ganic boron which might be present. Part of the ether was then distilled and the residue was treated with 5.0 ml. of 2 *N* sodium hydroxide and 5.0 ml. of 30% hydrogen peroxide added in small amounts. The reaction mixture was refluxed for 5 minutes on the water-bath, cooled, and titrated for boric acid. The yield of organoborane was equated to the yield of boric acid obtained in this procedure.

The results are summarized in Table VI.

**Acknowledgment.**—We wish to express our appreciation to Dr. Walter Korytnyk who carried out several of the experiments listed in Tables I and III, permitting a more extensive examination of the scope of the hydroboration reaction.

LAFAYETTE, IND.

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[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

# Organoboranes. I. Isomerization and Displacement Reactions of Organoboranes. A Convenient Procedure for the Conversion of Internal Olefins into Primary Alcohols

BY HERBERT C. BROWN AND B. C. SUBBA RAO[1]

RECEIVED MAY 15, 1959

The hydroboration of 2-hexene yields an organoborane which, oxidized directly without prior isolation, yields 2- and 3-hexanol in equimolar amounts. However, if the organoborane is heated in refluxing diglyme (160°) for four hours prior to oxidation, the product obtained is essentially pure 1-hexanol. In the same manner 2-octene, mixed 2-, 3-, 4- and 5-decenes, and a similar mixture of tetradecenes have been converted into 1-octanol, 1-decanol and 1-tetradecanol. It is proposed that the isomerization of the organoborane proceeds through a sequence of eliminations to form olefin and dialkylborane, followed by readditions, until the borane has been completely converted into the more stable tri-*n*-alkylborane. In confirmation of this mechanism is the observation that treatment of a trialkylborane with a higher olefin readily liberates the lower olefin with the concurrent formation of a new trialkylborane. In this way, tri-*n*-pentylborane, refluxed with 1-hexene, 1-octene and 1-decene, yields 1-pentene and, in turn, tri-*n*-hexyl-, tri-*n*-octyl- and tri-*n*-decylborane. 2-Octene, in the presence of organoborane as a catalyst, has been partially isomerized in a fractionating column to 1-octene.

The hydroboration of olefins provides a new, simple synthetic route to the organoboranes.[2] The ready availability[2] and high reactivity[3] of the organoboranes suggest that these compounds should have wide utility in organic synthesis and may well become a valuable adjunct to the organomagnesium compounds for such purposes. Accordingly, we have undertaken a systematic investigation of the chemistry of the organoboranes. The present paper is the first of a group which will present our results on the utility of these intermediates in organic syntheses.

Originally, in our hydroboration studies,[2] we isolated the organoboranes from the reaction mixture and then oxidized the products with alkaline hydrogen peroxide to obtain the alcohol. In this way we observed that the hydroboration of 2-pentene yields a tri-*sec* -pentylborane, b.p. 81–82° at 2 mm., with oxidation of this distilled material yielding 63% 2-pentanol and 37% 3-pentanol (infrared analysis).

Later we developed a simplified procedure in which the hydroboration product could be oxidized *in situ*, without isolation. In this procedure, the organoborane from 2-pentene yielded 2- and 3-pentanol in essentially equimolar amounts. During the earlier distillation a partial shift of the boron atom from the 3- to the 2-position of the alkyl group had occurred. Isomerization of a 2-alkylborane to a 1-alkylborane was first reported by Hennion, McCusker, Ashby and Rutkowski in their attempt to synthesize tri-*t*-butylborane by the reaction of *t*-butylmagnesium chloride with boron trifluoride.[4] Instead of the expected product, the organoborane contained both isobutyl and *t*-butyl groups.[5,6] They also reported that tri-*sec*-butylborane could be converted into tri-*n*-butylborane by heating under reflux (200–215°) for 20 hours.

In the course of our studies we observed that the isomerization proceeded far more rapidly in diglyme solution, usually being complete in 2 to 4 hours refluxing in that solvent (b.p. 160°).[7] Since the organoborane is conveniently synthesized in diglyme solution, it is evident that a simple conversion of internal olefins to terminal organoboranes and to primary alcohols is feasible. Accordingly, we undertook a study of this possibility.

