Synthetic Methods

Highly Efficient Reduction of Unactivated Aryl and Alkyl Iodides by a Ground-State Neutral Organic Electron Donor**

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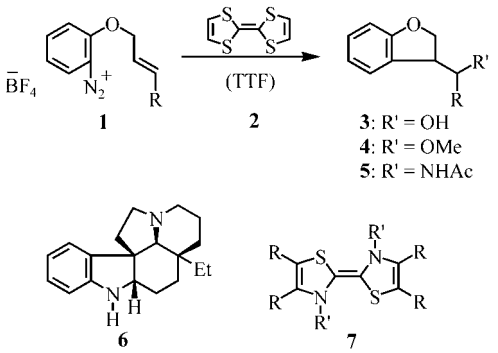
Reactive intermediates, namely radicals and organometallic species, can be formed by reduction of an organic substrate with an electron donor. Metals in low oxidation states[1] frequently perform this role, and indeed, most electron-transfer reduction processes feature this route. Alternative methods include electrochemical reduction at a (usually metal) cathode,[2,3] reduction by solvated electrons,[4] reduction by lithium naphthalenide[5] or related radical anions of organic molecules,[6] or photochemically assisted electron transfer.[7] The use of neutral ground-state organic molecules as powerful reducing agents is a novel and attractive idea. This would allow reductions to be carried out 1) under very mild conditions because of their neutrality, 2) in the absence of metal ions, a worthwhile feature as metal residues cause environmental problems, and 3) with wider applicability than in the case of photochemically assisted reactions.

Our initial studies[8] featured the reactions between arenediazonium salts **1** and tetrathiafulvalene (TTF, **2**). TTF (**2**) reacts with diazonium salts in a radical–polar crossover reaction that leads to the formation of alcohols **3**, ethers **4**, and amides **5** (Scheme 1). This protocol has been substantially developed and has even been used to prepare complex products such as aspidospermidine (**6**).[9,10] However, a limitation of this process is that only arenediazonium substrates can act as electron acceptors; attempts to extend this reaction to the much more common aryl halides or to alkyl halides have not been successful as these substrates are more difficult to reduce.[11] It is well known that diazadithiafulvalenes **7** (see Scheme 1) are more powerful reducing agents,[12] but we have shown that these compounds undergo a complicating side reaction when treated with arenediazonium salts[13] and are not powerful enough electron donors to react with organic halides.



Scheme 1. The radical–polar crossover reaction, useful in the synthesis of aspidospermidine (**6**), depends specifically on the use of tetrathiafulvalene (TTF, **2**). Conditions: **3**: acetone, water; **4**: MeOH; **5**: MeCN, then H_2O.

More recently, the reagent TDAE (1,1,2,2-tetra-(dimethylamine)ethane, **8**) has been reacted with very electron-deficient organic halides by Médebielle and co-workers.[14,15] Thus, iodotrifluoromethane (**9**) was treated with TDAE and benzoyl chloride to afford the products **10** and **11**, which indicate the intermediacy of trifluoromethyl anions,[14] and *p*-nitrobenzyl chloride (**12**) was similarly transformed to its anion[15] upon treatment with the same reagent (Scheme 2). Accordingly, our efforts began by testing the reaction of TDAE (**8**) with unactivated aryl and alkyl halides. In all cases, we found that this reagent is not sufficiently powerful to perform the reaction.

Powerful sulfur-containing organic electron donors such as **14** (Scheme 2) are available,[16] and here the driving force for the electron donation derives from the considerable

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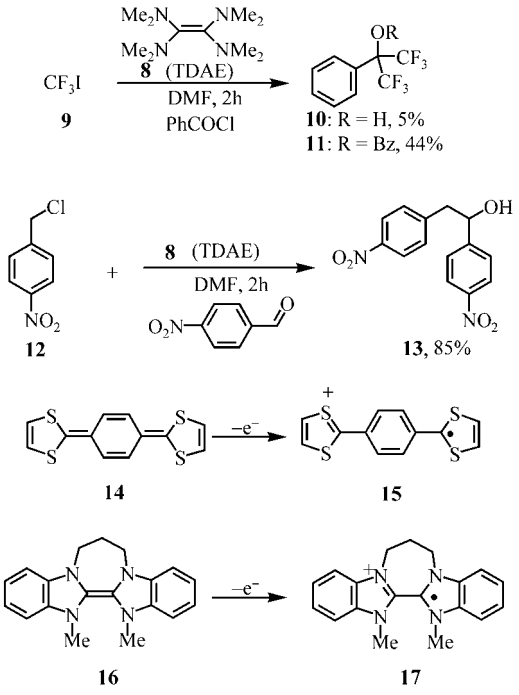
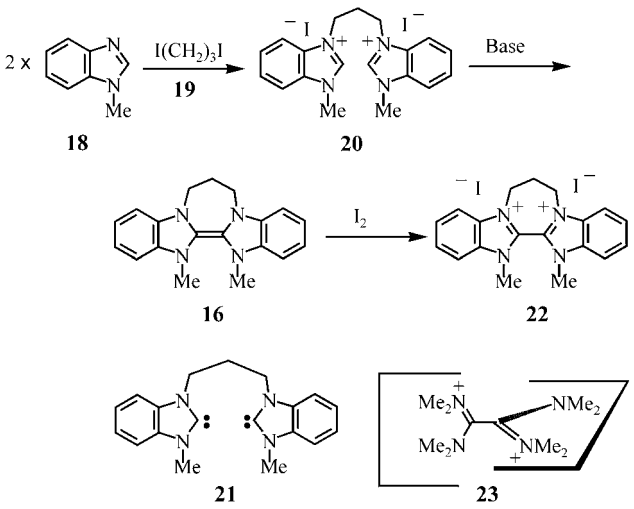


