*Anal.* Calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.91. Found: C, 87.06; H, 7.83.

The second material eluted was a gummy solid which yielded 3.6 g. of microscopic white crystals of **1,5-dibenzoylpentane**, m.p. 65–67° (lit.[8] m.p. 64°), upon crystallization from petroleum ether.

*Anal.* Calcd. for $C_{19}H_{20}O_2$: C, 81.43; H, 7.14. Found: C, 81.53; H, 7.27.

It formed a **bis-2,4-dinitrophenylhydrazone**, m.p. 235° dec.

*Anal.* Calcd. for $C_{31}H_{28}N_8O_8$: C, 58.12; H, 4.41. Found: C, 58.13; H, 4.67.

An additional 2.3 g. of this diketone was obtained by chromatography of the distillation residue; total yield 5.9 g. (21%). Additional oily material whose infrared spectrum indicated the presence of hydroxyl groups was obtained by exhaustive elution of the column, but identification was not possible.

**Disproportionation of 1-Phenyl-2-benzoylcyclohexene.**—Two grams of the 88° ketone was dissolved in 30 ml. of *p*-cymene containing 0.2 g. of palladium-on-charcoal and the resulting mixture was heated overnight at reflux under dry nitrogen. Upon filtration and concentration, a gummy yellow solid was obtained which produced white needles, m.p. 116–117°, upon recrystallization from methanol.

*Anal.* Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.67; H, 8.07.

*cis*-**1-Phenyl-2-benzoylcyclohexane** is reported[26] to melt at 116.5–117°. An authentic sample was prepared by addition of phenylmagnesium bromide to benzoylcyclohexene[26] and proved to be identical to the disproportionation product.

**Dehydrohalogenation of 1-Phenyl-2-bromo-2-benzoylcyclohexane.**—In an attempt to obtain 1-phenyl-2-benzoylcyclohexene by an independent route, a sample of 1-phenyl-2-bromo-2-benzoylcyclohexane[26] was prepared and refluxed with 2,6-lutidine. Upon evaporation of the solvent a dark red solid was obtained which yielded white crystals, m.p. 100–102°, upon recrystallization from ether. Its infrared spectrum was identical to that of **1-benzoyl-6-phenylcyclohexene** previously obtained by addition of phenylmagnesium bromide to 6-phenyl-1-cyanocyclohexene,[11] m.p. 95–96°. The reason for the difference in melting points is not known.

**Reaction of Ethyl 2-Cyclopentanone-1-carboxylate with Phenylmagnesium Bromide.**—The same procedure was used as for the cyclohexanone derivative, employing 175 ml. of 3 *M* phenylmagnesium bromide solution and 15.6 g. (0.1 mole) of ethyl 2-cyclopentanone-1-carboxylate. After steam distillation, the residue was taken up in ligroin and chilled. A white solid precipitated and was recrystallized from alcohol, m.p. 213–215°, yield 1.4 g. Its infrared spectrum showed a strong unassociated hydroxyl band at 3500 cm.$^{-1}$. An additional 2 g. was obtained during chromatography of the filtrate; yield 3.4 g. (8%).

*Anal.* Calcd. for $C_{30}H_{30}O_2$: C, 85.27; H, 7.16. Found: C, 84.96; H, 7.38.

**1,1,6,6-Tetraphenylhexane-1,6-diol** is reported[27] to melt at 212°. Upon treatment with acetic acid, a white solid, m.p. 107–108°, was obtained. 1,1,6,6-Tetraphenyl-1,5-hexadiene is reported[27] to melt at 106°. The diol was identical to an authentic sample prepared by the reaction of phenylmagnesium bromide with diethyl adipate.

The remaining ligroin solution was chromatographed on alumina. An oil, yield 6 g. (24%), whose infrared spectrum showed intense carbonyl absorption at 1660 cm.$^{-1}$ (cap. layer) was eluted first and converted to its 2,4-dinitrophenylhydrazone, m.p. 174° dec.