## Results and Discussion

The hydroboration of 2-pentene in diglyme solution[2] yields the corresponding tri-*sec*-pentylborane. Oxidation with alkaline hydrogen peroxide without isolation yields an equimolar mixture (infrared analysis) of 2- and 3-pentanol, b.p. 116–119° at 745 mm. On the other hand, if the diglyme solution of the hydroboration product is first heated for 4 hours under reflux, and then oxidized, the product is essentially pure 1-pentanol, b.p. 136–137° at 742 mm.

In a similar manner, 1-hexene yields 1-hexanol, b.p. 155–157° at 743 mm., whereas 2-hexene, yields an equimolar mixture of 2- and 3-hexanol,[8] b.p. 136–138° at 750 mm. After subjecting the

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[1] Post-doctorate research assistant, 1955–1957, on grants provided by The Upjohn Co., Parke, Davis and Co., and Merck and Co.

[2] (a) H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **81**, 6423 (1959); (b) **81**, 6428 (1959).

[3] H. R. Snyder, J. A. Kuck and J. R. Johnson, *ibid.*, **61**, 105 (1938); J. R. Johnson, M. G. Van Campen, Jr., and O. Grummitt, *ibid.*, **61**, 111 (1938); J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., *ibid.*, **61**, 115 (1938); J. R. Johnson and M. G. Van Campen, Jr., *ibid.*, **61**, 121 (1938).

[4] E. Krause and P. Nobbe, *Ber.*, **64**, 2112 (1931).

[5] G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, Abstracts of Papers, 130th Meeting of the American Chemical Society, September 16–21, 1956, p. 53-O.

[6] G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, THIS JOURNAL, **79**, 5190 (1957).

[7] A preliminary Communication reporting this observation was published: H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

[8] We are indebted to Dr. George Zweifel for this analysis utilizing gas chromatography.

intermediate organoborane to refluxing diglyme for 4 hours, the alcohol obtained was 1-hexanol, b.p. 155–157° at 745 mm.

Similarly, the hydroboration–isomerization procedure converted 2-octene into 1-octanol, b.p. 191–193° at 745 mm. In all of these cases, the yields of isolated alcohols were in the range of 75–90%.

In these reactions the boron atom must be approximately 50% on the 2- and 50% on the 3-position of the carbon chain. Yet it exhibits no difficulty in moving to the 1-position. It was of interest to establish whether a more extensive isomerization was possible.

Accordingly, an approximately equimolar mixture of 2-, 3-, 4- and 5-decenes, prepared by the isomerization of 1-decene over sodium-on-charcoal, was hydroborated and oxidized. There was obtained a mixture of secondary decanols, b.p. 190–220° at 742 mm. On the other hand, utilizing the usual isomerization technique prior to oxidation yielded 1-decanol, b.p. 226–229° at 742 mm., with only a small fore-fraction of the secondary alcohols. The product was identical with that realized directly from 1-decene.

Application of the same procedure to a sample of mixed tetradecenes provided a 40% yield of 1-tetradecanol, with a considerable quantity of the secondary alcohols. Evidently, in this case the 4-hour isomerization period is not adequate to achieve complete transfer of the boron to the terminal position. Increase of the heating period to 8 hours resulted in an increase in yield of the primary alcohol to 59%, and with an 18-hour heating period the yield rose to 70%.

In synthesizing the organoboranes we had utilized relatively low pressure and rapid distillation in order to minimize secondary reactions.[2,9] In view of our observation of the facile isomerization of organoboranes in diglyme solution, we reexamined the distillation of the hydroboration products. Organoboranes derived from the 1-olefins underwent no significant change either on refluxing under reduced pressure or during distillation at moderate pressures.[10,11] However, the organoborane from 2-hexene exhibited a slow increase in boiling point, from 168–170° at 30 mm., to 185–188° at 30 mm. as it was heated, first under reflux, followed by a very slow distillation over 24 hours. Thus, isomerization to tri-*n*-hexylborane, b.p. 185–188° at 30 mm., again occurred, but was very slow compared to the corresponding isomerization in diglyme solution.

The results of these studies are summarized in Table I.

