The Reaction of Bromine with Disubstituted Terminal Olefins. Hydrogen Bromide Catalyzed Isomerization of Olefins[1a]

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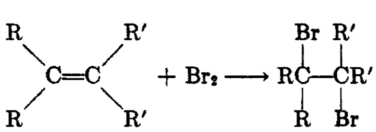
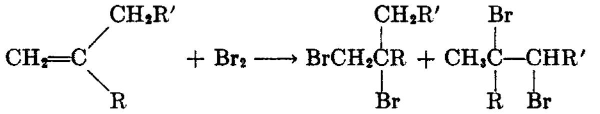
The addition of bromine to disubstituted terminal olefins in methylene chloride at 0° is shown to give 2,3-dibromides in addition to the expected 1,2-dibromides. The reaction is further complicated by the formation of appreciable amounts of monobromide and tribromide. The reaction is not appreciably affected by light, oxygen, peroxides, or inhibitors, but is markedly altered by changes in temperature and solvent and the presence of a soluble base such as pyridine. It is shown that allylic substitution competes with bromine addition and that the hydrogen bromide so formed rapidly isomerizes the terminal olefin to internal olefins which then add bromine to produce 2,3-dibromides.

The reaction of bromine with olefins has been known since the isolation of the element in 1826[2] and is universally acknowledged to follow the path summarized in eq 1. Exceptions to the general rule of 1,2 addition to an isolated carbon–carbon double bond are found with olefins which are prone to undergo molecular rearrangement. For example, cyclodecene[3] gives a low yield of the transannular product, 1,5-dibromocyclodecane, while camphene[4] and norbornenes[5] afford 2,10-dibromocamphane and 2,7-dibromonorbornane, respectively. In this communication we report another type of anamolous reaction, namely, the addition of bromine to disubstituted terminal olefins in methylene chloride or chloroform at 0° to yield 2,3-dibromides as well as the expected 1,2-dibromides (eq 2).

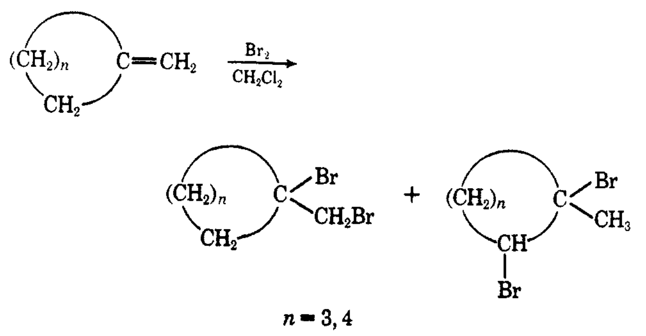


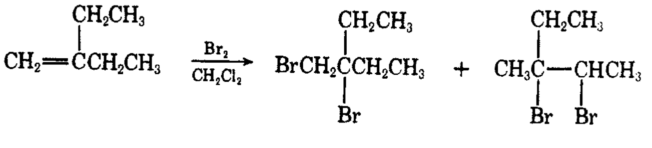
$$\mathrm{R_2C{=}CR'_2 + Br_2 \longrightarrow R\underset{R}{\overset{Br}{C}}-\underset{Br}{\overset{R'}{C}}R'} \qquad (1)$$



$$\mathrm{CH_2{=}C(CH_2R')(R) + Br_2 \longrightarrow BrCH_2\underset{Br}{\overset{CH_2R'}{C}}R + CH_3\underset{R}{\overset{Br}{C}}-\underset{Br}{C}HR'} \qquad (2)$$

The addition of bromine to methylenecyclopentane in methylene chloride at 0° gives 1,2-dibromo-1-methylcyclopentane and only a small amount of the expected 1-bromo-1-bromomethylcyclopentane, while methylenecyclohexane affords a dibromide fraction which contains, according to nmr analysis,[6] 32% 1,2-dibromo-1-methylcyclohexane and 68% 1-bromo-1-bromomethylcyclohexane.[7] Similar results were observed with 2-ethyl-1-butene and 2-ethyl-1-hexene.[8] Substantial and sometimes predominant amounts of monobromide and tribromide fractions are isolated from each of these olefins. A detailed study of the addition of bromine to 2-ethyl-1-hexene (vpc pure) has been carried out. Gas phase chromatography using a SF-96 temperature programmed column was employed to isolate and analyze the products. Each vpc peak was collected and characterized by nmr spectroscopy. The array of products formed in this reaction is shown in Chart I.





$$\mathrm{CH_2{=}\overset{CH_2CH_3}{C}CH_2CH_3 \xrightarrow[CH_2Cl_2]{Br_2} BrCH_2\underset{Br}{\overset{CH_2CH_3}{C}}CH_2CH_3 + CH_3\underset{Br}{\overset{CH_2CH_3}{C}}-\underset{Br}{C}HCH_3}$$

The addition of 1.25 equiv of bromine to 2-ethyl-1-hexene in methylene chloride at 0° was examined under a variety of conditions, and as shown in Table I is not markedly altered by the presence or absence of oxygen, light, an inert nitrogen atmosphere, peroxides, or an inhibitor such as *m*-dinitrobenzene. The composition of the dibromide fraction also remains relatively constant and is comprised of almost equal parts of the "normal" dibromide III and a mixture of the two "abnormal" dibromides IV and V.