*Anal.* Calcd. for $C_{24}H_{20}N_4O_4$: C, 67.27; H, 4.71. Found: C, 67.44; H, 4.89.

**The 2,4-dinitrophenylhydrazone of 1-phenyl-2-benzoylcyclopentene** is reported[12] to melt at 173°. An authentic sample of this derivative was prepared and the two samples proved to be identical. Continued elution with ether yielded 2.2 g. (8%) of **1,4-dibenzoylbutane**, m.p. 104–106° (lit.[28] m.p. 106–107°).

Nine fractions from the chromatographic column that came off between 1-phenyl-2-benzoylcyclopentene and 1,4-dibenzoylbutane were combined (wt. 0.6 g.) and treated with 2,4-dinitrophenylhydrazine reagent. An orange-red dinitrophenylhydrazone, m.p. 219–220°, isomeric with that from the phenylbenzoylcyclopentene, was obtained. The identity of this compound is unknown.

*Anal.* Calcd. for $C_{24}H_{20}N_4O_4$: C, 67.29; H, 4.67; N, 13.08. Found: C, 66.90; H, 4.65; N, 12.66.

**Reaction of 1-Phenyl-2-benzoylcyclohexene with Phenylmagnesium Bromide.**—A mixture of 5.2 g. (0.02 mole) of 1-phenyl-2-benzoylcyclohexene and 15 ml. of 3 *M* phenylmagnesium bromide was heated in 70 ml. of dry ether for 4 hours. The mixture was worked up in the usual manner and the crude product (5.5 g.) was heated for 30 minutes in 25 ml. of acetic anhydride containing two drops of sulfuric acid. The product from this treatment (3.7 g.) was chromatographed to give 1.6 g. of a hydrocarbon fraction which was heated in *p*-cymene with 0.2 g. of palladium-on-charcoal to produce a white solid, m.p. 122–126°. Recrystallization from methanol produced white crystals of 2-phenyltriphenylmethane, m.p. 136–138° (lit.[29] m.p. 138°). Its infrared spectrum was identical to that of an authentic sample.

A small ketonic fraction was eluted but could not be positively identified. Its infrared spectrum was very similar to but not identical to that of 1-phenyl-6-benzoylcyclohexene. It most probably was a mixture of materials.

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[26] H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

[27] M. Bouvet, *Bull. soc. chim. France*, [4] **17**, 202 (1915).

[28] Reference 25, p. 169.

[29] H. H. Hatt, A. Pilgrim and E. F. M. Stephenson, *J. Chem. Soc.*, 478 (1941).

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

# Isomerization of Saturated Hydrocarbons. XVI.[1] The Aluminum Bromide Catalyzed Isomerization of Ethyl-β-$C^{14}$-cyclohexane

BY HERMAN PINES, CHAO-TUNG CHEN[2a] AND ALFRED W. SHAW[2b]

RECEIVED NOVEMBER 13, 1957

Aluminum bromide catalyzed isomerization of ethyl-β-$C^{14}$-cyclohexane promoted by *sec*-butyl bromide was studied. The relative concentrations of a new species of ethylcyclohexane and 1,2-, 1,3-, and 1,4-dimethylcyclohexanes were found to be in the order of, although the first two compounds exceed, their thermodynamic equilibrium concentrations. About 9–11% of the $C^{14}$ was found in the ring of the dimethylcyclohexanes, which is equivalent to 12–15% of isotopic equilibration. The mechanism of isomerization is discussed and compared with that of hydroisomerization.

In a previous paper of this series[1] it was reported that ethyl-α- and ethyl-β-$C^{14}$-cyclohexane undergo a hydroisomerization reaction at 360° in the presence of a nickel–silica–alumina catalyst. The prod-

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[1] For paper XV of this series see H. Pines and A. W. Shaw, THIS JOURNAL, **79**, 1474 (1957).