TABLE I

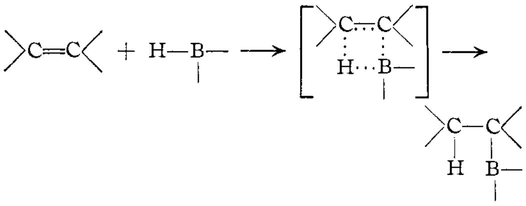
ISOMERIZATION OF ORGANOBORANES

| Olefin (0.3 mole) | Organoborane | Alcohol product G. | Alcohol product % | Alcohol product B.p., °C. (mm.) |
|---|---|---|---|---|
| 1-Pentene | Direct oxidation | 23.8 | 90 | 136–137 (742) |
| 2-Pentene | Direct oxidation | 21.6 | 82 | 116–119 (745) |
| 2-Pentene | Refl. in diglyme, 4 hr. | 22.4 | 85 | 136–137 (742) |
| 1-Hexene | 24.2 g., b.p. 185–188° (30 mm.) | 23.7 | 78 | 155–157 (743) |
| 2-Hexene | Direct oxidation | 24.7 | 81 | 136–138 (750) |
| 2-Hexene | Refl. in diglyme, 4 hr. | 22.8 | 75 | 155–157 (745) |
| 2-Hexene | Solvent removed, refl. for 6 hr., then slow distillation; 20.7 g., b.p. 186–188° (30 mm.) | 21.8 | 71 | 155–157 (743) |
| 2-Octene | Refl. in diglyme, 4 hr. | 32.4 | 83 | 191–193 (745) |
| 1-Decene | Direct oxidation | 40.3 | 85 | 227–229 (748) |
| Mixed decenes | Direct oxidation | 38.9 | 82 | 190–220 (742) |
| Mixed decenes | Refl. in diglyme, 4 hr. | 33.1 | 70 | 190–220 (742) |
| | | 37.8 | 80 | 226–229 (742) |
| Mixed tetradecenes | Refl. in diglyme, 4 hr. | 24.8 | 40 | 168–170[a] (15) |
| | Refl. in diglyme, 8 hr. | 38.1 | 59 | 168–170[a] (15) |
| | Refl. in diglyme, 18 hr. | 43.9 | 70 | 168–170[a] (15) |
| | Refl. in triglyme, 4 hr. | 34.1 | 53 | 168–170[a] (15) |

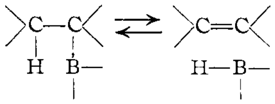
[a] M.p. of phenylurethan 73–74°.

The marked difference in the ease of isomerization of the pure tri-*sec*-alkylborane and that in diglyme solution is noteworthy. Thus, Hennion and his co-workers reported that tri-*sec*-butylborane was converted into tri-*n*-butylborane by heating under reflux at 200–215° for 1 to 2 days. Likewise, we observed a relatively slow isomerization in heating tri-*sec*-hexylborane under reflux. On the other hand, far more extensive isomerizations are complete in 2 to 4 hours at 160° in diglyme solution. It is evident that the ether solvent may be playing an important role in the isomerization. It was previously noted that ether solvents markedly catalyze the addition of diborane to olefins. In view of the mechanism to be proposed for the isomerization reaction, a catalytic effect of the solvent is quite reasonable.[12]

The addition of the boron–hydrogen bond to olefins appears to involve a simple 4-center *cis* addition (1).[13]


(1)

From Rosenblum's observation,[9] it is evident that this addition must be partially reversible at elevated temperatures (2).[11]


(2)

The isomerization of the boron atom from an internal position on a carbon chain to the terminal position can be formulated as a succession of such eliminations and additions (3).

Presumably, the preference of the boron atom for the terminal position is the result of decreased steric interactions in that location.

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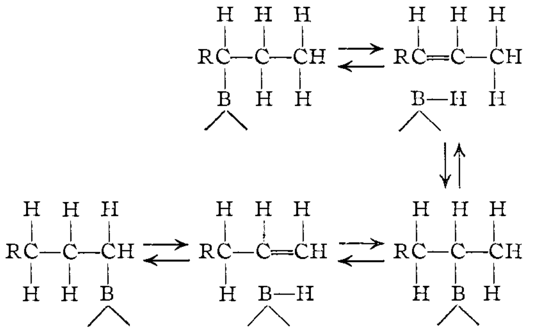
[9] L. Rosenblum, THIS JOURNAL, **77**, 5016 (1955), noted a slow decomposition of tri-*n*-butylborane into *n*-butyldiboranes and butene upon refluxing for 10 days at 125–130°.

