TABLE III

MONOMER REACTIVITY RATIOS FOR BUTADIENE (M_1) IN EMULSION COPOLYMERIZATION AT 5°

M_2	r_1	r_2
Methyl methacrylate	0.53 ± 0.05	0.06 ± 0.03
Methyl acrylate	.76 ± .04	.05 ± .02
Butyl acrylate	.99 ± .07	.08 ± .02
Methacrylonitrile	.36 ± .07	.04 ± .04
Vinylidene chloride	1.9 ± .2	< .05

TABLE IV

COMPARISON OF PROPERTIES OF BUTADIENE AND STYRENE RADICALS IN COPOLYMERIZATION

Radical	Butadiene rel. react.	r_1r_2	Styrene rel. react.	r_1r_2
Monomer	5°		60°	
Butadiene	1.00	...	1.28[a]	1.08
Styrene	0.72[a]	1.08	1.00	..
Methyl methacrylate	1.89	0.032	1.9[b]	0.24
Methyl acrylate	1.32	.038	1.34[b]	0.14
Methacrylonitrile	2.78	.014	3.3[a]	0.06
Vinylidene chloride	0.53	7.1	0.54[c]	0.16

[a] From ref. (6). [b] From ref. (18). [c] F. R. Mayo, F. M. Lewis and W. F. Hulse, THIS JOURNAL, **67**, 1701 (1945).

radicals and r_1r_2 products are compared for the monomers reported here.

The table permits two generalizations.[17] First, since the r_1r_2 products in the butadiene systems are smaller than those involving styrene, and since the monomers in general belong to the electron acceptor class,[15,18] butadiene must be a better electron donor than styrene.

Second, the close similarity of the two reactivity series reinforces the conclusion,[18] that styrene and butadiene must lie very close together in reactivity. Since a similar correspondence has been found in chain transfer with mercaptans,[19] styrene serves as a convenient substitute for butadiene in oil phase polymerizations where polymerization of butadiene is inconveniently slow.

[17] The two radicals have, of course, been compared at different temperatures. However, unpublished experiments by the authors indicate that the change in monomer reactivity ratios in these butadiene systems in going from 5 to 60° is small.

[18] F. R. Mayo, F. M. Lewis and C. Walling, THIS JOURNAL, **70**, 1529 (1948).

[19] W. V. Smith, *ibid.*, **65**, 2064 (1943).

PASSAIC, N. J. RECEIVED MAY 11, 1951

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

Isomerization of Saturated Hydrocarbons. IX.[1] Isomerization of Ethylcyclopentane, 1,3-Dimethylcyclopentane and 1,1-Dimethylcyclopentane in the Presence of Aluminum Bromide. Synthesis of 1,1-Dimethylcyclopentane

BY HERMAN PINES, F. J. PAVLIK[2] AND V. N. IPATIEFF

The relative ease of the isomerization of ethylcyclopentane, 1,3-dimethylcyclopentane and 1,1-dimethylcyclopentane to methylcyclohexane was studied. Under certain experimental conditions these hydrocarbons do not undergo ring expansion when subjected to aluminum bromide–hydrogen bromide unless traces of alkyl halides are added or when the reagents are exposed to ultraviolet light. In the presence of small amounts of oxygen, aluminum bromide *per se* acts as an isomerizing catalyst. The isomerization is inhibited by the presence of benzene. Ethylcyclopentane isomerizes more readily than 1,3-dimethylcyclopentane and the latter more readily than 1,1-dimethylcyclopentane; these results can be interpreted on the basis of the ionic chain mechanism. The synthesis of 1,1-dimethylcyclopentane is described.

It has previously been shown that under certain controlled conditions aluminum bromide–hydrogen bromide did not cause isomerization of *n*-butane to isobutane[3] or methylcyclopentane to cyclohexane[4] unless traces of olefins or alkyl halides were present.

It was also shown that ultraviolet light[5] promotes the isomerization of methylcyclopentane to cyclohexane in the presence of aluminum bromide–hydrogen bromide and that aluminum bromide in the presence of oxygen[6] and in the absence of hydrogen bromide causes a similar rearrangement. It was further shown[1,7] that benzene inhibits isomerization.

In order to explain the function of the various promoters an ionic mechanism was proposed[4,8] in which it was assumed that the alkyl halides, added as such or formed *in situ*, acted as chain initiators.

For methylcyclopentane a primary carbonium ion was assumed responsible for ring expansion. In the case of ethylcyclopentane the expansion of the five-membered ring to a six-membered ring would involve, according to the above ionic mechanism, a secondary carbonium ion. Since the latter is usually formed more readily than a primary carbonium ion such isomerization should proceed with greater ease.