[2] (a) Vladimir N. Ipatieff Fellow 1955–1956; (b) Universal Oil Products Co. Predoctoral Fellow 1953–1956.

uct consisted of alkylcyclohexane and alkylcyclopentane isomers. The relative concentration of the dimethylcyclohexanes produced corresponded to their thermodynamic equilibrium concentrations. A near statistical distribution of the radioactivity also was found between the ring and the methyl groups of 1,2-, and 1,4-dimethylcyclohexanes. The results obtained indicated that a deep seated skeletal rearrangement occurred, which must have involved repeated ring contractions and expansions. The extensive rearrangement of the $C^{14}$ isotope suggested that once the hydrocarbon molecule is activated by the formation of the carbonium ion on the solid catalyst it may undergo many rearrangements before the chain is terminated.

The present study was undertaken to provide further support for the proposed mechanism and in particular to determine whether isotopic equilibration occurs in a homogeneous catalytic system. Aluminum bromide was chosen as the catalyst for the isomerization of ethyl-$\beta$-$C^{14}$-cyclohexane on account of its high solubility in hydrocarbons. It was reported that aluminum chloride causes the isomerization of ethylcyclohexane to the isomeric dimethylcyclohexanes.[3,4]

## Results and Discussion

Ethyl-$\beta$-$C^{14}$-cyclohexane was subjected to the aluminum bromide catalyzed isomerization reaction promoted by *sec*-butyl bromide[5] under the conditions listed in Table I. The reaction was conducted in the absence of air and moisture using vacuum technique[6] but substituting oil-pump for the mercury pump. Although a very small amount of yellow sludge was observed, the isomerization undoubtedly proceeded in a homogeneous system, as was the case when high vacuum technique was used. The method employed for analysis consisted in dehydrogenating the alkylcyclohexanes to the corresponding aromatic hydrocarbons, oxidizing the latter to the corresponding acids and analyzing the acids by the method described previously.[1]

TABLE I

THE REACTION OF ETHYL-$\beta$-$C^{14}$-CYCLOHEXANE AND THE COMPOSITION OF THE PRODUCT[a]

| Experiment | 1 | 2 |
|---|---|---|
| Ethyl-$\beta$-$C^{14}$-cyclohexane, g. | 15.240 | 14.000 |
| *sec*-Butyl bromide, g. | 0.064 | 0.058 |
| Aluminum bromide, g. | 0.356 | 0.334 |
| Mole ratio[b] | 100:1:1/3 | |
| Temperature, °C. | 31 | 28 |
| Reaction time, min. | 50 | 40 |
| Composition of product, wt. % | | |
| Ethylcyclohexane[c] | 55.5 | 57.0 |
| Ethylcyclohexane[d] | 1.9 | 0.9 |
| 1,2-Dimethylcyclohexane | 5.2 | 7.5 |
| 1,3-Dimethylcyclohexane | 20.2 | 19.1 |
| 1,4-Dimethylcyclohexane | 11.2 | 9.5 |
| 1,1-Dimethylcyclohexane and alkylcyclopentanes | 6.0 | 6.0 |

[a] Determined by the isotope dilution technique. [b] Ethylcyclohexane: aluminum bromide: *sec*-butyl bromide. [c] Recovered unreacted ethylcyclohexane. [d] New species of ethylcyclohexane.

The composition of the alkylcyclohexanes is given in Table I. The product distribution was calculated from the isotope dilution data which are summarized in Table II. The relative concentrations of the new species of ethylcyclohexane and of the isomeric dimethylcyclohexanes in the reaction product were found to be in the order of their thermodynamic equilibrium concentrations.[7]

