54% yield of 3-methyl-2,4-hexanediol, b. p. 109° (9 mm.); $n^{20}D$ 1.4450; d^{20}_4 0.9588 was obtained. Its identity was shown by analysis for carbon and hydrogen. Calcd. for $C_7H_{16}O_2$: C, 63.54; H, 12.18. Found: C, 63.48; H, 12.17.

3-Methyl-2,4-dibromohexane.—The method of preparation here was the same as that described for 2-methyl-2,4-dibromopentane. A 90% yield of crude product of high purity was obtained. It was purified by distillation under diminished pressure. The purified dibromide had the following physical constants, b. p. 71.5–72.5 (1 mm.); $n^{20}D$ 1.4967; d^{20}_4 1.4504. Analysis for bromine gave results in agreement with the formula assigned. Calcd. for $C_7H_{14}Br_2$: Br, 61.97. Found: Br, 62.07.

1,2-Dimethyl-3-ethylcyclopropane.—This hydrocarbon was prepared from the dibromide by the method described for 1,1,2-trimethylcyclopropane. A 90% yield of product, $n^{20}D$ 1.4048, was obtained. Analysis for carbon and hydrogen gave results in agreement with the formula C_7H_{14}. Calcd. for C_7H_{14}: C, 85.62; H, 14.38. Found: C, 85.51; H, 14.32. A spectral map was made of this product. A portion of this product was distilled in the vertical surface column. The distillation is shown in Fig. 6. The infrared absorption spectra of the two plateau fractions were determined, Figs. 8 and 9.

Acknowledgment.—We are indebted to the Chemical Research Laboratory of the Standard Oil Co. of Ohio for the use of the infrared spectrometer and to Dr. Martval J. Hartig of the Standard Oil Co. of Ohio for assistance in the interpretation of infrared data.

Summary

1,1,2-Trimethylcyclopropane was prepared in high yield from 2-methyl-2,4-dibromopentane by the Freund reaction at low temperatures.

In the ring closure reaction to form 1,1,2-trimethylcyclopropane from 2-methyl-2,4-dibromopentane the principal by-products were found to be 2-methyl-1-pentene and 2-methylpentane. These by-product hydrocarbons have the same carbon skeleton as the dibromide from which they were formed.

1,1,2-Trimethylcyclopropane was obtained in a purity of about 95% by fractional distillation in a high efficiency distilling column.

Infrared absorption spectra show that aqueous potassium permanganate was not very selective for removing 2-methyl-1-pentene from 1,1,2-trimethylcyclopropane.

1,2-Dimethyl-3-ethylcyclopropane was prepared in high yield from 3-methyl-2,4-dibromohexane. It was separated into two fractions by distillation.

An improved method is described for the preparation of secondary and tertiary organic bromides from alcohols or diols.

CLEVELAND, OHIO RECEIVED SEPTEMBER 20, 1945

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization of Alkanes. IV.[1] Deuterium Exchange in the Isomerization of *n*-Butane[2]

BY HERMAN PINES AND R. C. WACKHER

It was shown[2a] that under controlled conditions, aluminum bromide–hydrogen bromide catalyst does not cause isomerization of *n*-butane unless traces of olefins or their equivalent are present. On the basis of these results, a chain mechanism was suggested.[3] It was postulated that isomerization of *n*-butane proceeds in the presence of a catalyst and traces of olefins or their equivalent by a sequence of reactions as represented by the following equations.

$$R{-}CH{=}CH_2 + HX^a \rightleftharpoons [R{-}\overset{+}{C}H{-}CH_3]X^- \quad (1)$$

[a] HX is HBr or $HAlBr_4$.

$$CH_3{-}CH_2{-}CH_2{-}CH_3 + R{-}\overset{+}{C}H{-}CH_3 \rightleftharpoons CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 + R{-}CH_2{-}CH_3 \quad (2)$$

$$CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 \rightleftharpoons CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{+}{C}H_2 \rightleftharpoons CH_3{-}\underset{\underset{CH_3}{|}}{\overset{+}{C}}{-}CH_3 \quad (3)$$

$$CH_3{-}\underset{\underset{CH_3}{|}}{\overset{+}{C}}{-}CH_3 + CH_3{-}CH_2{-}CH_2{-}CH_3 \rightleftharpoons CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_3 + CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 \quad (4)$$

