2-Oxido-1,1-diphenyl-3-(*o*-chlorophenyl) Propanol.[5]—Ten grams of solid *o*-chlorobenzalacetophenone oxide was added to a stirred ethereal solution of two equivalents of lithium phenyl maintained at −15°. After forty-five minutes of stirring at −15°, the solution was decomposed with iced acid. The ether gave a good yield of the 107–108° oxanol previously obtained by the use of phenylmagnesium bromide. The oxanol was identified by comparison with a known sample.

The author gratefully acknowledges a gift from the Milton Fund of Harvard University, with which the starting materials used in this problem were purchased.

Summary

The action of lithium phenyl and of phenylmagnesium bromide on alpha oxido ketones is compared. The structure of the compound formed by the reaction of phenylmagnesium bromide and benzal-*p*-methoxyacetophenone oxide has been determined.

EXETER, N. H. RECEIVED DECEMBER 16, 1936

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[5] Kohler and Bickel, THIS JOURNAL, **57**, 1100 (1935).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND MILLS COLLEGE]

Stereochemistry of Deuterium Compounds. I. Optical Rotation of Methylhexyldeuterocarbinol

BY LEONA YOUNG AND C. W. PORTER

Many unsuccessful attempts have been made to obtain optically active compounds in which asymmetry is dependent upon differences between hydrogen and deuterium. It was our aim, a year ago, to prepare stereoisomeric compounds of the type RR′CHD and to isolate the *d* and *l* forms of these compounds. Attempts to prepare such compounds from optically active halides, through the Grignard reaction, led to complete racemization.[1] Attempts to isolate an optically active hydrocinnamic acid from the products formed when cinnamic acid was reduced by deuterium failed, presumably, on account of slight differences in the solubilities of the alkaloid salts. Failure to resolve racemic phenyldeuteroacetic acid, C_6H_5-CHD-COOH, into active components through fractional crystallization of alkaloid salts was attributed to the same cause.[2]

Biilman, Jensen and Knuth claim to have produced a measurable optical rotation in camphane through the substitution of deuterium for hydrogen in a methylene group[3] but their findings have not been confirmed and their technique has been the subject of adverse criticism.[4]

Recently we turned our attention to a comparison of the rotations of compounds in which the hydrogen and deuterium are not attached directly to the asymmetric carbon atom. One example of this type has been reported.[5] Methyl hexylcarbinol was resolved into active components and the dextrorotatory fraction was used in the experiments reported here. The active alcohol was esterified by treatment with acetyl chloride and the ester was, in turn, hydrolyzed with deuterium oxide. The rotation of the recovered alcohol was lower than that of the original sample. This alcohol was then reconverted into the original form through esterification and subsequent hydrolysis with ordinary water. The recovered compound had the same rotation as that of the original sample. The experiment was repeated several times and, within the limits of experimental error, the results were the same.

The measured rotations were as follows:[6]

	I	II	III
Original carbinol	17.45	19.00	17.90
Deuterium derivative	17.20	18.70	17.60

The average difference in rotations of the two compounds was 0.28 scale divisions or 0.11°. We feel justified, therefore, in reporting a real difference between the optical properties of ordinary methylphenylcarbinol and the compound formed

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[1] Porter, THIS JOURNAL, **57**, 1436 (1935).

[2] Schultz and Porter, unpublished work, 1935.

[3] Biilman, Jensen and Knuth, *Ber.*, **69**, 1031 (1936).

[4] Leffler and Adams, THIS JOURNAL, **58**, 1555 (1936).

[5] Clemo and McQuillen, *J. Chem. Soc.*, 808 (1936).

[6] The measurements were made with a Fric polarimeter. The scale divisions on this instrument are equivalent to 0.404 degrees. The reading +19.00 corresponds to 7.68°. The specific rotation of the pure dextro compound with green light (5461 Å.) is +11.80°. Our resolution of the racemic mixture was not quantitative but for the purpose of this study it was not necessary to have complete separation. It was necessary only to have a preparation of known rotatory power and to be sure that no racemization occurred in the treatment to which the compound was subjected.

by substituting deuterium for hydrogen in the hydroxyl group. The specific rotation of the deuterium compound, $[\alpha]^{17}_{5461}$, is +11.62°.[7]

In earlier attempts to replace the carbonyl hydrogen by deuterium the alcohol was converted into the sodium derivative and the sodium alcoholate was hydrolyzed by deuterium oxide. This treatment caused partial racemization. On the other hand, acetyl chloride acts upon the optically active alcohol without racemization and the acetyl derivative when hydrolyzed by dilute sodium hydroxide or by a solution of sodium ethylate yields the original alcohol without change in rotation.

