**Decarboxylation of 8-Benzoyl-1-naphthoic-*carboxy*-$C^{14}$ Acid.**—The acid (0.15 g.) having an assay of 2.238 $\mu$c/mmole was dissolved in quinoline (3 ml.) and treated with a pinch of copper chromite. The mixture was refluxed for 25 minutes while sweeping the system with helium which passed on exit through saturated barium hydroxide solution. The barium carbonate precipitated was filtered, rinsed with boiled water, and dried at 135° (1 mm.) for five hours. It weighed 0.07 g. (66%).

*Assay.* Calcd. 2.238 $\mu$c/mmole. Found: 2.156, 2.100; Average $2.128 \pm 0.028$ $\mu$c/mmole.

The low assay here is undoubtedly due to coprecipitation contamination of the barium carbonate.

The quinoline residue was rinsed into water, strongly acidified with hydrochloric acid, and the mixture extracted continuously with ether for 4.5 hours. Solvent evaporation left 0.14 g. of amber oil. This was recrystallized from methanol with decolorization and seeding to produce 0.02 g. of benzoylnaphthalene, m.p. 75.6°, no mixed m.p. depression with an authentic sample. Assay showed the material to be completely void of radioactivity.

**Action of Sodium Ethoxide on 2-Phenyl-1-acenaphthenone-1-$C^{14}$.**—The ketone (0.15 g.) in absolute ethanol (10 ml.) was treated with two drops of *ca.* 1.5% sodium ethylate solution. An immediate purple coloration was noted. On standing overnight, the color was discharged and the product had begun to crystallize from the solution. Another two drops of ethylate solution was added and the mixture again allowed to stand until colorless. This process was repeated until the further addition of ethylate engendered no coloration. The solid was filtered and rinsed with ethanol, 0.04 g., m.p. 237-239°. On concentration of the mother liquor an additional 0.02 g. of impure material resulted. The pure material showed an infrared spectrum identical with the previous high-melting product.

*Assay.* Calcd. for $C_{36}H_{24}O_2$: 2.322 $\mu$c/mmole. Found: 2.300 $\mu$c/mmole.

OAK RIDGE, TENNESSEE

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

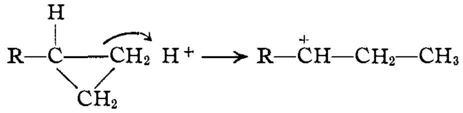
# Isomerization Accompanying Alkylation. IX.[1] The Reaction of Benzene with *n*- and Isopropylcyclopropane. The Synthesis of *n*- and Isopropylcyclopropane[2]

BY HERMAN PINES, WILLIAM D. HUNTSMAN[3a,3b] AND V. N. IPATIEFF[3c]

RECEIVED NOVEMBER 7, 1952

The alkylation of benzene with *n*- and isopropylcyclopropane in the presence of hydrogen fluoride has been studied. The reaction of benzene with *n*-propylcyclopropane produced a mixture of hexylbenzenes consisting of approximately 41% 2- and 46% 3-phenylhexane. With isopropylcyclopropane, the monoalkylated product consisted of approximately 80% 2-methyl-2-phenylpentane and possibly as much as 15% 3-methyl-3-phenylpentane. The three-membered ring in monoalkylcyclopropanes appears to cleave exclusively in one direction during acid-catalyzed alkylations. The synthesis of *n*- and isopropylcyclopropane in good yields and the infrared spectra of these compounds are reported. The infrared spectra of four of the hexylbenzenes are reported.