If the isomerization steps as given above are correct, then, by substituting deuterium bromide for hydrogen bromide, one would expect an exchange reaction to occur between the deuterium of the catalyst and hydrogen of the butanes. This can be represented by the equations

$$CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 \rightleftharpoons CH_3{-}CH{=}CH{-}CH_3 + H^+ \quad (3a)$$

$$H^+ + X^- \rightleftharpoons HX \quad (3b)$$

$$CH_3{-}CH{=}CH{-}CH_3 + DX \rightleftharpoons CH_3{-}CD{=}CH{-}CH_3 + HX$$

$$\uparrow\downarrow$$

$$CH_3{-}CHD{-}CHX{-}CH_3 \rightleftharpoons [CH_3{-}CHD{-}\overset{+}{C}H{-}CH_3]X^- \quad (3c)$$

$$CH_3{-}CHD{-}\overset{+}{C}H{-}CH_3 \rightleftharpoons CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{+}{C}HD \rightleftharpoons CH_3{-}\underset{\underset{CH_3}{|}}{\overset{+}{C}}{-}CH_2D \quad (3d)$$

(1) For paper III of this series, see R. C. Wackher and H. Pines, THIS JOURNAL, **68**, 1642 (1946).

(2) Presented before the Organic Division at the American Chemical Society Meeting, Atlantic City, April, 1946.

(2a) H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 595 (1946).

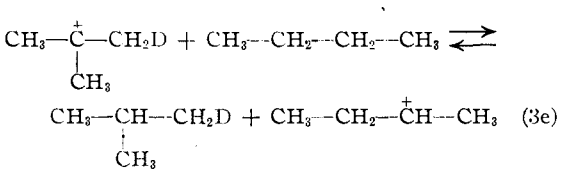
(3) H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, **68**, 153 (1946).

TABLE I

ISOMERIZATION OF *n*-BUTANE IN THE PRESENCE OF ALUMINUM BROMIDE–DEUTERIUM BROMIDE CATALYST

Experiment no.		1	2	3	4		
Reaction time, hrs.		20	20	20	7		
Temp., °C.		25					
Charge, mole	$AlBr_3$	0.01151	0.01021	0.01171	0.01031		
	DBr	.01054	.00942	0.1170	.01045		
	n-Butane	.1239	0	.1173	.1060		
	i-Butane	0	0.1156	0	0		
	n-Butenes	0	0	116×10^{-6}	98×10^{-6}		
Anal. of reaction product, mole %	DBr + HBr	7.9	6.3	9.4	8.1		
	Isobutane	0.0	93.3	36.6	19.1		
	n-Butane	92.1	0.4	53.0	72.4		
	Pentanes and higher	0		1.0	0.4		
Deuterium anal. and calc.		*n*-Butane	*i*-Butane	*i*-Butane	*n*-Butane	*i*-Butane	*n*-Butane
Atom % D in H_2O of combustion[a]		0.1352	0.1888	2.232	1.606	2.496	1.488
Average no. atoms of D per molecule of butanes		.0102	.0154	0.2198	0.1572	0.2462	0.1454
% D orig. present as DBr found in butanes		5.97	9.54	45.13	46.83	26.22	58.60

[a] 0.017% of deuterium oxide was subtracted from this column for succeeding calculation, inasmuch as this amount is present in natural water.



(3e)

By applying the same reasoning as given above, it becomes clear that deuterization of the *n*-butane can also take place. The equations also show the possibility of the existence of more than one atom of deuterium in a molecule of butanes.

In order to test the validity of the postulated mechanism of isomerization, deuterium bromide–aluminum bromide instead of hydrogen bromide–aluminum bromide was used as an isomerization catalyst. The reactions were carried out under controlled conditions using a high-vacuum technique as described previously.[2a,4] The experimental conditions are summarized in Table I. It was found that by treating either *n*-butane or isobutane with a 10 mole per cent. of deuterium bromide–aluminium bromide catalyst for twenty hours at 25°, no isomerization of the butanes occurred and only 6 and 9.5% of the deuterium exchanged with *n*-butane and isobutane, respectively. When, however, 0.1 mole per cent. of *n*-butenes was added to *n*-butane and the isomerization reaction was carried out under the same experimental conditions, over 40% of the butane isomerized to isobutane and 92% of the deuterium underwent an exchange reaction. The results given above indicate clearly that olefins take an active part in isomerization, and the results obtained are in agreement with the proposed mechanism of isomerization.

It was found that the decrease of the contact time between the catalyst and the hydrocarbons from twenty hours to seven hours, decreases only slightly the hydrogen–deuterium exchange reaction, namely, from 92 to 85%, as indicated by experiment 4, Table I.

The deuterium tracer technique also was used to throw some light on the mechanism of the isomerization of *n*-butane in the presence of hydroxyaluminum dibromide.