A significant change in the composition of the mono- and dibromide fractions is observed when the bromine addition is conducted in solvents of differing polarity (see Table II). When the reaction is conducted without solvent or in nonpolar solvents such as pentane, 1-bromo-2-ethylhexane (VIII), produced by anti-Markovnikov addition of HBr to 2-ethyl-1-hexene, was the predominant monobromide. The formation of this compound became less important and was replaced by bromide I as solvent polarity increased and VIII was not observed in methylene chloride, ethyl acetate or acetic acid.

Allylic bromides IIa–IId were found in 13–18% yield when cyclohexane, methylene chloride or acetic acid were used as solvents. Only trace amounts were discerned with ethyl acetate and benzene and none when the addition was conducted without solvent or in pentane. The vpc peaks for the allylic bromides are quite broad and it is possible that small amounts escaped detection in the latter cases.

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[1] (a) Preliminary report presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract 1S. (b) Gulf Oil Fellow, 1963–1964.

[2] A. J. Ballard, *Ann. Chim. Phys.*, [2] **32**, 337 (1826).

[3] J. Sicher, J. Zavada, M. Svoboda, *Collect. Czech. Chem. Commun.*, **27**, 1927 (1962).

[4] *Cf.* J. Wolinsky, *J. Org. Chem.*, **26**, 704 (1961).

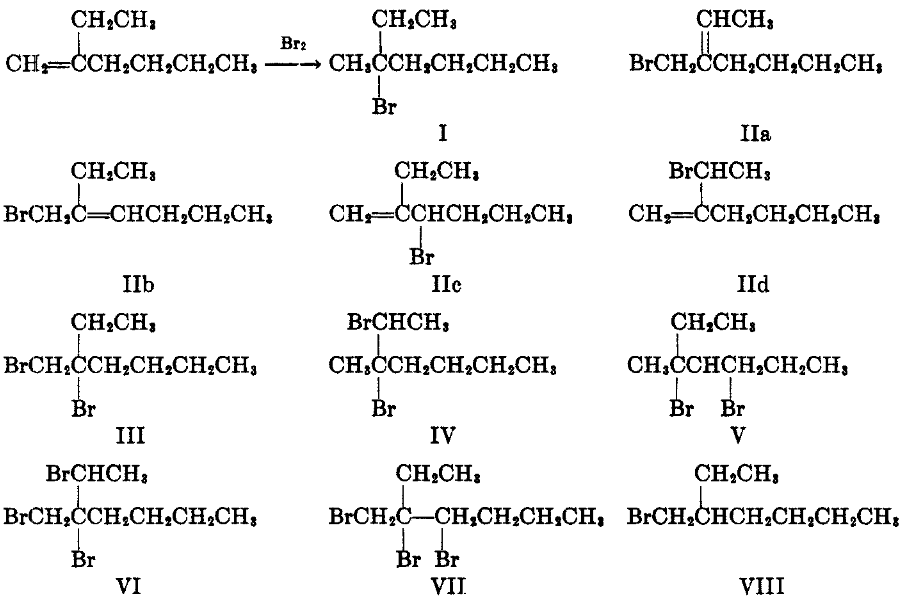
[5] H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

[6] 1-Bromo-1-bromomethylcyclohexane displays a sharp singlet at δ 3.38 ppm, whereas 1,2-dibromo-1-methylcyclohexane exhibits a triplet centered at 4.60 ppm.

[7] J. Wolinsky and K. L. Erickson, *J. Org. Chem.*, **30**, 2208 (1965).

[8] J. Privett, M. S. Thesis, Purdue University, 1962.

CHART I



The most dramatic effect on product composition brought about by a change in solvent concerned the make-up of the dibromide fraction (see Table III). In solvents of very low or very high polarity the normal dibromide III was the major or exclusive product. In solvents of intermediate polarity, such as methylene chloride and chloroform, the abnormal dibromides IV and V prevailed. Inverse addition of olefin to bromine in methylene chloride reduced the amount of abnormal dibromides IV and V from *ca.* 61 to 25% of the dibromide mixture. The change in ratio of dibromides when washed and unwashed chloroform was used can undoubtedly be attributed to the presence of 0.75% ethanol as a stabilizer in the unwashed solvent.

The amount of "abnormal dibromide" is substantially reduced when the addition of bromine is conducted at lower temperature as seen from a study with methylenecyclohexane shown in Table IV.

The most striking change is observed when the addition is conducted in methylene chloride in the presence of a soluble base such as pyridine. The monobromide fraction appears to be eliminated and only a small amount of tribromide fraction is formed. In general the dibromide can be isolated in 70–85% yield and in all cases examined to date is completely free of "abnormal" dibromides. As a preparative method for vicinal dibromides, the addition of bromine to disubstituted olefins in methylene chloride containing *ca.* 0.5 equiv of pyridine is highly recommended.

Turning next to the origin of the "abnormal" dibromides, it was shown that 1,2-dibromo-2-ethylhexane is stable to hydrogen bromide or a hydrogen

TABLE I

ADDITION OF BROMINE TO 2-ETHYL-1-HEXENE IN METHYLENE CHLORIDE AT 0°

Conditions	% monobromide I	% allylic bromides IIa–IId	% dibromides III, IV, and V	% tribromides VI and VII
Diffuse light, air	23.7	13.0	31.0	30.0
Diffuse light, oxygen	26.7	7.8	30.0	24.6
Diffuse light, air, MDB[a]	20.3	3.2	34.2	27.3
Dark, nitrogen	18.6	11.8	31.8	24.7
Dark, oxygen	32.0	5.8	30.0	38.3

[a] *m*-Dinitrobenzene.