The acid-catalyzed alkylation of benzene with cyclopropane at low temperatures is of interest because *n*-propylbenzene is formed to the exclusion of the isopropyl derivative.[4,5] Recent studies in this Laboratory, however, have shown that extensive isomerization of the type involving hydride ion shifts occurs during the alkylation of benzene with certain alkylcyclopropanes.[5] Ethylcyclopropane, for example, yields a mixture of 2- and 3-phenylpentane, this formation of the former involving an hydride ion shift. The production of the same mixture of pentylbenzenes during the alkylation of benzene with 2- or 3-pentanol[1] further exemplifies the ease with which this isomerization occurs. The formation of these substances to the exclusion of the other possible isomeric pentylbenzenes, coupled with the fact that the alkylation of benzene with methylcyclopropane furnishes pure *s*-butylbenzene, indicates that the three-membered ring cleaves exclusively in one direction during acid-catalyzed alkylations. This mode of cleavage is illustrated by the equation



This study has now been extended to include *n*- and isopropylcyclopropane. With these compounds it was found that the cyclopropane ring cleaves by the scheme outlined above, and extensive isomerization occurred during alkylation. Thus, the reaction of benzene with *n*-propylcyclopropane catalyzed by hydrogen fluoride produced a mixture of hexylbenzenes consisting of approximately 41% 2- and 46% 3-phenylhexane as determined by infrared analysis (Fig. 1). All of the bands present in the spectrum of the alkylated product are present in the spectra of either 2- or 3-phenylhexane. Hence, the spectrum of the impurity must be weak or else very similar to the spectra of 2- or 3-phenylhexane. The spectra of the latter compounds are very similar and it was necessary to resort to secondary bands at 9.94, 11.34 and 12.40 $\mu$ for analytical calculations.

The alkylation product from isopropylcyclopropane and benzene (Fig. 2) consisted of approximately .80% 2-methyl-2-phenylpentane (I) (Fig. 3) and may contain as much as 15% 3-methyl-3-phenylpentane (II)[6] (Fig. 4). According to infrared spectra 2-methyl-3-phenylpentane was not

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[1] For paper VIII of this series, see: H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, **73**, 4483 (1951).

[2] Presented, in part, before the Organic Division of the American Chemical Society, Chicago, Ill., Sept., 1950.

[3] (a) Universal Oil Products Co. Predoctoral Fellow, 1947–1950; (b) abstracted, in part, from the Ph.D. thesis of W.D.H.; August, 1950; (c) deceased November 29, 1952.

[4] J. H. Simons, S. Archer and E. Adams, THIS JOURNAL, **60**, 2955 (1938); V. N. Ipatieff, H. Pines and B. B. Corson, *ibid.*, **60**, 577 (1938); V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940); A. V. Grosse and V. N. Ipatieff, *ibid.*, **2**, 447 (1937).

[5] H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, **73**, 4343 (1951).

[6] Sample furnished by the Universal Oil Products Co.