TABLE II

REACTION OF ALUMINUM BROMIDE WITH DEUTERIUM OXIDE AND ISOMERIZATION OF *n*-BUTANE IN THE PRESENCE OF THE RESULTING REACTION PRODUCT

Part A

Experiment no.		5	6
Reaction time, hrs.	At 25°	16	17
	At 100°	0.5	0.75
Charge, mole	$AlBr_3$	0.01175	0.01137
	D_2O	0.01177	0.01142
	Moles D_2O per mole $AlBr_3$	1.00	1.00
DBr generated	Moles	0.01179	0.01186
	Moles per mole $AlBr_3$	1.00	1.04

Part B

Isomerization of *n*-Butane in the Presence of the Catalyst Described in Part A—Isomerization of *n*-Butane in the Presence of $DOAlBr_2$

Reaction time, hrs.	20	42
Reaction temp., °C.	25.0	25.0
n-Butane charged, moles	0.1189	0.1179
Anal. of product, mole %		
HBr and DBr	0.0	0.6
i-Butane	3.7	21.0
n-Butane	96.3	78.1
Pentanes and higher	0.0	0.3

Deuterium anal. and calc.	*i*-Butane	*n*-Butane	*i*-Butane	*n*-Butane
Atom % D in H_2O of combustion[a]	[b]	0.1224	0.1604	0.1288
Average no. atoms of D per molecule of butanes		.0088	.0126	.0094
% D orig. present as $DOAlBr_2$ found in butanes		4.32	1.44	3.99

[a] 0.017% of deuterium oxide was subtracted from this column for succeeding calculation, inasmuch as this amount is present in natural water. [b] Quantity too small for analysis.

(4) H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 599 (1946).

It was of special interest to determine whether the hydrogen or the halogen of the catalyst took an active part in the isomerization. In order to study the mechanism of this isomerization, deuteroxyaluminum dibromide was prepared by the action of one mole of deuterium oxide on one mole of aluminum bromide (Part A, Table II), using the technique described previously.[1] The reaction proceeded probably according to the equation

$$AlBr_3 + D_2O \longrightarrow DOAlBr_2 + DBr$$

The deuteroxyaluminum dibromide freed of the deuterium bromide formed, was used as a catalyst for the isomerization of *n*-butane (Part B, Table II). The reaction was carried out at 25° for twenty and forty-two hours; the yield of isobutane produced was 3.7 and 21%, respectively. It was found that very little exchange between deuterium and hydrogen occurred; in the isomerization reaction carried out over a period of twenty hours, 4.3% of the deuterium exchanged, while in the experiment carried out over a period of forty-two hours and in which 21% of isobutane was formed, only 5.4% of the deuterium exchanged.

On the basis of the experimental results obtained, it is reasonable to conclude that the isomerization of *n*-butane, by means of deuteroxyaluminum dibromide, involves the bromine atoms. As described in a previous paper,[1] the chain is probably initiated by an exchange reaction as given in equation 5.

$$CH_3{-}CH_2{-}CH_2{-}CH_3 + DOAlBr_2 \rightleftharpoons$$
$$CH_3{-}CH_2{-}CHBr{-}CH_3 + [DOAlBrH] \text{ or } [AlOBr + HD]$$
$$\downarrow\uparrow$$
$$[CH_3{-}CH_2{-}\underset{+}{C}H{-}CH_3]\,Br^- \quad (5)$$

The isomerization from that point proceeds according to equations 3 and 4.

Experimental

The isomerization reactions and purification of materials were carried out in the high-vacuum apparatus in the same manner (except as noted below) as described in previous publications.[2a,4] Before any experiments were made in the apparatus, it was equilibrated with deuterium oxide and deuterium bromide by allowing these to stand in the apparatus for twelve hours.

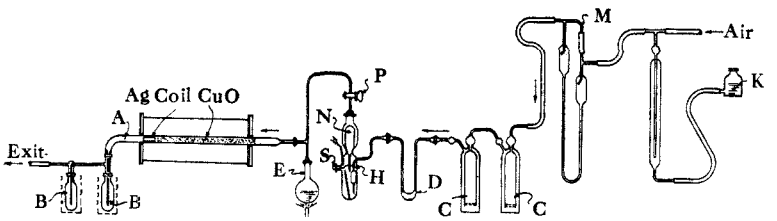


Fig. 1.—Combustion apparatus.

