tions and comparison with tropone, Smyth[56] has interpreted the dipole moment as showing a small but definite interaction between the phenyl rings and the central ring.

Acknowledgment.—The authors hereby express their thanks to Mr. Edwin Conner and to Misses Cecelia Vitiello and Betty Blasko, all of the Schering Corporation, for the infrared and ultraviolet spectra and for help in interpreting the spectra.

BROOKLYN 1, NEW YORK

[56] A. Di Giacomo and C. P. Smyth, THIS JOURNAL, **74**, 4411 (1952).

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization of Saturated Hydrocarbons. XII.[1] The Effect of Experimental Variables, Alkyl Bromides and Light upon the Isomerization of Methylcyclopentane in the Presence of Aluminum Bromide

BY HERMAN PINES, EUGENE ARISTOFF[2] AND V. N. IPATIEFF[3]

RECEIVED APRIL 17, 1953

The effect of temperature, contact time and concentration of reactants upon the isomerization of methylcyclopentane in the presence of aluminum bromide–hydrogen bromide has been investigated. The effect of alkyl bromides as chain initiators for the isomerization reaction has been studied and it was found that methyl bromide and ethyl bromide do not act as chain initiators. The effect of ultraviolet light upon the isomerization of methylcyclopentane in the presence of methyl bromide has been investigated. The mechanism of the isomerization of methylcyclopentane is discussed.

In the previous papers of this series it was shown that under certain controlled experimental conditions methylcyclopentane does not undergo isomerization to cyclohexane unless small amounts of olefins, alkyl halides or other chain initiators are present. This investigation was now extended to study the effect of experimental variables upon the isomerization and the type of alkyl bromides which can act as promoters for the reaction.

The experiments were made using a high vacuum apparatus for the purification of the reactants and for charging and discharging the reaction tubes.[4] The experimental procedure was the same as described previously.[5]

1. **Effect of Time and Temperature.**—The study of the effect of time and temperature upon the isomerization of methylcyclopentane was made in an attempt to determine the kinetics of this reaction. *s*-Butyl bromide was used as a chain initiator since it seems to be the most efficient of all the alkyl bromides investigated. The results obtained are represented graphically in Fig. 1. The rate of isomerization tends to approach a limit after a certain period of time, and the levelling off occurs much sooner as the temperature at which the reaction occurs is increased. It seems that the chain initiator or the chain propagator is destroyed through secondary reactions such as a condensation reaction which involves a transfer of hydrogen[6] or conjunct polymerization.[7] The latter reaction occurs more readily at higher temperatures and involves the conversion of the olefinic hydrocarbons into highly unsaturated cyclic hydrocarbons which form complexes with the aluminum bromide. These complexes cannot function as chain propagators or initiators.

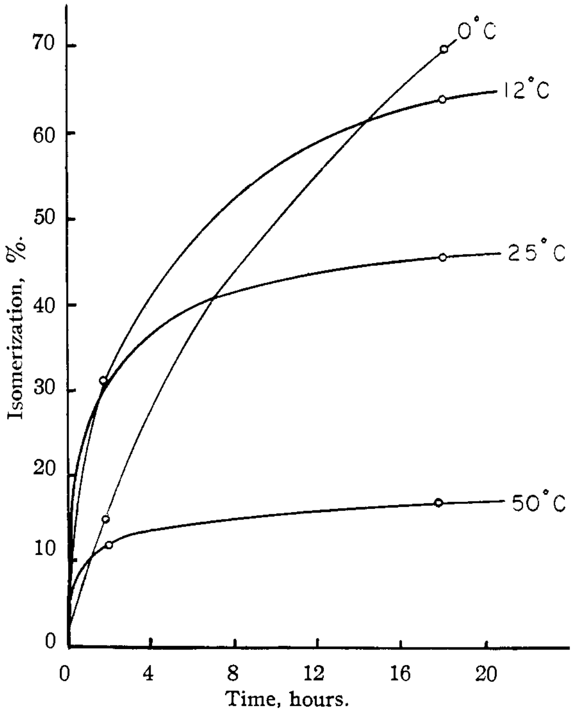

Fig. 1.—Effect of temperature: 100 moles methylcyclopentane, 2 moles aluminum bromide, 0.9 mole hydrogen bromide and 0.1 mole *s*-butyl bromide.

