

TABLE V

RELATION OF VISCOSITY TO BOILING POINT AND VAPOR PRESSURE OF *n*-ALKYL β -ETHOXYPROPIONATES^a

Equation	Pressure or temperature	Equations	Esters excluded	Deviation, cps. Max.	Average
23	760 mm.	$\text{Log } \eta_{25} = 4.5 (10^{-4}) T^2 - 0.794$	1	0.07	0.04
24	50 mm.	$\text{Log } \eta_{25} = 6.0 (10^{-4}) T^2 - 0.700$	1	.06	.035
25	760 mm.	$\text{Log } \eta_{40} = 3.87 (10^{-4}) T^2 - 0.804$	0	.053	.02
26	50 mm.	$\text{Log } \eta_{40} = 5.10 (10^{-4}) T^2 - 0.72$	0	.036	.023
27	150°	$\text{Log } \eta_{25} = 0.877 - 0.3 \log p$	0	.08	.05
28	150°	$\text{Log } \eta_{40} = 0.628 - 0.257 \log p$	0	.046	.029

^a η = Viscosity, cps.; T = boiling point, °K., and p = vapor pressure, mm.

point (or vapor pressure) should be of interest in the evaluation of plasticizers, particularly when it

is desired to combine minimum viscosity with minimum vapor pressure.

Summary

Carefully purified samples of the methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, *n*-octyl and *n*-decyl esters of β -ethoxypropionic acid were used in the determination of boiling points at various pressures, density (d^{20}_4 and d^{40}_4), refractive index (n^{20}_D and n^{40}_D), viscosity at 20 and 40°, and solubility in water at room temperature. Straight-line relationships between certain functions of these physical properties and the number of carbon atoms are given. From the data given here and in previous papers, it should be possible to estimate the boiling points at various pressures, densities, refractive indices, viscosities and water solubilities of all the *n*-alkyl β -alkoxypropionates.

PHILADELPHIA 18, PA.

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

Reduction of Organic Compounds by Lithium Aluminum Hydride. III. Halides, Quinones, Miscellaneous Nitrogen Compounds¹

BY ROBERT F. NYSTROM² AND WELDON G. BROWN

In two previous publications³ we have described the reduction of various carboxylic acid derivatives and of the free carboxylic acids to primary alcohols, and of aldehydes and ketones to the corresponding alcohols, by means of lithium aluminum hydride. Our survey of the potentialities of this reagent in organic synthesis revealed several additional types of organic compounds which are readily reduced. The experimental observations with respect to any one class of compounds have not been as extensive as might be desired but the present results will at least serve to indicate a greatly broadened range of applications.

Collectively, the data now available on the reactions of lithium aluminum hydride with organic compounds point to a far-reaching analogy with the Grignard reagent with respect to the types of compounds which are attacked. This analogy provides a useful basis for prediction; thus the alkyl halides which we find to be smoothly reduced are those which can be made to react with Grignard reagents. There are of course important differences with respect to the nature and extent of the reactions. These differences arise in part from the higher reactivity of the hydride. Thus the smooth reduction of acetomesitylene by the hydride³ is to be contrasted with the hindrance shown in its behavior toward Grignard reagents.

(1) The major portion of the results recorded herein were contained in a paper presented before the Symposium on Hydrides and Related Compounds at the Chicago meeting of the American Chemical Society, September 10, 1946.

(2) Present address: University of Illinois, Urbana, Illinois.

(3) Nystrom and Brown, *THIS JOURNAL*, **69**, 1197, 2548 (1947).

The reduction of carboxylic acids, previously reported, has its analogy in the formation of tertiary alcohols by the action of Grignard reagents on acids but the latter reaction takes place less readily and less completely.

The similarity between lithium aluminum hydride and the Grignard reagent is shown also by the response of the former to the Gilman-Schulze⁴ color test. This test, which is based on a reaction with Michler ketone, is considered to be characteristic for compounds having carbon-metal bonds. The observation that the hydride produces similar color phenomena strongly suggests that the first step is a reduction forming Michler hydrol. An example showing the usefulness of this test in determining the stoichiometry of a reaction with lithium aluminum hydride is given in the experimental part of this paper.

The reduction of nitriles and of cyanohydrins is likely to become an important method for the synthesis of pharmacologically active amines and aminoalcohols. For this reason it seems desirable to point out that cyanohydrins and di-nitriles tend to form highly insoluble precipitates which remove hydride from the solution and hence are reduced in relatively poor yield. A substantial improvement would doubtless result from the use of a greater excess of hydride in such cases, or from the use of solvents which would permit elevated reaction temperatures. The absence of secondary and tertiary amines in the product is a highly advantageous feature of this method of reduction.

(4) Gilman and Schulze, *ibid.*, **47**, 2002 (1936).

The intermediate complexes formed from lithium aluminum hydride and nitriles are stable in a nitrogen atmosphere, but are *pyrophoric* in contact with air.

Further study will be required to clarify the behavior of amides and to determine if the cleavage of the carbon-nitrogen bond observed in the reduction of diethylbenzamide is an isolated instance.