Scheme 2. Chemistry of TDAE (**8**) and structures of potentially more-powerful electron donors. TDAE = 1,1,2,2-tetra-(dimethylamine)ethene, DMF = *N*,*N*-dimethylformamide, Bz = benzoyl.

aromatization energy residing in the corresponding radical cation, **15**. The easiest way to visualize this aromatization is by looking at the particular canonical form, **15**, in which two of the rings are represented as aromatic. However, the syntheses of such compounds are not straightforward, so it is unlikely that they could ever be used as routine reagents. Even their characterization has proved challenging. However, the message is clear: aromatic stabilization energy can greatly assist electron donation.

The presence of nitrogen is also helpful to the creation of a good electron donor, as shown by both the diazadithiafulvalenes **7** and TDAE (**8**), particularly because of the stabilization imparted to the resulting cation by the adjacent nitrogens.[13]

These two stabilizing factors that act in concert, for example, in **16**, should therefore afford excellent electron donors. Thus, electron loss from **16** would initially afford radical cation **17**, which features the dual stabilization. Although compound **16** has not previously been prepared, a number of similar compounds, which are formally derived from the dimerization of cyclic carbenes, have been prepared[17,18] and used in mechanistic studies of the behavior of Wanzlick carbenes[17] or to test their ability to form carbene ligands on metals.[18] Their reductive organic chemistry appears not to have been explored, except from an electrochemical viewpoint.[17b,o] Reaction of benzimidazole **18** with 1,3-diiodopropane (**19**) afforded the stable crystalline salt **20**, which upon treatment with base[17a,b,d,e,18a,18g,18h] under argon then afforded a yellow solution of the "dimer" **16**, which is highly reactive towards air (Scheme 3). The dimer was characterized upon formation in situ in deoxygenated [D_7]DMF (*N*,*N*-dimethylformamide) under argon, and the



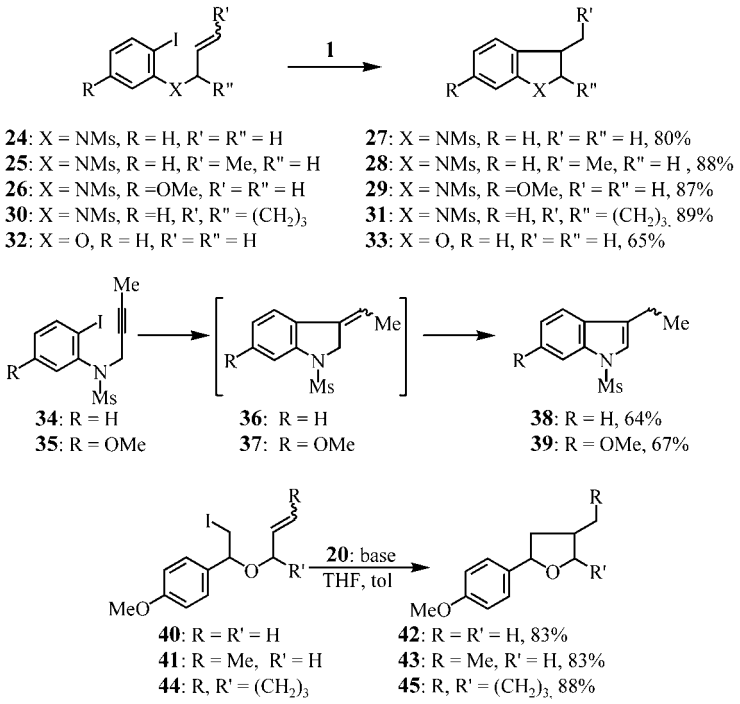
Scheme 3. Formation and reactions of tetraazaalkene **16**.

solution showed the appearance of a key signal at $\delta =$ 123.1 ppm corresponding to the central quaternary carbon in the dimer. No trace[19] of the corresponding biscarbene **21** or of a monocarbene species were evident.

To show that the dimer **16** had formed, it was treated with one equivalent of molecular iodine. With such an easily reduced compound as I_2, we would expect that **16** would behave like TDAE in forming a dication—in this case, **22**. Molecular modeling of $TDAE^{2+}$ indicates that the repulsion between the two positive charges would be minimized by twisting into orthogonal planes as in **23**. So the expected product **22**, being somewhat restrained by the 3-carbon strap, should subsequently undergo a helical twist to impart diastereotopicity to the protons of each of its -NCH_2- groups. Indeed reaction with one equivalent of iodine led to clean formation of the disalt **22** (see Scheme 3), which was characterized by HRMS (**22**−I^-) and by ^{1}H and ^{13}C NMR spectroscopy. As expected, the protons in the -NCH_2- groups are diastereotopic. Clean formation of **22** assured us that alkene **16** had also formed cleanly. Note that a study of a bis-bridged analogue[12d,17a] featuring 3-carbon bridges surprisingly showed no evidence for diastereotopicity.

