Acknowledgment.—The author wishes to acknowledge his indebtedness to Dr. J. D. Roberts for helpful suggestions in the course of this work.

Summary

The electric moments and ultraviolet absorption spectra of phenylcyclopropane, cyclopropyl methyl ketone, 2-methylcyclopropyl cyanide and 3,4-epoxybutene have been measured along with the moments and spectra of some related compounds containing an alkyl group or ethylenic double bond in place of the three-membered ring.

The ultraviolet absorption bands of the compounds containing a three-membered ring adjacent to a multiple bond are found at wave lengths intermediate between those of the corresponding compounds in which the small ring is replaced in turn by an alkyl group and by a double bond, at least when the bands correspond to an $N \rightarrow V_1$ transition. The behavior of the spectra and electric moments of small-ring compounds has been shown to be qualitatively that which would be expected if the small ring were "conjugated" with the double bond; this is in agreement with previous knowledge of the properties of these substances.

EAST LANSING, MICHIGAN RECEIVED APRIL 14, 1947

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Reduction of Organic Compounds by Lithium Aluminum Hydride. II. Carboxylic Acids

BY ROBERT F. NYSTROM AND WELDON G. BROWN

The reduction of various derivatives of carboxylic acids, *i. e.*, esters, anhydrides, and acid chlorides, to the primary alcohols by lithium aluminum hydride has been described in a previous paper.[1] It was not expected that the reduction of the free acids, or rather the lithium and aluminum salts which must be the primary product in the reaction of acids with lithium aluminum hydride, would proceed as readily. However, it has been found that in many cases the reduction does in fact occur readily and it has been possible thereby to prepare a number of alcohols which are not otherwise easily accessible.

The sole exception encountered in studying the behavior of a variety of carboxylic acids was triphenylacetic acid which was recovered unchanged upon acidification of the reaction mixture. This acid could be converted indirectly to the carbinol without difficulty by conversion to the acid chloride which is readily reduced by lithium aluminum hydride.

It is found that hydroxyl and amino groups do not interfere in the reduction of hydroxy- and amino-acids, other than by the decomposition of an amount of hydride equivalent to the active hydrogens. This process has been applied to the preparation of a number of substituted benzyl alcohols by the direct reduction of the corresponding hydroxy- and amino-benzoic acids. Numerous further applications of this kind will be obvious.

The possibility of selectively reducing one of the carboxyl groups of dibasic acids was explored with sebacic acid as a model. This acid was found to be reduced to the corresponding diol in excellent yield by an excess of lithium aluminum hydride. But when the calculated amount of lithium aluminum hydride for the reduction of one carboxyl group was added to an ether solution of the acid (reversing the usual order of addition) the product consisted of a mixture of diol and unchanged acid. The same products were obtained by reduction of the half ethyl ester of sebacic acid under similar conditions. Further experimentation at lowered temperatures is indicated.

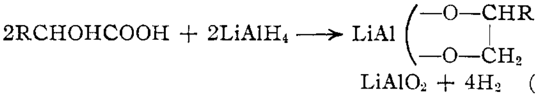
In conformity with previous observations on carboxylic acid derivatives, the double bonds of aliphatic unsaturated acids, *e. g.*, sorbic acid, are not affected by lithium aluminum hydride. However, cinnamic acid undergoes concurrent reduction at the double bond yielding hydrocinnamyl alcohol. It appears to be characteristic of the reagent that ethylenic nuclei, substituted on one side by a phenyl group and on the other by a reducible group (carboxyl, carbonyl, nitro, etc.) are hydrogenated. Further examples will be seen in forthcoming papers.

The equations given below are not intended to be literally accurate with respect to the constitution of the products but will serve to show the stoichiometry for the reduction of various classes of acids.

SIMPLE MONOCARBOXYLIC ACIDS

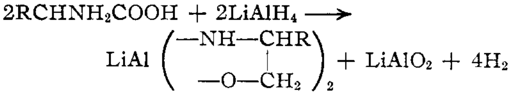
$$\mathrm{4RCOOH + 3LiAlH_4 \longrightarrow LiAl(OCH_2R)_4 + 2LiAlO_2 + 4H_2} \quad (1)$$

HYDROXY ACIDS



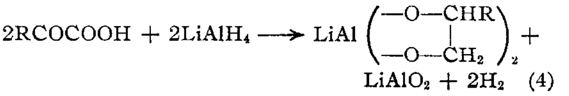
$$\mathrm{2RCHOHCOOH + 2LiAlH_4 \longrightarrow LiAl\left(\begin{array}{l}-O-CHR\\ \qquad | \\ -O-CH_2\end{array}\right)_2 + LiAlO_2 + 4H_2} \quad (2)$$

AMINO ACIDS



$$\mathrm{2RCHNH_2COOH + 2LiAlH_4 \longrightarrow LiAl\left(\begin{array}{l}-NH-CHR\\ \qquad\quad | \\ \ -O-CH_2\end{array}\right)_2 + LiAlO_2 + 4H_2} \quad (3)$$

KETO ACIDS



$$\mathrm{2RCOCOOH + 2LiAlH_4 \longrightarrow LiAl\left(\begin{array}{l}-O-CHR\\ \qquad | \\ -O-CH_2\end{array}\right)_2 + LiAlO_2 + 2H_2} \quad (4)$$

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[1] Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).

Experimental

The procedures followed in the reduction of carboxylic acids were similar to those previously described[1] except that it was generally desirable to work with somewhat more dilute solutions because of the greater tendency of the reaction mixtures to thicken. In some cases decomposition of the reaction mixture by alkali is preferable to acidification; this variant of the procedure is illustrated in the description below of the preparation of *o*-aminobenzyl alcohol. The experimental results are summarized in Table I.