Experimental

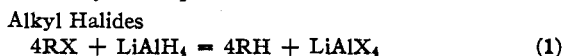
The reductions have been carried out by procedures similar to those described in previous papers with minor modifications. Allyl bromide and methyl iodide yielded gaseous products which were collected in cold traps and the yields were based upon the volume of gas obtained. Propene was identified as its adduct with bromine, 1,2-dibromopropane, b. p. 138°. Acid decomposition of the intermediate reaction complexes was employed except in those cases in which the reaction product is an amine. The procedure was then to decompose the intermediate by the addition of sodium hydroxide solution, as previously described, or by the use of sodium potassium tartrate solution. The latter technique is illustrated by the preparation of *o*-xylylamine described later.

The reduction of nitrobenzene to azobenzene by the usual process furnished a product which required steam distillation to achieve satisfactory purity. A better product was obtained by mixing the reactants (each in ether solution) at -80° and allowing the mixture to warm slowly to room temperature. Measurement of the hydrogen gas evolved during the reduction confirmed the stoichiometry shown in the accompanying equation (Equation 3). The product from the reduction (at room temperature) of *p*-nitrobromobenzene, 4,4'-dibromoazobenzene, being insoluble in water and only slightly soluble in ether, separated in crystalline form upon the addition of dilute sulfuric acid. It was obtained in very pure form merely by filtration and washing with hot water. In most other instances the products were isolated by repeated ether extractions as previously described.

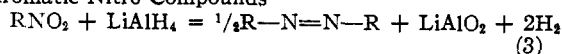
The immediate appearance of the azo color upon adding an aromatic nitro compound to lithium aluminum hydride solution at room temperature constitutes a simple and sensitive test for the nitro group.

Nitromethane, undiluted, reacted with the hydride at room temperature with explosive violence. The higher aliphatic nitro compounds were less reactive but it proved advantageous to add these in the form of dilute ether solutions.

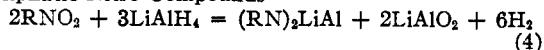
The quantities of lithium aluminum hydride taken for the reductions were in excess (generally 5-15%) of the stoichiometrical quantities indicated by the equations



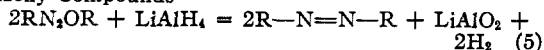
Aromatic Nitro Compounds



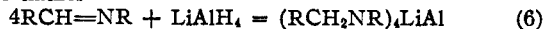
Aliphatic Nitro Compounds



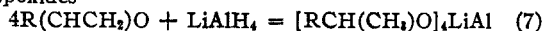
Azoxy Compounds



Aldimines



Epoxides



Amides



The experimental findings are summarized in the accompanying table (Table I). The yields pertain to pure products having acceptable physical constants and which were characterized wherever possible by standard methods. Since these experiments were in the nature of a preliminary survey the yields are not necessarily the best obtainable. The following description represents a typical experiment.

TABLE I
REDUCTIONS BY LITHIUM ALUMINUM HYDRIDE

Compound	Product	Yield, %
Allyl bromide	Propene	85
Methyl iodide	Methane	100
Cetyl iodide ^a	<i>n</i> -Hexadecane	95
Styrene dibromide	No reaction at 25°	
<i>n</i> -Butyl chloride	No reaction at 25°	
<i>p</i> -Benzoquinone	Hydroquinone	70
Anthraquinone ^b	Anthrahydroquinone	95
Phenanthraquinone	Phenanthrahydroquinone	98
Benzonitrile	Benzylamine	72
<i>o</i> -Tolunitrile	<i>o</i> -Xylylamine	88
Sebaconitrile	1,10-Diaminodecane	40
Mandelonitrile	β -Hydroxy- β -phenyl-ethylamine	48
Lauroitrile	Tridecylamine	90
Triphenylacetoneitrile	No reaction at 25°	
Nitrobenzene	Azobenzene	84
<i>p</i> -Nitrobromobenzene	4,4'-Dibromoazobenzene	88
Nitromesitylene	Azomesitylene	71
2-Nitrobutane	2-Aminobutane	85
ω -Nitrostyrene	β -Phenylethylamine	60
Azobenzene	No reaction at 25°	
Azoxybenzene	Azobenzene	99
Benzalaniline	<i>N</i> -Benzylaniline	93
<i>N</i> -Diethylbenzamide	Benzyl alcohol	
Acetanilide ^c	<i>N</i> -Ethylaniline	60
<i>N</i> -Methylacetanilide ^c	<i>N</i> -Methylethylaniline	91
<i>p</i> -Dimethylamino-benzaldehyde	<i>p</i> -Dimethylamino-benzylalcohol	95
Cinnamaldehyde	Hydrocinnamyl alcohol	87
Styrene oxide	α -Phenylethylalcohol	94 ^d
γ -Valerolactone	Pentandiol-1,4	85

^a Mixture refluxed for six hours, then allowed to stand overnight. ^b Soxhlet extractor technique used to introduce the compound. ^c Experiments by Mr. J. S. Ingraham. ^d B. p. 105-106° (20 mm.), n_D^{20} 1.5275, identified as the *N*-phenylcarbamate, [Straus and Grindel, *Ann.*, **439**, 299 (1924)] m. p. 91°.