After the reaction period and condensation of the products in a small tube on the vacuum apparatus, all the sample, including any hydrogen or deuterium bromide, was transferred to the low-temperature Podbielniak distillation apparatus and fractionated, thus eliminating the sodium hydroxide scrubber used in previous work. Only about the middle two-thirds of the distillation product of the *i*- and *n*-butane were used for the combustion and analysis. These portions were condensed in small ampules sealed on the Podbielniak low-temperature distillation apparatus. The ampules were then sealed off and transferred to the combustion apparatus shown in Fig. 1.

The apparatus shown in Fig. 1, besides being used for combustion of the hydrocarbons, was used for final purification of the water sample. It consisted essentially of a quartz combustion tube A filled with copper oxide and a silver coil and kept at 700°; condensers (about 10 cc.) B cooled in ordinary ice and Dry Ice; the purifying train with sulfuric acid scrubbers C and trap D kept in Dry Ice; the water still E and the vessel H where the hydrocarbon sample is contained and fed to the combustion tube. The air rate was regulated by means of the leveling bulb K and determined either by the flow meter M or by counting the bubbles in the scrubber. For operation, the sealed ampule N containing the hydrocarbon was inserted as shown and with the stopcock P closed and the vessel cooled in Dry Ice; its tip was broken by means of the breaker S. With the sample in the bottom of the vessel the stopcock was then opened and the vessel warmed to about −70°, and the combustion allowed to proceed until all the sample was burned.

After the sample was completely burned, the water sample in B was transferred to the still E, a small quantity of potassium permanganate and sodium carbonate added and the water sample redistilled over the copper oxide.

The deuterium content of the water of combustion was determined by the float method described by J. Aman,[5] and made available to us through the courtesy of Dr. Adelbert L. Farkas.

The sample of heavy water was obtained from the Norsk Hydro-Elektrisk Kraelstofaktieselskab and their analysis by density showed that it contained 99.65 mole per cent. deuterium oxide on the basis of a d^{20}_{20} of 1.10714 for 100% deuterium oxide. Recalculated on the basis of a more recent determination[6] of 100% deuterium oxide in which d^{25}_{25} 1.10764, however, showed it to contain 99.51 mole per cent. deuterium oxide. The density of this sample was checked by picnometer method and found to be d^{25}_{25} 1.10723 which corresponds to 99.62 mole per cent. deuterium oxide, the value of which was used in further calculations. All weighings were corrected to weight *in vacuo*.

In calculating the deuterium oxide content of the samples, account was made of the normal deuterium oxide content (0.017 mole per cent.) of ordinary water.[7]

The deuterium bromide was prepared by the reaction of deuterium oxide and aluminum bromide, and is a by-product in the preparation of the deuteroxyaluminum dibromide catalyst. The procedure used was the same as the one described previously.[1]

The deuterium bromide produced had a normal boiling point of −66.9° as determined by vapor pressure measurements. (Assuming equal reaction rates of deuterium oxide and water the product contained 0.38 mole per cent. hydrogen bromide as impurity.) The above value compares very favorably with the measurements of Bates, Halford and Anderson[8] and Erlenmeyer,[9] all of whom found a value of −66.8°.

In the preparation of the deuteroxyaluminum dibromide this compound did not become molten, even at 100°, as did the hydroxyaluminum dibromide prepared in previous work.[1]

(5) J. Aman, Ph.D. Thesis, Hebrew University, Jerusalem, Palestine, 1941.

(6) E. Swift, Jr., THIS JOURNAL, **61**, 198 (1939).

(7) L. G. Longsworth, *ibid.*, **59**, 1483 (1937).

(8) J. R. Bates, J. D. Halford and L. C. Anderson, *J. Chem. Phys.*, **3**, 331 (1935).

(9) H. Erlenmeyer, *Z. Elektrochem.*, **44**, 8 (1938).

Acknowledgment.—The authors wish to thank Professor V. N. Ipatieff for the encouragement and the interest shown in the progress of this investigation.

Summary

Exchange reaction between hydrogen of butanes and deuterium of deuterium bromide–aluminum bromide catalyst has been studied in order to elucidate the mechanism of butane isomerization.

Very little exchange reaction and no isomerization occurred when butanes were treated with deuterium bromide–aluminum bromide. In the presence of 0.1 mole per cent. of butenes, isomerization of *n*-butane to isobutane occurred and 82–92% of the deuterium was exchanged for hydrogen.

Deuteroxyaluminum dibromide acted as a catalyst for the isomerization of *n*-butane; less than 6% of the deuterium underwent an exchange reaction.

Mechanism of isomerization of butanes was discussed.