In the case of 1,3-dimethylcyclopentane although the chance for formation of a tertiary carbonium ion as the probable primary step in the reaction is twice that for ethylcyclopentane it was assumed that the isomerization would proceed less readily than in the case of ethylcyclopentane because of the necessary formation of a primary carbonium ion for ring expansion.

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[1] For paper VIII of this series see H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, **72**, 4304 (1950).

[2] Universal Oil Products Company Predoctorate Fellow 1949–1951.

[3] H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 595, 2518 (1946).

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

[5] H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **72**, 4055 (1950).

[6] H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **71**, 749 (1949).

[7] J. M. Mavity, H. Pines, R. C. Wackher and J. A. Brooks, *Ind. Eng. Chem.*, **40**, 2374 (1948).

[8] H. S. Bloch, H. Pines and L. Schmerling, THIS JOURNAL, **68**, 153 (1946).

For 1,1-dimethylcyclopentane a tertiary carbonium ion cannot be formed; the ring expansion must involve a prior shift of a methyl group; therefore, this compound should be most stable and isomerization should proceed less readily than for the ethyl- and 1,1-dimethylcyclopentane. In order to test the validity of the above indicated assumptions a comparative study of the three cyclopentanes has been carried out.

Discussion of Results

Ethylcyclopentane.—The results obtained from the study of ethylcyclopentane are summarized in Table I.

TABLE I

ISOMERIZATION OF ETHYLCYCLOPENTANE

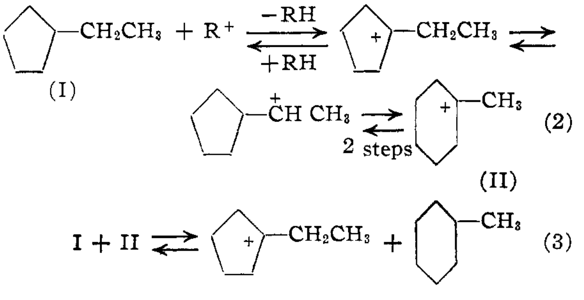
The amount of ethylcyclopentane used in the various experiments varied from 3–6 g.; temperature 25°.

Expt.	Reagents: moles per 100 moles of ethylcyclopentane AlBr$_3$	HBr	s-C$_4$H$_9$Br	Time, hours	Methylcyclohexane, %
1	3	1	0	9	4
2	1.5	1	0.05	2	97
3[a]	1.2	0	0	2	80
4	2	1	0	2[b]	45
5[c]	1.5	1	0.1	2	1

[a] 0.58 mole per cent. of oxygen was added. [b] Irradiation by ultraviolet light. [c] 0.15 mole per cent. of benzene was present.

The data show that the effect of a chain initiator such as *s*-butyl bromide, oxygen or the effect of irradiation by ultraviolet light upon the isomerization of ethylcyclopentane is much greater than in the case of methylcyclopentane,[3] 1,3-dimethylcyclopentane or 1,1-dimethylcyclopentane as will be seen below. As in the case of methylcyclopentane benzene inhibits the isomerization of ethylcyclopentane. The mechanism of isomerization of ethylcyclopentane is similar to that of *n*-butane and of methylcyclopentane[7] and can be expressed as

$$RBr + AlBr_3 \rightleftarrows [R^+][AlBr_4^-] \qquad (1)$$



Oxygen or ultraviolet light cause the formation of a chain initiator, while benzene removes it and therefore causes the inhibition of the reaction.[5,6]

It was observed that ethylcyclopentane when exposed to air underwent oxidation forming most probably hydroperoxides which act as chain initiators for isomerization. For that reason, it was imperative to store this hydrocarbon in sealed tubes or under an atmosphere of nitrogen. Even in the latter case, after a few weeks certain products were formed which promoted isomerization. These promoters were removed by percolating ethylcyclopentane through silica gel. The quantity of promoters "impurities" present in ethylcyclopentane could not be detected by physical tests or spectroscopic analysis. It was found expedient to make control experiments at frequent intervals using aluminum bromide–hydrogen bromide as a catalyst. Ethylcyclopentane was considered pure when the extent of isomerization after 9 hours was less than 4%. Similar control tests were made with the other two cyclopentanes to ascertain that isomerization promoters were absent.

1,3-Dimethylcyclopentane.—Table II contains the summary of results obtained from the study of the isomerization of 1,3-dimethylcyclopentane.

TABLE II

ISOMERIZATION OF 1,3-DIMETHYLCYCLOPENTANE

The experiments were made at 25°; 3–6 g. of 1,3-dimethylcyclopentane was used in each experiment.

