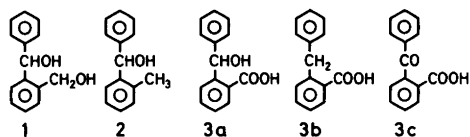


Development of Hydrogen Gas during an Organic Reaction

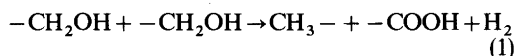
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Reducing 2-benzoylbenzoic acid by means of LiAlH_4 led to 1-(2-hydroxymethylphenyl)-1-phenylmethanol, **1**. In attempts to transfer **1** to other products it was, in one instance, mixed with pulverized potassium hydroxide and heated in a thick-walled glass tube. At about 200°C melting took place, followed by a lively gas evolution and separation of a slightly discoloured solid substance on top of the fluid alkali. It was first thought that water had been split from the diol, giving 1-phenyl-2-oxaindan as a result, but the latter substance prepared separately did not react with alkali under the same conditions.



On investigation, the melted mass was found to consist of a neutral substance containing a methyl group, namely 1-(2-methylphenyl)-1-phenylmethanol (**2**), and the potassium salt of a carboxylic acid (**3a**, **3b** or **3c**) referred to below. An explanation of the chemical process taking place during the melting was arrived at when it was suggested, and in fact proved, that the evolved gas was hydrogen. The process actually consists of a reaction between two molecules containing a primary alcohol group, so that one becomes a methyl group and the other a carboxyl group, at the same time leaving one molecule of hydrogen free, as according to reaction (1).



As will be seen in **2**, the secondary alcohol group from **1** has remained unchanged. This may be due to the fact that **2** is a neutral substance remaining undissolved in the melted alkali. On the other hand, when coming to the carboxylic acid, three formulae **3a**, **3b** and **3c** have been considered. The reason for this is that separate experiments have shown that diphenylmethanol, on heating in the presence of potassium hydroxide, partly turns into a mixture

containing diphenylmethane and benzophenone also. In the present case it is, therefore, probable that the crude product is a mixture from which **3b** and **3c** have been isolated.

Subsequently, it was found that other organic compounds containing a primary alcohol group, on heating with potassium hydroxide, undergo the same reaction with evolution of hydrogen gas. In the case of low-boiling substances, such as benzyl alcohol, the reaction was rather restricted as the required temperature was not reached, but it was obvious that an evolution of gas took place and benzoic acid could be isolated from the molten mass. In the same way, when 3-methylbenzyl alcohol was used, *m*-toluic acid could be isolated.

Using 2-naphthylmethanol the reaction went much easier and the reaction products 2-methylnaphthalene and 2-naphthoic acid were identified.

Finally, it was found that even a higher aliphatic alcohol, such as 1-decanol, to a certain although small degree underwent the same reaction, giving decanoic acid which in the mass spectrometer showed the correct value of m/z 172. On standing, the acid crystallized and had a melting point of 32°C , being the value given for decanoic acid. The corresponding hydrocarbon decane, which should be expected, was obviously too volatile to be isolated in this case.

Experimental. The diol **1** (2 g) was mixed with powdered KOH (8 g) and heated in a thick-walled glass tube, with an arrangement made for collecting the ca. 50 ml gas which evolved. By gas chromatography this gas was proved to be hydrogen. After cooling, the melted mass was dissolved in water and a neutral substance extracted with diethyl ether. The substance (0.6 g) was found to be identical with the 1-(2-methylphenyl)-1-phenylmethanol (**2**) prepared synthetically from *o*-methylbenzyl chloride which, after a Friedel-Crafts reaction with benzene followed by a reduction, gave **2** with m.p. 91°C . Found: C 85.27, H 7.00. Calc. for $\text{C}_{14}\text{H}_{14}\text{O}$: C 84.80, H 7.12. $^1\text{H NMR}$ (CDCl_3): δ 7.2 (m, 10 H), 5.47 (1 H,s), 2.25 (3 H,s).

By acidifying the aqueous solution, an organic acid mixture separated, from which in some cases **3b**, (2-benzoylbenzoic acid, m.p. 118°C) in others **3c**, (2-benzoylbenzoic acid, m.p. 126°C) could be isolated. The authenticity of the two acids was checked by mass spectrometry.

The methyl ester of 2-naphthoic acid was reduced with LiAlH_4 to 2-naphthylmethanol, m.p. 80°C . The latter (1.5 g) mixed with 5 g powdered KOH was heated in a glass tube and at about 210°C gas began to evolve. When about 50 cm^3 gas had been collected, heating was discontinued and the content of hydrogen in the gas confirmed. The hydrocarbon formed, being rather volatile, was adsorbed in

diethyl ether and found to be a liquid which, on the mass spectrometer, showed m/z 129. The value calculated for methylnaphthalene is 130. Acidifying the alkaline solution, 2-naphthoic acid (0.82 g; m.p. 187°C) was isolated.

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