TABLE I

REDUCTION OF CARBOXYLIC ACIDS BY LITHIUM ALUMINUM HYDRIDE

Acid	Product	Yield, %
Trimethylacetic acid	Neopentyl alcohol	92
Stearic acid	Octadecanol-1	91
Sebacic acid	Decanediol-1,10	97
Ethyl hydrogen sebacate	Decanediol-1,10	91
Sorbic acid	Sorbyl alcohol	92
Furoic acid	Furfuryl alcohol	85
Phenylacetic acid	β-Phenylethanol	92
Cinnamic acid	Hydrocinnamyl alcohol	85
Triphenylacetic acid	No reduction at 25°	
Benzoic acid	Benzyl alcohol	81
Salicylic acid	*o*-Hydroxybenzyl alcohol	99
o-Chlorobenzoic acid	*o*-Chlorobenzyl alcohol	97
Anthranilic acid	*o*-Aminobenzyl alcohol	97
Phenylglyoxylic acid	Phenylethyleneglycol	80

Reduction of an Ether-soluble Acid. Phenylacetic Acid to β-Phenylethanol.—A solution of 4.75 g. (0.125 mole) of lithium aluminum hydride in 180 ml. of ether is placed in a one-liter three-necked flask equipped with reflux condenser, dropping funnel, and mechanical stirrer, and protected from moisture until completion of the reaction by calcium chloride tubes attached to the openings. Through the dropping funnel, a solution of 13.6 g. (0.1 mole) of phenylacetic acid in 150 ml. of ether is added at a rate such as to produce gentle reflux. Fifteen minutes after the addition has been completed and with continued stirring and cooling of the flask, water is added cautiously to decompose excess hydride. Then 150 ml. of 10% sulfuric acid is added (the flask may again have to be cooled in ice-water at this point) and a clear solution results. The contents of the flask are transferred to a separatory funnel and worked up in the usual way. The product is purified by fractional distillation through a 24-inch column under reduced pressure and there is obtained a 92% yield of β-phenylethanol, b. p. 112° (18 mm.), n^{20}_D 1.5318.

Reduction of a Compound Slightly Soluble in Ether. Anthranilic Acid to o-Aminobenzyl Alcohol.—The apparatus differs from that described above in that a continuous extractor is inserted between the flask and the reflux condenser. A solution containing 9.1 g. (0.24 mole) of lithium aluminum hydride in 600 ml. of ether is placed in the flask, and 13.7 g. (0.1 mole) of anthranilic acid is placed in the extractor thimble. The solution is warmed until all of the anthranilic acid has been transferred to the reaction flask. The flask is then cooled and the excess hydride is decomposed by the addition of water. To the mixture is then added 250 ml. of 10% sodium hydroxide solution. The ether layer is separated and the water layer extracted with two 200-ml. portions of ether. The residue from the combined ether extracts is dried *in vacuo* over calcium hydride for five hours. The product, *o*-aminobenzyl alcohol, m. p. 82°, is obtained in 97% yield.

Summary

Various types of carboxylic acids are smoothly converted to the corresponding primary alcohols by lithium aluminum hydride. Free hydroxyl and amino groups do not interfere. The double bonds in cinnamic acid, but not in sorbic acid or furoic acid, are simultaneously hydrogenated.

CHICAGO, ILLINOIS RECEIVED APRIL 25, 1947

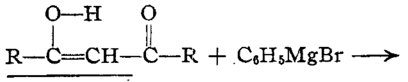
[CONTRIBUTION FROM THE LABORATORIES OF THE UNIVERSITY OF MARYLAND]

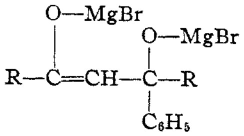
The Reaction of 5,5-Dimethylcyclohexanedione-1,3 (Dimedone) and its Ethyl Enol Ether with Phenylmagnesium Bromide

BY G. FORREST WOODS

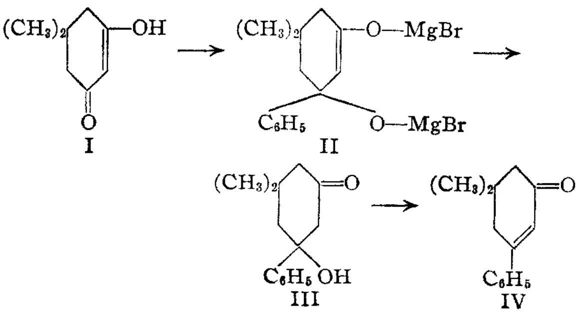
The addition of ethyl cyanoacetate to 5,5-dimethyl-3-phenyl-Δ^2-cyclohexenone in the Michael reaction would make available compounds rather closely related to morphine. The preparation of the above α,β-unsaturated ketone and the reaction of dimedone with phenylmagnesium bromide forms the subject of the present paper.

It was anticipated that the reaction of the strongly enolic dimedone[1] with phenylmagnesium bromide would proceed in accordance with the observations made by Kohler and Erickson[2] for the reaction of strongly enolic α,β-diketones with phenylmagnesium bromide. Kohler's representation of this reaction is as follows


$R-\overset{O-H}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-R + C_6H_5MgBr \longrightarrow$


$R-\overset{O-MgBr}{\overset{|}{C}}=CH-\underset{C_6H_5}{\overset{O-MgBr}{C}}-R$

In the case of dimedone (1) the reaction was expected to proceed as shown below whereby product III would be obtained



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[1] Schwarzenbach and Felder, *Helv. Chim. Acta*, **27**, 1044 (1944).

[2] Kohler and Erickson, THIS JOURNAL, **53**, 2301 (1931).