Expt.	Reagents: moles per 100 moles of 1,3-dimethylcyclopentane AlBr$_3$	HBr	s-C$_4$H$_9$Br	Time, hours	Methylcyclohexane, %
1	2	1	0	9	1
2	1.5	1	0.05	2	39
3[a]	1.2	0	0	2	5
4	2	1	0	9[b]	6
5[c]	1.5	1	0.10	2	2

[a] 0.57 mole % of oxygen was added. [b] Ultraviolet irradiation. [c] 0.15 mole % of benzene was present.

The isomerization of this compound occurs to a lesser extent than that of ethylcyclopentane. This is especially noticeable when oxygen or ultraviolet light is used to form the chain initiator. The isomerization of 1,3-dimethylcyclopentane is also inhibited by benzene. The mechanism of isomerization is analogous to that of methylcyclopentane.

1,1-Dimethylcyclopentane.—The experimental results given in Table III indicate that 1,1-dimethylcyclopentane is the most stable of the three alkylcyclopentanes toward isomerization.

TABLE III

ISOMERIZATION OF 1,1-DIMETHYLCYCLOPENTANE

From 3 to 6 grams of 1,1-dimethylcyclopentane was used in each experiment. The reactions were made at 25°.

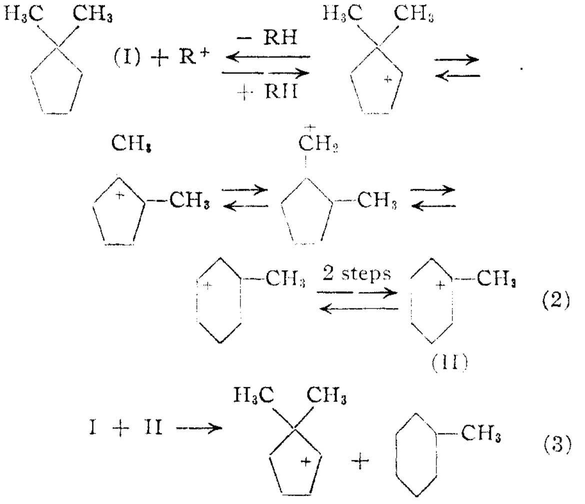
Expt.	Reagents: moles per 100 moles of 1,1-dimethylcyclopentane AlBr$_3$	HBr	Time, hours	Methylcyclohexane, %
1	3	1	9	1
2[a]	1.5	1	9	11
3[b]	1.5	0	9	2
4	2	1	9[c]	0
5	2	1	26[c]	2

[a] 0.05 mole per cent. of *s*-butyl bromide was used. [b] 0.5 mole per cent. of oxygen was added. [c] Ultraviolet irradiation.

The results obtained are in line with the prediction based on the mechanism of isomerization. The stability of 1,1-dimethylcyclopentane toward isomerization is best illustrated by experiment 2 which indicates that even after 9 hours of contact time only 11% of this hydrocarbon was converted to methylcyclohexane as compared with 97 and 39% isomerization, respectively, for ethylcyclopentane and 1,3-dimethylcyclopentane after 2 hours of contact time. The relative resistance of 1,1-dimethylcyclopentane toward isomerization is also shown by the slight effect oxygen and ultraviolet light exercised upon this compound.

The mechanism of the isomerization of 1,1-dimethylcyclopentane can be presented as

$$\mathrm{RBr + AlBr_3 \rightleftharpoons [R^+][AlBr_4^-]} \qquad (1)$$

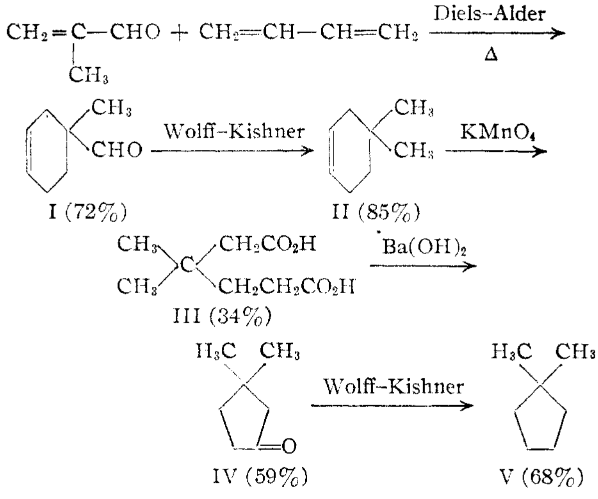


Materials

Ethylcyclopentane and 1,3-dimethylcyclopentane were prepared from cyclopentanone and ethylmagnesium bromide and from 3-methylcyclopentanone and ethylmagnesium bromide, respectively, according to the procedure described previously.[9]

Ethylcyclopentane distilled at 102–103°, n^{20}_D 1.4194. 1,3-Dimethylcyclopentane distilled at 90–91°, n^{20}_D 1.4078. According to infrared analysis, it consisted of *cis* and *trans*-isomer.

