

one hour gave a halogen-free product, b.p. 121–123° (60 mm.), n_D^{20} 1.4938. Careful fractionation of this material through a Piros-Glover micro column gave pure 2-phenyl-2-methylpentane, b.p. 126.8–127° (66 mm.), n_D^{20} 1.4929. This product was completely stable to 2% permanganate.

2-Phenylhexane.—2-Phenyl-2-hexanol, synthesized from acetophenone and *n*-butylmagnesium bromide, was dehydrated and the resulting olefin hydrogenated by the procedure described above. The 2-phenylhexane thus obtained had the following constants: b.p. 207.5–209.5°, n_D^{20} 1.4868 (lit.¹⁷ b.p. 214°, n_D^{20} 1.4882).

2-Methyl-3-phenylpentane.¹⁸—2-Methyl-3-phenyl-3-pentanol, synthesized from propiophenone and isopropylmagnesium bromide was dehydrated and the resulting olefin hydrogenated by the procedure described above. The 2-methyl-3-phenylpentane thus obtained had the following constants: b.p. 199–200°, n_D^{20} 1.4890 (lit.¹⁷ b.p. 209°, n_D^{20} 1.4912).

Alkylation Experiments.—The general procedure for alkylations using hydrogen fluoride catalysts was followed.¹⁹

(17) A. W. Francis, *Chem. Revs.*, **42**, 107 (1948).

(18) Synthesized by W. S. Postl.

(19) H. Pines, A. Edeleanu and V. N. Ipatieff, *THIS JOURNAL*, **67**, 2193 (1945).

1. ***n*-Propylcyclopropane.**—The reaction of 8.4 g. (0.1 mole) of *n*-propylcyclopropane with 78 g. (1 mole) of benzene in the presence of 15.0 g. (0.75 mole) of hydrogen fluoride produced 13.6 g. (84% yield) of monoalkylated product, b.p. 207–210°, n_D^{20} 1.4861.

2. **Isopropylcyclopropane.**—The reaction of 5.7 g. (0.07 mole) of isopropylcyclopropane with 78 g. (1 mole) of benzene using 10 g. of hydrogen fluoride as catalyst gave 6.0 g. (55% yield) of monoalkylated product, b.p. 203–208°, n_D^{20} 1.4928.

Infrared Spectra.—The infrared spectra of 2- and 3-phenylhexane, and the alkylation product from benzene and *n*-propylcyclopropane were determined on a Beckman Model IR2 instrument. The remaining spectra of hexylbenzenes were determined on a Beckman Model IR2T instrument. Sodium chloride cells were used. The spectra of *n*- and isopropylcyclopropane were taken on a Perkin-Elmer Model 21 infrared recording spectrophotometer.

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Isomerization of Saturated Hydrocarbons. XI.¹ The Isomerization of Alkylcyclopropanes and Alkylcyclobutanes in the Presence of Aluminum Halide Catalysts

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The behavior of a number of alkylcyclopropanes and alkylcyclobutanes in the presence of aluminum halide catalysts has been studied to determine if they would isomerize to hydrocarbons containing five- or six-membered rings. 1,1-Dimethyl-, 1,2-dimethyl-, ethyl-, and *n*-propylcyclopropane showed no tendency to isomerize but underwent polymerization instead. The polymerization of 1,1-dimethylcyclopropane was much more rapid and more extensive than that of the other alkylcyclopropanes mentioned above. In the cyclobutane series, methylcyclobutane polymerized and no detectable amount of isomerization to cyclopentane occurred. Ethylcyclobutane isomerized to methylcyclopentane and cyclohexane, but the isomerization was accompanied by considerable amounts of polymerization. With isopropylcyclobutane, however, extensive isomerization to methylcyclohexane and dimethylcyclopentanes occurred with very little polymerization. The difference in the behavior of methyl-, ethyl- and isopropylcyclobutane can be rationalized on the basis of the relative ease of formation of intermediate carbonium ions. The dehydration of cyclobutyl dimethylcarbinol by heating with phenyl isocyanate occurs without rearrangement and provides a convenient route for the synthesis of isopropylcyclobutane.

