

Synthesis of 2,3-Dihydrobenzofuran

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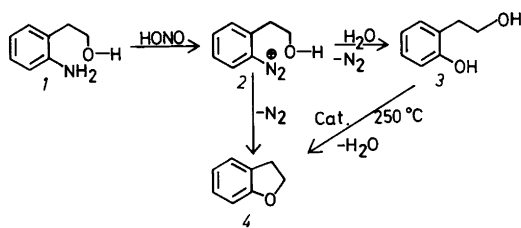
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A new, one-step indole synthesis from 2-(*o*-nitrophenyl)ethanol was reported some time ago.¹ The evidence indicated that the reaction involves a heterogeneously catalysed cyclisation of 2-(*o*-aminophenyl)ethanol (**1**) to 2,3-dihydroindole followed by dehydrogenation to indole.¹ The same principle might also be used in the synthesis of other heterocyclic compounds, and we now report the formation of 2,3-dihydrobenzofuran (**4**) from 2-(*o*-hydroxyphenyl)ethanol. A recent monograph by Mustafa reviews methods for the formation of substituted 2,3-dihydrobenzofurans. However, none of these are well suited for the preparation of **4** itself.²

2-(*o*-Hydroxyphenyl)ethanol (**3**) was obtained (50% yield) together with **4** (35% yield) on diazotisation of **1**. A 70% yield of **3** and traces only of **4** have earlier been obtained by the same reaction.³

2-(*o*-Aminophenyl)ethanol was completely converted to 2,3-dihydroindole by passage over silica gel at 250 °C.¹ In contrast to this, only 1.5% of 2,3-dihydrobenzofuran was obtained when **3** was reacted under these conditions.

However, when a more acidic catalyst, alumina with 6% silica, was used, **3** reacted completely and gave **4** in 75% yield. 2,3-Dihydrobenzofuran



was not dehydrogenated by passage over a catalyst treated to contain copper, which might have been expected from the analogous dehydrogenation of 2,3-dihydroindole.¹ However, the dehydrogenations of **4** over other catalysts are well-known.⁴ A mechanism was proposed for the cyclisation of **1** to 2,3-dihydroindole in which the *o*-amino group undergoes nucleophilic attack on the 1-carbon atom.¹ Phenols are generally weaker nucleophiles than anilines, and the lower reactivity of **3** than **1** over silica gel is thus in accordance with the mechanism proposed earlier. One would also expect the rate of reaction to increase with the acidity of the

catalyst,⁵ as was observed when silica gel was substituted with the more acidic alumina-silica.

Experimental. The facilities for the heterogeneously catalysed reactions, the catalysts, and the analytical method have been described.⁵

2-(*o*-Hydroxyphenyl)ethanol (**3**). Sodium nitrite (22 g) in water (90 ml) was added to **1** (45 g) in water (150 ml), sulfuric acid (30 ml, 98%) and ice (250 g) during 30 min. The temperature was raised to 50 °C for 30 min, the solution made basic and extracted with ether to give **4** (13.8 g, 35% yield). Acidification and ether extraction gave **3** (22.7 g, 50% yield).

Reaction of 2-(*o*-hydroxyphenyl)ethanol (**3**) over silica gel. **3** (3.3 g) in 1,2-dimethoxyethane (4.4 g) was injected on the reactor containing silica gel (10 g) at 250 °C during 1 h. The reactants were passed through with nitrogen (26 l h⁻¹). The product contained **3** (1.8 g, 55%) and **4** (50 mg, 1.5%). The weight of the catalyst increased by 1.2 g during the reaction.

Reaction of 2-(*o*-hydroxyphenyl)ethanol (**3**) over alumina-silica. **3** (3.6 g) in 1,2-dimethoxyethane (4.7 g) was injected on alumina with 6% silica (10 g) at 250 °C during 1 h, nitrogen flow rate 27 l h⁻¹. The product was **4** (2.4 g, 75%). The weight of the catalyst increased by 0.6 g during the reaction.

1. Bakke, J. M., Heikman, H. and Hellgren, E. B. *Acta Chem. Scand. B* 28 (1974) 393.
2. Mustafa, A. *Benzofurans*, Wiley, New York 1974.
3. Bennet, G. M. and Hafez, M. M. *J. Chem. Soc.* (1941) 652.
4. Karakhanov, E. A., Vagabov, M. V. and Viktorova, E. A. *Vestn. Mosk. Univ. Khim.* 13 (1972) 133; *Chem. Abstr.* 78 (1973) 15935 t.
5. Bakke, J. M. and Roholdt, H. M. *Acta Chem. Scand. B* 33 (1979) 152.

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