TABLE II

THE ADDITION OF BROMINE TO 2-ETHYL-1-HEXENE IN VARIOUS SOLVENTS AT 0–5°

Solvent	% monobromide I	% monobromide VIII	% allylic bromides IIa–IId	% dibromides III, IV, V	% tribromides VI, VII
Neat	15.9	24.8		36.4	18.7
Pentane	4.5	27.9		36.6	9.0
Benzene	13.8	6.2		30.8	27.8
CH_2Cl_2	23.7		13.0	31.0	30.0
Ethyl acetate	9.8			41.4	9.4
Acetic acid	17.0		14.7	48.9	Trace
DMF				75[a]	

[a] The normal dibromide III was the only dibromide in this fraction. The dibromide was contaminated with at least two formate esters, the first appeared to be identical with 3-methyl-3-heptyl formate and the second showed an nmr spectrum consistent with its formulation as 3-bromomethyl-3-heptyl formate. These minor products most likely result from DMF participation during the bromine addition.

TABLE III

COMPOSITION OF THE DIBROMIDE FRACTION FROM THE ADDITION OF BROMINE TO 2-ETHYL-1-HEXENE IN VARIOUS SOLVENTS

Solvent	% "normal" dibromide III	% "abnormal" dibromides IV and V
Neat	100	0
Pentane	100	0
CCl_4	88	12
Benzene	76	24
Chloroform[a]	86	14
Chloroform (washed)[b]	42	58
Methylene chloride	39	61
Methylene chloride inverse addition	73	27
Ethyl acetate	83	17
Acetic acid	90	10
Ethanol	100	0
Dimethylformamide	100	0

[a] Analytical grade chloroform containing 0.75% ethanol. [b] Chloroform washed with concentrated sulfuric acid, water dried and distilled.

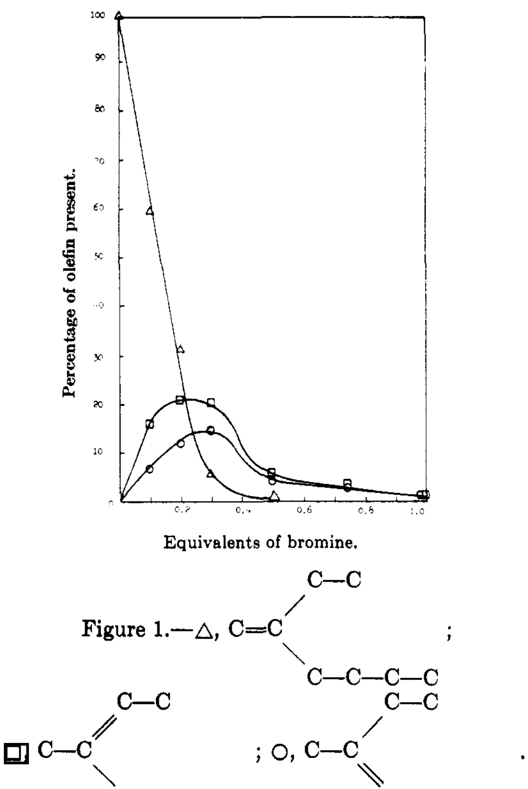


Figure 1.—△, ; □, ; ○, .

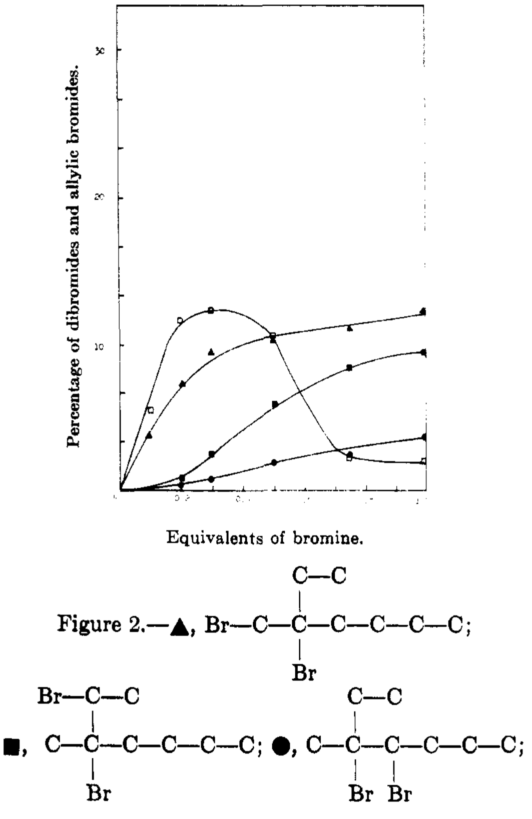
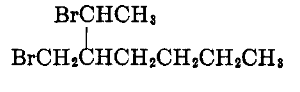


Figure 2.—▲, $Br—C—\overset{C—C}{\underset{Br}{C}}—C—C—C—C$; ■, $C—\overset{Br—C—C}{\underset{Br}{C}}—C—C—C—C$; ●, $C—\overset{C—C}{\underset{Br}{C}}—\underset{Br}{C}—C—C—C$; □, allylic bromides.

bromide–bromine mixture. 3-Bromo-3-methylheptane (I) did not react with bromine at an appreciable rate.[9] These observations rule out the possibility of IV and V forming *via* rearrangement of dibromide III or bromination of bromide I.

