Free radical hydrobromination of propargyl bromide and bromoallene[1]

KARL R. KOPECKY AND SHIMA GROVER[2]
Department of Chemistry, University of Alberta, Edmonton, Alberta

Received November 22, 1968

Rearrangement is observed in the free-radical hydrobromination of propargyl bromide. Between −20 and +30 °C in *n*-pentane or ether solution, 1,2-dibromopropene is the major product. A detailed stereochemical and kinetic study of the reaction indicates that the 1,2-dibromopropene is formed via bromoallene which results from the loss of a bromine atom from the first formed 1,3-dibromo-2-propenyl radical. Only 1/3 to 1/2 of the bromoallene diffuses away from its bromine atom partner. The remainder of the bromoallene recombines within the solvent cage with its bromine atom partner at a rate which is competitive with its rate of rotation with respect to the bromine atom. When the free radical hydrobromination of propargyl bromide is carried out at −78° in liquid hydrogen bromide, the 1,3-dibromo-2-propenyl radical can be trapped to a large extent by the hydrogen bromide to form *cis*-1,3-dibromopropene. The stereochemistry of this addition reaction > 99% *trans*. A small amount of 1,2-dibromopropene which is 77% *trans* is also formed. Under the same conditions a 3:1 mixture of 1,2- and 1,3-dibromopropenes is produced from bromoallene. The 1,3-dibromopropene produced from bromoallene is > 95% *cis*, while the 1,2-dibromopropene consists of a 49:51 *cis*:*trans* mixture of isomers.

Canadian Journal of Chemistry, **47**, 3153 (1969)

In connection with another problem in these laboratories a large amount of 1,3-dibromopropene was required. The free radical hydrobromination of propargyl bromide appeared to be a more convenient route to this compound than

[1] $HC{\equiv}CCH_2Br + HBr \rightarrow CHBr{=}CHCH_2Br$

those already available (1–3). Free radical hydrobromination of terminal acetylenes has been shown to give anti-Markovnikov products (4–6). However, when hydrogen bromide was bubbled through propargyl bromide containing benzoyl peroxide at 0 °C, only ca. 15% of 1,3-dibromopropene was formed. The major product was 1,2-dibromopropene which was isolated in 54% yield. A rearrangement, presumably migration of a bromine atom, has clearly occurred in this transformation. In view of the interest in bromine migrations (7, 8) and the mechanism of free radical addition of hydrogen bromide to unsaturated systems (7–16), the course of this reaction was examined in detail.

Products and Nature of Reaction

It was found that up to 7 compounds can be present in reaction mixtures from the hydrobromination of propargyl bromide. These are *cis*- and *trans*-1,2-dibromopropene, *cis*- and *trans*-1,3-dibromopropene, 2-3-dibromopropene, bromoallene, and propargyl bromide. Clean separation by gas–liquid chromatography of all these compounds could be achieved using a 9.5 ft × 1/4 in. column of 10% UCON 50HB5100 on Chromosorb W. All analyses reported were obtained by gas–liquid chromatography using this column. The identification of these compounds is described in the Experimental.

Some preliminary experiments were carried out in order to confirm that the formation of 1,2-dibromopropene from the hydrobromination of propargyl bromide was the result of a free radical process. These are summarized in Table I.

High yields of 1,2-dibromopropene were obtained only in the presence of benzoyl peroxide or under illumination. Addition of the free radical inhibitors hydroquinone and ferrous chloride to the reaction mixtures resulted in the formation of considerable amounts of 1,3- and 2,3-dibromopropenes, presumably by an ionic process or processes. Reaction in the dark is very slow in the absence of initiators. This evidence confirms that hydrobromination of propargyl bromide under free radical conditions results in almost exclusive formation of a product of a rearrangement, 1,2-dibromopropene, at 0 °C.

No evidence was found for the formation of any 3,3-dibromopropene by either the free radical or ionic addition of hydrogen bromide to

---

[1](*a*) Presented in part at the 48th Chemical Conference of the Chemical Institute of Canada, Montreal, Quebec, May, 1965. Abstracts, p. 61. (*b*) Abstracted from a Thesis submitted by S. Grover to the Faculty of Graduate Studies of the University of Alberta in partial fulfillment of the requirements for the M.Sc. Degree, May, 1966.

[2]Holder of a Province of Alberta Scholarship 1963–1964 and 1964–1965 and a NRCC Studentship 1965–1966.

TABLE I

Product distribution from preliminary hydrobrominations of propargyl bromide at 0 °C*

Run	Solvent	Conditions and additives	% Dibromopropene† 1,2-	2,3-	1,3-
1	None	Benzoyl peroxide	54‡	0‡	15‡
2	None	$FeCl_3$ + hydroquinone	59	26	15
3	Pentane	Benzoyl peroxide	98	0.1	2
4	Ether	Dark, $FeCl_3$ + hydroquinone	21	79	0
5	Acetic acid§	$FeCl_2$ + hydroquinone	64	25	11
6	Pentane	Dark, no additive	91¶	5¶	4¶

*Except for run 5 reactions were carried out by passing HBr gas into the reaction mixture. Reactions were complete after 2–8 h.
†Analysis by g.l.c. except for run 1. Yields are relative yields at the end of the reaction except for runs 1 and 6. Total absolute yield of products > 98%, except in run 1.
‡Isolated yield from a preparative run.
§Propargyl bromide added to solution of 30% HBr in acetic acid containing the additives.
¶More than 95% starting material left after 48 h.

propargyl bromide. Product balances of 95–100% were obtained indicating that little, if any, polymer or tribromide was formed in either the ionic or free radical reactions and that these reactions stopped cleanly at the dibromide stage.

The 1,2- and 1,3-dibromopropenes produced in these reactions are mixtures of *cis* and *trans* isomers. It was shown that these mixtures are equilibrium mixtures. The equilibrium compositions of the 1,2- and 1,3-dibromopropenes were determined by irradiating with a sun lamp, the pure geometric isomers in pentane solution saturated with hydrogen bromide until no further change in isomer composition was observed. These results are shown in Table II.

TABLE II

Equilibration of isomers of 1,2- and 1,3-dibromopropene at 0 °C.

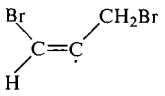
Starting compound	Equilibrium composition
cis-1,2-Dibromopropene	76.8% *trans*
trans-1,2-Dibromopropene	77.1% *trans*
cis-1,3-Dibromopropene	84.5% *cis*
trans-1,3-Dibromopropene	83.1% *cis*

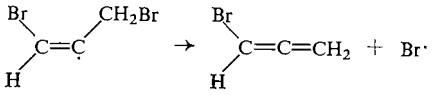
Bromoallene was detected in reactions which were interrupted before completion. Continuous monitoring of several hydrobromination reactions in pentane containing benzoyl peroxide as initiator revealed that the concentration of bromoallene always increases to a maximum of about 10% of the initial propargyl bromide concentration at about 20 to 40% reaction, and then slowly decreases as the reaction progresses further. The amount of propargyl bromide smoothly decreases and that of 1,2-dibromopropene smoothly increases as the reaction progresses. This behavior is independent of the rate of hydrogen bromide addition and of the initial propargyl bromide and benzoyl peroxide concentrations. The propargyl bromide initially contained less than 0.5% bromoallene. These observations, coupled with the observation that no bromoallene is produced in the dark in the absence of benzoyl peroxide under otherwise identical conditions (run 6, Table I), show that formation of bromoallene from propargyl bromide also is a free radical process under these conditions.