[10] R. Köster has reported that he observed a breakdown of the tri-*n*-decylborane into 1-decene and di-*n*-decylborane on attempted distillation (ref. 11). On the other hand, we distilled tri-*n*-hexylborane, b.p. 185–188° at 30 mm., and tri-*n*-octylborane, b.p. 144–145° at 2 mm., with no noticeable difficulty. In both cases, boron analysis of the distilled products indicate the essential absence of appreciable decomposition (ref. 2a). We also distilled tri-*n*-decylborane, b.p. 205–208 at 5 mm., without observable difficulty. Unfortunately, in this case we did not attempt to analyze the product for boron (ref. 2b). We are unable to account for this apparent difference in our observations (see discussion ref. 2b).

[11] R. Köster, *Ann.*, **618**, 31 (1958).

[12] An alternative mechanism has been suggested (ref. 6).

[13] H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 247 (1959).


(3)

We have observed that ether solvents greatly catalyze the addition of diborane to olefins.[2] Consequently, ethers may be expected to catalyze the reverse elimination stage (2). On this basis, the marked enhancement of the isomerization rate observed in diglyme solution is reasonable.

It is a consequence of this mechanism that under conditions of the isomerization reaction, a high concentration of an added olefin should bring about the displacement of that formed in the elimination stage, ultimately forming a new organoborane. Accordingly, we treated tri-*n*-pentylboron in the flask of a fractionating column with 1-hexene, 1-octene and 1-decene. In each case, 1-pentene was collected as distillate and tri-*n*-hexylborane, tri-*n*-octylborane and tri-*n*-decylborane, respectively, were isolated in yields of 85–93%(Table II).[14]

In contrast to the ease with which these straight-chain terminal olefins replace one another, we noted that the corresponding reaction of 2,4,4-trimethyl-1-pentene with tri-*n*-pentylborane was relatively sluggish proceeding only to approximately 60% of completion in 12 hours. It is apparent that the methyl branch in the 2- position markedly reduces the ability of the olefin to participate in the reaction.

In Köster's recent study of this reaction, he utilized triisobutylborane in a number of displacement experiments. In this case the displacement of the branched-chain olefin, isobutylene, proceeds readily even with α-methylstyrene and cyclohexene.

The results of our displacement experiments are summarized in Table II.

TABLE II

ORGANOBORANES BY REACTION OF OLEFINS WITH TRI-*n*-PENTYLBORANE

| Reactants | | | Products | | | | |
|---|---|---|---|---|---|---|---|
| Tri-*n*-pentyl-borane, g. | Olefin | G. | Organo-borane | G. | % | 1-Pentene G. | 1-Pentene % |
| 20.0 | 1-Hexene | 22.2 | Tri-*n*-hexyl- | 20.9 | 93 | 17.1 | 90 |
| 20.3 | 1-Octene | 30.2 | Tri-*n*-octyl- | 28.2 | 90 | 17.0 | 90 |
| 19.9 | 1-Decene | 37.0 | Tri-*n*-decyl- | 32.4 | 85 | 17.2 | 93 |
| 20.0 | 2,4,4-Trimethyl-1-pentene | | Mixed | 13.9 | | 11.7 | 62 |

It is apparent that the ready isomerization of trialkylboranes to place the boron atom in the terminal position provides a simple synthetic route for the conversion of internal olefins to primary alcohols. Moreover, since the isomerized tri-*n*-alkylboranes readily undergo displacement reactions with other olefins, it should be possible to convert the isomerized product into the terminal olefin and a new organoborane. In this way a cyclic process to isomerize internal to terminal olefins appears feasible.

We examined briefly the possibility of a catalytic process for such an isomerization by partially converting 2-octene to the organoborane in triglyme solution and then slowly fractionating 1-octene out of the reaction mixture. The distillate was indeed enriched in 1-octene (28%). However, the equipment at our command at the time these experiments were carried out was not quite suitable and we therefore deferred exploration of this route.

It should be stated that since the above study was completed, the isomerization of organoboranes derived from a wide variety of olefinic structures has been subjected to quantitative study by Dr. George Zweifel in these laboratories. The results fully support the proposed mechanism and open up a number of new and interesting synthetic possibilities. These results will be reported shortly.