CHICAGO, ILLINOIS RECEIVED AUGUST 5, 1946

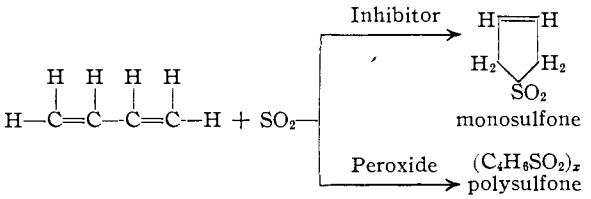
[CONTRIBUTION FROM THE PHYSICAL RESEARCH LABORATORY OF THE DOW CHEMICAL CO.]

Kinetics of the Diene Sulfur Dioxide Reaction[1]

BY L. R. DRAKE, S. C. STOWE AND A. M. PARTANSKY[2]

Introduction

It is well known in the literature[3] that conjugated dienes react in the liquid phase with sulfur dioxide to form sulfones. The course of the reaction, as determined by H. Staudinger,[4] can be directed to the formation of the monomeric sulfone by the addition of a polyhydric phenol or to the polysulfone by the addition of a peroxide.



He also has shown that the concentration of the reactants and the nature of the diene employed affect the ratio of monomeric to polymeric sulfone.

Early work by Staudinger[3c] and Eigenberger[3d] demonstrated that the monosulfones decomposed and the decomposition temperature was dependent upon the substituent groups of the diene but no mention was made as to whether these decomposition temperatures were measured at approximately equal decomposition rates.

H. J. Backer[5] and his co-workers have studied many substituted dienes that undergo this addition reaction. In the course of measuring the physical properties of the sulfones they noted the decomposition temperatures of each material. D. Craig[6] has remeasured the decomposition temperature of the sulfones of butadiene, 2-methylbutadiene-1,3, 2,3-dimethylbutadiene-1,3 and 4-methylpentadiene-1,3 at approximately the same decomposition rates.

This work has been carried out to study the equilibrium of the diene sulfur dioxide reaction and to study the decomposition rates of the resulting sulfones.

Experimental

Starting Materials.—Sulfur dioxide was obtained from the Ansul Chemical Company.

Butadiene, 99.8% or better was obtained by decomposing recrystallized butadiene sulfone, removing the sulfur dioxide with a sodium hydroxide solution, drying the gaseous butadiene over Drierite and storing it at −20° in a five-pound cylinder as liquid butadiene, f. p. −108.9°.

The butadiene sulfone used for this work was recrystallized from water and dried in vacuum over calcium chloride, m. p. 63–64°.

The isoprene was obtained by decomposing its sulfone and removing the sulfur dioxide. The resulting material had the following physical properties: b. p. 34.0 ± 0.1°; f. p. −146.6°; d^{20}_4 1.4164.

The isoprene sulfone was recrystallized from water, m. p. 63–64°, solubility 7.85 mg./100 g. of water at 25°.

Piperylene was obtained by decomposing its liquid sulfone, b. p. 40–42°.

Equilibrium Study

Butadiene Sulfone.—Butadiene and the sulfur dioxide were mixed in weighed quantities sufficiently large to make a complete set of experimental determinations and 0.1% *p-t*-butylcatechol (based on the weight of the hydrocarbon) was added as an inhibitor. The composition of the mixture was checked by the standard Orsat technique. The reaction mixture, in liquid phase, was poured into glass ampoules of 1.5-ml. capacity. These ampoules were sealed, weighed, then placed in an electrically heated aluminum block capable

(1) Prepared for the 1945 Meeting-in-Print of the Division of Physical and Inorganic Chemistry, American Chemical Society.

(2) Present address: Great Western Division of The Dow Chemical Company, Pittsburgh, California.

(3) (a) F. E. Matthews, German Patent 236,386; *Friedländer*, **10**, 1039 (1913); (b) G. de Briun, *Verslag Akad. Wetenschappen*, **23**, 445–446 (1914); *C. A.*, **9**, 634 (1915); (c) H. Staudinger, German Patent 506,839; *C. A.*, **25**, 522 (1913); (d) E. Eigenberger, *J. prakt. Chem.*, **127**, 307–335 (1930).

(4) H. Staudinger, *Ber.*, **68A**, 455–471 (1935).

(5) J. H. Baker, *et al.*, *Rec. trav. chim.*, **51**, 294 (1932); **53**, 524 (1934); **54**, 170 (1935); **54**, 538 (1935); **55**, 898 (1936); **56**, 1063 (1937); **56**, 1069 (1937); **58**, 778 (1939); **59**, 422 (1940); **59**, 890 (1940); **59**, 1141 (1940).

(6) D. Craig, THIS JOURNAL, **65**, 1006 (1943).