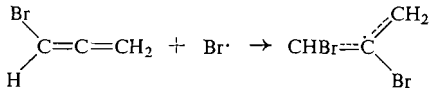
When pure bromoallene is hydrobrominated at 0° in pentane solution in the presence of benzoyl peroxide, a mixture of 95% 1,2-dibromopropene and 5% 1,3-dibromopropene is formed. This product composition is essentially identical to that obtained from propargyl bromide under these conditions (run 3, Table I). Only trace amounts of propargyl bromide are formed during the hydrobromination of bromoallene under these conditions.

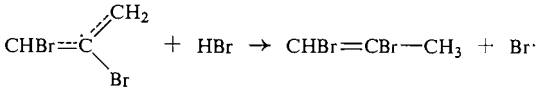
Attempts to Trap Radical Intermediate

It seemed possible that all the dibromide produced from the free radical hydrobromination of propargyl bromide is formed from bromoallene after a prior isomerization of the propargyl bromide to bromoallene under the reaction conditions, eqs. [2]–[5]. The bromoallene could be formed from propargyl bromide by addition of a bromine atom to the terminal carbon atom of the acetylene, followed by loss of the bromine atom originally present, see

[2] $Br\cdot + H{-}C{\equiv}C{-}CH_2Br \rightarrow$ 

[3] 

[4] 

[5] 

reactions [2] and [3]. In the free radical hydrobromination of propyne to form *cis*-1-bromopropene (6) the bromine atom adds to the terminal carbon atom, and it has been shown that a bromine atom is readily lost from a carbon atom adjacent to a radical center (17). Addition of a bromine atom to the center carbon atom of bromoallene would give a long-lived allylic radical, reaction [4], which would react with hydrogen bromide to form 1,2-dibromopropene.

Several attempts were made to trap the postulated intermediate *cis*-1,3-dibromo-2-propenyl radical with hydrogen bromide at 25° in solution, reaction [6*a*]. Increasing the rate of introduction of hydrogen bromide into hydrobromination reactions of propargyl bromide in pentane solution did not result in any change in product composition. The maximum concentration of hydrogen bromide in pentane which could have been attained under these conditions is ca. 0.6 *M* (18). More concentrated hydrogen bromide solutions can be prepared in ether. A hydrobromination under illumination by a sun lamp of propargyl bromide in ether saturated with hydrogen bromide (ca. 40% HBr) did result in formation of significant amounts of 1,3-dibromopropene. The distribution of dibromides formed was 1,2-dibromopropene (11%), 2,3-dibromopropene (19%), and 1,3-dibromopropene (70%). The presence of a considerable quantity of 2,3-dibromopropene in the product mixture indicates that a significant amount of ionic reaction had occurred. This makes uncertain what amount of 1,3-dibromopropene was formed by trapping of any intermediate radical. A hydrobromination under illumination of propargyl bromide in ether solution 1.3 *M* in hydrogen bromide resulted in the formation of a 90:10 mixture of 1,2-:1,3-dibromopropene and only traces of 2,3-dibromopropene. This product composition is not significantly different from those of numerous runs carried out in ether solution 0.32 *M* in hydrogen bromide at 25° (see below) or in one run at −20°. Hydrobromination under illumination of propargyl bromide in ether solution more concentrated than about 1.3 *M* in hydrogen bromide always resulted in formation of significant amounts of 2,3-dibromopropene. The intermediate radical cannot be trapped to any significant extent by hydrogen bromide at hydrogen bromide concentrations of up to 1.3 *M* at 25°. Above this concentration ionic reactions begin to interfere.

An earlier attempt to carry out free radical addition of hydrogen bromide to unsaturated systems in ether solution failed (10). In the present study free radical hydrobrominations in ether solution occurred only if ether was carefully treated prior to reaction (see Experimental).

The intermediate 1,3-dibromo-2-propenyl radical would be expected to have a longer life at lower temperatures and experiments designed to trap it at −78° were carried out.

Attempts to carry out free radical hydrobromination of propargyl bromide in ether or pentane solution at low temperature were

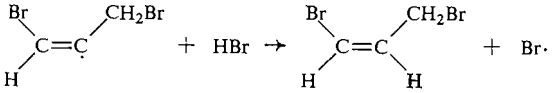
[6*a*] 

TABLE III

Product distribution and stereochemistry of free radical hydrobromination of propargyl bromide and bromoallene in liquid hydrogen bromide at −78°

		% Dibromopropene	
Conversion (%)	Bromoallene (%)	1,2- (% *trans*)	1,3- (% *cis*)
	From propargyl bromide		
0	0.3	—	—
1.8	0.5	0.1 (77.0)	1.5 (98.8)
10.7	2.0	0.7 (77.1)	8.3 (97.5)
27.7	1.4	2.0 (77.2)	24.6 (96.0)
	From bromoallene		
9.3	—	6.8 (51.4)	2.5 (95.5)
48.0	—	36.1 (50.8)	11.9 (92.6)

frustrated by the formation of solid phases. When a 0.32 *M* solution of hydrogen bromide in ether was cooled to −78° a large amount of white precipitate formed. A pentane solution 0.32 *M* in hydrogen bromide was homogeneous at −78°. However, introduction of even small amounts of propargyl bromide resulted in immediate formation of a precipitate.

Both bromoallene and propargyl bromide form homogeneous solutions with hydrogen bromide at −78°. A number of free radical hydrobrominations of bromoallene and propargyl bromide were carried out in degassed liquid hydrogen bromide solution at this temperature. Reactions were initiated by illumination from a sun lamp. Similar conditions have previously been used for the free radical hydrobromination of propyne (6). No addition or isomerization occurred in the absence of illumination. No reaction products with molecular weight higher than that of dibromopropene were detected. Results from a number of experiments are summarized in Table III. Propargyl bromide and bromoallene gave different product distributions under these conditions and product distributions from both were different from those observed in reactions at room temperature in solution. The ratio 1,2-:1,3-dibromopropene formed in the radical hydrobromination of either bromoallene or propargyl bromide in solution at room temperature is always in the range 10:1 to 30:1. In reactions at −78° the 1,2-:1,3-dibromopropene ratio obtained from propargyl bromide was ca. 1:12 and that obtained from bromoallene was ca. 3:1. Radical hydrobromination of propargyl bromide can yield either 1,2-dibromopropene almost exclusively or 1,3-dibromopropene almost exclusively depending upon reaction conditions. The very predominant formation of 1,3-dibromopropene at low temperature shows that the bromine atom adds at the terminal acetylenic carbon atom of propargyl bromide. That only small amounts of bromoallene and 1,2-dibromopropene are formed from propargyl bromide in these reactions can be explained by postulating that in liquid hydrogen bromide at −78° (*a*) the intermediate *cis*-1,3-dibromo-2-propenyl radical, if formed, abstracts a hydrogen atom from hydrogen bromide much more rapidly than it loses a bromine atom to form bromoallene, or (*b*) the bromine atom reacts with a propargyl bromide–hydrogen bromide complex and hydrogen atom transfer is rapid (10).