The data as shown in Fig. 1 indicate that the study of the kinetics of the isomerization of saturated hydrocarbons might lead to erroneous conclusions, unless the disappearance of a chain initator or a chain propagator is taken into consideration.

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[1] For paper XI of this series see H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, **75**, 2315 (1953).

[2] Universal Oil Products Company Predoctoral Fellow 1947–1949.

[3] Deceased, November 29, 1952.

[4] H. Pines, B. H. Abraham and V. N. Ipatieff, THIS JOURNAL, **70**, 1742 (1948).

[5] H. Pines, F. J. Pavlik and V. N. Ipatieff, *ibid.*, **73**, 5738 (1951).

[6] V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **6**, 242 (1941); THIS JOURNAL, **70**, 531 (1948).

[7] V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **1**, 464 (1936); L. Schmerling and V. N. Ipatieff, "The Mechanism of the Polymerization of Alkenes" in "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., p. 63.

2. Effect of Concentration of Reactants.—The effect of concentration of reactants upon the isomerization of methylcyclohexane is presented graphically in Figs. 2, 3 and 4. These experiments were carried out for two hours at 25°. In the experiments shown in Fig. 4, the amount of hydrogen bromide used was so adjusted as to have the total amount of bromides present in the reaction mixture equivalent to 1 mole per 100 moles of methylcyclopentane used. The results obtained confirm previously made observations that small changes in the concentration of the chain initiator greatly influence the extent of isomerization of saturated hydrocarbons.[8] By increasing the concentration of *s*-butyl bromide from 0.025 mole per cent. based on methylcyclopentane used to 0.105% the amount of cyclohexane formed is increased from 15 to 49%. The changes in the concentration of aluminum bromide and hydrogen bromide have a lesser effect upon the degree of isomerization.

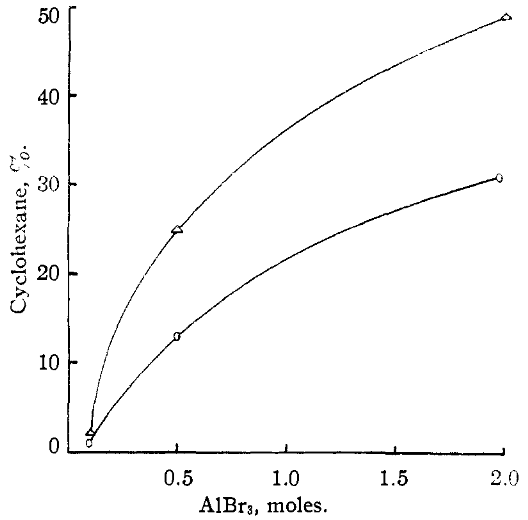

Fig. 2.—Effect of aluminum bromide: Δ, 100 moles methylcyclopentane, 0.10 mole *s*-butyl bromide and 0.90 mole hydrogen bromide; O, 100 moles methylcyclopentane, 0.10 mole *s*-butyl bromide and 0.40 mole hydrogen bromide.