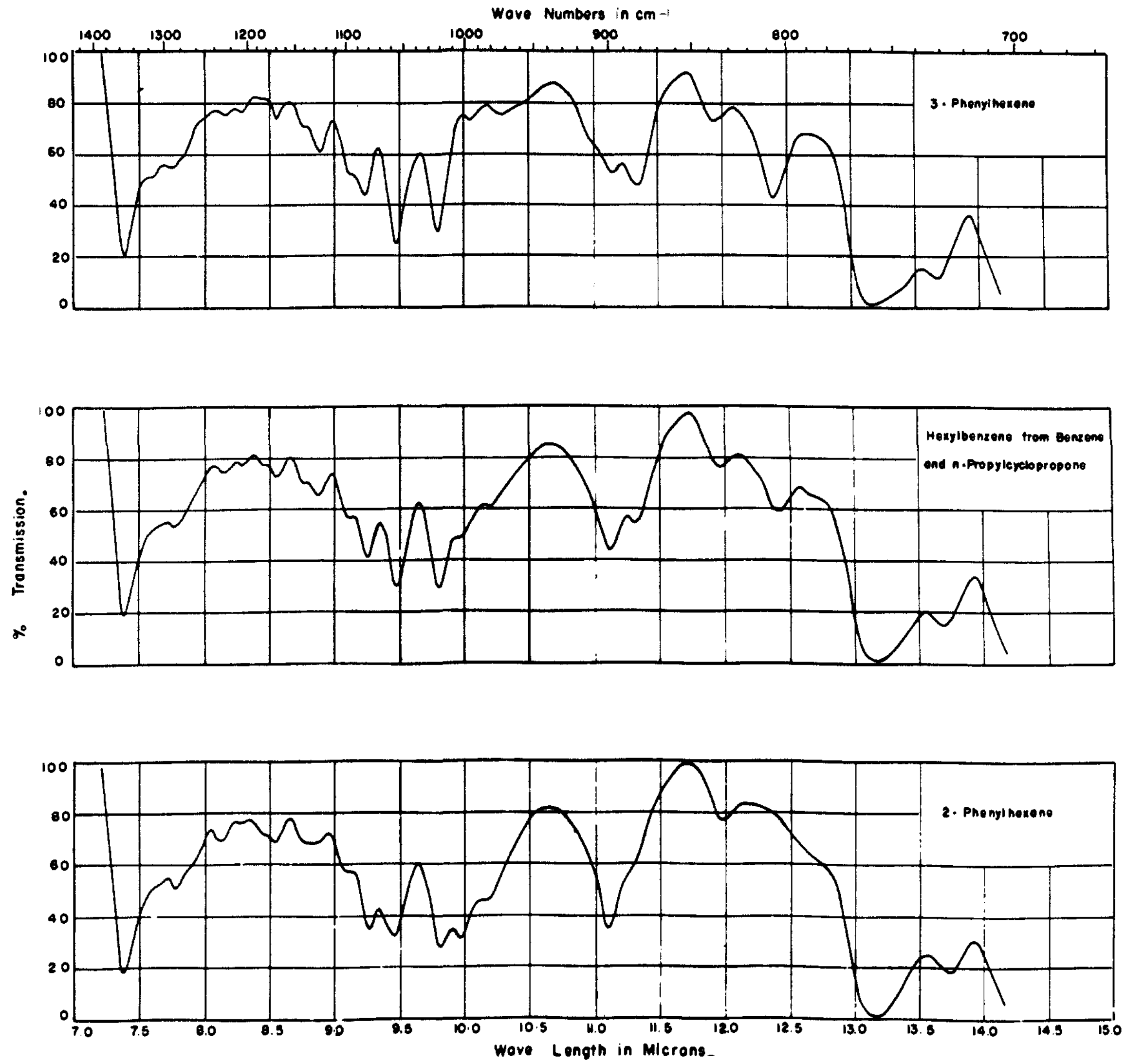
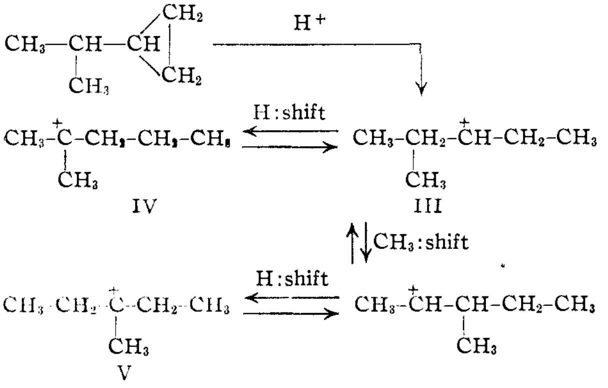
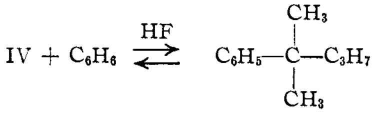


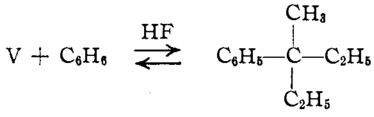
Fig. 1.—Cell thickness, 0.1 mm.; temperature, 25°.

