "R" preparative v.p.c. column at 136° and 220 ml./min. The purified product (99.0%) had a refractive index $n^{20}\mathrm{D}$ 1.4782. The 1,1- and 1,2-dihalobutanes were fractionated from the material b.p. 69–75° (75 mm.); 1-chloro-1-bromobutane (99.9% pure), $n^{20}\mathrm{D}$ 1.4680; 1-chloro-2-bromobutane (99.4% pure), $n^{20}\mathrm{D}$ 1.4800 (reported, Beilstein, $n^{20}\mathrm{D}$ 1.4800). Kharasch[6] reported that 1-chloro-1-bromobutane and 1-chloro-3-bromobutane isolated from the bromination of 1-chlorobutane had the respective refractive indices $n^{20}\mathrm{D}$ 1.4670 and 1.4770 which are about 0.001 unit lower than our observed values. His reported values for the 1-chloro-2-bromobutane of $n^{20}\mathrm{D}$ 1.4788 is also about 0.001 unit lower than ours. The value which we have observed was identical with that reported in Beilstein for a sample of the 1,2-dihalide prepared by an independent synthesis, suggesting that the products isolated by Kharasch were not completely pure. However, our structural assignments resulting from the preparation of the 1,2- and 1,3-bis-(S-alkyl)-isothiourea picrates of 1-chloro-2-bromo- and 1-chloro-3-bromobutane and comparison (by means of infrared) with authentic samples prepared from the corresponding dibromides agree with those made by Kharasch. The identification of 1-bromo-1-chlorobutane was confirmed by hydrolysis in a sealed tube at 150° with lead oxide and comparison of the 2,4-dinitrophenylhydrazone of the hydrolyzed product by melting point with that of butyraldehyde.

Quantitative analysis of isomeric products was obtained using a 2-m., 0.25-in. Perkin–Elmer column "R" at 134° and 50 ml./min. The results are presented in Table II.

Chlorination of 1-Bromobutane.—Quantitative v.p.c. analysis of reaction mixtures was carried out under the identical conditions used for the analysis of the 1-chlorobutane bromination. The products 1,2-dichlorobutane, 1-bromo-1-chlorobutane, and 1-bromo-4-chlorobutane were identified by comparison with the v.p.c. of authentic samples. The identity of 1-bromo-2-chlorobutane and 1-bromo-3-chlorobutane was inferred by analogy with the v.p.c. of the 1-chloro-2-bromo- and 1-chloro-3-bromobutanes, with which they showed almost identical retention times. These v.p.c. peaks were sufficiently displaced to demonstrate that different 1,2- and 1,3-dihalides were produced in the chlorination of 1-bromobutane from those of the 1-chlorobutane bromination.

Bromination of 2-Bromobutane.—Analysis of reaction mixtures using a Perkin–Elmer 2-m., 0.25-in. "R" column at 130° and 50 ml./min. revealed two incompletely resolved peaks corresponding to *meso*-2,3-dibromobutanes (Eastman) and *dl*-2,3-dibromobutane (prepared from bromine and *cis*-2-butene). A smaller peak, which was eluted first, had a retention time different from that all the other previously observed dibromobutanes. This peak was therefore assumed to be 2,2-dibromobutane, which was the only remaining dibromobutane. The results are presented in Table III.

Bromination of 2-Chlorobutane.—Vapor phase chromatographic analysis using a Perkin–Elmer 2-m., 0.25-in. "R" column at 125° and 35 ml./min. showed the same three-peak pattern observed in the bromination of 2-bromobutane—a single peak followed by a pair of incompletely resolved peaks. In this case the single peak was the principal product. Hydrolysis of this material at 150° with lead oxide (sealed tube) and preparation of the 2,4-dinitrophenylhydrazone showed the hydrolysis product to be methyl ethyl ketone. The pair of small peaks which comprised about 8% of the total product (Table III) were assumed to be the *meso*- and *racemic*-2,3-dihalides.

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(17) (a) S. Winstein, *J. Am. Chem. Soc.*, **64**, 2792 (1942); (b) S. Winstein and R. M. Roberts, *ibid.*, **75**, 2297 (1953).

Acknowledgment.—The author wishes to express his thanks to Prof. P. S. Skell for his discussions and suggestion regarding the influence of bromine atom bridging in alkyl bromide brominations.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC., WILMINGTON 98, DEL.]

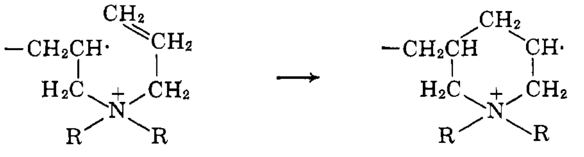
Bicyclo-copolymerization of Sulfur Dioxide and *cis,cis*-1,5-Cyclooctadiene[1]

BY A. H. FRAZER AND W. P. O'NEILL

RECEIVED MARCH 28, 1963

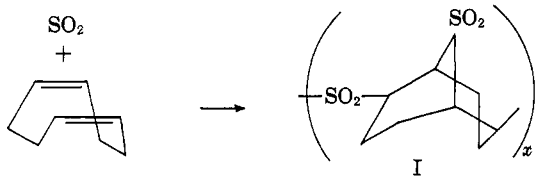
The copolymerization of sulfur dioxide with *cis,cis*-1,5-cyclooctadiene has been effected using radical initiation in dilute solutions. The soluble copolymer which was obtained in film- and fiber-forming molecular weights has no unsaturation and contains two moles of sulfur dioxide per mole of cyclooctadiene. A cyclization polymerization mechanism is proposed. The properties of the copolymer were determined and the thermal and hydrolytic stability studied.