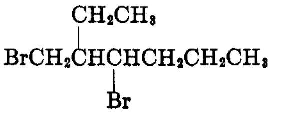
Another path to IV and V visualizes allylic substitution[10] followed by ionic addition of hydrogen bromide to the resulting allylic bromides. An allylic bromide mixture[11] was prepared by heating 2-ethyl-1-hexene with N-bromosuccinimide. This mixture could be partially separated into three fractions by glpc. The nmr spectra suggested fraction A was composed of IIc and IId, fraction B was IIb and fraction C was IIa.

Hydrogen bromide was passed into a methylene chloride solution of the allylic bromide mixture and after isolation the dibromide fraction showed five vpc peaks. The first three peaks exhibited retention times identical with III, IV, and V. The last two were collected and on the basis of nmr analysis were assigned structures IX and X, that is dibromides arising from the free radical addition of HBr[12] to the allylic bromides. No traces of IX or X were found among the products of the bromine addition to 2-ethyl-1-hexene, nor were these bromides produced when the bromine addition was carried out in the presence of free radical initiators such as benzoyl peroxide, *t*-butyl peroxide or *t*-butyl hydroperoxide.



$BrCH_2\overset{BrCHCH_3}{C}HCH_2CH_2CH_2CH_3$

IX



$BrCH_2\overset{CH_2CH_3}{C}H\underset{Br}{C}HCH_2CH_2CH_3$

X

A competitive experiment involving the addition of a limited amount of hydrogen bromide to a mixture of 2-ethyl-1-hexene and the allylic bromides IIa–d demonstrated that the olefin is consumed before the allylic bromides are attacked. The possibility of hydrogen bromide addition to allylic bromides II as an important path to dibromides IV and V during bromine addition to 2-ethyl-1-hexene can be discarded since this addition occurs too slowly and leads to dibromides which are not observed in the bromination reaction.

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(9) G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.*, **77**, 4025 (1955).

(10) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961); R. T. Arnold and W. W. Lee, *J. Amer. Chem. Soc.*, **75**, 5396 (1953).

(11) For the isomerization of allylic bromides see S. Winstein and W. G. Young, *J. Amer. Chem. Soc.*, **58**, 104 (1936); H. Van Risseghem and D. Gredy, *C. R. Acad. Sci., Paris*, **202**, 489 (1936); I. E. Muskat and H. E. Northrup, *J. Amer. Chem. Soc.*, **52**, 4043 (1930); W. G. Young and J. F. Lane, *ibid.*, **59**, 205 (1937); M. S. Kharasch, E. T. Margolis, and F. R. Mayo, *J. Org. Chem.*, **1**, 393 (1936).

(12) M. S. Kharasch and F. R. Mayo, *J. Amer. Chem. Soc.*, **55**, 2468 (1933).

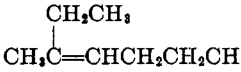
TABLE IV

ADDITION OF BROMINE TO METHYLENECYCLOHEXANE

Temp, °C	Base present	1-Bromo-1-bromomethylcyclohexane	1,2-Dibromo-1-methylcyclohexane
0	None	62	38
0	$NaHCO_3$	72	28
0	Pyridine	100	0
−78	None	90	10

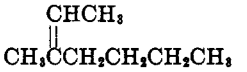
An important clue to the pathway for formation of dibromides IV and V was provided by following the bromine addition to 2-ethyl-1-hexene by vapor phase chromatography (see Figures 1 and 2). At the outset dibromide III is formed and only after an appreciable quantity of bromine has been added (0.2–0.3 equiv) is the formation of dibromides IV and V noted. Allylic bromides IIa–d are formed somewhat more rapidly than dibromide III at the initial stages of the addition. The amount of allylic bromide approaches a maximum by the time 0.3–0.4 equiv of bromine has been added and thereafter falls off as it is converted into tribromide.

Analysis of the unreacted olefin revealed that 2-ethyl-1-hexene disappears rapidly and by the time 0.5 equiv of bromine has been added only traces remain. Rearranged olefins XI and XII are detected soon after the addition starts, rising to a maximum by the time 0.3–0.4 equiv of bromine has been added, and then falling off during the latter stages of addition.



$\mathrm{CH_3\overset{\overset{CH_2CH_3}{|}}{C}{=}CHCH_2CH_2CH_3}$

XI



$\mathrm{CH_3\overset{\overset{CHCH_3}{\|}}{C}CH_2CH_2CH_2CH_3}$

XII

It is clear that allylic bromination competes with bromine addition throughout the course of the reaction, and, in particular, occurs more rapidly at the initial stages. Hydrogen bromide produced by the substitution reaction converts the terminal olefin into the more thermodynamically stable internal olefins XI and XII. Normal bromine addition to XI and XII then produces dibromides IV and V.

It was independently established that hydrogen bromide in methylene chloride rapidly isomerized disubstituted terminal olefins. Hydrogen bromide was bubbled through several olefins dissolved in methylene chloride and aliquots were withdrawn and analyzed for residual olefin. Ionic addition took place quite rapidly as indicated by the disappearance of olefin and formation of tertiary bromide, but most significantly was the appearance of the isomerized olefin, including XI and XII from 2 ethyl-1-hexene and 2-methyl-2-pentene from 2-methyl-1-pentene. Qualitatively it was observed that the isomerization of 2-ethyl-1-hexene occurs more rapidly than 2-methyl-1-pentene, which, in turn, isomerized many times faster than 1-heptene.