formed in detectable amounts. The remaining product is unknown and may consist of other isomeric hexylbenzenes. The predominant formation of I in this reaction would be expected on the basis of the relative stability of the tertiary carbonium ion IV as compared with the secondary carbonium ion III. The possible formation of II, however, is interesting since it would involve the shift of a methyl group as indicated below.





$$\mathrm{IV} + C_6H_6 \underset{}{\overset{HF}{\rightleftarrows}} C_6H_5-C(CH_3)_2-C_3H_7 \qquad \mathrm{I}$$



$$\mathrm{V} + C_6H_6 \overset{HF}{\rightleftarrows} C_6H_5-C(CH_3)(C_2H_5)-C_2H_5 \qquad \mathrm{II}$$

The syntheses of most of the hexylbenzenes that were used for the reference spectra were conventional. It has been reported[7] that the alkylation of benzene with 2-methyl-2-pentanol in the presence of aluminum chloride produces pure 2-methyl-2-phenylpentane; however, examination of the spectrum of the product prepared this way showed it to contain considerable quantities of isomeric hexylbenzenes. The synthesis of pure 2-methyl-2-phenylpentane was accomplished by the reaction of 2-phenyl-2-methyl-propylmagnesium chloride with ethyl *p*-toluenesulfonate.

The synthesis of *n*- and isopropylcyclopropane is

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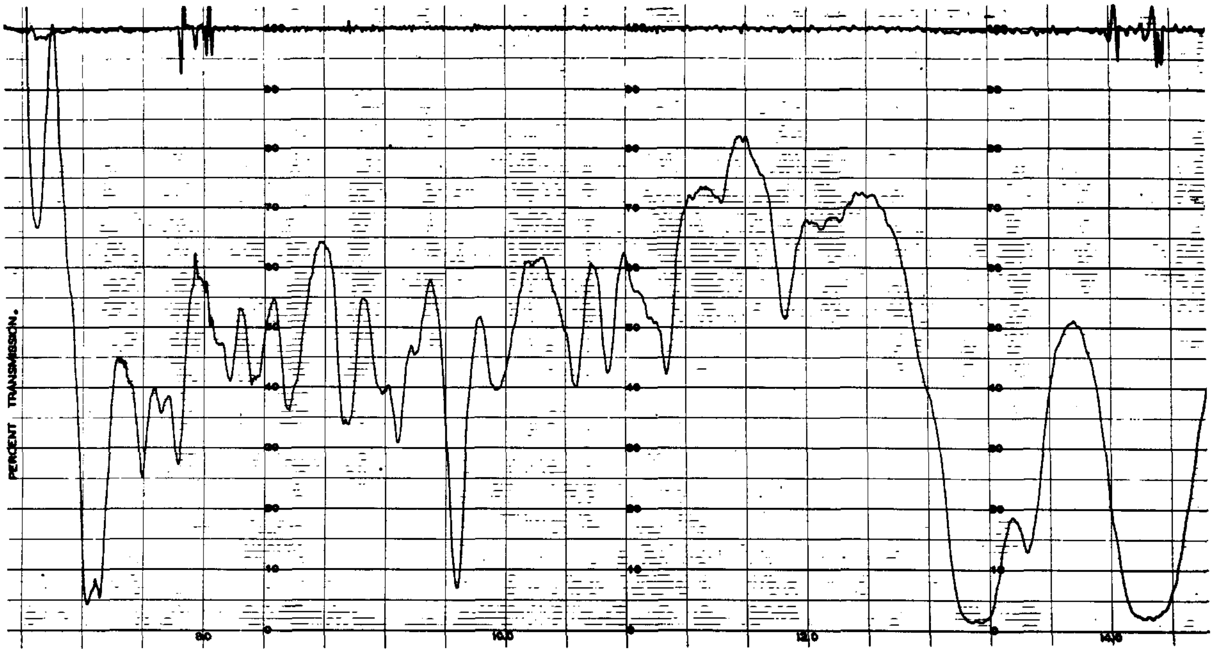
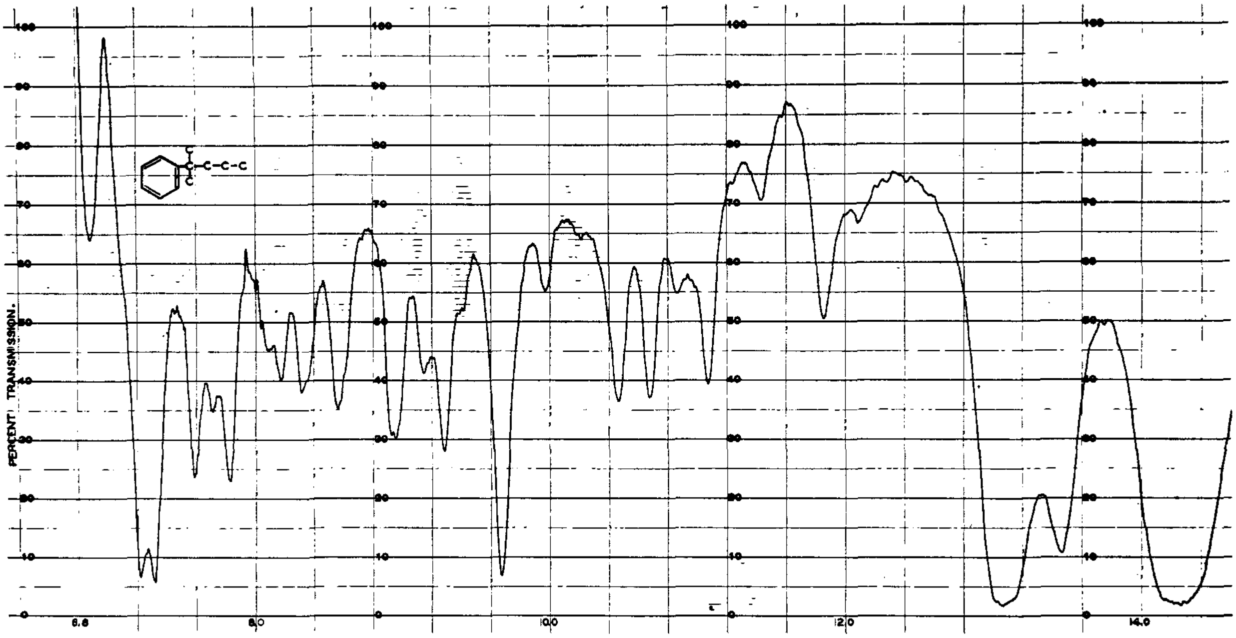
[7] R. C. Huston, W. Fox and M. Binder, *J. Org. Chem.*, **3**, 251 (1938).



Wave length in microns.

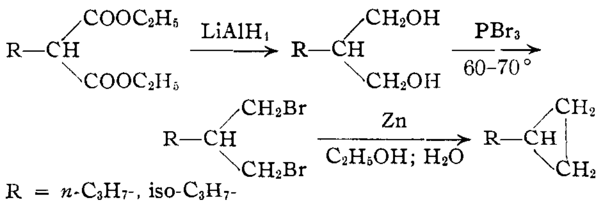
Fig. 2.—Hexylbenzenes from benzene and isopropylcyclopropane; cell thickness, 0.1 mm.



Wave length in microns.