In order to explain the solubility of polymers obtained from diallyl quaternary ammonium salts, Butler and Angelo[2] proposed an intermolecular–intramolecular propagation mechanism in this radical polymerization, the intramolecular step producing piperidinium units



A number of examples of inter–intramolecular polymerization have since appeared. These include, in addition to the free-radical type of initiation of Butler and Angelo, Ziegler–type,[3] anionic,[4a] and cationic.[4b] Recently, the inter–intramolecular polymerization of triallyl- and tetrallylammonium bromide has been reported to yield polymers containing methylene-linked bicyclic and tricyclic rings.[5] Similarly the transannular polymerization of bicyclodienes has been reported to yield nortricyclene repeating units.[6]

Recently, the cyclo-copolymerization of 1,5-hexadiene and sulfur dioxide has been reported.[7] This paper reports the bicyclo-copolymerization of sulfur dioxide with *cis,cis*-1,5-cyclooctadiene *via* inter–intramolecular propagation. To our knowledge, this is the first example of such a bicyclo-copolymerization.



I

Discussion and Results

Polymerization.—The copolymerization of sulfur dioxide with *cis,cis*-1,5-cyclooctadiene has been effected by using free radical initiators in solvents or diluents. Solvents and diluents such as tetramethylene sulfone, dimethyl sulfoxide, diethyl ether, and excess sulfur dioxide were found to be operable. Radical initiators such as ascaridole–hydrochloric acid, ascaridole–hydrogen chloride, and methyl ethyl ketone peroxide were found to be effective. Unlike other radical polymerizations, this polymerization could be initiated with oxygen alone, and oxygen acted as a "promoter" for other radical initiators. Although initiation of polysulfone preparation with "combined oxygen" has been reported,[8] polymerization in this case was initiated by merely bubbling oxygen through the reaction mixture. This "oxygen effect" will be discussed in greater detail in a later paper.

The preferred procedure for the preparation of high molecular weight polymer in high conversion consisted of using tetramethylene sulfone as reaction medium with methyl ethyl ketone peroxide as initiator and oxygen as a "promoter." In this manner, quantitative yields of soluble high molecular weight polymer were obtained. Representative copolymerizations of sulfur dioxide and 1,5-cyclooctadiene are summarized in Table I.

TABLE I[a]

Reaction medium	Initiators[d]	Temp., °C.	Time, hr.	Atmosphere	Yield,[g] %	η_{inh}[h]	S, %
Diethyl ether	A	15	2	N_2	37	0.62	26.42
. . .	B	−5	10	N_2	23	.90	26.93
DMSO[b]	A	22	8	N_2	84	.21	26.51
TMS[c]	A	25	16	N_2	83	1.55	26.94
TMS[c]	A	25	16	Air[e]	89	1.95	26.85
TMS[c]	A	25	16	Air[f]	93	2.10	26.93
TMS[c]	. .	25	16	Air[f]	50	1.20	26.84
DMSO[b]	C	22	16	N_2	88	0.21	26.43
TMS[c]	C	25	16	N_2	80	1.4	26.86
TMS[c]	C	25	16	Air[e]	98	2.2	26.76
TMS[c]	C	−4	2	N_2	15	1.13	26.87

[a] All reactions carried out with 10% wt. concn. of monomers; $M_{SO_2}/M_{C_8H_{12}}$ = 0.25/0.10. [b] DMSO, dimethyl sulfoxide. [c] TMS, tetramethylene sulfone. [d] A initiator, 5 drops of ascaridole and 5 drops of concd. HCl; B initiator, 1 drop of ascaridole and 400 cc. of HCl (gas); C initiator, 5 drops of methyl ethyl ketone peroxide. [e] Reaction mixture opened to air. [f] Air bubbled through reaction mixture. [g] Yield, per cent based on 1,5-cyclooctadiene. [h] η_{inh}, inherent viscosity ($\ln \eta_{rel}/C$) for 0.5 g. of polymer/100 ml. of dimethyl sulfoxide solution.

Radical initiators usually effective in the copolymerization of sulfur dioxide with olefins or dienes such as cumene hydroperoxide, α,α'-azobis-(α,γ-dimethylvaleronitrile), benzoyl peroxide, ammonium nitrate, and hydrogen peroxide were ineffective in this system. As might be expected, cationic initiators such as boron trifluoride and boron trifluoride etherate gave low molecular weight hydrocarbon oligomers of 1,5-cyclooctadiene, but no polysulfone. Similarly, lithium naphthalene and a Ziegler-type catalyst from aluminum triisobutyl

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(1) Presented at the 144th National Meeting of the American Chemical Society, March 31–April 5, 1963, Los Angeles, Calif.

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