TABLE II

RADIOCHEMICAL ASSAY AND DILUTION DATA FOR THE ISOMERIZATION OF ETHYL-$\beta$-$C^{14}$-CYCLOHEXANE

| Experiment | 1 | 2 |
|---|---|---|
| Initial specific activity, c.p.m. | 8 × 3173 | 8 × 6653 |
| Wt. of product taken for analysis, g. | 12.258 | 9.797 |
| Carrier hydrocarbon, g. | | |
| 1,2-Dimethylcyclohexane | 1.686 | 2.712 |
| 1,3-Dimethylcyclohexane | 1.768 | 2.181 |
| 1,4-Dimethylcyclohexane | 1.491 | 2.048 |
| Aromatic acid and spec. activity, c.p.m. | | |
| Benzoic | 7 × 120 | 7 × 123 |
| *o*-Phthalic | 8 × 876 | 8 × 1425 |
| Isophthalic | 8 × 1850 | 8 × 3074 |
| Terephthalic | 8 × 1519 | 8 × 2086 |

1,2-Dimethylcyclohexane and the new species of ethylcyclohexane were produced in amounts remarkably more than their thermodynamic equilibrium concentrations[7] at the expense of 1,3-dimethylcyclohexane in particular (Table III). These results were unexpected in view of the nearly thermodynamic equilibration observed when nickel–silica–alumina was used as a catalyst,[1] and because in the present study likewise the extent of ethylcyclohexane reacted was approximately the same as in the case of the nickel catalyst. The lack therefore of thermodynamic equilibration in the presence of aluminum bromide catalyst as compared with the solid catalyst can be interpreted that on the solid catalyst the carbonium ions produced are chemisorbed on the surface of the catalyst, and they remain there long enough to undergo repeated ring contractions and expansions leading to complete equilibration before encountering another hydrocarbon molecule. On the other hand, in the liquid phase homogeneous catalysis the close proximity of the parent hydrocarbon would interfere with the repeated ring expansions and contractions inasmuch as the chain termination and the chain transfer reaction would be more apt to occur. It has been demonstrated previously[8] that the exchange reaction between a carbonium ion and a hydrocarbon proceeds very rapidly. The deviation of 1,2-dimethylcyclohexane from the thermodynamic equilibration may be due to some factors which favor ring expansion (**a**) over (**b**) in one of the reaction chains. At present, however, such controlling factors are not clearly understood; the preferred **a** step may be due to the inductive effect of the methyl group or/and greater stability

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(3) G. Chiurdoglu, P. J. C. Fierens and C. Henkart, *Bull. soc. chim. Belges*, **59**, 140 (1950).

(4) N. D. Zelinsky, M. B. Turova-Pollak, N. F. Tsvetkova and E. G. Treshchova, *J. Gen. Chem. U.S.S.R.*, **21**, 2409 (1951).

(5) H. Pines and R. W. Myerholtz, THIS JOURNAL, **77**, 5392 (1955).

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

(7) J. E. Kilpatrick, H. G. Werener, C. W. Beckett, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **39**, 523 (1947).

(8) P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1531 (1944).

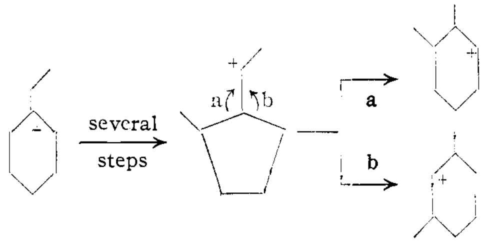
TABLE III

COMPARISON OF EXPERIMENTAL AND THEORETICAL THERMODYNAMIC EQUILIBRIUM CONCENTRATION OF THE ALKYLCYCLOHEXANES[a]

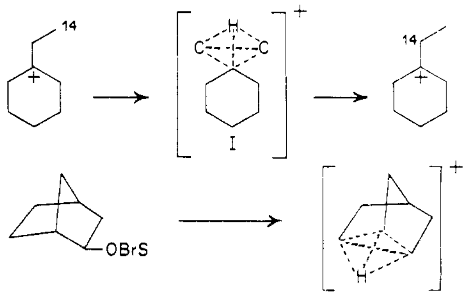
| Experiment | 1[b] | 2[b] | Calcd.[c] |
|---|---|---|---|
| Ethylcyclohexane | 4.9 | 2.4 | 1.3 |
| 1,2-Dimethylcyclohexane | 13.5 | 20.4 | 9.4 |
| 1,3-Dimethylcyclohexane | 52.5 | 51.5 | 60.4 |
| 1,4-Dimethylcyclohexane | 29.1 | 25.7 | 29.0 |

