

## Reduction of Esters to Related Alcohols

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Aluminium amalgam in alcohol has been found to be an efficient reducing agent for converting an ester grouping to the related alcohol. The method is easy to perform in the laboratory and is superior to other methods, when small quantities are to be reduced. Copper-chromium oxide method is hardly worthwhile with small quantities.

Bouveault-Blanc reduction of esters (*Compt. rend.*, 1903, 136, 1676; *Chem. Zentr.* 1903, II, 418; *Bull. soc. chim.*, 1904, 31, 666; Hansley, *Ind. Eng. Chem.*, 1947, iii, 39, 55) is the only method of converting esters into related alcohols, both in the laboratory and in large-scale practice. This method is not entirely satisfactory from the point of view of yield and the ease of operation on a large scale. The other method of producing alcohols in the laboratory, apart from high pressure reduction, is to convert acids into acid chlorides and then reduce them to aldehydes catalytically and thence to alcohols by standard methods.

Catalytic hydrogenation over copper-chromium oxide under high pressure is now being increasingly used in industry, but in every-day laboratory practice with small quantities it is not very feasible.

Aluminium with a standard electrode potential of -1.67 volts should serve as a good reducing agent though less powerful than metallic sodium ( $E_0 = -2.71$  volts). The usually inert aluminium becomes highly reactive due to removal of the oxide layer from the surface of the metal. It is also possible that in amalgam formation two of the valency electrons of aluminium become temporarily concerned with the two electrons of mercury, leaving one electron of aluminium in a slightly different status. Whatever may be the reason, there is a striking similarity between sodium and amalgamated aluminium. It occurred to us that esters could possibly be reduced by amalgamated aluminium to alcohols in the manner of the Bouveault-Blanc reaction. This expectation has been fully justified. We have found that ethyl benzoate is reduced to benzyl alcohol, ethyl phenylacetate to phenyl ethyl alcohol, and ethyl phenylpropionate to phenyl propyl alcohol. In every case tried, the reaction is facile and reasonably good yields are obtained. In some cases yields are diminished due to inherent difficulty of isolating the end product. The alcohol used had water in it and the reaction was not hindered in any way. We found best yields with 95% alcohol. In some cases it is better to add water to the reaction mixture as the reaction proceeds so that the strength of alcohol remains 95% (ca).

The most striking case was the reduction of *o*-acetoxyethyl salicylate. The product isolated was *o*-ethoxysalicyl alcohol. We are at present unable to provide a clear picture of the mechanism of the reaction. It was thought that the acetoxy group was double decomposed by aluminium ethoxide, forming aluminium acetate and *o*-ethoxymethyl salicylate in the first stage, and then this was reduced to ethoxysalicyl alcohol in the normal manner. But this view does not seem to be correct as using methanol we have not been able to isolate *o*-methoxysalicyl alcohol. The reaction remains largely incomplete and the

only recognisable product that can be isolated in very poor yield is *o*-ethoxysalicyl alcohol. Moreover, by increasing the quantity of water in the alcohol used in reduction, the yield of *o*-ethoxysalicyl alcohol was not much diminished. In the presence of a relatively large amount of water, aluminium ethoxide would have been decomposed to a large extent and would not have been available for the double decomposition reaction. Therefore we are inclined to the view that the group  $-O-COCH_3$  was reduced to  $-O-CH_2CH_3$ . If this view is correct, then it must be regarded as a most remarkable case of reduction. The facile reduction of diethyl phthalate to phthalyl alcohol makes us think that aluminium amalgam is indeed a powerful reducing agent and its possibilities are immense. The reduction of heterocyclic esters should give valuable intermediates for synthetic work.

We are naturally extending the reaction to cover as large a field as possible.

## EXPERIMENTAL

### *Reduction of Ethyl Benzoate to Benzyl Alcohol*

Ethyl benzoate (30 g.), dissolved in hot 95% ethanol (150 c.c.) (temperature 70°), was treated with aluminium (20 g., freshly amalgamated in 4 portions). The amalgam was not dried. The mixture was thoroughly shaken. Water (30 c.c.) was added during the course of reduction to maintain the temperature at about 75°. After the whole of aluminium had reacted, the mixture was filtered and washed with hot ethanol (250 c.c.). After removal of the ethanol from the filtrate, the residue was taken in a solvent, dried, and then distilled; b.p. 205°; carbanilate m.p. 78°; yield 20 g.

