A consideration of the mechanism of the ester cleavage reaction suggests that methyl crotonate would be much more susceptible than methyl β-bromobutyrate to reaction with hydrogen bromide.

The Kinetic Studies.—For the optical rotation studies samples of the pure bromoesters were sealed in small Pyrex glass tubes. The tubes had previously been exposed for 24 hours to hot concentrated nitric acid, washed with distilled water, dried and stored in a desiccator over phosphorus pentoxide. The rate samples were immersed in the vapor of a refluxing liquid of appropriate boiling point. Substances such as water, toluene, chlorobenzene and *n*-butyl ether were used. The tubes were removed from time to time, quenched in ice water and opened. The optical rotations of the contents were determined using a 0.5-dm. micropolarimeter tube. Samples were ordinarily allowed to equilibrate to bath temperature for one hour before the first sample was withdrawn. The optical rotation of this sample was used as α_0 in the calculation of rate constants, k_{obsd}, reported in Table I.

To follow the kinetics of dehydrobromination weighed samples of the bromoesters were heated in the Pyrex tubes as described above. Tubes removed for analysis were broken in a beaker of ice-water, and the contents of the beaker were titrated with 0.1 *N* sodium hydroxide to the phenolphthalein end-point using a microburet.

The reaction tubes were again allowed to equilibrate to bath temperature for at least one hour before withdrawal of the first sample. The time of withdrawal of this sample was chosen as zero time in calculating rate constants. Analyses of samples withdrawn subsequently were corrected on the assumption that all samples underwent the same per cent. dehydrobromination during the equilibration period.

To establish that unreacted bromoester did not consume standard base under the conditions of the titration approximately 0.2 g. of the pure esters were treated with cold aqueous hydrochloric acid in amounts approximating the hydrogen bromide content of some of the rate samples. By titration with sodium hydroxide the added hydrochloric acid could be accounted for with an accuracy of ±0.5%.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Rearrangement of 2-Methylbutane-1-C^{14} over Aluminum Bromide[1,2]

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Liquid-phase rearrangement of 2-methylbutane-1-C^{14} at room temperature over water-promoted aluminum bromide appears to yield 2-methylbutane-4-C^{14} considerably more rapidly than 2-methylbutane-2(or 3)-C^{14}. Very extensive rearrangement of C^{14} was observed in the conversion of 2-methylbutane-1-C^{14} to *t*-amyl bromide by treatment with *t*-butyl bromide and aluminum bromide even with a contact time of about 0.005 sec. Photochemical vapor-phase halogenations of isopentane were found to give essentially pure *t*-amyl bromide with bromine and a serious mixture of products with chlorine.

In an earlier investigation,[3] isotope-position rearrangements of C^{14}-labeled *t*-amyl and *t*-butyl chlorides over aluminum chloride were found to proceed as would be expected on the basis of the carbonium ion theory of molecular rearrangements. The pattern of results was quite unlike that obtained in the isomerization of C^{13}-labeled butanes over water-promoted aluminum bromide[4] and it seemed possible that the discrepancy was due to differences in: (1) the behavior of halides and hydrocarbons; (2) the natures of the catalysts; (3) four- and five-carbon systems; or (4) liquid- and vapor-phase operations. The last possibility seemed very likely since, if hydrocarbon isomerizations involve carbonium ion chain mechanisms,[5] a given cation, at the surface of a solid catalyst, would have a far better chance in a vapor-phase than a liquid-phase system to undergo several isotope position rearrangements before encountering a hydrocarbon molecule and being converted to isomerized hydrocarbon and a new cation in the very rapid exchange reaction demonstrated by Bartlett, Condon and Schneider.[6] The purpose of the present research was to study the isomerization of 2-methylbutane-1-C^{14} over water-promoted aluminum bromide in liquid and vapor phases. The work has had to be indefinitely suspended and we report at this time some interesting preliminary experiments on liquid-phase systems.