Double-bond migrations in steroidal systems catalyzed by hydrogen chloride in chloroform at 0° have been known for many years[13] and vitamin A acetate has been converted into retro-vitamin A[14] with hydrogen bromide. Outside of these systems the rapid isomerization of olefins by hydrogen halides under mild conditions has not been noted. The gas phase isomerization of 1-butene by hydrogen bromide occurs above 290° and Maccoll[15] has suggested the involvement of a molecular mechanism. A bromine atom promoted rearrangement has been proposed to explain the formation of 2-butene during the gas phase photolysis of 1-butene and hydrogen bromide.[16]

Preliminary investigations have shown that the isomerization of 2-ethyl-1-hexene by hydrogen bromide in pentane is slow and that hydrogen bromide addition involves competition between a free-radical pathway to give primary bromide VIII (impeded by inhibitors) and an ionic reaction to give bromide I. In methylene chloride the isomerization is complete within 20–40 sec, while addition requires 2–3 min. Neither the isomerization nor the addition reaction is retarded by the presence of inhibitors. Investigation of the hydrogen bromide catalyzed isomerization of olefins continues and will be described in a later report.

Experimental Section[17]

The Addition of Bromine to 2-Ethyl-1-hexene. A. Methylene Chloride.—To a solution of 20 g (0.178 mol) of 2-ethyl-1-hexene[18] in 30 ml of methylene chloride maintained at 0° was added dropwise, over a 40-min period, a solution of 28.0 g (0.178 mol) of bromine in 40 ml of methylene chloride. The solvent was carefully removed and analysis of the residue using a 4-ft SF-96 column at 150° showed four large peaks with retention times of 6.75, 19, 21 and 23 min in a ratio of *ca.* 2:4:4:6, respectively. Small peaks at 8, 9.5 and 10.5 min were attributed to allyl bromides IIa–d. Temperature programming to 190° caused two more peaks, with retention times of 49 and 51 min, to appear.

Each major peak was collected and identified by analysis of its nmr spectrum. The 6.75-min peak exhibited a sharp singlet at δ 1.66 (CH_3CBr) superimposed on a complex multiplet from 1.3 to 2.0 and a three-signal pattern centered at 1.0 ppm [two superimposed (CH_3CH_2–)] suggesting its assignment as bromide I.

The 19-min peak exhibited a one-proton multiplet at δ 4.02 ($CHBrCH_2$), a quartet centered at 1.9 (J = 7 Hz, –CH_2CH_3), a singlet at 1.73 (CH_3CBr), and a triplet at 1.07 ppm (J = 7 Hz, –CH_2CH_3) allowing its formulations as dibromide V.

The 21-min peak showed a quartet at 4.39 (J = 7 Hz, –$CHBrCH_3$), a doublet methyl resonance at 1.91 (J = 7 Hz, –$CHBrCH_3$), a singlet methyl resonance at 1.79 and a triplet methyl centered at 0.98 ppm permitting its assignment as dibromide IV.

The 23-min peak displayed a sharp singlet at 3.74 (–CH_2Br) a triplet overlapping another multiplet at 1.84, complex multi-

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(13) I. M. Heilbron and F. S. Spring, *J. Chem. Soc.*, 2807 (1929); A. Windaus, K. Dithmar, H. Murke, and F. Suckfüll, *Ann.*, **488**, 91 (1931).

(14) S. Patai, "The Chemistry of Alkenes," Interscience Publishers, Inc., New York, N. Y., 1964, p 434.

(15) A. Maccoll and R. A. Ross, *J. Amer. Chem. Soc.*, **87**, 4997 (1965).

(16) P. I. Abell, *ibid.*, **88**, 1346 (1966).

(17) All boiling points are uncorrected. Nuclear magnetic resonance spectra were determined at 60 Mc on a Varian Associates A-60 spectrometer. Chemical shifts are recorded in parts per million with reference to tetramethylsilane as an internal standard. Gas chromatographic analyses and separations were performed using Aerograph A-90-O and A-90-P chromatograms. Bromides were analyzed using a 4 ft × 0.25 in. SF-96 on 60-80 firebrick column. This column was satisfactory throughout the course of most of this study. It was replaced by a fresh column after it deteriorated and failed to give reproducible results. Olefins were analyzed using a 15 ft × 0.25 in., 25% adiponitrile on Chromosorb W column. This column was occasionally checked to determine whether olefin isomerization was catalyzed by the column. Microanalyses were performed by Dr. C. S. Yeh and associates.

(18) 2-Ethyl-1-hexene was prepared by pyrolysis of 2-ethyl-1-hexylacetate and purified by fractional distillation using a Todd column, bp 120-122°. It was shown to be free of isomeric olefins by vpc.

plets between 1.3 and 1.7 and a triplet centered at 1.04 ppm ($2CH_3CH_2$–) requiring its formulation as dibromide III.

The mixture of tribromides VI and VII, 49- and 51-min peaks, exhibited complex multiplets between 4.0 and 4.5 (–$CHBrCH_2$), singlets at 3.84 and 3.9 (–CH_2Br), complex signals between 0.9 and 2.0, but a distinguishable doublet at 1.86 ppm (–$CHBrCH_3$).