Fig. 3.—2-Methyl-2-phenylpentane; cell thickness, 0.1 mm.

indicated in the scheme below. The reduction of the alkylmalonic esters with excess lithium aluminum hydride proceeded in good yields and this reaction would appear to be very useful for the synthesis of 1,3-diols as intermediates for the



$$\mathrm{R{-}CH}\begin{cases}\mathrm{COOC_2H_5}\\ \mathrm{COOC_2H_5}\end{cases} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{R{-}CH}\begin{cases}\mathrm{CH_2OH}\\ \mathrm{CH_2OH}\end{cases} \xrightarrow[60\text{-}70^\circ]{\mathrm{PBr_3}}$$

$$\mathrm{R{-}CH}\begin{cases}\mathrm{CH_2Br}\\ \mathrm{CH_2Br}\end{cases} \xrightarrow[\mathrm{C_2H_5OH;\ H_2O}]{\mathrm{Zn}} \mathrm{R{-}CH}\begin{cases}\mathrm{CH_2}\\ \mathrm{CH_2}\end{cases}$$

R = $n$-$C_3H_7$-, iso-$C_3H_7$-

preparation of a wide variety of alkylcyclopropanes. The alkylcyclopropanes prepared in this fashion were free of olefins as evidenced by stability to 2% permanganate. Strong absorption bands at about 9.9 μ, characteristic of the cyclopropane ring[8] are present in the spectra of both compounds. The boiling point and refractive index of the isopropylcyclopropane prepared in this fashion agree well with those recently reported for a sample of 98% purity.[9]

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[8] J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 2482 (1949).

[9] V. A. Slabey and P. H. Wise, *ibid.*, **74**, 3887 (1952).

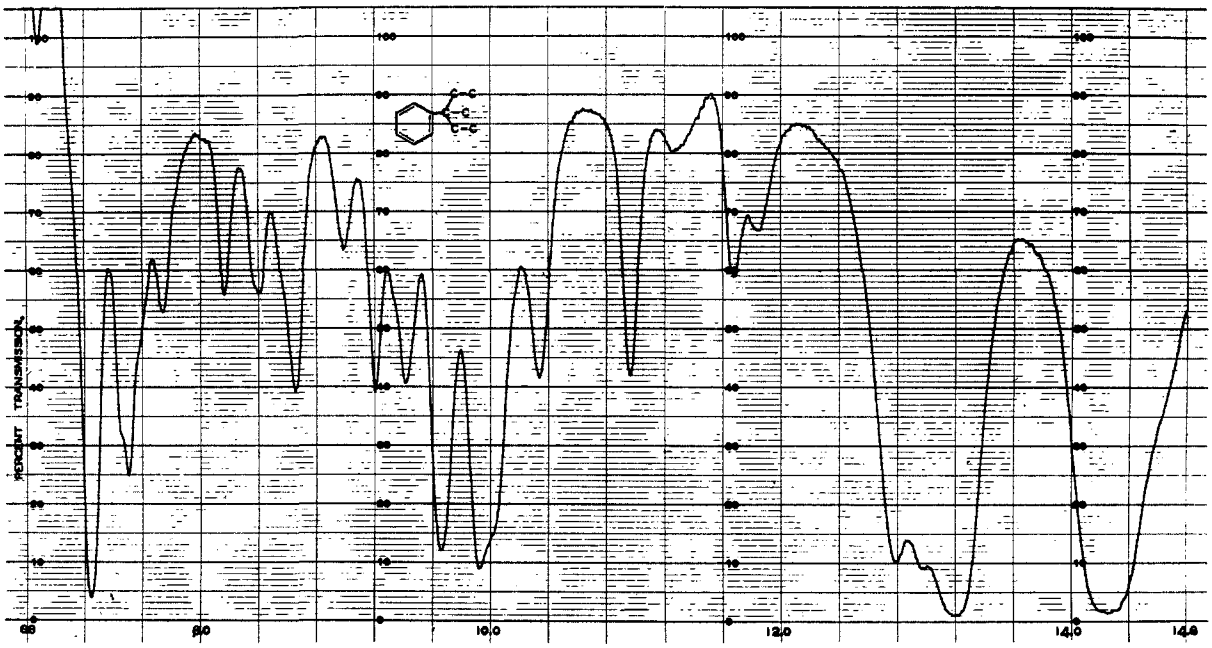

Fig. 4.—3-Methyl-3-phenylpentane; cell thickness, 0.1 mm.