1,1-Dimethylcyclopentane was synthesized by the following series of reactions, using butadiene and methacrolein as the starting materials:



Compound I has not been reported previously. The ultimate yield of 1,1-dimethylcyclopentane was 8.4%.

a. **4-Methyl-4-formylcyclohexene** (I).—A solution consisting of 102 g. (1.45 moles) of methacrolein (b.p. 68°, n^{20}_D 1.4140), 88 g. (1.63 moles) of butadiene, one gram of hydroquinone and 100 ml. of benzene was heated in an 850-cc. capacity rotating autoclave at 150° for five hours. The yield of I was 129 g. (72%); b.p. 164–166, n^{20}_D 1.4640, d^{20}_4 0.9447. MR_D calcd.: 34.75. MR_D found: 34.22. Semicarbazone. Melted at 170–172° from ethanol.

Anal. Calcd. for $C_8H_{12}O$: C, 76.50; H, 9.73. Found: C, 76.53; H, 9.80.

b. **4,4-Dimethylcyclohexene** (II).—The aldehyde (I), 102 g. (0.83 mole) was reduced by the Wolff–Kishner reaction according to the general procedure of Huang-Minlon[10] with the exception that the potassium hydroxide was not added until the hydrazone had been formed. The yield of 4,4-dimethylcyclohexene was 77.5 g. (85%); b.p. 115.5–118°, n^{20}_D 1.4414.

c. **β,β-Dimethyladipic Acid** (III).—To a solution of 77 g. (0.7 mole) of 4,4-dimethylcyclohexene, 15 g. of sodium carbonate and three liters of water in a five-liter three-neck flask was added, over a period of 15 minutes, at 0–5° and with stirring, 295 g. (1.9 mole) of potassium permanganate. The mixture was stirred for eight hours after addition of permanganate. The aqueous solution was filtered from the manganese dioxide, evaporated to a small volume, acidified with phosphoric acid, filtered again and extracted with ether by means of a liquid–liquid extractor. The β,β-dimethyladipic acid melted at 80°; yield 44 g. or 34%.

d. **3,3-Dimethylcyclopentanone** (IV).—The β,β-dimethyladipic acid, 44 g. (0.25 mole) and 5 g. of crystalline barium hydroxide were heated to 300°. The 3,3-dimethylcyclopentanone formed distilled at 153–154°, n^{20}_D 1.4342; yield 14 g. or 50%. Semicarbazone which was crystallized from dilute ethanol melted at 179–180°.

Anal. Calcd. for $C_8H_{14}ON_3$: C, 57.14; H, 8.32; N, 25.00. Found: C, 57.16; H, 8.85; N, 25.1.

e. **1,1-Dimethylcyclopentane** (V).—The ketone (IV) was reduced by the procedure of Huang-Minlon.[10] From 35 g. (0.29 mole) of the ketone 19.4 g. (68%) of 1,1-dimethylcyclopentane was obtained; b.p. 88°, n^{20}_D 1.4139.

Apparatus

The high vacuum apparatus and technique used was essentially that described previously.[4] A round bulb of clear fused quartz was used for the reactions involving irradiations to ultraviolet light. A Cenco quartz cadmium–mercury vapor arc lamp was used at a distance of 20 cm. from the reaction tube at room temperature as the source of irradiation.

The chain initiators, such as *s*-butyl bromide or oxygen were placed in an ampoule having a thin-walled break-off. The sealed ampoule was carefully placed in the reaction tube, and the latter was evacuated. After the other reactants had been added the reaction tube was sealed off, then brought to the temperature of the reaction and shaken, in order to break the thin bulb of the ampoule containing the promoter. The use of this technique which brings the chain initiators in contact with the reagents only at the temperature at which the reactions are carried out, gave good reproducibility.

Analysis

The composition of the hydrocarbons obtained from the isomerization was determined by means of infrared spectral analysis. Spectra of the three alkylcyclopentanes were identical with those reported by the American Petroleum Institute Project #44.

The several wave lengths used for calculating the composition of the various samples are given in Table IV.

TABLE IV

WAVE LENGTHS USED FOR QUANTITATIVE CALCULATIONS OF HYDROCARBONS

Wave lengths in microns			
Methylcyclohexane	Ethylcyclopentane	1,3-Dimethylcyclopentane	1,1-Dimethylcyclopentane
7.70	7.70	8.04	7.7
8.04	8.04	8.80	8.26
8.80	10.40	10.40	8.60
9.24	10.80	10.80	9.24
10.20	11.06	11.06	10.80
10.40			11.06
10.80			
11.06			

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(9) H. Pines and V. N. Ipatieff, THIS JOURNAL, **61**, 1076 (1939).

(10) Huang-Minlon, *ibid.*, **68**, 2487 (1946).