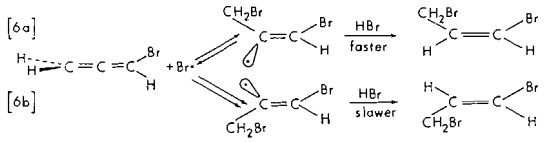
Stereochemistry of Hydrogen Bromide Addition at −78°

The proportion of the *cis*-isomer in the 1,3-dibromopropene mixture decreases somewhat as the reaction proceeds. This appears to be due to a slow isomerization catalyzed by hydrogen bromide. Extrapolation of a plot of % *cis*-1,3-dibromopropene vs. % conversion to 0% conversion gives an intercept of 99.2% *cis*. This value is significantly different from the equilibrium value which is calculated to be ca. 90% *cis* at −78°. The radical hydrobromination of propargyl bromide under these conditions is a stereospecific *trans* addition reaction. The hydrobromination of propyne has also been shown to be a stereospecific *trans* addition reaction under the same conditions (6).

Unexpectedly, the 1,3-dibromopropene formed from bromoallene under these conditions is also

mainly the *cis*-isomer. Extrapolation to 0% conversion indicates that the proportion of *cis*-isomer formed initially in this reaction is > 96%.

The radical addition of hydrogen bromide to olefins at low temperature has been shown to be a stereospecific *trans*-process (11, 12, 19) and there is no obvious reason why addition of a bromine atom could not occur equally well at either side of the bromoallene molecule to give a mixture of *cis*- and *trans*-1,3-dibromo-2-propenyl radicals, at least in incipient form, reactions [6*a*] and [6*b*]. Perhaps hydrogen transfer



from hydrogen bromide to the *trans*-radical is sterically hindered. Inspection of Fisher–Hirschfelder–Taylor molecular models indicates that there may be some interference by the vinyl bromine atom to approach of hydrogen bromide to the adjacent vinylic radical center in the *trans* radical. In the case of the reaction involving a hydrogen bromide–allene complex, the hydrogen bromide would have to shift from a symmetrical position between the terminal and central carbon atoms toward the central carbon atom before hydrogen atom transfer could occur, and this shift would also be more difficult in the process leading to the *trans*-dibromide.

The 1,2-dibromopropene produced from bromoallene has a different isomer composition from that produced from propargyl bromide. At −78° the equilibrium mixture is calculated to contain ca. 82% of the *trans*-isomer. In neither reaction is the equilibrium mixture formed. The isomer ratio of 1,2-dibromopropene remains essentially constant during both reactions, so that 1,2-dibromopropene is isomerized much more slowly than 1,3-dibromopropene under these reaction conditions.

Kinetic Evidence for Radical Intermediate in Solution

The results of the low temperature hydrobrominations of propargyl bromide show that the initial point of attack of the bromine atom is at the terminal carbon atom of the acetylernic group. This would indicate that in ether and pentane solution bromoallene is formed by way of the *cis*-1,3-dibromo-2-propenyl radical, reactions [2] and [3]. In order to obtain kinetic evidence for the formation of this intermediate, several runs were made in ether with known concentrations of reactants and were continuously monitored.

Oxygen-free solutions of propargyl bromide and hydrogen bromide in ether were irradiated at room temperature. These reactions were homogeneous. As was observed in the more qualitative runs carried out in pentane, the bromoallene concentration increased to ca. 10–12% of the initial propargyl bromide concentration and then decreased as the reaction progressed further. No variation in behavior was observed when the initial hydrogen bromide concentrations were varied from 0.32 to 1.3 *M*. Results from two runs at the extremes of hydrogen bromide concentration used are shown in Fig. 1. No reaction was observed in the absence of illumination.

Although the 1,2-dibromopropenes formed in hydrobromination reactions carried out in pentane solution were always equilibrated, this was not the case when the reactions were carried out in ether solution. Here the isomer ratio varied during the course of a reaction and always contained less than the equilibrium amount of the *trans*-isomer.

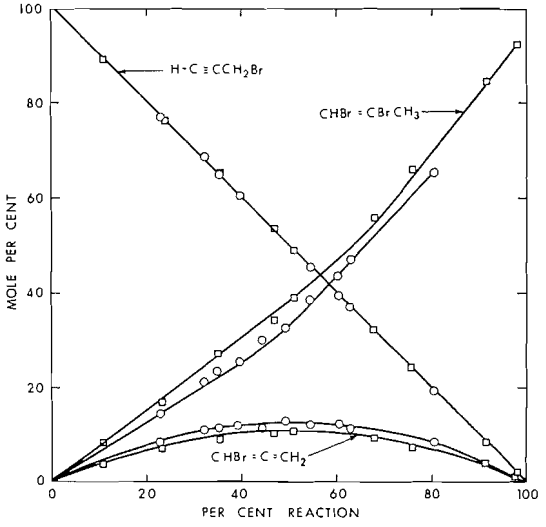


FIG. 1. Disappearance of starting material and formation of products in radical hydrobromination of propargyl bromide in ether at 25°. □, run 8, $[HBr]_0$ = 1.32 *M*, $[PB]_0$ = 0.032 *M*, 6% 1,3-dibromopropene present at 80% reaction; ○, run 10, $[HBr]_0$ = 0.32 *M*, $[PB]_0$ = 0.032 *M*, 5% 1,3-dibromopropene present at the end of the reaction.

The equilibrium ratio was determined in ether by irradiating a solution of pure *trans*-1,2-dibromopropene and hydrogen bromide in this solvent. Equilibration proceeded much more slowly than did the equilibration in pentane, but afforded essentially the same isomer composition as formed in pentane: 77.8% *trans*- and 22.2% *cis*-1,2-dibromopropene.

It appeared at first that the 1,2-dibromopropene formed initially contained more of the *cis*-isomer than the equilibrium mixture and that equilibration occurred slowly as the reaction progressed. However, when the isomer composition was monitored early in the reaction, it was found that the reaction was more complex. The upper curve of Fig. 2 shows the variation of the % of *trans*-isomer in the 1,2-dibromopropenes formed from propargyl bromide during ca. the first 30% of reaction. Extrapolation of the curve to 0% reaction gives an intercept of ca. 74% *trans*-1,2-dibromopropene. The % of *trans*-isomer present actually decreases from near the equilibrium % early in the reaction, to 67%, and only later beings to increase again.

The lower curve of Fig. 2 shows the variation during approximately the first 30% of reaction of the % of the *trans*-isomer of the 1,2-dibromopropenes formed in hydrobromination of bromoallene under illumination in ether. The results are entirely different from those obtained with propargyl bromide. Initially, nearly equal amounts of *cis*- and *trans*-isomers are present. As the reaction progresses the proportion of *trans*-isomer increases slowly.

It is clear that mechanism of formation of 1,2-dibromopropene in the radical hydrobromination of propargyl bromide is more complex than is indicated by reactions [2]–[5]. In ether solution at 25° a significant portion of the product must arise by a process not involving free bromoallene.