## Experimental Part

**Materials.**—The solvents, olefins, sodium borohydride and boron trifluoride etherate have been described in earlier papers.[2] The isomeric decenes and tetradecenes were supplied by Dr. Carl Johnson of the Standard Oil Co. (Indiana). Infrared examination confirmed the absence of the 1-isomers.

**Thermal Isomerization of Organoboranes.**—The reaction apparatus consisted of a 200-ml. two necked flask fitted with sintered glass dispersion tube, a reflux condenser, and an outlet connected to the top of the condenser leading to a mercury bubbler and an acetone wash bottle. In the flask was placed 25.2 g. (0.300 mole) of 1-hexene in 100 ml. of diglyme and the apparatus flushed with nitrogen. Diborane, 60 mmoles (20% excess), was generated as previously described[2] in 90% yield from 100 mmoles of sodium borohydride in 100 ml. of diglyme and 200 mmoles of boron trifluoride etherate, 28.4 g. in 50 ml. of diglyme. The diborane was passed into the olefin solution over a period of 2 hours and then the reaction mixture permitted to stand for 1 hour at room temperature. The solvent was removed under reduced pressure and the organoborane recovered by fractionation at reduced pressure. There was obtained 25.2 g. of tri-*n*-hexylborane, b.p. 185–188° at 30 mm. This was dissolved in diglyme, 10 ml. of water added (hydrogen evolved), followed by 40 ml. of 3 *N* sodium hydroxide, and oxidized carefully with 40 ml. of 30% aqueous hydrogen peroxide. There was obtained 26.4 g. of crude alcohol, b.p. 152–156° at 745 mm. On redistillation, there was obtained 23.9 g. of 1-hexanol, b.p. 155–157° at 743 mm.

In the same manner 25.2 g. of 2-hexene was hydroborated and the product oxidized without isolation. There was obtained 24.7 g. of crude alcohol, b.p. 135–138° at 745 mm.; refractionated: 23.8 g. of an equimolar mixture of 2- and 3-hexanol,[8] b.p. 136–138°. No 1-hexanol could be detected.

In a duplicate experiment 25.2 g. of 2-hexene was treated with diborane and the reaction mixture, diglyme solution, was heated under reflux for 4 hours. The reaction solution was cooled, water added, followed by 40 ml. of 3 *N* sodium hydroxide, and the product oxidized in the usual manner with 40 ml. of 30% aqueous hydrogen peroxide. From 25.2 g. of crude alcohol, b.p. 152–156° at 745 mm., 22.8 g. of 1-hexanol, b.p. 155–157° at 745 mm., was obtained.

Similarly, 25.2 g. of 2-hexene was converted to the organoborane. The solvent was removed under reduced pressure and the residue was heated under reflux for 6 hr. (bath temp.

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[14] These observations were originally published in a Communication which appeared in 1957 (ref. 7). At that time we unfortunately overlooked a Communication by R. Köster, *Angew. Chem.*, **68**, 383 (1956), which included the statement, "Eine Addition von Boralkylen an die C=C Doppelbindung gibt es offenbar nicht. Dagegen existiert die sog. Verdrängungsreaktion

$$B(C_nH_{2n+1})_3 + 3C_mH_{2m} = B(C_mH_{2m+1})_3 + 3C_nH_{2n}\text{''}$$

We regret our oversight and wish to express our appreciation to Dr. Köster for calling it to our attention in a considerate manner.

220–225°). The organoborane was slowly distilled. There was obtained 20.7 g. of organoborane, b.p. 186–188°; at 30 mm., evidently tri-*n*-hexylborane. (Tri-*sec*-hexylborane distills at 168–170° at 30 mm.) The product was oxidized. There was obtained 21.8 g. of 1-hexanol, b.p. 155–157° at 743 mm. No 2- or 3-hexanol was detected.

The procedures utilized for the conversion of 2-pentene, 2-octene, the mixed decenes and tetradecenes into the corresponding primary alcohols were identical and need not be described individually. The experimental results are summarized in Table I.

**Displacement Reactions of Tri-*n*-pentylborane.**—A stock of tri-*n*-pentylborane was prepared by hydroborating 1-pentene.