2-Methylbutane-1-C^{14} (I) was synthesized from 2-methyl-2-butanol-1-C^{14} by dehydration and hydrogenation. Treatment with permanganate was employed to remove the last traces of olefin. Location of the tracer atoms in I required a route to *t*-amyl halides or trimethylethylene, either of which could be further degraded as described previously.[3] The aluminum bromide-catalyzed halogen–hydrogen exchange between *t*-butyl halides and isopentane to yield *t*-amyl bromide seemed well suited for the purpose since the reaction appears to be clean and fast.[6] However, when this type of exchange was carried out with I using a contact time of 0.2 sec. it was found that complete isotopic equilibrium was established between C-1 and C-4 of the *t*-amyl bromide (*cf.* Table I). Even with a contact time as short as *0.005 sec.*, the C^{14} was *completely* equilibrated between C-1 and C-4 and a total degradation showed some radioactivity at C-2 and C-3. The speed of these reactions compared with the rearrangements of labeled *t*-amyl chloride over aluminum chloride is probably partly due to

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(2) Presented at the Symposium on Reaction Mechanisms at the 75th Anniversary Meeting of the American Chemical Society, September 7, 1951.

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TABLE I

RADIOACTIVITY ANALYSES OF LABELED ISOPENTANE DEGRADATION PRODUCTS

Source of *t*-$C_5H_{11}Br$[a]	Glycol[b]	CHI_3 (C-1)[b]	Acetone DNPH[b,c]	Acetaldehyde dimethone[b]	CHI_3 (C-4)[b]	Activity of products[d], % C-1	C-2	C-3	C-4
C_5H_{12} (I) with C_4H_9Cl and $AlBr_3$ (0.2 sec. contact time)	.....[e]	911 ± 7	218 ± 2	...[e]	437 ± 7	56 ± 2	8 ± 3	(8 ± 3)[f]	27 ± 2
C_5H_{12} (I) with C_4H_9Br and $AlBr_3$ (~0.005 sec. contact time)	318 ± 3	480 ± 7	115 ± 3	34 ± 2	490 ± 3	59 ± 2	5 ± 3	7 ± 3	30 ± 1
C_5H_{12} (I) with Br_2 ($h\nu$)	432 ± 4	1045 ± 4	237 ± 5	4 ± 2	10 ± 3	97 ± 1	2 ± 3	3 ± 2	1 ± 1
C_5H_{12} (I) over $AlBr_3 \cdot H_2O$ followed by Br_2 ($h\nu$)	904 ± 20	1164 ± 24	302 ± 5	98 ± 2	1154 ± 20	52 ± 1	9 ± 2	13 ± 2	26 ± 1

[a] *t*-$C_5H_{11}Br$ = *t*-amyl bromide used in the degradation scheme of ref. 3. [b] Measured activities of "infinitely thick" barium carbonate precipitates in counts/min. corrected for background with standard deviations. The samples were prepared as described by J. D. Roberts, W. Bennett, E. W. Holroyd, Jr., and C. H. Fugitt, *Anal. Chem.*, **20**, 904 (1948), and counted with a windowless methane-filled proportional counter ("Nucleometer"). [c] DNPH = 2,4-dinitrophenylhydrazone. [d] Calculated from the measured activities as described in ref. 3. [e] Not obtained pure. [f] Not measured, assumed to be the same as at C-2.

the solubility of aluminum bromide in hydrocarbons and its efficacy in converting alkyl halides to carbonium ions. The only other simple procedure for production of *t*-amyl halides from labeled isopentane without rearrangement seemed to be direct halogenation. Vapor-phase photochemical chlorination was found to give an impractically small fraction of *t*-amyl chloride but the corresponding bromination was quite satisfactory and gave about a 70% yield of *t*-amyl bromide which was apparently free of isomeric bromides.[7,8] A trial degradation of I by the bromination procedure indicated no significant rearrangement (*cf.* Table I).

Liquid-phase isomerization of I over water-promoted aluminum bromide was carried out using techniques similar to those employed by Pines and Wackher.[9] Under conditions where *n*-butane would be partially isomerized to *i*-butane[9b] (approximately 1:1 mole ratio of $AlBr_3$ to H_2O with excess hydrogen bromide pumped off, room temperature, 16 hr.), it was found that the C^{14} of I was very extensively rearranged (*cf.* Table I) even though there was but little change in the appearance of the reaction mixture. Complete equilibration of C-1 and C-4 occurred and substantial activity appeared at C-2 and C-3. The apparently large difference in rate of transfer of C^{14} between C-1 and C-4 as compared to between these atoms and C-2 and C-3 corresponds to the results of our earlier experiments on isotope position rearrangements of *t*-alkyl chlorides over aluminum chloride and strengthens our belief in the applicability of the carbonium ion theory to aluminum halide-catalyzed hydrocarbon isomerizations.

Acknowledgment.—We are indebted to Miss Winifred Bennett and Mrs. Clare M. Regan for the C^{14}-analyses reported in this paper.

