Reductive Rearrangement of 4-Phenyl-1,3-dioxans to 2-Phenylbutane-1,4-diols upon Treatment with Sodium–Potassium Alloy

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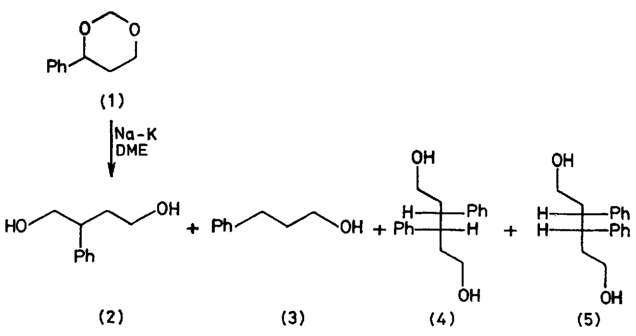
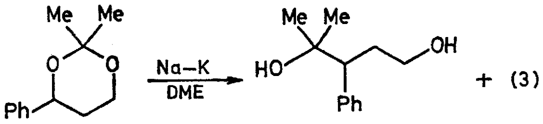
Summary Reduction of 4-phenyl-1,3-dioxan with Na–K alloy affords 2-phenylbutane-1,4-diol as the major product along with smaller amounts of 3-phenylpropan-1-ol and 3,4-diphenylhexane-1,6-diols.

Several years ago it was reported that a naphthalene radical anion is produced upon treatment of 4-phenyl-1,3-dioxan (**1**) in dimethoxyethane (DME) solution with Na–K alloy.[1] The formation of a naphthalene radical anion was inferred from analysis of the e.s.r. spectrum of the product mixture[1] and we were prompted to reinvestigate this potentially useful reaction by isolation and identification of the products. In our hands, reduction of (**1**) with Na–K alloy under a variety of conditions afforded 2-phenylbutane-1,4-diol (**2**) along with smaller amounts of 3-phenylpropan-1-ol (**3**) and 3,4-diphenylhexane-1,6-diols [(±)-(**4**) and *meso*-(**5**)]. Neither naphthalene nor any other bicyclic product was detected in the product mixture.



Reductions were performed under an argon atmosphere in a Morton flask fitted with an efficient stirrer. Solutions of (**1**) in dry DME (2.5×10^{-2} M to 0·5 M) and excess of Na–K eutectic[2] (previously cleaned by washing with dry DME) were rapidly stirred at low temperature (−42 to 0 °C in various runs) until the initially red suspension turned a deep green in colour[1] (2—18 h, depending on concentration, temperature, and stirring rate). Following the sudden colour change, the DME solution was carefully transferred *via* a cannula on to ice, and the resulting aqueous solution was acidified to pH *ca.* 6·5. Exhaustive extraction with diethyl ether, concentration of the extract, and fractionation of the residue afforded 2-phenylbutane-1,4-diol[3] (**2**) (60%), 3-phenylpropan-1-ol[4] (**3**) (23%), (±)-(**4**)[5] (6%), and *meso*-3,4-diphenylhexane-1,6-diol[5] (**5**) (2·5%). The products were identical in all respects to authentic samples prepared by standard methods.[3–5] As previously noted,[1] the reaction displays a dramatic solvent-dependence characteristic of many such reductions:[6] solutions of (**1**) in diethyl ether are inert to the action of Na–K alloy.

Reduction of (**1**) most likely[6] proceeds *via* benzylic C–O cleavage and loss† of H_2CO from the initially formed radical anion of (**1**) to give $Ph\dot{C}HCH_2CH_2O^-$ (or the corresponding dianion). The formation of (**3**), (**4**), and (**5**) by hydrogen abstraction and/or dimerization from such an intermediate finds ample precedent in the literature.[4–6] The major pathway, a formal reductive rearrangement of (**1**) to (**2**), must involve either a purely intramolecular rearrangement or, more likely, bimolecular recombination of the liberated H_2CO (or its ketyl) with the benzylic dianion (or radical anion) on the surface of the alloy. The possibility that the high yield of (**2**) resulted from incorporation of an H_2CO unit generated by *in situ* fragmentation of the DME solvent[7] was eliminated by the following observation: 2,2-dimethyl-4-phenyl-1,3-dioxan (**6**) in DME was cleanly reduced by excess of Na–K alloy to 2-methyl-3-phenylpentane-2,5-diol (**7**) (31%: m.p. 89—90 °C; lit.[8] m.p. 89—90 °C) and (**3**) (68%). No trace of (**2**) could be detected in the reaction product.



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† Sweeping the reaction mixture with argon and passage of the effluent through dimedone solution resulted in precipitation of small amounts of the formaldehyde–dimedone adduct.

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