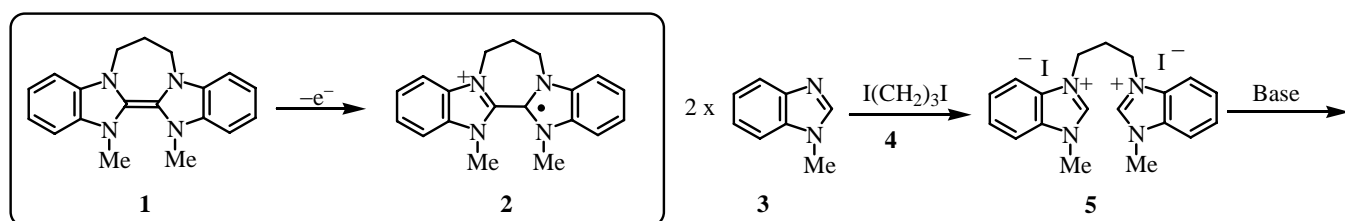


The Birth of 'Super-S.E.T.' Reagents

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Reactive intermediates, namely radicals and organometallics, can be formed by reduction of an organic substrate with an electron-donor. Metals in low oxidation states frequently perform this role, and indeed, most electron-transfer reduction processes feature this route. Alternative methods include electrochemical reduction at a (usually metal) cathode,¹ reduction by solvated electrons, reduction by lithium naphthalenide¹ or related radical anions of organic molecules or photochemically assisted electron transfer. The idea of using neutral ground-state organic molecules as powerful reducing agents in synthesis is a novel and attractive one. This would allow reductions to be carried out (i) under very mild conditions because of their neutrality, (ii) in the absence of metal ions, a worthwhile feature when metal residues cause environmental problems and (iii) with wider applicability than in the case of the photochemically assisted reactions.

We have now prepared the first neutral organic, ground-state molecule that is powerful enough to reduce aryl iodides to aryl radicals, and alkyl iodides to alkyl radicals. The compound is **1** and has two special features: (a) it incorporates 4 nitrogen atoms that are very well able to stabilise positive charge in the radical-cation **2** (b) the radical-cation **2** can be represented as a quasi-aromatic species (see the new 5-membered aromatic heterocycle depicted below).



We reasoned that the combination of these two stabilising factors, acting in concert as in **1**, should therefore afford excellent electron donors.

Further work has allowed better understanding of the mechanisms involved and character of these species and the first reductions of unactivated aryl and alkyl iodides by a neutral ground-state organic molecule have been described. Considerable variation of these super-S.E.T. structures is now possible to afford reducing agents of greater power, or to tailor reductions to particular substrates. They should have applications in synthesis and materials chemistry.

Our work has been completely dependent on the EPSRC National Mass Spectrometry Service. Mass spectrometry at the NMSSC has been invaluable in resolving ambiguities arising from NMR data. With rapid turn-around of samples, and with the facility to deal with many unstable and sensitive samples, and to provide spectra from different ionisation modes, we have been massively helped in our work. Interestingly, the most recent novel reaction actually occurred in the mass spectrometer, and we were alerted to this by the vigilant staff at Swansea, who noted that our samples were behaving anomalously in their mass spectrometers. We were surprised to see that our colleagues at Swansea not only provide an excellent technical service, but think about the chemistry of their samples too.

Publications:

J. A. Murphy, T. A. Khan, S. -Z. Zhou, D. W. Thomson and M. Mahesh, *Angew. Chem Int. Ed.*, **2005**, *44*, 1356-1360.