

REDUCTION BY DISSOLVING METALS

XI. THE ACTION OF POTASSIUM AND ALCOHOLS ON SOME MONOBENZENOID SUBSTANCES

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Summary

An investigation has been made of some of the effects of structure and of conditions on the extent of reduction by potassium and alcohols of a number of monobenzenoid substances (see Table 1).

I. INTRODUCTION

It is well known (Birch 1950) that alkali metals and alcohols in liquid ammonia can reduce monobenzenoid compounds to $\alpha\delta$ -dihydro-derivatives. It was briefly reported (Birch 1947) that potassium and alcohols can bring about the same reduction in anisole derivatives. A further study has now been carried out with the object of comparing the yields obtainable from benzenes variously substituted with alkyl-, methoxy- and dimethylamino-groups in relation to possible reaction mechanisms. The process has the advantage for this purpose over the metal-alcohol-ammonia combinations that completely homogeneous solutions of the organic substances can be obtained. It has the disadvantage that the potassium forms a separate phase. However, all reductions were carried out as far as possible under the same conditions, and the results in any given case were usually reproducible within several per cent.

Estimation of the extent of reduction was carried out in two entirely different ways. The first method depends on the fact that the dihydroanisole and dihydroaniline derivatives on acid treatment give rise to ketones. These can then be quantitatively estimated as their 2,4-dinitrophenylhydrazones (method A or B). The second method, applicable to alkyldihydrobenzenes or dihydroanisoles, depends on the fact that they are quantitatively oxidized to the benzene or anisole by the action of lead tetra-acetate, and can accordingly be titrated using standard methods (method C). Usually these methods give results in good agreement, Table 1. They were checked against one another by using a sample of 2,5-dihydroanisole prepared by reduction with sodium and ethanol in liquid ammonia: method A 92.6 per cent.; method C 93.9, 93.7 per cent. This material, after standing for 5 days, gave the values: method A 83.4 per cent.; method C 83.8 per cent. It is well known that autoxidation to aromatic material occurs on leaving in air.

In Table 1 the amounts of different substances and alcohols employed are in molar ratios throughout, unless otherwise indicated, being based on the

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clusive; it may be that the slightly lower yield at higher temperature is due to increasing side-reactions such as conjugation of the double bonds and further reduction.

Owing to an interruption in collaboration the effects of a number of alterations in structure have not yet been examined; discussion of the mechanism will therefore be postponed. It is worth noting, however, that the order of ease of reduction anisole > dimethylaniline > toluene is in the order of the inductive effects of the groups attached to the ring. The process may be of some practical importance for compounds insoluble in liquid ammonia.

II. EXPERIMENTAL

(a) *Reduction Process*.—The potassium was purified by heating with pure dioxan, thus being obtained as clean metallic spheres which floated on the surface; the impurities sank to the bottom. The alcohols were purified by standard methods to obtain completely anhydrous material. The compound to be reduced (5.00 g of tolyl methyl ether or the mol. equiv. of other ethers) was dissolved in the alcohol (40.0 c.c. of ethanol or the mol. equiv. of other alcohols) in a flask (100 c.c.) fitted with a stirrer and reflux condenser. Potassium (3.2 g) was added in small pieces with vigorous stirring, the total time of addition being 45–60 min according to the rate of reaction; the temperature was kept at about 50–60 °C.

(b) *2,4-Dinitrophenylhydrazine Estimation*.—(i) *Method A*. After reduction, water (50 c.c.) was added and the solution extracted with ether (2 × 25 c.c.). The extract was added to a freshly prepared solution of 2,4-dinitrophenylhydrazine (4 g) in ethanolic sulphuric acid (5% ; 400 c.c.). Ether was evaporated on the water-bath, ethanol added to make up the original volume, and the solution left for several days. The crystalline precipitate was then removed by filtration, washed with warm aqueous sulphuric acid (2N) and with hot water, dried at 110 °C, and weighed. In several cases (notably that of anisole) the cold ethanolic solution of the reagent was saturated with the 2,4-dinitrophenylhydrazone to avoid loss due to its slight solubility.

(ii) *Method B*. The ether extract (method A) was added to 2,4-dinitrophenylhydrazine (4 g) in hydrochloric acid (2N ; 300 c.c.), the mixture shaken and then warmed. Finally the remaining ether and unreduced aromatic ether were removed by warming under reduced pressure, while hydrochloric acid (2N) was added to make up loss by evaporation. After leaving overnight the derivative was removed by filtration, washed with hot water (2 l.), dried, and weighed.

The derivative in each case was recrystallized and the m.p. agreed with that expected for the $\alpha\beta$ -unsaturated ketone derivative (cf. Birch 1946) with the exception of that from 4-methylanisole which appeared to be a mixture of the derivatives from 4-methylcyclohex-2- and 3-enone. For anisole the unreduced material was shown to be unchanged by its b.p. and n_D ; acidification of the alkaline solution from the original reduction gave no phenol, so demethylation does not occur.

(c) *Lead Tetra-acetate Oxidation*.—(i) *Method C*. Lead tetra-acetate (Dimroth and Schweker 1923) was dissolved to a 0.1N solution in acetic acid purified by refluxing with chromium trioxide for 24 hr. To a weighed aliquot portion (c. 5%) of the ether extract from the reduction (see method A) an excess of lead tetra-acetate (0.1N ; 10–25 c.c.) was added, and the solution shaken for a few minutes. To it was added 20 c.c. of a solution containing potassium iodide (20 g) and crystallized sodium acetate (500 g) in water (1 l.). The liberated iodine was titrated with thio-sulphate (0.1N) in the usual manner. A blank consisting of ether and the alcohol used in the reduction showed only a very small consumption of lead tetra-acetate.

III. REFERENCES

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