[a] 1,1-Dimethylcyclohexane was excluded from the calculation. [b] The Data of Table I converted to 100% reaction. [c] Taken from the data for 27° of Kilpatrick, *et al.*[6]

of the resulting carbonium ion owing to hyperconjugation.



The production of a new species of ethylcyclohexane in amounts more than the thermodynamic equilibrium concentrations could be explained by a relatively rapid 1,2-shift of the cyclohexylethylcarbonium ion. It is, however, not excluded that the isomerization may take place, to some extent, through an intermediate function of bridged carbonium ions I, which may not be in equilibrium with other species. The side chain carbon atoms then would be made equivalent isotopically, and the $\alpha$-labeled ethylcyclohexane can be produced directly. The occurrence of such ions in reactions of cyclohexane derivatives have not been suggested before, but a very close similarity may be found in the acetolysis of exo-norbornyl *p*-bromobenzenesulfonate, in which a nortricyclonium ion could be one of the intermediates.[9]



It was observed that the isomerization products underwent only 94% dehydrogenation. The remaining 6% may be taken as the total amount of 1,1-dimethylcyclohexane and alkylcyclopentanes. The theoretical thermodynamic equilibrium concentrations according to Kilpatrick, *et al.*,[6] are 6% for the former and 0.5% for the latter for the temperatures studied. Although the distribution of the alkylcyclohexanes deviates to some extent from the theoretical values, the total value of 6% for the two compounds is reasonable.

The radioactivity distribution between the ring and side chain of the alkylcyclohexanes is summarized in Table IV. The values obtained are based on the radiochemical assay data for the degradation experiments of the corresponding acids; Table V and VI. The radioactivity distribution data show that the distribution of $C^{14}$ in the ring for 1,2-, 1,3- and 1,4-dimethylcyclohexanes is 11% and 9% for experiments 1 and 2, respectively. These values correspond to 15% and 12% isotopic equilibration as compared with 80% in the case of the solid catalyst.[1] This difference in equilibration may also be attributed to the difference between homogeneous and heterogeneous catalysis as discussed above. It is seen from Table IV that the radioactivity on the ring of the alkylcyclohexanes increases with the increase in contact time. This is also in agreement with the proposed mechanism.

TABLE IV

THE RADIOACTIVE DISTRIBUTION BETWEEN RING AND SIDE CHAIN OF THE ALKYLCYCLOHEXANES FROM THE ISOMERIZATION OF ETHYL-$\beta$-$C^{14}$-CYCLOHEXANE

| Experiment | 1 | | | 2 | | |
|---|---|---|---|---|---|---|
| Cyclohexane | Ring | Side chain | Diff.[a] | Ring | Side chain | Diff.[a] |
| Ethyl- | 0.8 | 98.6 | −0.6 | 0.3 | 99.6 | −0.1 |
| 1,2-Dimethyl- | 11.2 | 84.2 | −4.6 | 9.4 | 85.6 | −5.0 |
| 1,3-Dimethyl- | 10.6 | 84.4 | −5.0 | 9.8 | 86.3 | −3.9 |
| 1,4-Dimethyl- | 11.6 | 83.4 | −5.0 | 8.6 | 87.2 | −4.2 |

[a] Difference between recovered radioactivity and 100% recovery.