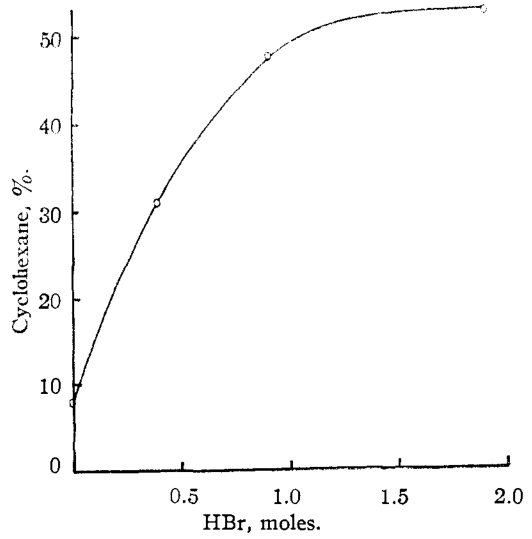

Fig. 3.—Effect of hydrogen bromide: 100 moles methylcyclopentane, 2 moles aluminum bromide and 0.1 mole *s*-butyl bromide.

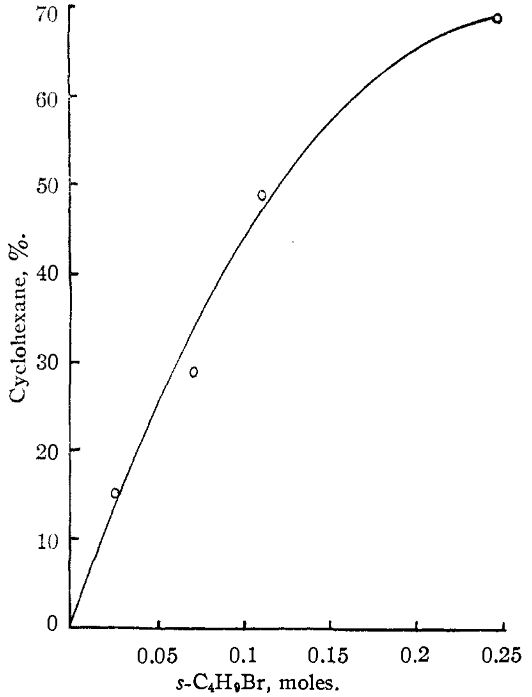

Fig. 4.—Effect of *s*-butyl bromide: 100 moles methylcyclopentane, 2 moles aluminum bromide. Moles of HBr used = 1.0 mole–mole *s*-C_4H_9Br.

3. Effects of Alkyl Bromides.—Table I represents the results which were obtained from the study of the effect of alkyl bromides upon the isomerization of methylcyclopentane. It is of interest to note that under the experimental conditions used methyl and ethyl bromide do not act as chain initiators for the isomerization of methylcyclopentane in the presence of aluminum bromide–hydrogen bromide catalyst. The lack of activity of methyl and ethyl bromide toward promoting the isomerization of methylcyclopentane could be interpreted by the possible difficulty with which an exchange reaction between the hydrogen of the hydrocarbon and the primary bromides occurs. Using an ionic interpretation it could be stated that a primary alkyl carbonium ion produced by the action of aluminum bromide upon the alkyl bromide does not remove a hydride from the methylcyclopentane.

The observation that primary carbonium ions do not abstract a hydride from methylcyclopentane could be used to explain the absence of neopentane during the isomerization of *n*- or isopentane. According to the calculated equilibrium of isomerization of pentanes[9] at 25°, neopentane should be the main constituent of the equilibrium mixture of pentanes. No neopentane, however, was reported to be formed during the isomerization of pentanes.[10]

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

(9) F. C. Rossini, E. J. R. Prosen and K. S. Pitzer, *J. Research, Natl. Bur. Standards*, **27**, 529 (1941).

(10) H. Pines, "Isomerization of Alkanes" in "Advances in Catalysis," Vol. 1, Academic Press Inc., New York, N. Y., 1948, p. 201.

TABLE I

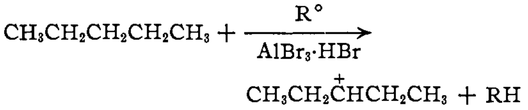
EFFECT OF ALKYL BROMIDE PROMOTERS UPON THE ISOMERIZATION OF METHYLCYCLOPENTANE

The experiments were made at 25° using about 8.00 to 10.00 ± 0.01 g. of methylcyclopentane.