Distillation of the reaction product gave 8.4 g of monobromide fraction [bp 31–46° (2 mm), $n^{24}\mathrm{D}$ 1.4601–1.4690], 21.8 g of dibromide fraction [bp 46–66° (2 mm), $n^{24}\mathrm{D}$ 1.4971–1.5061], and 14.9 g of distillate which was largely tribromide ($n^{24}\mathrm{D}$ 1.5430). Vpc analysis of these fractions indicated only those materials found in the crude reaction product.

B. Methylene Chloride under Various Conditions.—To a solution of 5 g (44.6 mmol) of 2-ethyl-1-hexene in 25 ml of methylene chloride maintained at 0° was added dropwise a solution of 9.0 g (56.2 mmol) of bromine in 20 ml of methylene chloride. The system was preflushed for 90 min in the event an oxygen atmosphere was employed and 45 min if a nitrogen atmosphere was used. The reaction mixtures were either quenched with solid sodium carbonate and the excess bromine removed with a stream of nitrogen, or quenched with aqueous sodium carbonate, washed with water and dried over anhydrous magnesium sulfate. The solvent was removed and distillation proceeded to give three fractions and a liquid residue: fraction 1, bp 40–60° (4 mm), $n^{20}\mathrm{D}$ 1.46; fraction 2, bp 60–90° (4 mm), $n^{20}\mathrm{D}$ 1.50; fraction 3, bp 90–100° (4 mm), $n^{20}\mathrm{D}$ 1.53 and residue, $n^{20}\mathrm{D}$ 1.54. The weighed fractions were individually analyzed using a 4-ft SF-96 column: fraction 1 was largely monobromide I; fraction 2 was allylic bromides IIa–d and dibromides III, IV, and V; and fraction 3 was dibromides and tribromides VI and VII; the residue was largely tribromides VI and VII. These data are collected in Table I.

C. Various Solvents.—Pentane was washed with concentrated sulfuric acid, potassium permanganate solution, and distilled using a Todd column. Chloroform was washed with water, distilled employing a Todd column, and used immediately. Ethyl acetate and methylene chloride were distilled through a Todd column. Benzene (Baker spectral grade), carbon tetrachloride (Baker spectral grade) and absolute ethanol were used without further purification. Glacial acetic acid was dried over triacetylborate and distilled. Dimethylformamide was shaken with potassium hydroxide and distilled.

Bromine was added to 2-ethyl-1-hexene in various solvents. The reaction mixtures were worked up by washing with water and adding pentane when necessary to extract the bromides. After the solvent was removed the residue was analyzed by vpc using a 4 ft SF-96 column at 140°.

When the addition was conducted without solvent or in pentane, cyclohexane, or benzene, the monobromide fraction contained a new component which was isolated by vpc. This monobromide displayed a doublet at 3.44 ($BrCH_2CH$–), a broad signal between 1.2 and 1.6 and two methyl resonances centered at 0.95 ppm leading to its assignment as bromide VIII.

D. Methylene Chloride–Pyridine.—Freshly distilled 2-ethyl-1-hexene (50 g, 0.454 mol) in methylene chloride containing 35 g of pyridine was treated at Dry Ice temperature with 72.8 g (0.455 mol) of bromine in methylene chloride. The solution was washed with sodium bisulfite solution, 5% hydrochloric acid and water. The solution was dried and distilled to give 105 g (85%) of 1,2-dibromo-2-ethylhexane (III), bp 78–79° (2 mm), $n^{19}\mathrm{D}$ 1.5033. No monobromide was isolated; however, *ca.* 10 g of distilland was left containing a small amount of pyridine hydrobromide.

E. The Course of Bromine Addition Followed by Vpc.—To an ice-cooled solution of 5.88 g (0.0577 mol) of 2-ethyl-1-hexene (freshly passed through alumina), 2.0 g of cyclohexane, and 0.5 g of *n*-dodecane[19] in 20 ml of methylene chloride was added dropwise over a 45-min period a solution of 9.85 g (0.0615 mol) of bromine in 20 ml of methylene chloride. Aliquots were periodically withdrawn as the addition proceeded and the olefin content was determined on an adiponitrile column, while the bromides were analyzed on an SF-96 column at 160°. These data are shown in Figures 1 and 2.

Addition of Bromine to Olefins. 2-Ethyl-1-butene.—To a cooled solution of 100 g (1.19 mol) of 2-ethyl-1-butene in 250 ml of chloroform was slowly added a solution of 195 g (1.22 mol) of bromine in 250 ml of chloroform. Distillation gave 209.5 g of a dibromide fraction [bp 80–90° (18 mm), $n^{19}\mathrm{D}$ 1.5063] and 60 g of tribromide [bp 120–135° (18 mm)]. The forerun and material isolated from the distillation trap amounted to *ca.* 20 g [lit. for 1,2-dibromo-2-ethylbutane, bp 80–81° (18 mm);[20] 87° (21 mm)[21]]. A redistilled sample of the dibromide fraction was submitted for analysis.

Anal. Calcd for $C_6H_{12}Br_2$: C, 29.6; H, 4.92. Found: C, 29.96; H, 5.26.

The nmr spectrum of the dibromide fraction showed a singlet at 3.80 and a quartet at 4.20 ppm which indicated the presence of a mixture of 1,2-dibromo-2-ethylbutane and 2,3-dibromo-2-ethylbutane.