Since it was first shown that the presence of traces of alkyl halides or their equivalent are necessary to effect the butane-isobutane isomerization in the presence of aluminum halide catalysts,³ a large amount of evidence has been accumulated which indicates that acid-catalyzed isomerizations of this type proceed *via* a carbonium ion chain mechanism.⁴ Recent communications from this Laboratory have dealt with various methods of producing chain initiators, *e.g.*, by ultraviolet irradiation^{4d} and addition of oxygen^{4a,4e} and the effects of structure upon the relative rates of isomerization.^{1,4f}

Isomerization of alkylcyclopentanes and cyclohexane, *i.e.*, ring expansion and contraction, has been shown to occur under the same conditions as the butane-isobutane reaction. Very little work,

however, has been reported on the isomerization of alkylcyclopropanes and alkylcyclobutanes.⁵ The isomerization of ethylcyclobutane in the presence of aluminum chloride has been reported to yield methylcyclopentane and cyclohexane in addition to considerable amounts of polymeric material.⁶ This has been confirmed in the present study.

Discussion of Results

Alkylcyclopropanes.—The behavior of 1,1-dimethyl-, 1,2-dimethyl-, ethyl- and *n*-propylcyclopropane in the presence of aluminum halide or aluminum hydroxy dichloride catalysts was studied. Details of representative experiments are summarized in Table I. Detectable amounts of isomerization did not occur with any of these compounds, and polymerization was the predominant reaction.

Very rapid and complete polymerization of 1,1-dimethylcyclopropane occurred in the presence of aluminum bromide and hydrogen bromide or alu-

⁵ Throughout this paper, isomerization of cyclic hydrocarbons refers to ring expansion and contraction rather than the formation of olefins.

⁶ M. Turova-Pollak and M. Lukina, *J. Gen. Chem. U.S.S.R.*, **18**, 179 (1948).

(1) For paper X of this series see H. Pines, F. J. Pavlik and V. N. Ipatieff, *THIS JOURNAL*, **74**, 5544 (1952).

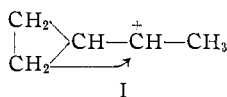
(2) (a) Universal Oil Products Company Predoctoral Fellow 1947–1950. (b) Deceased, November 29, 1952.

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

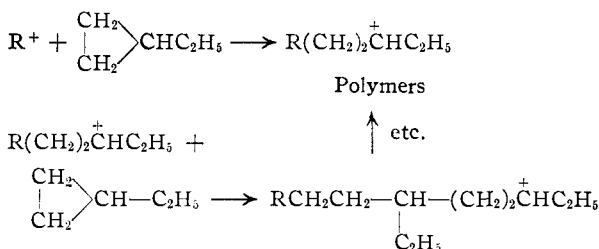
(4) (a) H. Pines and R. C. Wackher, *ibid.*, **68**, 599 (1946); (b) H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, **70**, 1742 (1948); (c) H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **71**, 749 (1949); (d) **72**, 4055 (1950); (e) **72**, 4304 (1950); (f) H. Pines, F. J. Pavlik and V. N. Ipatieff, *ibid.*, **73**, 5738 (1951).

minum bromide alone even at -50° (Expt. 1 and 2). This polymerization occurred during the period when the reaction mixture was warming up from liquid air temperature and was complete within a few minutes. Absence of highly colored sludge in the reaction mixtures indicated that the process was one of true addition polymerization. Polymerization of the other three alkylcyclopropanes was much slower and less extensive. Furthermore, the formation of orange-red sludge in the reaction mixture indicated the occurrence of conjunct polymerization. The detection of *n*-hexane and 2-methylpentane in the unpolymerized product from experiment 4 is additional evidence for this belief.⁷

Failure of these compounds to isomerize can be ascribed to the so-called "olefinic character" of the cyclopropane ring. On the basis of the ionic mechanism which has been proposed for acid-catalyzed isomerization, ring expansion would necessitate the formation of intermediate ions such as I by abstraction of hydrogen with its pair of electrons. Polymerization, on the other hand, would involve cleavage of the three-membered ring by an



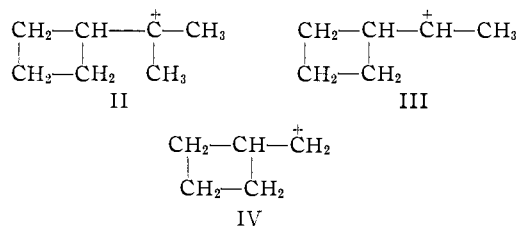
attacking carbonium ion as indicated in the following scheme. This scheme is similar to ones that have



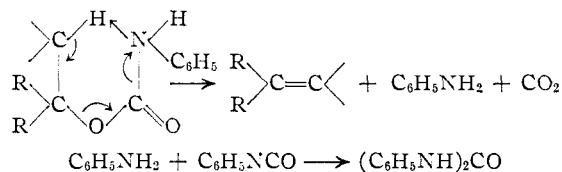
been proposed for the polymerization of olefins.⁸ The ability of 1,1-dimethylcyclopropane to act as a chain initiator for the isomerization of methylcyclopentane to cyclohexane provides further evidence of the olefinic character of the cyclopropane ring.⁹ Evidently, cleavage of the three-membered ring occurs more readily than the formation of ions such as I.