## Experimental

**2-Isopropyl-1,3-propanediol.**—The usual procedure for reductions with lithium aluminum hydride was followed.[10] Ethyl isopropylmalonate, 101 g. (0.5 mole), was added dropwise to a solution of 30.4 g. (0.8 mole) of lithium aluminum hydride in 650 ml. of anhydrous ether. The reaction mixture was worked up in the usual fashion and furnished 41 g. (70% yield) of 2-isopropyl-1,3-propanediol, b.p. 148-148.5° (18 mm.), $n^{20}_D$ 1.4505, $d^{20}_4$ 0.9762.

*Anal.* Calcd. for $C_6H_{14}O_2$: C, 61.0; H, 11.9; *MR*D, 33.05. Found: C, 61.4; H, 11.8; *MR*D, 32.52.

**2-Isopropyl-1,3-dibromopropane.**—2-Isopropyl-1,3-propanediol, 35.4 g. (0.30 mole), was placed in a 250-ml. 3-neck flask fitted with dropping funnel, mercury seal stirrer, thermometer, and reflux condenser holding a calcium chloride tube leading to a gas trap. The diol was warmed to 70° and 60.0 g. (0.22 mole) of phosphorus tribromide was added, with stirring, at such a rate as to maintain the temperature at 65–75°. Stirring and heating at 65–75° were continued for one hour and then the mixture was heated on the steam-bath overnight. The reaction mixture was cooled, poured into ice-water and extracted with ether. The extracts were washed successively with water, 10% potassium carbonate and water until neutral to litmus and then dried over calcium chloride. The ether was stripped, and distillation furnished 46 g. (63% yield) of 2-isopropyl-1,3-dibromopropane, b.p. 106-107° (16 mm.), $n^{20}_D$ 1.5056, $d^{20}_4$ 1.611.

*Anal.* Calcd. for $C_6H_{12}Br_2$: Br, 65.5; *MR*D, 45.43. Found: Br, 65.6; *MR*D, 44.97.

**Isopropylcyclopropane.**—The procedure for conducting the Gustavson cyclization previously described[11a,11b] was followed. The reaction of 40.0 g. (0.16 mole) of 2-isopropyl-1,3-dibromopropane with a well-stirred slurry of zinc dust, 50 g. (0.76 mole) in 80 ml. of 80% ethanol at the reflux temperature produced 11.0 g. (80% yield) of isopropylcyclopropane. The product was fractionated in an 8-plate column, b.p. 58.3-58.5° (750 mm.), $n^{20}_D$ 1.3857 (lit.[9] b.p. 58.31°, $n^{20}_D$ 1.3865). This material was stable to 2% permanganate.

**2-*n*-Propyl-1,3-propanediol.**—The reduction of ethyl *n*-propylmalonate by the procedure outlined above for 2-isopropyl-1,3-propanediol furnished 2-*n*-propyl-1,3-propanediol in 75% yield, b.p. 132–137° (18 mm.), $n^{20}_D$ 1.4480. The bis-phenylurethan melted at 123-125° (lit.[12] m.p. 124.5-125.5°).

**2-*n*-Propyl-1,3-dibromopropane.**—The reaction of phosphorus tribromide with 2-*n*-propyl-1,3-propanediol by the procedure given above for the corresponding isopropyl derivative furnished 2-*n*-propyl-1,3-dibromopropane in 80% yield, b.p. 95–96° (13 mm.), $n^{20}_D$ 1.5030, $d^{20}_4$ 1.583.

*Anal.* Calcd. for $C_6H_{12}Br_2$: Br, 65.5; *MR*D, 45.43. Found: Br, 65.7; *MR*D, 45.40.

