

## Reduction by Dissolving Metals. XXI\* Some Deuteroanisoles

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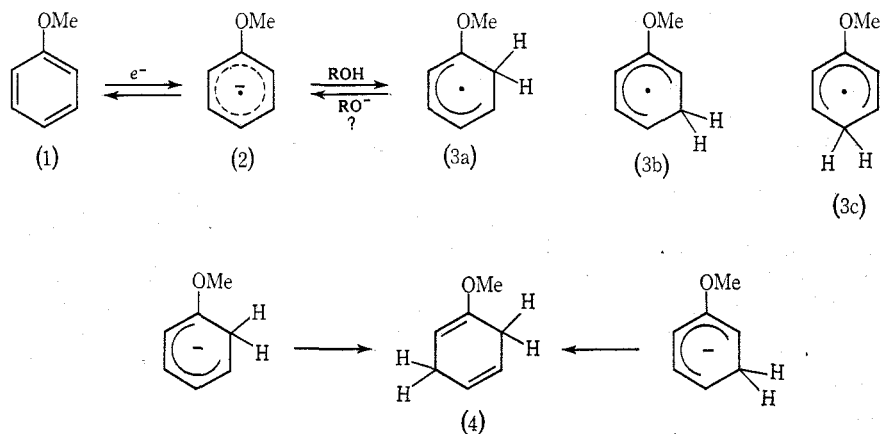
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### Abstract

The reversibility of the protonation steps in the metal-ammonia reduction of anisole has been investigated. Use of deuterated substrates has indicated that the product, in this case, is determined by kinetic protonation at both stages.

The structure of the product of a metal-ammonia reduction of a substituted benzene, e.g. anisole (1), is determined (Scheme 1) by the positions of addition of the two protons in the stages shown.<sup>1</sup> It could be affected by the reversibility of either of the protonations. Reversal of the second protonation has been examined in some detail,<sup>2</sup> and kinetic control gives mainly unconjugated diene. Highly basic conditions are required for reversibility, e.g. the presence of  $\text{NH}_2^-$ . Reversal of the first protonation would regenerate the initial radical anion (2), no matter what ring position was involved. The final product could therefore be determined by which of the possible initial products, e.g. (3a), (3b), (3c), is the least acidic rather than by the relative rates



Scheme 1

\* Part XX, *J. Chem. Soc., Perkin Trans. 1*, 1974, 545.

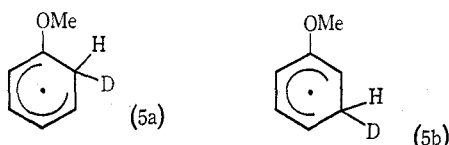
<sup>1</sup> Birch, A. J., and Nasipuri, D., *Tetrahedron*, 1959, 6, 148; Krapcho, A. P., and Bothner-By, A. A., *J. Am. Chem. Soc.*, 1959, 81, 3658.

<sup>2</sup> Birch, A. J., *J. Chem. Soc.*, 1950, 1551; *Q. Rev., Chem. Soc.*, 1950, 4, 84.

of addition to the charged system at the *ortho*, *meta* and *para* positions. Protonated radical anions such as (3a) would be expected to show much higher acidities than (4)<sup>2-4</sup> and reversibility under reduction conditions might be possible.

Furthermore, since 2,5-dihydro derivatives (4) result as the first observable product, it is not clear which of these positions marks the point of reaction of the first proton, an important theoretical point which has led to some controversy<sup>4</sup> so far not settled by experiment. Use of deuterated substrates might indicate if the protonation to (3a) or (3b) is reversible.

We have now found that reduction of anisole[2-D] and anisole[3-D] with sodium in liquid ammonia in the presence of ethanol as a proton source gave no evidence of loss of deuterium from an intermediate such as (5a) or (5b).



Addition of *t*-butoxide anion, to encourage reversal of protonation of (3), did cause some loss of deuterium in the anisole[2-D] case. However, treatment of the dihydro derivative of anisole[2-D] (a mixture of 2,5-dihydroanisole[2-D] and 2,5-dihydroanisole[6-D]) resulted in a similar loss under the same conditions. The 2-position of 2,5-dihydroanisoles is known to be quite highly acidic<sup>2</sup> and exchange of a deuterium in that position would not be unexpected.

Furthermore, the reduction of anisole, anisole[2-D] and anisole[3-D] with sodium in deuterated ammonia in the presence of ethanol[OD] gave no indication of incorporation of more than two deuterium atoms.

We conclude that the product, at any rate in similar cases to (1), is determined by kinetic protonation at both stages.

## Experimental

The deuterium content of the deuterated anisoles and the corresponding reduction products were determined by mass spectrometry. Mass spectra were determined on an A.E.I. MS-902 mass spectrometer operating at 8 eV.

The deuteroanisoles were prepared by the usual Grignard procedure.<sup>5</sup>

### Reduction of Deuteroanisoles

Liquid ammonia (250 ml) was distilled from sodium into a flask containing the deuteroanisole (7.5 g) in anhydrous ethanol (13 ml). Sodium (5.1 g) was added as rapidly as possible (*c.* 5 min) and the blue solution allowed to stir for an additional 20 min. Methanol was added to discharge the blue colour and the ammonia allowed to evaporate. Water was added and the solution thoroughly extracted with ether. The ethereal layer was washed with water and brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The concentrated residue was distilled to afford 7.1 g (93%) of the corresponding dihydroanisole, b.p. 85°/85 mm.

### Reduction of Anisole in Deuterated Ammonia

The procedure was the same as above except ethanol[OD] and ammonia[D<sub>3</sub>] replaced the non-deuterated materials and the reaction was quenched with ethanol[OD] instead of methanol.

<sup>3</sup> Zimmerman, H. E., *Tetrahedron*, 1961, **16**, 169; Brown, J. K., and Burnham, D. R., *Mol. Phys.*, 1968, **15**, 173.

<sup>4</sup> Burnham, D. R., *Tetrahedron*, 1969, **25**, 897, and references therein.

<sup>5</sup> Satchell, D. P. N., *J. Chem. Soc.*, 1956, 3911.

*Reduction of Deuteroanisole in the Presence of Butoxide Anion*

The procedure was the same as that for the reduction of deuteroanisoles but powdered potassium t-butoxide (2 g) was added to the reaction mixture.

**Acknowledgment**

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