Alkylcyclobutanes.—The behavior of methyl-, ethyl- and isopropylcyclobutane is interesting. Data obtained from representative experiments with these compounds are summarized in Table II. It is seen (Expt. 7 and 8) that no detectable amount of isomerization occurred with methylcyclobutane in the presence of aluminum bromide, hydrogen bromide and *s*-butyl bromide or aluminum chloride and hydrogen chloride. Considerable polymerization occurred. In the presence of aluminum chloride and hydrogen chloride (Expt. 9), ethylcyclobutane polymerized to the extent of 40%. In addition, however, the unpolymerized product con-

tained approximately 8% methylcyclopentane, the remainder being unreacted ethylcyclobutane. Extensive amounts of polymerization and isomerization occurred in the presence of aluminum hydroxydichloride catalysts¹⁰ (Expt. 10). It has been found that the addition of small amounts of benzene suppresses the cracking of certain hydrocarbons upon treatment with aluminum halide catalysts.¹¹ It failed to reduce the amount of polymerization of these small ring compounds. In contrast to methyl- and ethylcyclobutane, isopropylcyclobutane underwent extensive isomerization and very small amounts (1–2%) of polymerization (Expt. 65 and 66). Methylcyclohexane, *cis*- and *trans*-1,2-dimethylcyclopentane, and *cis*- and *trans*-1,3-dimethylcyclopentane constituted the reaction product. The striking difference in the tendency of these compounds to isomerize is probably related to the decreasing ease of formation of the ions II > III > IV.



Dehydration of cyclobutyl dimethylcarbinol by heating with phenyl isocyanate followed by hydrogenation of the resulting olefins, proved to be a convenient synthesis of pure isopropylcyclobutane. The use of phenyl isocyanate for the dehydration of tertiary alcohols has been reported in the literature¹²; however, no mention is made of the fact that the reaction proceeds without rearrangement. The reaction may proceed by the formation of the phenylurethan which decomposes by a mechanism similar to ones proposed for the Chugaev reaction¹³ and the formation of olefins by pyrolysis of esters.¹⁴



Experimental

Starting Materials. Alkylcyclopropanes.—The synthesis of 1,1-dimethyl-, 1,2-dimethyl-, ethyl- and *n*-propylcyclopropane was described previously.¹⁵

Methylcyclobutane.—Methylenecyclobutane contaminated with about 5% spiro-pentane was obtained by the Gustavson debromination of pentaerythrityl bromide.¹⁶ Precise fractionation of this material furnished methylenecyclobutane of 99% purity as determined by infrared analysis. The material thus obtained was hydrogenated to methylcyclo-

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TABLE I

Experiment	1	2	3	4	5	6
Alkylcyclopropane						
Kind	1,1-Dimethyl	1,1-Dimethyl	Ethyl ^b	<i>n</i> -Propyl	<i>n</i> -Propyl	1,2-Dimethyl
Mole	0.040	0.042	0.054	0.0192	0.015	0.034
Aluminum halide						
Kind	AlBr ₃	AlBr ₃	AlCl ₃	AlBr ₃	AlCl ₃	Al(OH)Cl ₂
Mole	0.0008	0.001	0.0015	0.0008	0.0007	^c
Hydrogen halide						
Kind	HBr	..	HCl	HBr
Mole	0.004	..	0.00015	0.0004
Time, hours	0.25 ^a	0.1	4	1	1	3
Temp., °C.	24	-50	25	24	24	24
Polymn., %	100	100	50	90	22	7
Unpolymd. material	Ethylcyclopropane	<i>n</i> -Hexane 35% 2-methylpentane 54%	<i>n</i> -Propylcyclopropane	1,2-Dimethylcyclopropane

^a Reaction tube opened at the end of this period of time. Polymerization was undoubtedly complete before end of this time. ^b *s*-Butyl bromide, 0.0001 mole, added. ^c Catalyst prepared from reaction of 0.0023 mole of AlCl₃ and 0.0027 mole of H₂O; 0.0017 mole of HCl evolved.