Further support for this conclusion is obtained from the kinetic analysis of the reaction. If all the product were formed via free bromoallene then the reactions may be formulated as in reactions [2]–[5]. Since the loss of a bromine atom from the 1,3-dibromo-2-propenyl radical is fast and the amount of bromoallene present in the reactions is independent of hydrogen bromide concentration, Fig. 1, rate-determining steps may be represented as

$$[7] \qquad PB + Br\cdot \xrightarrow{k_1} BA + Br\cdot$$

$$[8] \qquad BA + Br\cdot \xrightarrow{k_2} DB$$

where PB = propargyl bromide, BA = bromoallene, and DB = 1,2-dibromopropene. The following expressions may now be written

$$[9] \qquad \frac{-d[PB]}{dt} = k_1[PB][Br\cdot]$$

$$[10] \qquad \frac{-d[BA]}{dt} = k_2[BA][Br\cdot] - k_1[PB][Br\cdot]$$

$$[11] \qquad \frac{d[BA]}{d[PB]} = \frac{k_2[BA] - k_1[PB]}{k_1[PB]}$$

$$[12] \qquad \frac{d[BA]}{d[PB]} - \frac{k_2[BA]}{k_1[PB]} = -1$$

This expression may be integrated (20) using $[PB_0]$ and [0] as the initial limits, and [PB] and [BA] as the final limits of the variables to give

$$[13] \qquad [BA] = \frac{[PB]}{1 - k_2/k_1}\left[\left(\frac{[PB]}{[PB_0]}\right)^{k_2/k_1 - 1} - 1\right]$$

This result is identical to that obtained by McMillan (21) using a somewhat different method. The ratio k_2/k_1 may be determined from the maximum concentration of bromoallene.

$$[14] \qquad \frac{-d[BA]}{dt} = 0 = k_2[BA][Br\cdot] - k_1[PB][Br\cdot]$$

$$[15] \qquad k_2/k_1 = [PB]/[BA] \text{ at maximum BA}$$

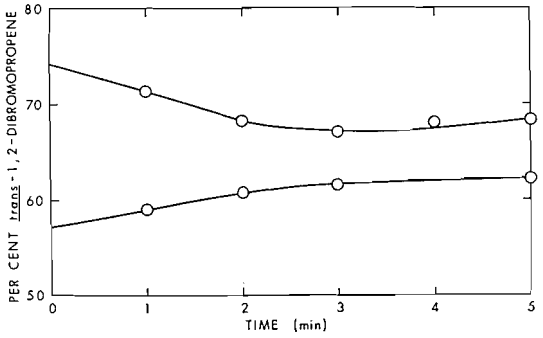


FIG. 2. Variation of isomer composition of 1,2-dibromopropene with time in radical hydrobromination of propargyl bromide (upper curve) and bromoallene (lower curve) in ether at 25°.

Unfortunately the concentration of bromoallene passes through a broad maximum and the concentration of propargyl bromide varies considerably, while the concentration of bromoallene varies but little. In each of a number of runs the ratio k_2/k_1 calculated in this manner varied from about 5 at the beginning of the broad maximum to about 3.5 at the end of the broad maximum. The ratios used for calculations were taken from concentrations at the estimated midpoint of the broad maximum and were 4.0 for three runs and 4.7 for one run. Using eq. [13] the upper curve of Fig. 3 was calculated for the concentration of bromoallene during run 10. This curve is clearly different from the experimental curve. Bromoallene is neither being formed as rapidly nor consumed as rapidly as required were all the intermediate *cis*-1,3-dibromo-2-propenyl radicals converted to free bromoallene. It appears that only a portion of the intermediate radicals formed yields free bromoallene.

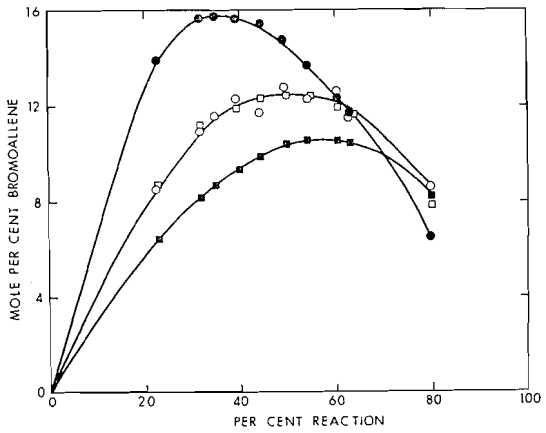


FIG. 3. Variation of bromoallene concentration with time in hydrobromination of propargyl bromide in ether at 25° in run 10. ○, Observed; ●, calculated using eq. [13]; □, calculated using eq. [16] with $F = 1/2$; ■, calculated using eq. [16] with $F = 1/3$. The middle curve is drawn through the experimental points.

If only a fraction, F, of the intermediate *cis*-1,3-dibromo-2-propenyl radicals formed is diverted to free bromoallene, the following equation may be derived to represent the concentration of bromoallene during the course of the reaction

$$[16] \quad [BA] = \frac{F[PB]}{1 - k_2/k_1}\left[\left(\frac{[PB]}{[PB_0]}\right)^{k_2/k_1 - 1} - 1\right]$$

A series of curves was calculated for each run using various values of F. The ratio k_2/k_1 in these cases is given by

$$[17] \quad k_2/k_1 = F\,[PB]/[BA] \text{ at maximum BA}$$

Figure 3 shows curves obtained using eq. [16] for run 10 using different values of F. The curve calculated using $F = 1/2$ gives a very close fit to the experimental curve. For four runs very close agreement between the calculated and experimental curves was obtained, with the values of F and k_2/k_1 shown in Table IV. These results indicate that about 50% of the reaction proceeds by a process not involving free bromoallene.

TABLE IV

Values of F and k_2/k_1 for hydrobrominations of propargyl bromide in ether at 25°

Run	$[PB]_0$, * M	$[HBr]_0$, M	F	k_2/k_1
7	0.354	0.354	1/2	2.0
8	0.032	0.324	1/3	1.6
9	0.100	0.324	1/2	2.0
10	0.032	1.30	1/2	2.0

*Propargyl bromide contained less than 0.5% bromoallene initially.

Reactions of the Radical Intermediate

There appear to be two possible processes which could account for that part of the reaction which does not form free bromoallene. One process involves an intramolecular bromine atom migration, Fig. 4, to form the allylic 1,2-dibromopropenyl radical. The other process could be a

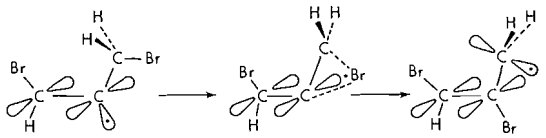


FIG. 4. Stereochemistry of bromine atom migration.

cage reaction between bromoallene and its bromine atom partner which results from loss of a bromine atom from the 1,3-dibromo-2-propenyl radical, Fig. 5. A choice can be made between these two processes by considering the stereochemistry of the reaction in ether solution at short reaction times, Fig. 2, and the geometric requirements of the two processes.