TABLE V

RADIOCHEMICAL ASSAY DATA FOR THE DECARBOXYLATION OF THE AROMATIC ACIDS DERIVED FROM THE ALKYLCYCLOHEXANES

| | Specific activity | | |
|---|---|---|---|
| | Benzoic | Isophthalic | Terephthalic |
| | Experiment 1 | | |
| Acid | 7 × 31 | 8 × 1850 | 8 × 1519 |
| Benzene | 6 × 9 | 6 × 262 | 6 × 236 |
| Carbon dioxide | 1 × 126 | 2 × 6246 | 2 × 5070 |
| | Experiment 2 | | |
| Acid | 7 × 123 | 8 × 3074 | 8 × 2086 |
| Benzene | 6 × 29 | 6 × 401 | 6 × 271 |
| Carbon dioxide | 1 × 666 | 2 × 10612 | 2 × 7275 |

TABLE VI

RADIOCHEMICAL ASSAY DATA: RESULTS OF THE SCHMIDT REACTION ON *o*-PHTHALIC ACID

| | Specific activity | |
|---|---|---|
| Expt. | 1 | 2 |
| *o*-Phthalic acid | 8 × 210 | 8 × 139 |
| Carbon dioxide | 1 × 707 | 1 × 476 |
| Anthranilic acid | 7 × 128 | 7 × 83 |

Statistical scrambling of the carbon atoms was observed when propane-1-$C^{13}$ was contacted with aluminum bromide promoted with water.[10] Similarly, when *n*-butane-1-$C^{13}$ was contacted with same catalyst for 12 hours, 11.6% of the *n*-butane which underwent isomerization was equilibrated isotopically.[11] On the other hand in the rearrangement of 2-methylbutane-1-$C^{14}$ over water promoted

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(9) J. D. Roberts and C. C. Lee, THIS JOURNAL, **73**, 5009 (1951); J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

(10) O. Beeck, J. W. Otvos, J. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **16**, 255 (1948).

(11) J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *ibid.*, **16**, 745 (1948).

aluminum bromide catalyst only a partial scrambling of the carbon atoms occurred.[12] The differences of the extent of scrambling of the isotopic carbons in *n*-butane and 2-methylbutane was attributed to the respective vapor and liquid phase operations.[12] In the present study the less deep seated scrambling of the $C^{14}$ in ethylcyclohexane as compared with previous experiment[1] can also be attributed to the difference in the two phases of operations.

## Experimental

**Ethyl-β-$C^{14}$-cyclohexane** used in this work was from the preparation described previously.[1]

**Aluminum bromide** was prepared according to Walton.[13] As a preliminary purification it was refluxed in an all-glass apparatus with aluminum turnings and then distilled. The receiver test-tubes were immediately sealed after distillations. Further purification and transfer into small ampoules were carried out as described previously,[5] except that a vacuum of 3 mm. by means of an ordinary oil-pump was used instead of a high vacuum.

***sec*-Butyl Bromide Ampoule.**—Freshly distilled *sec*-butyl bromide, b.p. 91.3°, was weighed into a small apparatus, Fig. 1. A was connected to a three-way stopcock which was attached to a vacuum line. Dry nitrogen was passed through the system and B sealed. After *sec*-butyl bromide was frozen with liquid nitrogen bath, the system was evacuated (3 mm.). Admission of nitrogen followed by evacuation was repeated three times, and C sealed off.

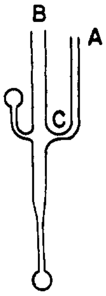

Fig. 1.—*sec*-Butyl bromide ampoule.

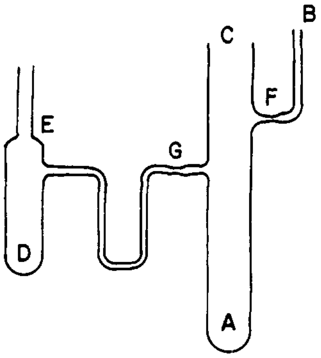

Fig. 2.—Reactor assembly.