2-Ethyl-1-butene in the Presence of Pyridine.—To a cooled and stirred solution of 15 g (0.179 mol) of 2-ethyl-1-butene and 12.2 g (0.155 mol) of pyridine in methylene chloride was added a methylene chloride solution of 29.8 g (0.180 mol) of bromine. The resulting solution was washed with aqueous sodium bisulfite, 5% hydrochloric acid and water. The methylene chloride layer was dried and distilled to give 31.0 g (71%) of 1,2-dibromo-2-ethylbutane: bp 64–66° (11 mm); $n^{20}\mathrm{D}$ 1.5110; nmr signals at 3.8 (s, CH_2Br), 1.93 (q, –CH_2CH_3), and 1.10 ppm (t, –CH_2CH_3).

2-Methyl-1-pentene.—To an ice cooled solution of 50.2 g (0.6 mol) of 2-methyl-1-pentene in 125 ml of chloroform was added a solution of 94.5 g (0.59 mol) of bromine in 125 ml of chloroform. Distillation gave 68 g of dibromide [bp 57–62° (3 mm); $n^{20}\mathrm{D}$ 1.5032] and 56 g which was predominantly tribromide [bp 62–80° (0.5–3.0 mm)]. A portion of the first fraction was redistilled for analysis, bp 34–35° (1.0 mm), $n^{15}\mathrm{D}$ 1.5057.

Anal. Calcd for $C_6H_{12}Br_2$: C, 29.52; H, 4.96. Found: C, 30.16; H, 5.35.

When the bromine addition to 15 g of olefin was carried out in the presence of 12.2 g of pyridine there was obtained 35 g of dibromide: bp 63–68° (11 mm); $n^{18}\mathrm{D}$ 1.5057; nmr singlet at 3.8 ($BrCH_2$), methyl singlet at 1.80 superimposed on a broad multiplet from 1.3 to 1.85, and a triplet methyl resonance centered at 1.0 ppm.

Methylenecyclohexane.—To a stirred and Dry Ice cooled mixture of 5 g of methylenecyclohexane in 25 ml of methylene chloride and 5 g of sodium bicarbonate was added dropwise a solution of 8.0 g of bromine in 25 ml of methylene chloride. The solid was removed and distillation gave a forerun [bp 37–38° (1 mm); $n^{19}\mathrm{D}$ 1.5220], 6 g [bp 78–88° (1 mm), $n^{19}\mathrm{D}$ 1.5441–1.5474], and 4 g [bp 88–90° (1 mm), $n^{19}\mathrm{D}$ 1.5503] [lit.[10] for bromomethyl-1-bromocyclohexane, bp 112° (16 mm), $n^{20}\mathrm{D}$ 1.5422]. Nmr analysis of these fractions indicated they were comprised of about 90% 1-bromomethyl-1-bromocyclohexane and 10% 1,2-dibromo-1-methylcyclohexane on the basis of the relative areas of the signals at 3.38 (s, –CH_2Br) and 4.60 ppm (t, –CHBr).

1-Methylcyclohexene.—A solution of 3.4 g (0.021 mol) of bromine in methylene chloride was added at 0° to a stirred solution of 2.0 g (0.021 mol) of 1-methylcyclohexene containing 1 equiv of sodium bicarbonate. The solid was removed and distillation gave 4.0 g of 1,2-dibromo-1-methylcyclohexane: bp 66–67° (1 mm); $n^{18}\mathrm{D}$ 1.5415; nmr signals at 4.60 (t, –$CHBrCH_2$), and 1.95 (s, $CH_3C(Br)<$) superimposed on a complex multiplet from 1.55 to 2.1 ppm.

Methylenecyclopentane.—When a solution of bromine in methylene chloride was added at 0° to a mixture of 52% of methylenecyclopentane and 1-methylcyclopentene in methylene chloride there was obtained a low-boiling fraction whose nmr spectrum showed a sharp singlet at 1.88 ppm ($CH_3C(Br)<$). The dibromide fraction distilled at 55–62° (4 mm) and was shown by nmr to be almost exclusively 1,2-dibromo-1-methylcyclopentane (doublet at 4.65 for >CHBr and singlet at 2.05 ppm for $CH_3C(Br)<$). A higher boiling fraction appeared to be largely tribromide.

When 2 g of the original olefin mixture was brominated in

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[19] Cyclohexane was added to serve as an internal standard for the analysis of the unreacted olefins. Dodecane served as an internal standard in the analysis of the bromides. Weighed amounts of each pure standard, olefin, and bromide were injected several times and peak areas were measured. These calibrations were used to correct for differences in the thermal conductivities of these compounds.

[20] H. Van Risseghem, *Bull. Soc. Chim. Fr.*, 369 (1955).

[21] C. Schmitt and C. Boord, *J. Amer. Chem. Soc.*, **54**, 760 (1932).