As Fig. 4 shows, bromine atom migration must produce the 1,2-dibromopropenyl radical with the bromine atoms *trans*. This would also

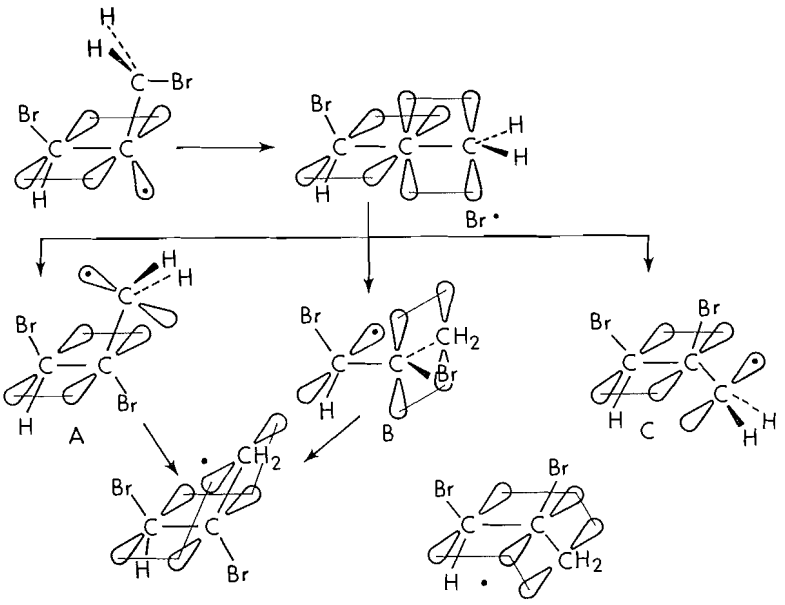


FIG. 5. Stereochemistry of bromine atom elimination followed by recombination.

be so if the initial radical were a bridged radical instead of a vinyl radical as depicted. However, it is difficult to account for the formation of bromoallene from a bridged radical without first opening it to *cis*-1,3-dibromo-2-propenyl radical, and it is not required to account for any of the results. From the stereochemical results illustrated in Fig. 2, it can be concluded that the 1,2-dibromopropenyl radicals must maintain their geometry under these reaction conditions. It has already been shown that other types of allylic radicals are geometrically stable (22). Thus, any 1,2-dibromopropene formed via bromine atom migration must be completely *trans*. The stereochemistry of the first formed 1,2-dibromopropene can be determined by reference to Fig. 2. The intercept at 0% reaction of the upper curve gives the stereochemistry of the initial product before isomerization and before any reaction of bromoallene. The result is 74% *trans*. It can be shown in another way from the data illustrated in Fig. 2 that the initial stereochemistry cannot be 100% *trans*. The lower curve in Fig. 2 shows that isomerization of the products (to 78% *trans*) is very slow under these conditions and that at reaction times of 2–5 min the stereochemistry of the 1,2-dibromopropenes formed from bromoallene is about 60% *trans*. Assuming that 50% of the 1,2-dibromopropenes produced in the hydrobromination of propargyl bromide under these conditions arises via free bromoallene (a maximum amount based on the kinetic results) and the other 50% arises via a process giving 74% *trans*, then the net isomer distribution during this time should be about 67% *trans*. This agrees well with the value of 68–69% *trans* shown by the upper curve of Fig. 2. Were the other 50% to arise via a process giving 100% *trans* rather than 74% *trans*, then the net isomer distribution would be about 80% *trans* during the first 2–5 min of reaction. This is not observed. Clearly the stereochemistry of the first formed 1,2-dibromopropenes must be quite different from 100% *trans* which indicates that a bromine atom migration cannot be involved. This is not unexpected as the initial radical formed upon bromine atom migration would not be the stabilized allyl radical but one in which the odd electron is localized in an atomic p orbital which is perpendicular to the plane of the adjacent π-orbital. There is no driving force for the migration as the primary radical formed would not be expected to show stability over the initial vinyl radical.

This leaves the cage reaction as the only alternative for the ca. 50% of the reaction which does not proceed via bromoallene. The cage

reaction must be stereoselective since the initial stereochemistry of the 1,2-dibromopropene formed from bromoallene is different from that of the 1,2-dibromopropene formed from propargyl bromide. Loss of a bromine atom from the 1,3-dibromo-2-propenyl radical must occur from a conformation in which the carbon–bromine bond that is breaking is parallel to the orbital containing the odd electron. The conformation of lower energy is shown in Fig. 5. The other conformation in which the bromomethyl group has rotated by 180° with respect to the conformation shown is seen by inspection of Fisher–Hirschfelder–Taylor models to be severely strained due to steric interference between the bromine atoms. In fact, that conformation cannot be made with the models. When initially formed the bromoallene molecule and the bromine atom have the steric relationship shown in Fig. 5 in which the bromine atom is on the opposite side of the molecule from the bromine atom in the molecule and in the plane defined by the bromomethylene group. Radical A, formed by recombination of the bromine atom with the p orbital in the plane of the bromomethylene group on the side opposite to the bound bromine, will give the *trans*-1,2-dibromopropenyl radical upon rotation of the methylene group and will finally give *trans*-1,2-dibromopropene. Reaction at the same orbital at the side *cis* to the bound bromine will give radical C which will then give the *cis*-1,2-dibromopropenyl radical and thus *cis*-1,2-dibromopropene. Reaction with the other p orbital will give radical B. Rotation of the bromomethylene group in either direction will give a stable allylic radical so that one would expect radical B to give approximately equal amounts of *cis*- and *trans*-1,2-dibromopropenyl radicals, and hence equal amounts of *cis*- and *trans*-1,2-dibromopropene. Since the cage recombination gives more *trans*-1,2-dibromopropene than does recombination outside the cage, the cage recombination to give radical A must compete with rotation of the bromoallene molecule with respect to its bromine atom partner. This is, then, an example of a stereoselective atom–molecule cage recombination reaction.

Relaxation times for molecular rotation of a number of small molecules in the liquid phase are near 10^{-11} s (23–25). This corresponds to the time that two particles will be confined to a solvent cage (26). It is thus reasonable that a reaction which can compete with diffusion can also compete with molecular rotation. Cage recombination of radicals derived from optically active azo compounds is a stereoselective process (27).

The addition of a bromine atom to bromoallene must have a very low activation energy if it is to compete with diffusion and molecular rotation. It has been suggested that the addition of a bromine atom to allene requires little or no activation energy (28). The energetic requirements for the bromine atom – bromoallene addition reaction are expected to be very similar. An atom–molecule cage recombination appears to occur in the radical chlorination of *t*-butyl bromide by *t*-butyl hypochlorite (29).

In an excellent study of the radical hydrobromination of allene it was shown that bromine atoms add to the terminal and central carbon atoms of allene at equal rates, and that the radical resulting from addition to the central carbon has a longer lifetime with respect to loss of the bromine atom than the radical resulting from terminal addition (28). As a result only products resulting from an initial addition of a bromine atom at the central carbon of allene are isolated when the concentration of hydrogen bromide is low or at high temperatures (30–32), while products resulting from initial addition at the terminal carbon are observed only at high hydrogen bromide concentrations and lower temperatures. It was suggested that a bromine-bridged radical was not required to account for these results (28). The results of the present study are in complete agreement with these conclusions, and provide stereochemical evidence against the intervention of bromine-bridged radicals in allenic systems.