***n*-Propylcyclopropane.**—This hydrocarbon was prepared in 85% yield from 2-*n*-propyl-1,3-dibromopropane by the same procedure used for isopropylcyclopropane; b.p. 69-70° (757 mm.), $n^{20}_D$ 1.3926 (lit.[13] b.p. 68.5°, $n^{18}_D$ 1.3957).

*Anal.* Calcd. for $C_6H_{12}$: C, 85.63; H, 14.37; *MR*D, 28.41. Found: C, 85.70; H, 14.08; *MR*D, 28.28.

**3-Phenylhexane.**—3-Phenyl-3-hexanol was prepared in 87% yield by the method of Gilman and Meals.[14] This alcohol was dehydrated over activated alumina at 330° and the resulting olefin hydrogenated at 50°, under a hydrogen pressure of 100 atmospheres, in the presence of nickel-Kieselguhr using an equal volume of pentane as solvent. The 3-phenylhexane thus obtained was fractionated through an eight-plate column and had the following constants: b.p. 207° (752 mm.), $n^{20}_D$ 1.4859 (lit.[15] b.p. 209-212°, $n^{20}_D$ 1.4859).

**2-Phenyl-2-methylpentane.**—2-Phenyl-2-methylpropylmagnesium chloride was prepared by the reaction of 67.2 g. (0.4 mole) of 1-chloro-2-methyl-2-phenylpropane[16] with 9.7 g. (0.4 mole) of magnesium in 500 ml. of anhydrous ether. The reaction mixture was stirred and refluxed for one hour after the addition was complete and then a solution of 160 g. (0.8 mole) of ethyl *p*-toluenesulfonate in 200 ml. of anhydrous ether was added dropwise over a period of 1.5 hr. The reaction mixture was hydrolyzed by pouring over a mixture of cracked ice and 50 ml. of concentrated hydrochloric acid and dried over anhydrous potassium carbonate. Fractionation through an 18-inch column packed with glass helices furnished 28 g. (43% yield) of product, b.p. 113-120° (68 mm.), $n^{20}_D$ 1.4950. This material decolorized 2% permanganate and gave a positive Beilstein test for halogen. Refluxing over sodium at 140° under reduced pressure for

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[10] R. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

[11] (a) N. D. Zelinsky and M. N. Ujedinoff, *J. prakt. Chem.*, [2] **84**, 543 (1911); (b) G. Gustavson, *ibid.*, **36**, 300 (1887).

[12] H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 3121 (1948).

[13] J. Böeseken and H. Takes, *Rec. trav. chim.*, **56**, 858 (1937).

[14] H. Gilman and R. Meals, *J. Org. Chem.*, **8**, 126 (1943).

[15] G. Egloff, "Physical Constants of Hydrocarbons," Vol. 3, Reinhold Publishing Corp., New York, N. Y., 1946, p. 129.

[16] F. C. Whitmore, C. A. Weisgerber and A. C. Shabica, Jr., THIS JOURNAL, **65**, 1469 (1943).

one hour gave a halogen-free product, b.p. 121-123° (60 mm.), $n^{20}D$ 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.), $n^{20}D$ 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°, $n^{20}D$ 1.4868 (lit.[17] b.p. 214°, $n^{20}D$ 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°, $n^{20}D$ 1.4890 (lit.[17] b.p. 209°, $n^{20}D$ 1.4912).

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

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°, $n^{20}D$ 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°, $n^{20}D$ 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.

**Acknowledgment.**—The authors wish to thank Mr. Edmond Baclawski of the Universal Oil Products Company for many of the infrared spectral analyses.

EVANSTON, ILLINOIS

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[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).

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

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

BY HERMAN PINES, WILLIAM D. HUNTSMAN[2a] AND V. N. IPATIEFF[2b]

RECEIVED NOVEMBER 7, 1952

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 iosmerized 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 cyclobutyldimethylcarbinol 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-

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[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).

[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).