In a 100-ml. round-bottom flask were placed 20.0 g. of tri-*n*-amylborane (0.09 mole) and 22.2 g. of 1-hexene (0.26 mole). The reaction mixture was heated under reflux for 1 hour under a dry nitrogen atmosphere. The reaction mixture was then fractionated through a Todd column. There was obtained, 17.0 g. of 1-pentene, b.p. 30–31° at 746 mm. The residue distilled through a Vigreux yielded 20.9 g. of tri-*n*-hexylborane, b.p. 124–126° at 1 mm., a yield of 93%.

The procedures were similar in the corresponding reactions involving 1-octene and 1-decene. In the corresponding experiment with 2,4,4-trimethyl-2-pentene, 30.0 g., and tri-*n*-pentylborane, 20.0 g., there was realized only 11.7 g. of 1-pentene after 12 hours of distillation. The residue yielded only 13.9 g. of mixed organoborane with a wide boiling range. The results are summarized in Table II.

**Isomerization of 2-octene.**—In a 200-ml. round-bottomed flask were placed 50 ml. of triglyme and 40 ml. of 2-octene. The mixture was treated with 15 mmoles of diborane to form a catalytic amount of organoborane. The reaction mixture was heated under reflux for 12 hours (nitrogen) and then slowly fractionated in a Todd column, removing distillate at b.p. 120–121°. There was obtained 22.9 g. of olefin, containing 28% of 1-octene, as indicated by infrared analysis.

LAFAYETTE, IND.

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# Mechanism of Acid-catalyzed Isomerization of the Hexanes

BY D. A. MCCAULAY

RECEIVED JUNE 4, 1959

A kinetic study was made of the relative rates of interconversion of all the hexane isomers and of the rates of side reactions at different temperatures, at different concentrations of the HF and HF-BF$_3$ catalysts, and in the presence of inhibitors. A conventional carbonium-ion mechanism accounts for all the facts observed: the need for initiators and a high-dielectric medium, the increase in rate with acidity, the relative rates of conversion of the various isomers, the autocatalytic nature of the cracking reaction, and the change in rates with the concentration of substances that could be carbonium-ion precursors. Cracking inhibitors, such as benzene, were found to function by maintaining the carbonium-ion concentration at a low but constant level and thereby preventing run-away cracking.

The mechanism of the isomerization of alkanes in the presence of a strong acid catalyst has been studied extensively.[1-13] The most favored view is one suggested by Bloch, Pines, and Schmerling[3] and established by Pines and Wackher.[11] They showed that traces of carbonium-ion precursors are necessary to initiate the reaction, and concluded that isomerization proceeds via a chain-carrying, carbonium-ion intermediate. For various reasons, other workers consider a complex between the catalyst and the saturated hydrocarbon as the active intermediate.[5,7,13] Because of these conflicting points of view, additional work to elucidate the mechanism in more detail appeared justified.

In the present study, the relative rates of interconversion of all the hexane isomers and the rates of side reactions were measured at different temperatures, at different catalyst acidities, and in the presence of inhibitors and accelerators. The hexanes were chosen for study because isomerization from a straight-chain configuration to singly and doubly branched forms is possible, side reactions can be controlled, and the products can be analyzed simply. As catalyst, anhydrous hydrogen fluoride promoted by boron trifluoride was chosen because the acidity of this system could be varied over the extremely wide range necessary to measure the widely different rates of isomerization of the methylpentanes and *n*-hexane. Correlations of the rates of isomerization and cracking with the structure of the hydrocarbon and with the other variables could then be expected to shed light on the mechanism of isomerization.

## Experimental

The hexanes studied were *n*-hexane, which isomerizes slowly, and 3-methylpentane, which isomerizes much more rapidly. Both were Phillips Petroleum Company technical-grade hydrocarbons. Gas chromatography showed the *n*-hexane to contain about 1% 3-methylpentane and 2.6% methylcyclopentane, and the 3-methylpentane to contain about 0.5% 2-methylpentane. Most of the impurities other than saturated hydrocarbons were removed by extraction with sulfuric acid, percolation through silica gel, and distillation through a short column. *n*-Hexane and 3-methylpentane receiving this treatment were designated "treated feed." For studying the effect of trace impurities, portions of the two hydrocarbons were further purified by shaking for five minutes with aluminum chloride, decanting,

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