Experimental

2-Methylbutane-1-C^{14}.—A mixture of 15.3 g. of 2-methyl-2-butanol-1-C^{14} (prepared as previously described[3]) with 56 ml. of 18 *N* sulfuric acid contained in a flask equipped with a 10-cm. indented column was heated at 140° with an oil-bath. The effluent gases were passed through a tower packed with potassiun hydroxide pellets and then condensed in a Dry Ice-cooled trap. When the reaction was complete, the last of the product was swept into the trap with a stream of nitrogen. The yield of crude labeled 2-methylbutenes was 8.6 g. (82%).

The product was dissolved in 25 ml. of acetic acid (in a flask carrying a gas inlet tube and Dry Ice condenser) and reduced using 0.8 g. of platinum oxide as a catalyst by bubbling in hydrogen at atmospheric pressure over nine hours. The reaction flask was immersed in a water-bath at room temperature to prevent the acetic acid from freezing. The isopentane was removed from the mixture under reduced pressure, bubbled through 50% potassium hydroxide solution and condensed in a Dry Ice-cooled trap. The product was vaporized, passed through a potassium hydroxide tower, condensed and fractionated through a 20-cm. indented column. The yield of 2-methylbutane-1-C^{14} was 4.9 g. (39% based on 2-methyl-2-butanol-1-C^{14}). The material used in the isomerization experiments was refluxed for six hours over alkaline sodium permanganate, dried and distilled.

Conversion of 2-Methylbutane-1-C^{14} to *t*-Amyl Bromide by Hydrogen–Halogen Exchange.—The procedures were similar to those previously described[6] except for modifications necessitated by the fact that the labeled isopentane could not practically be used in excess. After a large number of trials with non-isotopic materials, a flow apparatus was adopted which was patterned after that of Swain and Kent.[10] In a typical experiment, a mixture of 7.0 g. (0.097 mole) of 2-methylbutane-1-C^{14}, 54 g. (0.36 mole) of *t*-butyl bromide and 15 ml. of olefin-free *n*-pentane and a solution of 21 g. (0.080 mole) of aluminum bromide in 75 ml. of olefin-free *n*-pentane were forced under nitrogen pressure through opposed orifices into vigorously stirred ice-water. The rates of flow and dimensions of the "cross-fire" were such as to give a contact time of ~ 0.005 sec. before quenching. The organic layer was separated, washed with water and dried over magnesium sulfate. Fractionation of the products gave 9.0 g. (61%) of *t*-amyl bromide, b.p. 106–108°. The bromide was degraded by the scheme described for C^{14}-labeled *t*-amyl chloride.[3]

Photochemical Bromination of 2-Methylbutane-1-C^{14}.—Bromination of 8.0 g. of 2-methylbutane-1-C^{14} was carried out in the illumination of two No. 2 Photoflood lamps at 20 cm. using the chlorination apparatus described earlier.[11] The halogen was conveyed into the reaction zone by a dry nitrogen stream bubbling through liquid bromine maintained at room temperature. The yield of *t*-amyl bromide, b.p. 105–106°, was 10.7 g. (71%). No isomeric monobromides were detected.

Photochemical chlorination of isopentane by the usual procedure[11] gave a 90% yield of mixed monochlorides, b.p. 91–96.5°. Hydrolysis of this product with boiling water[3] gave less than 1 g. of trimethylethylene.

Liquid-phase Isomerization of 2-Methylbutane-1-C^{14} over Water-promoted Aluminum Bromide.—The apparatus and

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[7] M. S. Kharasch, W. Hered and F. R. Mayo, *J. Org. Chem.*, **6**, 818 (1941), similarly report that *t*-butyl bromide is the sole monobromination product from the liquid-phase bromination of isobutane.

[8] The differences in product composition in the chlorination and bromination of isopentane are similar to those observed with ethylpentachlorobenzene and admit of the same explanation, S. D. Ross, M. Markarian and M. Nazzewski, THIS JOURNAL, **69**, 1914, (1947); **71**, 396 (1949).

[9] (a) H. Pines and R. C. Wackher, *ibid.*, **68**, 595, 599 (1946); (b) R. C. Wackher and H. Pines, *ibid.*, **68**, 1642 (1946).

[10] C. G. Swain and L. Kent, *ibid.*, **72**, 518 (1950).

