Formation of Naphthalene Anion by the Reaction of 4-Phenyl-1,3-dioxan with Sodium–Potassium Alloy

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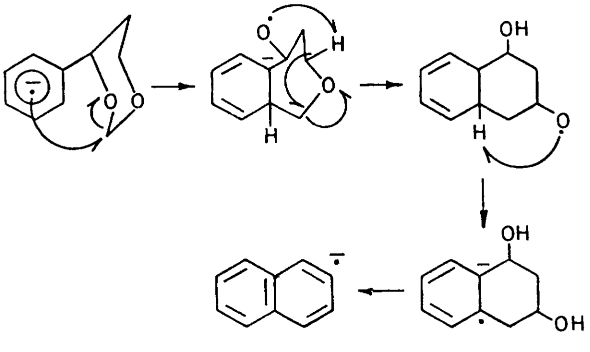
Summary The reaction of 4-phenyl-1,3-dioxan with sodium—potassium alloy produced the naphthalene radical anion.

DURING the course of an e.s.r. investigation of the radical anion of 4-phenyl-1,3-dioxan (**1**), it was observed that the naphthalene radical anion is formed through the rearrangement of the radical anion of (**1**).

Treatment of a solution of 4-phenyl-1,3-dioxan in 1,2-dimethoxyethane (*ca.* 10^{-2}M) with clean sodium–potassium alloy at low temperature (below −30°) *in vacuo* caused the solution to go red. The solution exhibited a strong e.s.r. signal which is attributed to the radical anion of (**1**).[1] The reduction did not proceed either in THF or when potassium and sodium metals were used separately. After a few



SCHEME

hours contact with sodium-potassium alloy at around −30°, the red solution of the radical turned green. The e.s.r. signal due to the radical anion of (**1**) was transformed gradually to a 25-line pattern which consisted of two quintets with a binomial intensity ratio and with hyperfine splitting constants of 5·00 and 1·84 gauss. This hyperfine structure and the colour of the solution fit in well with those reported for the naphthalene radical anion.[2] The naphthalene radical anion was only observed after prior formation of the radical anion of (**1**). It is likely, therefore, that the naphthalene structure is formed *via* the anion radical of (**1**). No appreciable acceleration of the reaction rate with increasing concentration of (**1**) was observed, suggesting that the reaction proceeded through an intramolecular rearrangement.

The mechanism in the Scheme is suggested.

Rough estimation of the e.s.r. signal intensities for both radical anions showed that the yield of the naphthalene radical anion from the radical anion of (**1**) is higher than 50%.

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