The significance of the results obtained in the present study with respect to other systems in which bromine-bridged radicals or bromine atom migrations have been postulated (6–8, 33–35) is unclear. As was pointed out above there appears to be little, if any, driving force for bromine atom migration in the 1,3-dibromo-2-propenyl radical. In most of the other systems migration would lead directly to a more stable radical. Also, in the present system the orbital bearing the odd electron is directed more away from the adjacent carbon–bromine bond than is the case in a saturated system, Fig. 6. Both factors would make either bridging or migration in the 1,3-dibromo-2-propenyl radical less favorable than in the saturated systems. Thus, although the present

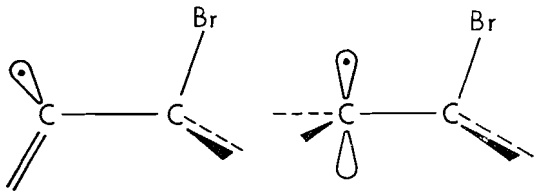


FIG. 6. Geometry of the 3-bromo-2-propenyl and the 1-bromo-2-propyl radicals.

study provides additional evidence that the loss of a bromine atom adjacent to a radical center is very rapid (17, 29) and that recombination at a different carbon atom is very rapid, the present system does not serve as a good model for an analogous process in the saturated systems.

The ratio of terminal to center addition of a bromine atom to bromoallene observed in liquid hydrogen bromide in this study, 1:3, differs from the ratio of 1:1 to be expected from the limiting ratio found in the case of allene (28). It is difficult to tell if the difference is significant as no effort was made in the present study to determine whether the ratio found was the limiting ratio.

Gas Phase Reactions

The gas phase hydrobromination of propargyl bromide was also briefly studied in an attempt to confirm that a considerable amount of the bromoallene formed in solution from propargyl bromide is consumed by a cage recombination reaction. There can be no cage reaction in the gas phase and in the absence of bromine atom migration; all the 1,2-dibromopropene formed should result from free bromoallene. If bromine atom migration is occurring in solution it should also occur in the gas phase, and there would be, as in solution, two routes to 1,2-dibromopropene. Reactions were carried out in an oxygen-free system at room temperature under illumination. All the reactions had an inhibition period of ca. 5 min. No reaction was observed in the dark. In contrast to the reactions in solution, bromoallene was always formed much more rapidly than was 1,2-dibromopropene. The isomer composition of the 1,2-dibromopropene formed initially is ca. 54% *trans*, Fig. 7. Isomerization is rapid and the equilibrated mixture was present after only 2.6% 1,2-dibromopropene had been formed. About 35% bromoallene was present by this time. No structurally isomeric dibromopropenes were detected at these amounts of conversions. At higher conversions a thin film

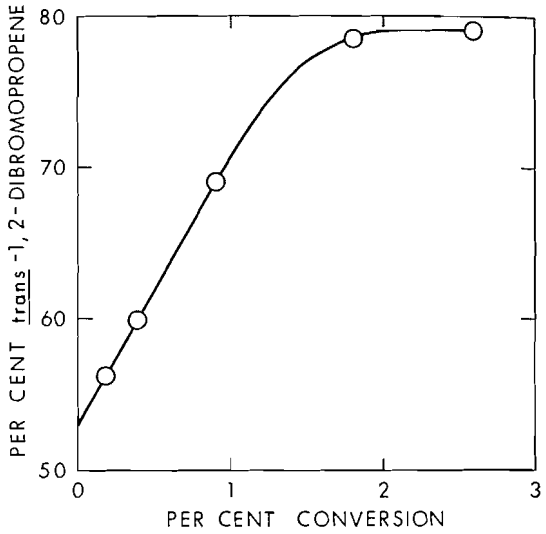


FIG. 7. Variation of isomer composition of 1,2-dibromopropene with conversion in the gas phase hydrobromination of propargyl bromide at 25°.

deposited on the walls of the reaction vessel so the reaction was not investigated at higher conversions. The stereochemistry of the 1,2-dibromopropenes formed is quite similar to that found from hydrobromination of bromoallene in solution. This indicates that in the gas phase the 1,2-dibromopropenes are formed entirely from free bromoallene and that bromine atom migration is unimportant.

A recent report describes the equilibration of propargyl bromide and bromoallene catalyzed by hydrogen bromide under illumination at 135–200° (36). Equilibrium could be reached starting with either component and propargyl bromide was found to be more stable than bromoallene by 0.83 kcal at 400 °K. No more than traces of propargyl bromide were observed in any of the radical hydrobrominations of bromoallene in solution in the present study, even though at 25° the equilibrium mixture should consist of about 80% propargyl bromide. The route to propargyl bromide from bromoallene would be the reverse of reaction [3] followed by the reverse of reaction [2]. That this process does not occur at 25° indicates that the activation energy for the loss of the vinyl bromine atom from the 1,3-dibromo-2-propenyl radical to give propargyl bromide, reaction [2], is significantly greater than is that for loss of the allylic bromine atom to give bromoallene, reaction [3]. This is

[18–19] $$H{-}C{\equiv}C{-}CH_2Br + Br\cdot \rightleftarrows HBr + \begin{matrix} H{-}C{\equiv}C\dot{C}HBr \\ \updownarrow \\ HC{=}C{=}CHBr \end{matrix} \rightleftarrows Br\cdot + H_2C{=}C{=}CHBr$$

to be expected as aryl bromides, and, therefore, quite probably, vinyl bromides, have much stronger carbon bromine bonds than do allylic bromides (37).

The mechanism proposed for the propargyl bromide–bromoallene equilibration (36) consists of reversible hydrogen atom abstractions by bromine atoms, reactions [18–19]. From the results of the present study it is clear that propargyl bromide can be converted to bromoallene simply by addition and subsequent elimination of bromine atoms, reactions [2] and [3]. These steps should be reversible at the temperatures used in the equilibration studies (36) and such a reversible addition–elimination sequence surely contributes significantly to the equilibration process and may well account for almost all the equilibration.

Hydrogen chloride was also reported to catalyze the equilibration and a reversible hydrogen abstraction reaction by chlorine atoms was invoked to account for it. However, an addition–elimination sequence probably contributes in this case also. Such a sequence would initially produce chloroallene and bromine atoms, reactions [20] and [21]. After only a few per cent conversion to chloroallene there would be enough bromine atoms produced, so that they would then become the exclusive chain carriers.

Experimental

Boiling points are uncorrected values. Infrared (i.r.) spectra were recorded on a Perkin–Elmer recording infrared spectrophotometer, model 421, equipped with sodium chloride optics. Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian analytical spectrophotometer, Model A-60. Tetramethylsilane was used as internal standard.