[11] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

procedures were modeled after those of Pines and Wackher.[9] The isomerization was carried out in a sealed glass tube in the following manner. The reaction tube was evacuated and 2 g. (0.0075 mole) of aluminum bromide sublimed in. Water (0.10 g., 0.0055 mole) was distilled into the tube and, after its reaction with the aluminum bromide was complete, the hydrogen bromide was pumped off. 2-Methylbutane-1-C^{14} (10.8 g., 0.15 mole) was distilled into the tube which was then cooled in a liquid nitrogen trap and sealed off *in vacuo*. The tube was allowed to stand at room temperature for 15 hours with occasional shaking. The isopentane was then removed under reduced pressure and, on photochemical bromination, yielded 9.6 g. (45%) of labeled *t*-amyl bromide, b.p. 106°. This material was degraded as before.[3]

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The Stereochemistry of the Free Radical Addition of Hydrogen Bromide to 1-Bromocyclohexene and 1-Methylcyclohexene

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The addition of hydrogen bromide to 1-bromocyclohexene proceeds rapidly when catalyzed by benzoyl peroxide or ultraviolet light. The addition is apparently a free radical reaction as it does not occur in the presence of inhibitors of "abnormal" addition. The single addition product isolated appears to be the previously unreported *cis*-1,2-dibromocyclohexane. The formation of this product indicates a preferred *trans* addition. The addition of hydrogen bromide to 1-methylcyclohexene proceeds rapidly without catalysts and yields 1-bromo-1-methylcyclohexane. In pentane in the presence of benzoyl peroxide or ultraviolet light normal and abnormal addition products are formed simultaneously. The abnormal addition product is dehydrobrominated to 1-methylcyclohexene indicating that it is *cis*-1-bromo-2-methylcyclohexane. The formation of this isomer indicates that free radical addition in this case is also *trans*.

The "abnormal" addition of hydrogen bromide to carbon–carbon double bonds has been investigated in considerable detail by Kharasch and coworkers[2] and found to involve a radical chain reaction.[3] In order to obtain additional information concerning the nature of free radical additions we have investigated the stereochemistry of the free radical addition of hydrogen bromide to double bonds.

The stereochemistry of this addition can be determined by selecting systems where *cis* and *trans* addition give different products, provided that the ethylenic compound and addition products are not isomerized under the conditions of the reactions. As bromine atoms promote *cis–trans* isomerizations[4] presumably by a reversible addition of a bromine atom to the double bond, it is apparent that open chain ethylenic compounds may be partially or completely isomerized prior to addition. Indeed it has been shown that *cis* to *trans* isomerization of stilbene is much faster than free radical addition of hydrogen bromide.[5] Chlorostilbene[6] and 2-bromobutene[7] are also rapidly isomerized by bromine atoms.

In the present work the stereochemistry of the free radical addition of hydrogen bromide to 1-bromocyclohexene (I) and 1-methylcyclohexene (III) was investigated. With cyclic systems complications due to *cis–trans* isomerization of the double bond are avoided. From earlier work concerning the orientation of the abnormal addition of hydrogen bromide[2] the expected adduct from I would be 1,2-dibromocyclohexane and that from III would be 1-bromo-2-methylcyclohexane. The stereochemistry of the addition can be deduced from the configuration of the addition products.

From available information concerning the orientation of elimination reactions[8] and by assuming *trans* elimination[9] to be required in base-promoted dehydrobrominations *cis*-1,2-dibromocyclohexane should be converted to I by dehydrobromination whereas the *trans* isomer could not yield this product. It has been shown[10] that *trans*-1,2-dibromocyclohexane is primarily converted to cyclohexadiene by dehydrobromination in quinoline although small amounts of I are also formed. By similar reasoning III would be the predominating elimination product of *cis*-1-bromo-2-methylcyclohexane whereas 3-methylcyclohexene would have to be the exclusive product from the *trans* isomer.

The data obtained for the addition of hydrogen bromide to 1-bromocyclohexene are summarized in Table I. The additions were catalyzed by benzoyl peroxide[2] and ultraviolet light[11] and were carried out in purified pentane.

Addition proceeds rapidly when catalyzed by benzyl peroxide or ultraviolet light (expt. 1, 2 and 3), but does not occur in the presence of inhibitors of abnormal addition[2] (expt. 4) or under ionic conditions (expt. 5 and 6). In the last two experiments nearly all of the unchanged I was recovered indicating ionic addition to be extremely slow. These observations indicate that addition proceeds by a radical process exclusively and as ionic addition is not competing, 1,1-dibromocyclohexane presumably is not formed.

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[1] (a) Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. (b) Rohm and Haas Co., Philadelphia, Pennsylvania.

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