**Isomerization Reaction.**—An apparatus shown in Fig. 2 was used. A weighed amount of ethyl-β-$C^{14}$-cyclohexane was placed in A with glass beads and a *sec*-butyl bromide ampoule. B was attached to the vacuum line and C sealed. Nitrogen was passed through the apparatus. An aluminum bromide ampoule, cut at its neck, was dropped into D, and E sealed immediately. The system was isolated, the hydrocarbon frozen with a liquid nitrogen-bath and the system evacuated (3 mm.). Admission of nitrogen and evacuation were repeated three times and the system was isolated again. The cooling bath was removed, the solidified hydrocarbon allowed to melt, the bath placed again to freeze the hydrocarbon and the system evacuated. This was repeated twice and F sealed off. The aluminum bromide was distilled from D to A, and G sealed off. The reaction tube was allowed to warm up to the room temperature, gently rotated to dissolve the catalyst, and shaken to break the *sec*-butyl bromide ampoule. The mixture immediately turned yellow at this moment. Then the tube was shaken for a period of time and at the temperature listed in Table I. After the reaction the mixture was clear and colorless with a very small amount of yellow sludge at the bottom. The tube was cut open and the content poured onto ice. The cold aqueous organic mixture was extracted with ether. The ethereal solution was washed with water, 10% sodium carbonate and water, and dried with Drierite overnight. The ether was distilled on an 8 inch Vigreux column. The residue was distilled from a small Claisen flask to give a clear, colorless distillate, maximum b.p. 127°, $n^{20}D$ 1.4291, 80% recovery.

**Analysis.**—The product for analysis was diluted with inactive 1,2-, 1,3- and 1,4-dimethylcyclohexanes as shown in Table II. The mixture was dehydrogenated by passing twice over 20 ml. of platina–alumina catalyst at 285° at an H.L.S.V. of 0.5. Subsequent chromatography, oxidation of aromatic mixture, separation, purification and decarboxylation of acids, purification of benzene and radioactivity assay, etc., were carried out according to the methods previously described.[1] The results are shown in the tables.

**Dehydrogenation** of a synthetic mixture of 15% 1,1-dimethylcyclohexane and 85% ethylcyclohexane under the conditions mentioned above did not give toluene, as confirmed by infrared spectrum.

EVANSTON, ILLINOIS

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(12) J. D. Roberts and G. R. Coraor, THIS JOURNAL, **74**, 3586 (1952).

(13) H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1950, pp. 103-105.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY]

# Stereospecific Vinyl Polymerization by Asymmetric Induction[1]

BY NICKY BEREDJICK[2] AND CONRAD SCHUERCH

RECEIVED NOVEMBER 2, 1957

*l*-α-Methylbenzyl methacrylate has been polymerized and copolymerized with maleic anhydride. The *l*-α-methylbenzyl groups have been removed from the polymer and copolymer by reaction with phosphonium iodide. The resulting polymeric methacrylic acid exhibited some crystallinity and the reduced copolymer had optical activity of opposite sign (+) to that of the polymeric ester. This appears to be the first demonstration that asymmetric induction can produce a degree of stereospecificity in vinyl polymerization.

The probable presence of stereoisomeric structures in vinyl polymers having the structure $(-CH_2CR_1R_2-)_n$ has been recognized for many years,[3-6] and has been considered the case of the generally poor crystallinity of polystyrene, polyvinyl acetate, polymethacrylates, acrylates and the

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(1) Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956. Abstracted from a portion of a thesis presented by Nicky Beredjick in partial fulfillment of the requirements of Ph.D. at the State University College of Forestry.

(2) Standard Oil Co. (Indiana), Whiting, Indiana.

(3) H. Staudinger, "Die Hochmolekularen Organische Verbindungen," Julius Springer, Berlin, 1932, p. 114.

(4) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 56.

(5) C. S. Marvel, "Chemistry of Large Molecules," Interscience Publishers, Inc., 1943, p. 240.

(6) M. L. Huggins, paper presented at the Rochester Meeting of the A.C.S., June 24, 1944.