Analytical gas–liquid chromatography (g.l.c.) was carried out with an Aerograph 202 fractometer using a 9.5 ft × 1/4 in. stainless steel column packed with 10% Ucon-50-HB5100 (Polyglycol) on Chromosorb W. For preparative g.l.c. an Aerograph Autoprep equipped with a 20 ft × 3/8 in. stainless steel column packed with 10% Ucon-50-HB280X (Polyglycol) on Diaport W.A.W. was used. The order of elution was the same on both columns and was bromoallene, propargyl bromide, *trans*-1,2-dibromopropene, *cis*-1,2-dibromopropene, 2,3-dibromopropene, *cis*-1,3-dibromopropene, and *trans*-1,3-dibromopropene. Heptane was used as internal standard. Areas were measured by peak height × width at half-peak height. Controls using authentic mixtures showed that the thermal response factors of all the above materials were within 2% of the internal standard and no corrections were applied.

Reactions carried out under irradiation were irradiated with a General Electric sun lamp. Solutions were dried with anhydrous magnesium sulfate. Matheson 99.8% hydrogen bromide was used without further purification.

Pentane was purified by shaking 500 ml technical grade material with 50 ml portions of concentrated sulfuric acid until the sulfuric acid layer remained colorless. The pentane was then shaken several times with water, dried, and distilled through a 40 cm vigreaux column. Heptane was purified in the same manner.

Diethyl ether used as solvent for photoinitiated hydrobrominations was purified in the following way. Mallinckrodt absolute reagent grade material was distilled, anhydrous hydrogen bromide added to the distillate, and the resulting solution irradiated for 1 h. The ether was then washed with saturated salt solution until the aqueous layer was neutral, dried, distilled, and stored over sodium. Photoinitiated hydrobrominations in ether which was not purified in this manner had very long induction periods and produced impurities which interfered with product analysis by g.l.c.

Propargyl bromide was prepared according to the method of Jacobs and Brill (38), b.p. 79° (695 mm), n_D^{25} 1.4906; reported b.p. 81.8° (750 mm), n_D^{20} 1.4929 (38). This material always contained less than 0.5% bromoallene according to g.l.c. analysis.

Bromoallene was prepared according to a modification of the method of Jacobs and Brill (38). The crude product

[20] $$Cl\cdot + H{-}C{\equiv}C{-}CH_2Br \rightarrow \begin{matrix} Cl & & CH_2Br \\ & C{=}\dot{C} & \\ & H & \end{matrix}$$

[21] $$\begin{matrix} Cl & & CH_2Br \\ & C{=}\dot{C} & \\ & H & \end{matrix} \rightarrow \begin{matrix} Cl & & \\ & C{=}C{=}CH_2 & \\ & H & \end{matrix} + Br\cdot$$

was purified by preparative g.l.c. to give material containing less than 0.5% propargyl bromide, n_D^{25} 1.5182, reported n_D^{20} 1.5200 (38).

Hydrobromination Reactions at Room Temperature

Reactions in pentane were carried out by bubbling hydrogen bromide through a stirred solution of 5 g propargyl bromide or bromoallene and 5 g heptane in 20 ml pentane in a 3-necked round bottomed flask fitted with a dry ice condenser. Peroxide-initiated runs were carried out using 0.5 g benzoyl peroxide as additive. Dark reactions were carried out in a darkened hood in apparatus wrapped with aluminium foil. Before g.l.c. analysis the reaction mixtures were poured into ice water. The organic layer was washed twice more with ice water, once with sodium bicarbonate solution, and dried. Results are summarized in Table I.

Ionic reactions in ether were carried out in the dark by adding 0.6 g propargyl bromide or bromoallene to 10 ml of an ether solution saturated with hydrogen bromide and containing 0.5 g of hydroquinone and/or 0.5 g ferrous chloride. Before analysis, solutions were freed from hydrogen bromide as described for the reactions in pentane.

Free radical reactions in ether were carried out in a 3-necked flask attached to a vacuum line using as solvent ether purified as described above. The system was purged with nitrogen by several cycles of evacuating and filling with purified nitrogen before each run. Ether and hydrogen bromide which had been stored under nitrogen were distilled into the flask. Propargyl bromide or bromoallene were introduced through a serum cap with a hypodermic syringe and the solution was irradiated. The reactions had induction periods of 1–2 min and were complete in about 1 h. Samples were withdrawn through the serum cap periodically, freed of hydrogen bromide as described above, and analyzed.

One run was carried out in ether solution at −20° with propargyl bromide. The product distribution was the same as in the runs carried out at room temperature. Homogeneous hydrobrominations of propargyl bromide at −78° in pentane and ether solution could not be carried out. When propargyl bromide was added to a solution of hydrogen bromide in pentane at −78° a white precipitate formed immediately. This presumably was a complex of hydrogen bromide and propargyl bromide (39). A 1 *M* solution of hydrogen bromide in ether formed white crystals on cooling to −40°.

Hydrobromination Reactions in Liquid Hydrogen Bromide

A 10 ml pear-shaped flask was charged with 0.83 g (0.01 *M*) hydrogen bromide and 1.25 g (0.01 *M*) propargyl bromide. A homogeneous solution formed. The solution was degassed with two freeze–thaw cycles, −195° to −78°, before irradiation. The flask was then irradiated from 20 cm while immersed in a bath at −78°. After irradiation the flask was evacuated and the contents distilled twice from flask to flask under 2 mm pressure before analysis. Extensive *cis–trans* isomerization occurred when analyses were performed without prior distillation of the reaction mixture.

Gas Phase Hydrobromination of Propargyl Bromide

Hydrogen bromide and propargyl bromide were introduced into a 200 ml evacuated flask to partial pressures of 34 and 49 mm respectively. The contents were stirred for 5 min with a magnetic stirrer. The flask and its contents were irradiated after which a 5 ml portion of anhydrous ether was injected into the flask. The ether solution was freed of hydrogen bromide as described previously, before analysis. All the reactions had an inhibition period of ca. 5 min and formed a thin film on the wall of the flask after ca. 7 min of irradiation. Irradiations were not carried on beyond this point.

Product Identification

The products of the hydrobromination reactions were identified by comparison of their retention times on the g.l.c. column used and by comparison of n.m.r and i.r. spectra of samples collected from the effluent of the g.l.c. with those of authentic samples, with the exception of 2,3-dibromopropene.

trans-1,2-Dibromopropene was prepared by the slow addition of bromine to a solution of propyne in methylene chloride at −78°. The product was 99% *trans*-1,2-dibromopropene, b.p. 124–125° (688 mm), n_D^{25} 1.5323; reported b.p. 125.9°, $n_D^{17.4}$ 1.5369 (40). The n.m.r. spectrum (neat) showed absorption at τ 3.58 (multiplet) and τ 7.67 (doublet, J = 1.1 c.p.s.) with relative areas 1.0:3.0.

cis-1,2-Dibromopropene was prepared by isomerization of the *trans*-compound. *trans*-1,2-Dibromopropene was dissolved in pentane containing some hydrogen bromide and the solution was irradiated for 1 h. The solution was then washed several times with ice water, dried, and distilled. The fraction boiling at 45° at 18.5 mm was collected and contained 77% *trans*- and 23% *cis*-1,2-dibromopropene. A sample of the *cis*-isomer was collected by preparative g.l.c., b.p. 133–134° (688 mm), n_D^{25} 1.5290; reported b.p. 135.2°, $n_D^{17.4}$ 1.5337 (40). The n.m.r. spectrum (neat) showed absorption τ 3.91 (multiplet) and τ 7.66 (doublet, J = 1.1 c.p.s.) with relative areas of 1.0:3.0.