Experiment	Promoter RBr	Mole ratio of reactants[a] HBr	RBr	Product composition, mole % cyclohexane
	A. (one-hour duration)			
1	n-C_3H_7Br	0.39	0.099	10
2	i-C_3H_7Br	.40	.099	25
3	s-C_4H_9Br	.42	.105	15
4	t-C_4H_9Br	.41	.100	16
	B. (2-hour duration)			
5	None	1.00	0	0
6	CH_3Br	0.88	0.113	0
7	C_2H_5Br	.79	.214	1
8	n-C_3H_7Br	.40	.100	16
9	i-C_3H_7Br	.40	.103	18
10	s-C_4H_9Br	.40	.100	31
11	t-C_4H_9Br	.40	.103	17
	C. (18-hour duration)			
12	None	1.00	0	0
13	CH_3Br	0.39	0.123	0
14	C_2H_5Br	.40	.098	0
15	n-C_3H_7Br	.40	.100	24
16	i-C_3H_7Br	.40	.106	23
17	s-C_4H_9Br	.41	.102	43
18	t-C_4H_9Br	.41	.103	17

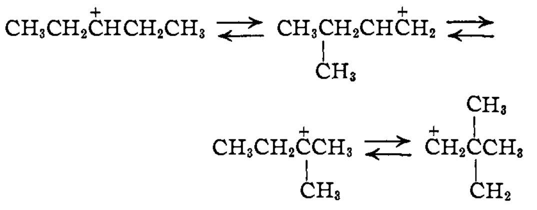
[a] Based on methylcyclopentane = 100 and aluminum bromide = 2.03 ± 0.05.

This is not surprising now since for the neopentane to be formed it would be necessary for a neopentylcarbonium ion to abstract a hydride from *n*- or isopentane, according to the following simplified equations



$$CH_3CH_2CH_2CH_2CH_3 + \xrightarrow[AlBr_3\cdot HBr]{R^\circ} CH_3CH_2\overset{+}{C}HCH_2CH_3 + RH \quad (1)$$

R° = olefin



$$CH_3CH_2\overset{+}{C}HCH_2CH_3 \rightleftarrows CH_3CH_2\underset{CH_3}{CH}\overset{+}{C}H_2 \rightleftarrows CH_3CH_2\underset{CH_3}{\overset{+}{C}}CH_3 \rightleftarrows \overset{+}{C}H_2\underset{CH_2}{\overset{CH_3}{C}}CH_3 \quad (2)$$

The two propyl bromides cause the same extent of isomerization when the reaction is carried out for two hours or longer. It is probable that *n*- and isopropylcarbonium ions reach equilibrium prior to withdrawal of a hydride ion from methylcyclopentane.

When *t*-butyl bromide is used as a promotor the amount of isomerization is relatively low and it is irrelevant whether the reaction is of one hour or eighteen hours duration. It is probable that a part of the *t*-butyl bromide in the presence of aluminum bromide underwent conjunct polymerization and therefore was prevented from acting as a chain initiator for the isomerization reaction. The highest conversion of methylcyclopentane to cyclohexane was achieved when *s*-butyl bromide was used as a chain initiator.

4. **Effect of Hydrogen Bromide.**—It has been shown previously that at room temperature the isomerization of methylcyclopentane does not take place in the presence of aluminum bromide–hydrogen bromide unless a chain initiator is present or the reactants are exposed to ultraviolet light.[11] The latter caused the dissociation of the hydrogen bromide into hydrogen and bromine atoms which reacted with the methylcyclopentane and thus initiated the chain reaction. It has now been found that a similar result could be achieved by raising the temperature of isomerization to 80°. The experimental results are summarized in Table II. It is very probable that at the higher temperatures some of the hydrogen bromide is dissociated into the corresponding atoms.