Reduction of *o*-Tolunitrile to *o*-Xylylamine.—A solution of 7.6 g. (0.2 mole) of lithium aluminum hydride in 300 ml. of ether is placed in a one-liter, three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. Openings are protected from atmospheric moisture, until completion of the reaction, by calcium chloride tubes. Through the dropping funnel, a solution of 23.4 g. (0.2 mole) of *o*-tolunitrile in 200 ml. of ether is introduced at a rate such as to produce gentle reflux. Shortly after completing the addition, sufficient water is added dropwise, and with cooling of the flask in ice-water, to decompose the excess hydride. There is then added 500 ml. of a 20% solution of sodium potassium tartrate. The clear mixture is transferred to a separatory funnel and after separating the ether layer, the aqueous layer is extracted with two 100-ml. portions of ether. From the combined ether extracts there is obtained, after drying over calcium sulfate, an 88% yield of *o*-xylylamine, b. p. 134° (85 mm.), n_D^{20} 1.5412. The product was further characterized by conversion to *o*-xylylbenzamide,⁵ m. p. 88°.

Gilman-Schulze Color Test.—The test was carried out in the following manner. Ten drops of a 1% solution of Michler ketone in thiophene-

(5) Krober, *Ber.*, **23**, 1027 (1890), m. p. 88°.

free benzene are added to 1 ml. of an ethereal solution of lithium aluminum hydride. Thirty seconds later, 1 ml. of water and then 8 drops of a 0.2% solution of iodine in glacial acetic acid are added. Two layers appear and the lower aqueous layer is blue or purple depending upon the concentration of the hydride solution. This test was used to determine the stoichiometry of the reaction of lithium aluminum hydride with *p*-tolunitrile by adding successive portions of the latter to a known quantity of the hydride in ether solution and withdrawing a small sample of the solution after each addition for testing as described above. The test was positive when the quantity of nitrile, in terms of moles per mole of lithium aluminum anhydride, was 1.65 and 1.87, and negative with amounts of 2.09 and 2.31. The combining ratio was thus indicated as lying between 1.87 and 2.09.

Summary

The reduction of alkyl halides to hydrocarbons, nitriles to primary amines, aromatic nitro and azoxy compounds to azo compound, aliphatic nitro compounds to primary amines, and miscellaneous other reductions by lithium aluminum hydride are described.

CHICAGO, ILLINOIS

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Chain Transfer in the Polymerization of Styrene. V. Polymerization of Styrene in the Presence of Mercaptans

BY R. A. GREGG, D. M. ALDERMAN¹ AND FRANK R. MAYO

Chain transfer is the process whereby a polymerizing free radical removes an atom from some molecule, forming an inactive polymer molecule and a new radical.^{1a} The ratio of the rate constants for radical reaction with solvent and with monomer is called the transfer constant,² C , and measures the reactivity of the solvent toward the radical. The polymerization of styrene in carbon tetrachloride³ showed the transfer constant to be independent of the solvent concentration and of the average length of the radicals except for the very shortest⁴ radicals. Application of the same methods to hydrocarbons showed that the relatively unreactive substituted benzyl radical in polymerizing styrene is excellent for determining small differences in reactivities of hydrocarbons.⁵ The present work shows some effects of structure on the reactivities of mercaptan⁶ hydrogen atoms in chain transfer.

Two methods were used to determine the transfer constants of the mercaptans. In the first, the transfer constant, C , is given by^{2,3}

$$1/\bar{P} = C[SX]/[M] + 1/\bar{P}_0 \quad (1)$$

where \bar{P} is the degree of polymerization of the polymer formed at solvent and monomer concentrations $[SX]$ and $[M]$; \bar{P}_0 is a constant equal to the degree of polymerization in the absence of solvent. Experimentally, $[SX]/[M]$ must remain sensibly unchanged and \bar{P} must be large in comparison with unity.^{3,4} In the second method, the rates of disappearance of monomer and solvent are measured, from which⁶

$$\frac{d \log [SX]}{d \log [M]} = C \quad (2)$$

assuming that essentially all chains are terminated by chain transfer. The method is applicable to both catalyzed and uncatalyzed reactions at any conversion, but modification is necessary when the number of moles of monomer and solvent reacting are nearly equal.⁴

(1) Deceased, October 16, 1944.

(1a) Flory, *THIS JOURNAL*, **59**, 241 (1937).

(2) Mayo, *ibid.*, **65**, 2324 (1943).

(3) Gregg and Mayo, *ibid.*, **70**, 2373 (1948).

(4) Mayo, *ibid.*, **70**, 3689 (1948).

(5) Gregg and Mayo, *Trans. Faraday Soc.*, in press.

(6) Cf. also W. V. Smith, *THIS JOURNAL*, **68**, 2059 (1946).