The acetyl derivative of 2-octanol is very slightly soluble in water and the hydrolysis is necessarily accomplished in alcoholic solution. To guard against an exchange between the hydrogen of the hydroxyl group in the ethyl alcohol (used as a solvent) and deuterium in the hydroxyl group of the octyl alcohol, we hydrolyzed the ester in a mixture of NaOD, C_2H_5OD and D_2O when the heavy derivative was wanted and we used a mixture of NaOH, C_2H_5OH and H_2O when the light alcohol was wanted.

Experimental

The Resolution of Methylhexylcarbinol.—The standard method for the resolution of a racemic mixture of methylhexylcarbinol into its optical isomers was employed.[8]

Preparation of the Acetyl Derivative.—Thoroughly dried dextrorotatory methylhexylcarbinol was converted into the acetyl derivative by means of acetyl chloride. Slightly more than the equivalent weight of acetyl chloride was added to the alcohol, drop by drop and with constant stirring, at a temperature of from 10 to 15°. The mixture was allowed to stand overnight at room temperature. The excess of acetyl chloride was then distilled off on a water-bath. The remaining acetyl derivative of the alcohol was obtained by distillation under reduced pressure.

Preparation of the Deuterium Derivative.—One half of the acetyl derivative of the dextrorotatory methylhexylcarbinol (17.68 g.) was dissolved in 120 cc. of C_2H_5OD and 40 cc. of D_2O. To this was added 10 g. of NaOD. The solution was heated for one hour under a reflux condenser on a water-bath. The ethyl alcohol was then distilled off by immersing the flask in boiling water. When nearly all the ethyl alcohol had been removed the remaining mixture separated into two layers. The upper layer (methylhexylcarbinol) was removed and dried with anhydrous potassium carbonate. It was then fractionated to remove traces of ethyl alcohol and treated again with potassium carbonate. The process of alternate distillation and treatment with potassium carbonate was continued until there was no further change in rotatory power, *i. e.*, until all water and ethyl alcohol had been removed. The rotation was lower than that of the original alcohol as indicated in the table above.

The remaining half of the acetyl derivative of the methylhexylcarbinol was treated in the same way with NaOH, C_2H_5OH and H_2O. The final product showed no difference in optical rotation from that of the original substance. The result indicates that this method of esterification and hydrolysis does not cause racemization of the alcohol.

Conversion of the Deuterium Derivative of Methylhexylcarbinol to the Hydrogen Derivative.—The deuterium derivative of methylhexylcarbinol was converted into the acetyl derivative as described above. The ester was hydrolyzed in a solution of NaOH, C_2H_5OH and H_2O. The product was dried and distilled as previously described and its rotation returned to the original value.

Summary

Substitution of deuterium for hydrogen in the hydroxyl group of methylhexylcarbinol lowers the optical rotation of the compound.

BERKELEY, CALIF.

RECEIVED NOVEMBER 23, 1936

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(7) Calculated from the measured rotation and known composition of the sample used. The specific rotation of ordinary 2-octanol is 11.80°. Our mixture consisting of *d*- and *l*-octanol had a rotation of +7.68°. This value is equal to $11.80\,M_1 - 11.80M_2$ with M_1 and M_2 representing the mole fractions of the dextro and levo rotatory forms, respectively. The mole fraction of the *d*-form in the mixture is, therefore, 0.825 and of the *l*-form 0.175. The mole fractions are the same after conversion to the deuterium derivatives and this mixture in a 10-cm. tube has a rotation of 7.55°. From the equation $7.55 = 0.825\alpha - 0.175\alpha$ we obtain $\alpha = 11.62°$.

(8) "Organic Syntheses," Vol. VI, 1926, p. 68.