A mixture of *cis*- and *trans*-1,3-dibromopropene prepared by the method of Hatch (1) was separated into the two components by g.l.c. The n.m.r. spectrum (neat) of the *cis*-isomer, n_D^{25} 1.5519, reported n_D^{25} 1.5516 (41), liquid at −78°, showed absorption at τ 3.6 (multiplet) and τ 5.95 (multiplet) with relative areas 1.0:1.0. The n.m.r. spectrum of the *trans*-isomer, n_D^{25} 1.5572, reported n_D^{25} 1.5570 (41), solid at −78°, showed absorption at τ 3.6 (multiplet) and τ 6.15 (multiplet) with relative areas of 1.0:1.1. Hatch reports that *cis*-1,3-dibromopropene is a liquid at −78° while *trans*-1,3-dibromopropene is a solid at −78° (1).

The material with retention time between those of *cis*-1,2-dibromopropene and *trans*-1,3-dibromopropene was identified only on the basis of its n.m.r. spectrum (neat) which showed absorption at τ 3.91 (multiplet), τ 4.32 (doublet, J = 2.2 c.p.s.), and τ 5.75 (doublet, J = 1.0 c.p.s.) with relative areas 1.0:1.0:2.0. The data are in agreement with those reported for 2,3-dibromopropene (42).

No evidence was obtained in any of the reactions for the formation of 3,3-dibromopropene.

Determination of cis–trans Equilibria

A stirred solution of 0.29 g of a pure isomer of dibromopropene in 125 ml pentane was irradiated while a very slow stream of hydrogen bromide was slowly

bubbled into the solution. Aliquots were withdrawn periodically and analyzed directly by g.l.c. Irradiation was continued until there was no further change in isomer composition.

Acknowledgments

We wish to thank Professors D. Darwish and D. D. Tanner for helpful discussions.

1. L. F. HATCH and K. HARWELL. J. Am. Chem. Soc. **75**, 6002 (1953).
2. M. R. LESPIEAU. Ann. chim. et phys. [7] **11**, 232 (1897).
3. F. STITZ. Öester. Chemiker Zg. **48**, 186 (1947).
4. P. L. HARRIS and J. C. SMITH. J. Chem. Soc. 1572 (1935).
5. C. A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND. J. Am. Chem. Soc. **58**, 1807 (1936).
6. P. S. SKELL and R. G. ALLEN. J. Am. Chem. Soc. **80**, 5997 (1958).
7. P. S. SKELL, R. G. ALLEN, and N. D. GILMOUR. J. Am. Chem. Soc. **83**, 504 (1961).
8. P. S. SKELL, D. L. TULEEN, and P. D. READIO. J. Am. Chem. Soc. **85**, 2849 (1963).
9. H. L. GOERING, P. I. ABELL, and B. F. AYCOCK. J. Am. Chem. Soc. **74**, 3588 (1952).
10. H. L. GOERING and L. L. SIMS. J. Am. Chem. Soc. **77**, 3465 (1955).
11. H. L. GOERING and D. W. LARSEN. J. Am. Chem. Soc. **81**, 5937 (1959).
12. P. S. SKELL and R. G. ALLEN. J. Am. Chem. Soc. **81**, 5883 (1959).
13. P. I. ABELL and C. CHIAO. J. Am. Chem. Soc. **82**, 3610 (1960).
14. N. A. LEBEL. J. Am. Chem. Soc. **82**, 623 (1960).
15. L. D. BERGEL'SON. Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk, 887 (1960); Chem. Abstr. **57**, 24334*g* (1962).
16. L. D. BERGEL'SON. Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk, 1499 (1958); Chem. Abstr. **53**, 7969*f* (1959).
17. H. STEINMETZ and R. M. NOYES. J. Am. Chem. Soc. **74**, 4141 (1952).
18. E. R. BOEDEKER and C. C. LYNCH. J. Am. Chem. Soc. **72**, 3234 (1950).
19. P. S. SKELL and P. FREEMAN. J. Org. Chem. **29**, 2524 (1964).
20. A. L. NELSON, K. W. FOLLEY, and M. CORAL. Differential equations. D. C. Heath and Co., Boston, Massachusetts. 1952. p. 39.
21. W. G. MCMILLAN. J. Am. Chem. Soc. **79**, 4838 (1957).
22. C. WALLING and W. THALER. J. Am. Chem. Soc. **83**, 3877 (1961).
23. W. P. PURALL, K. FISH, and C. P. SMYTH. J. Am. Chem. Soc. **82**, 6299 (1960).
24. A. J. CURTIS, P. L. MCGEER, G. B. RATHMAN, and C. P. SMYTH. J. Am. Chem. Soc. **74**, 644 (1952).
25. K. HIGASI, K. BERGMANN, and C. P. SMYTH. J. Phys. Chem. **64**, 880 (1960).
26. R. M. NOYES. J. Am. Chem. Soc. **77**, 2042 (1955).
27. (*a*) K. R. KOPECKY, T. GILLAN, and T. W. MOJELSKI. 51st Ann. Conf. Chemical Institute of Canada, Vancouver, British Columbia. June, 1968. Abstracts. p.57. (*b*) F. D. GREENE and M. A. BERWICK. 156th Meeting of the American Chemical Society, Atlantic City. September, 1968. Abstracts. ORGN, No. 112.
28. E. I. HEIBA and W. O. HAAG. J. Org. Chem. **31**, 3815 (1966).
29. W. D. HAAG and E. I. HEIBA. Tetrahedron Letters, 3683 (1965).
30. D. KOVACHIC and L. C. LEITCH. Can. J. Chem. **39**, 3636 (1961).
31. K. GRIESBAUM, A. A. OSWALD, and D. M. HALL. J. Org. Chem. **29**, 2404 (1964).
32. P. I. ABELL and R. S. ANDERSON. Tetrahedron Letters, 3727 (1964).
33. P. S. JUNEJA and E. M. HODNETT. J. Am. Chem. Soc. **89**, 5685 (1967).
34. W. THALER. J. Am. Chem. Soc. **85**, 2607 (1963).
35. P. S. SKELL and P. D. READIO. J. Am. Chem. Soc. **86**, 3334 (1964).
36. H. G. MEUNIER and P. I. ABELL. Tetrahedron Letters, 3633 (1967).
37. T. L. COTTRELL. The strengths of chemical bonds. 2nd ed. Butterworths, London. 1958. p. 205.
38. T. L. JACOBS and W. F. BRILL. J. Am. Chem. Soc., **75**, 1314 (1953).
39. O. MAAS and J. RUSSELL. J. Am. Chem. Soc. **43**, 1227 (1921).
40. H. VAN RISSEGHEM. Bl. Soc. Chim. Belg. **28**, 379 (1919).
41. A. T. BOTTINI, B. J. KING, and J. M. SNEAS. J. Org. Chem. **27**, 3688 (1962).
42. F. B. WHIPPLE, J. H. GOLDSTEIN, and G. R. MCCLURE. J. Am. Chem. Soc. **82**, 3811 (1960).