*Phenyl ethyl alcohol* was similarly prepared from ethyl phenylacetate (30 g.) and aluminium (15 g.) in hot ethanol (200 c.c.). After removal of the ethanol from the filtered reaction mixture, the residue was taken up in ether whence the product (20 g.), b.p. 220°, was obtained.  $\alpha$ -Naphthyl carbamate, m.p. 119°, was crystallised from hot ethanol.

*Phenyl Propyl Alcohol.*—The reduction was carried out as described before. Ethyl phenylpropionate (17 g.) Al (6 g.), ethanol (150 c.c.) were used. After the reduction was complete, ethanol was removed by distillation. Aluminium hydroxide was then dissolved with hydrochloric acid and the whole thing extracted with chloroform. From the dried chloroform solution, the product was isolated by distillation; b. p. 235°; phenylurethane m.p. 46-47°; yield 60% of theory. When methyl cinnamate (25 g.) was reduced with aluminium (9 g.) in ethanol (250 c.c. at 75°), but no water was introduced as the reduction proceeded. (The aluminium amalgam was not dried). A crystalline substance (m. p. 172°, 6 g.) was isolated after dissolving the aluminium hydroxide in acid and hydrolysing the residue with alkali to decompose any unchanged ester. The substance was crystallised from benzene-ligroin. (Found: C, 73.4; H, 6.7%). It had no alcoholic group. It was obviously formed by a bimolecular reduction. We are investigating the nature of this substance. But in the above reduction, when water (15+5 c.c.) was introduced as the reaction proceeded, phenyl propyl alcohol (5 g.) could be isolated.

### *Reduction of Diethyl Phthalate: Formation of Phthalyl Alcohol*

Diethyl phthalate (27 g.) in hot ethanol (350 c.c., 68-74°) was reduced with freshly amalgamated aluminium (20 g.). Water (30 c.c.) was added as the reaction proceeded to maintain the temperature to the above limits. The mixture in this experiment was very well shaken. After the amalgam was used up, ethanol was removed by distillation.

HCl was added to dissolve the precipitated aluminium hydroxide and the mixture was repeatedly extracted with chloroform. The residue from chloroform was then hydrolysed with 25% NaOH solution and extracted again with chloroform. The residue from chloroform gave the product (8.9 g.), m.p. 64-65° (cf. Perkin, *J. Chem. Soc.*, 1888, 53, 7). The substance is sparingly soluble in benzene. On oxidation it gave phthalic acid.

*Reduction of o-Acetoxyethyl Salicylate: Formation of o-Ethylsalicyl Alcohol*

*o*-Acetoxyethyl salicylate (25 g.) was reduced with aluminium (12 g.) in hot ethanol (150 c.c.) No extra water, except that came from the moist amalgam, was added. After removal of ethanol the mixture was treated with HCl and then repeatedly extracted with ether. The residue from ether was hydrolysed with 10% NaOH solution. Ether extract from the alkaline mixture gave an oil, b.p. 130-38°/9 mm (265°/760 mm), yield 12 g. (cf. Botsch, *Monats h*, 1880, 1, 621). It gave *o*-ethoxybenzoic acid by permanganate oxidation.

*Reduction of Diethyl Succinate: Formation of Tetramethylene Glycol*

Diethyl succinate (25 g.) was reduced with aluminium (19 g.) in hot ethanol (400 c.c.). The amalgamated aluminium was added in 5 instalments. Finally water (20 c.c.) was added towards the end of the reduction and the mixture refluxed for 2 hrs. After removal of ethanol by distillation, HCl was added and the mixture was extracted with chloroform (3 × 100 c.c.). The residue from chloroform was hydrolysed with NaOH (6 g. in water 20 c.c.) by heating at 100° for 2 hrs. The ice-cold solution was extracted with chloroform repeatedly whence tetramethylene glycol, b.p. 120°/10 mm (12 g.) was isolated. Dibenzoyl derivative m.p. 57-58°. The work is being continued.