TABLE II

Experiment	7	8	9	10	11	12
Alkylcyclobutane						
Kind	Methyl ^a	Methyl	Ethyl	Ethyl ^c	Isopropyl	Isopropyl
Mole	0.042	0.021	0.019	0.004	0.015	0.035
Aluminum halide						
Kind	AlBr ₃	AlCl ₃	AlCl ₃	Al(OH)Cl ₂	AlCl ₃	AlBr ₃
Mole	0.0011	0.0018	0.00091	^b	0.0017	0.0011
Hydrogen halide						
Kind	HBr	HCl	HCl	..	HCl	..
Mole	0.00048	0.00044	0.00049			
Time, hours	1.5	1.5	1.5	21	2	4
Temp., °C.	30	24	24	25	25	26
Polymn., %	30	50	46	65	2	<1
Unpolymd. material (% comp.)						
Methylcyclobutane	96	96				
Isopentane	4	2				
Ethylcyclobutane			91	16		
Methylcyclopentane			8	25		
Cyclohexane				11		
2-Methylpentane				13		
Methylcyclohexane					60	16
Dimethylcyclopentanes					40	84 ^d

^a *s*-Butyl bromide, 0.00014 mole used. ^b Aluminum hydroxy-dichloride catalyst prepared from 0.0011 mole of AlCl₃ and 0.0010 mole % H₂O; 0.0008 mole % HCl evolved. ^c Benzene, 0.00005 mole, added. ^d *cis*-1,2-Dimethylcyclopentane, 6%; *trans*-1,2-dimethylcyclopentane, 47%; *cis*-1,3-dimethylcyclopentane, 24%; *trans*-1,3-dimethylcyclopentane, 7%.

butane, b.p. 37.0–37.2°, *n*_D²⁰ 1.3851 (literature¹⁷ b.p. 36.0–36.5°, *n*_D²⁰ 1.3847). The infrared spectra of the methylcyclobutane were identical with those reported in the literature.¹⁸

Ethylcyclobutane.—Methyl cyclobutyl ketone which was synthesized by the method of Wibaut, *et al.*,¹⁹ had the following constants: b.p. 134.8–135° (751 mm.), *n*_D²⁰ 1.4315 (literature¹⁸ b.p. 136–136.5°, *n*_D¹⁹ 1.4322). The reduction of this ketone by the Huang-Minlon²⁰ modified Wolff-Kishner reaction furnished a 60% yield of ethylcyclobutane, b.p. 70–71°, *n*_D²⁰ 1.4020 (literature²¹ b.p. 70.6, *n*_D²⁰ 1.4020). The infrared spectra were identical with those reported in the literature.^{18,21}

Isopropylcyclobutane.—Cyclobutyl dimethylcarbinol was synthesized from methyl cyclobutyl ketone and methyl iodide *via* a Grignard reaction. After hydrolysis with ammonium chloride the cyclobutyl dimethylcarbinol obtained

in 70% yield distilled at 145°, *n*_D²⁰ 1.4454 (literature²² b.p. 144.5–145.5°, *n*_D²⁰ 1.4473).

Cyclobutyl dimethylcarbinol, 60 g. (0.53 mole), and phenyl isocyanate, 126 g. (1.06 moles) were mixed and heated in a 250-ml. distilling flask. The olefin began distilling when the flask temperature reached 150° and the reaction proceeded smoothly at 150–180°. A vigorous evolution of carbon dioxide occurred and diphenylurea crystallized in the flask. Five ml. of methanol was added to the crude olefin thus obtained to remove small amounts of phenyl isocyanate that distilled over. After standing overnight, the mixture was washed thoroughly with water, filtered and dried over calcium chloride. Distillation furnished 35 g. (70% yield) of olefin, b.p. 97–108°, *n*_D²⁰ 1.4355–1.4380. This olefin on hydrogenation yielded 28 g. of isopropylcyclobutane b.p. 93° (756 mm.), *n*_D²⁰ 1.4076. The infrared spectrum of this material was identical with the published spectra of isopropylcyclobutane.¹⁸

Isomerization Experiments.—A high vacuum line similar to the one previously described^{1b} was constructed for this study, and the techniques used were essentially those described by these workers. The composition of unpolymerized materials was determined by infrared analysis.

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