TABLE II

EFFECT OF TEMPERATURE UPON THE ISOMERIZATION OF METHYLCYCLOPENTANE IN THE PRESENCE OF ALUMINUM BROMIDE–HYDROGEN BROMIDE

Experiment	Temp., °C.	Time, hr.	Mole ratio of reactants,[a] HBr	Product composition, mole % cyclohexane
12	25	18	1.00	0
19	49	18	0.50	0
20	56	24	0.89	6
21	80	24	0.89	26

[a] Based on methylcyclopentane = 100 and aluminum bromide = 2.00 ± 0.01.

5. **Effect of Methyl Bromide and Light.**—It was shown in exp. 6, Table I that methyl bromide does not act as a chain initiator for the isomerization of methylcyclopentane. It was observed, however, that the irradiation of the reactants with ultraviolet light has an effect upon the isomerization reaction. In the presence of light a 20% yield of cyclohexane was produced while in the absence of light, under similar conditions, the extent of isomerization was only 2% (Table III).

TABLE III

EFFECT OF IRRADIATION UPON THE ISOMERIZATION OF METHYLCYCLOPENTANE IN THE PRESENCE OF ALUMINUM BROMIDE–METHYL BROMIDE

Experiment[a]	Irradiation time, hr.	Product composition, mole % clohexane
22	0	2
23	9	20

[a] The mole ratio of reagents used in each experiment was: methylcyclopentane = 100, aluminum bromide = 1.97 + 0.01, methyl bromide = 0.95. Total duration of each experiment was 18 hours.

The following equations serve to illustrate the probable mechanism of the reaction

$$CH_3Br \xrightarrow{h\gamma} CH_3\cdot + Br \quad (1)$$

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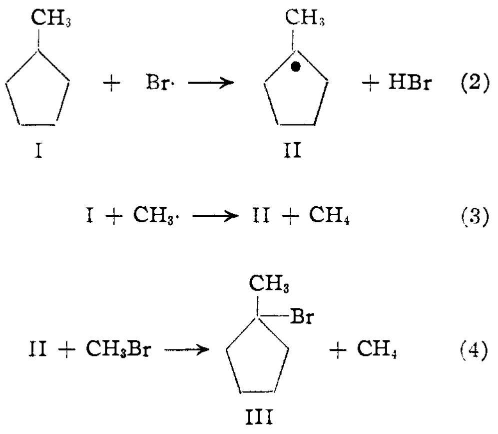
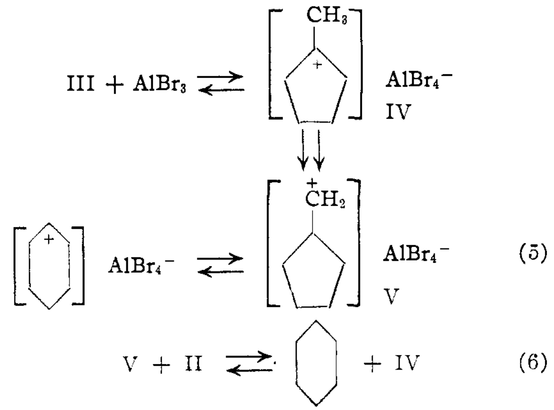
[11] H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, 72, 4055 (1950).





EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BUCKNELL UNIVERSITY]

On Cyclic Intermediates in Substitution Reactions. IV. The Hydrolysis of Trimethylene- and Tetramethylene Chlorohydrins[1]

BY HAROLD W. HEINE, ALFRED D. MILLER, WILLIAM H. BARTON AND RICHARD W. GREINER

RECEIVED MAY 7, 1953

The rates of hydrolysis for trimethylene- and tetramethylene chlorohydrins have been determined. It has been established that: (1) the rate of hydrolysis, as measured by the release of chloride ion, of trimethylene- and tetramethylene chlorohydrin is four times and a thousand times faster, respectively, than ethylene chlorohydrin; (2) the entropy of activation for tetramethylene chlorohydrin is more positive by about 6 e.u. than ethylene- or trimethylene chlorohydrin; (3) tetrahydrofuran is the main product of the hydrolysis of tetramethylene chlorohydrin.