TABLE V

Aliquot	Time, min	% 2-ethyl-1-hexene	% internal XI	% olefins XII	% unreacted olefin
0	0	100	0	0	100
1	1	70	20	10	53
2	5	38	37	25	47
3	15	9	57	35	41
4	23	4	56	40	33

TABLE VI
HYDROGEN BROMIDE AND OLEFINS

Aliquot	Time, hr	2-Methyl-1-pentene	2-Methyl-2-pentene	% unreacted olefin
0	0	100	0	100
1	1	71	29	60
2	10	58	42	48
3	20	39	61	40
4	35	18	82	30
		1-Heptene	2-Heptene	
0	0	98	2	100
1	35	98	2	
2	180	92	8	
3	360	89	11	72

methylene chloride in the presence of 2 g of pyridine there was obtained a dibromide fraction and a small amount of residue. No monobromide was found. Nmr analysis of the dibromide indicated it contained almost equal quantities of 1-bromomethyl-1-bromocyclopentane (singlet at 3.98) and 1,2-dibromo-1-methylcyclopentane (doublet at 4.65 ppm).

Reaction of 2-Ethyl-1-hexene with N-Bromosuccinimide.—A mixture of 15.85 g (89 mmol) of N-bromosuccinimide, 0.2 g of benzoyl peroxide, 30.2 g (270 mmol) of 2-ethyl-1-hexene, and 40 ml of carbon tetrachloride was stirred and refluxed for 20 min. The mixture was cooled and filtered to yield 8.6 g (98%) of succinimide. Distillation of the filtrate afforded 11.4 g (67%) of an allylic bromide mixture, bp 50–74° (3 mm), showing vpc retention times of 8, 9.5, and 10.5 min on a 4-ft SF-96 column at 150°. These peaks were collected and identified on the basis of their nmr spectra. The first vpc peak exhibited singlets at 4.82 and 5.05 ($CH_2{=}C$), a complex triplet at 4.52 (J = 7 Hz, $={=}CCHBrCH_2{-}$), and a doublet at 1.75 ppm ($-CHBrCH_3$). The relative area of the 4.52–1.75-ppm signal is roughly 2:3 suggesting this fraction is approximately a 50:50 mixture of 2-(1-bromoethyl)-1-hexene (IIa) and 3-bromo-2-ethyl-1-hexene (IIb). The second and third vpc peaks exhibited a singlet at 4.91 characteristic of $BrCH_2C{=}$ protons. The third peak displayed a quartet centered at 5.55 and a doublet at 1.66 attributed to a vinyl methyl group, allowing its assignment as 3-bromomethyl-2-heptene (IIa). The second vpc peak was formulated as 1-bromo-2-ethyl-2-hexene (IIb).

Addition of Hydrogen Bromide to the Allylic Bromide Mixture IIa–d.—Dry hydrogen bromide gas was passed at a rate of 80 bubbles/min into a solution of 1 g of allylic bromide IIa–d and 1 g of dodecane in 15 ml of methylene chloride cooled to 0°. After 20 min 57% of the allylic bromide was unreacted. The addition was essentially complete after 63 min. Vpc analysis indicated the formation of two new dibromides, in addition to dibromides III, IV, and V. These new dibromides, retention times 26 and 29 min, were collected and identified as IX and X on the basis of their nmr spectra. The 1,2-dibromides and 1,3-dibromides were produced in a ratio of *ca.* 1:9.

Isomerization of Olefins with Hydrogen Bromide. 2-Ethyl-1-hexene.—A 100-ml three-necked flask, equipped with a Drierite drying tube, a syringe stopple and an inlet tube fitted with a bubbler and a phosphorus pentaoxide drying tower connected to a hydrogen bromide cylinder (Matheson), was preflushed with hydrogen bromide at 50 bubbles/min. A solution of 2 g of 2-ethyl-1-hexene and 1 g of cyclohexane in 20 ml of methylene chloride was charged to the flask and bubbling of hydrogen bromide was continued. Aliquots were removed at given time intervals and the unreacted olefin was analyzed using an adiponitrile column at 25° (Table V).

Olefins XI and XII were isolated by vpc and characterized by their nmr spectra. Olefin XII exhibited a complex quartet centered at 5.1 (J = 6 Hz, $C{=}CHCH_3$), a complex multiplet at 1.92 ($={=}C(CH_3)CH_2{-}$), a doublet centered at 1.53 (J = 6 Hz, $C{=}CHCH_3$) and a triplet at 0.88 ppm ($-CH_2CH_2CH_3$). Olefin XI displayed a complex triplet at 5.02 ($C{=}CHCH_2$), a singlet at 1.58 ($C{=}CCH_3$) and two triplets centered at 0.96 and 0.87 ($-CH_2CH_3$). Olefins XI and XII are most likely mixtures of *cis* and *trans* isomers which were not separated by the adiponitrile column.

2-Methyl-1-pentene and 1-Heptene.—2-Methyl-1-pentene and 1-heptene were treated with hydrogen bromide using the exact conditions described above (Table VI).

Under these conditions *β*-pinene was 50% isomerized to *α*-pinene after 3 min (Carbowax column at 130°) and all olefin was converted into bornyl bromide in 10 min.

Registry No.—Hydrogen bromide, 10035-10-6; bromine, 7726-95-6; 2-ethyl-1-hexene, 1632-16-4; 2-ethyl-1-butene, 760-21-4; 2-methyl-1-pentene, 763-29-1; methylenecyclohexane, 1192-37-6; 1-methylcyclohexene, 591-49-1; methylenecyclopentane, 1528-30-9; I, 18908-60-6; III, 18908-61-7; IV, 18908-62-8; V, 18908-63-9; VI, 18908-64-0; VII, 18908-65-1; VIII, 18908-66-2; XI, 7300-03-0; XII, 3404-75-9.