Part I[2] of this series presented a study of the alkaline hydrolysis of some aliphatic bromoacids, in which the position of attachment of halogen ranged from α to γ, and which established that the reactivities increased in the order $\alpha < \beta \ll \gamma$. The increase of reactivity was interpreted as due to the increasingly strain-free character of the cyclic intermediate (lactone) formed.

It is of interest to investigate nucleophilic groups other than the carboxylate ion to see if they participate in the formation of cyclic intermediates as the distance between the nucleophilic group and the seat of substitution is increased. A suitable group of compounds for such a study would be the aliphatic chlorohydrins. In the present investigation the hydrolysis of trimethylene- and tetramethylene chlorohydrin has been studied. These substances are soluble in water at concentrations of 0.05–0.1 M and the kinetics of substitution (of oxygen for chlorine) are easily followed by measuring the release of the chloride ion. Here the hydroxyl group plays the role of the nucleophilic group.

The hydrolysis of ethylene chlorohydrin was investigated previously by Radulescu and Muresanu.[3]

Experimental

Trimethylene Chlorohydrin.—This compound was purchased from Matheson Chemical Company and redistilled. The fraction which boiled between 63–64° at 16 mm. was used in the rate studies.

Tetramethylene Chlorohydrin.—This compound was purchased from Matheson Chemical Company and redistilled. The fraction which boiled between 70–72° at 7 mm. was used.

Anal. Calcd. for C_4H_9OCl: Cl, 32.64. Found: Cl, 32.44.

Method of Rate Measurement.—The measurements were carried out in a water-bath in which the temperature was thermostatically controlled to ±0.02°. Ordinarily a quantity of chlorohydrin sufficient to make the concentration lie within the range 0.05–0.1 M was introduced into a 100-ml. volumetric flask. Water preheated to the bath temperature was added and at convenient time intervals, 10-ml. aliquots were removed with a pipet and immediately delivered into a solution of 5 ml. of 6 M HNO_3 and 30 ml. of distilled water. The unreacted chlorohydrin was extracted with two 10-ml. portions of chloroform and the chloride ion was determined by the Volhard method. In calculating the rate constants from the results of the titration the first sample was taken as the starting point of the reaction.

Typical rate data for the two chlorohydrins are given in Table I. Table II summarizes the complete data on first-order rate constants of trimethylene chlorohydrin and tetramethylene chlorohydrin.

TABLE I

RATES OF HYDROLYSIS OF TRIMETHYLENE- AND TETRAMETHYLENE CHLOROHYDRINS

Time, min.	Vol. of 0.05 N $AgNO_3$, ml.	$10^4 k_1$, min.$^{-1}$	Time, min.	Vol. of 0.05 N $AgNO_3$, ml.	$10^2 k_1$, min.$^{-1}$
Trimethylene chlorohydrin, $t = 86.30°$			Tetramethylene chlorohydrin, $t = 70.50°$		
358.2	1.06	3.96	10.25	0.89	1.71
659.7	1.84	3.95	20.00	1.59	1.69
1270	3.29	4.16	30.09	2.23	1.71
2060	4.48	3.97	40.17	2.76	1.72
2581	5.13	3.96	50.17	3.22	1.74
3163	5.75	3.99	60.50	3.55	1.69
∞	8.02	Mean 4.00	∞	5.54	Mean 1.71

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[1] Presented at the American Chemical Society Meeting-in-Miniature at Philadelphia, Penna., Jan. 29, 1953.

[2] J. F. Lane and H. W. Heine, THIS JOURNAL, **73**, 1348 (1951).

[3] D. Radulescu and F. L. Muresanu, *Bull. soc. sci. cluj. Roumanie*, 6, 198 (1932).