Compound **16** was then treated with a series of aryl iodides, **24**–**26** and **30** (Scheme 4). All of these compounds smoothly afforded the corresponding indolines in excellent yield (81–90%). The oxygen-linked substrate **32** also showed clean transformation to the product **33**; the lower yield (65%) may reflect a greater volatility of the product relative to the nitrogen series. The alkyne-containing substrates **34** and **35** also cyclized smoothly to give the exocyclic alkenes, which were not isolated but treated with acid under mild conditions to give the corresponding indoles **38** (64%) and **39** (67%). Similarly, aliphatic iodides **40**, **41**, and **44** reacted smoothly with **16**, which was formed in situ, and gave excellent yields of cyclized products (Scheme 4).

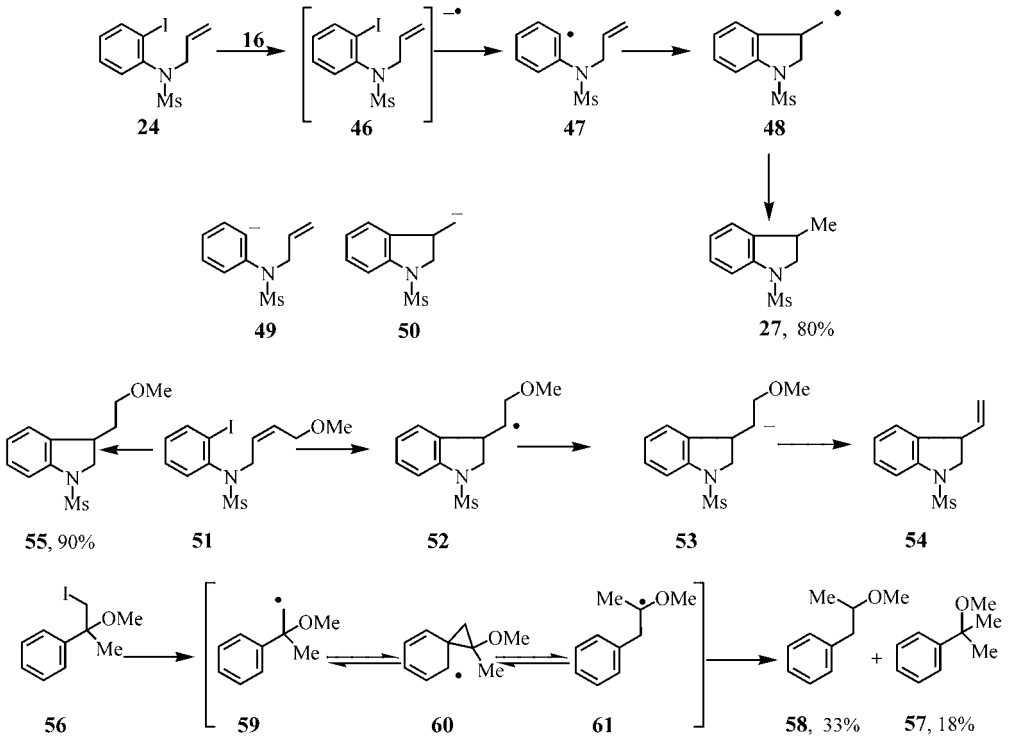
Questions arise over the mechanisms of the observed reactions and in particular over the nature of the intermediates. Initial electron transfer to the substrate, for example, aryl iodide **24**, would afford the radical anion **46** (Scheme 5).



Scheme 4. Reactions of aryl iodides and aliphatic iodides with tetraazaalkene **16**. Ms = methanesulfonyl, tol = toluene.

Dissociation of **46** would then afford the aryl radical **47**. Although, in principle, **47** could be further reduced to the anion **49**, this anion would be more likely to undergo nucleophilic attack on DMF, but this reaction was not observed. The excellent yields of the products obtained preclude these pathways from our reaction. Similarly, the cyclized radical **48** could, in principle, be reduced to the corresponding anion **50**, but again this should result in attack on DMF. No such product was seen, so we believe that the pathway featured radicals—but not anions—derived from the substrates throughout. The source of the hydrogen atom in the final hydrogen transfer, for example, in the conversion of **48** to **27**, has not yet been determined. A labeling experiment using anhydrous deuterated DMF as the exclusive solvent, sodium hydride as base rather than potassium hexamethyldisilazide (KHMDS), and **25** as substrate revealed no label in the product **28** (this point is currently under further investigation).

Similarly with the alkyl iodides **40**, **41**, and **44**, cyclization to **42**, **43**, and **45** should start with electron transfer followed by loss of iodide and formation of free-radical intermediates. In these substrates, a further opportunity exists to show the presence of carbanions prior to cyclization by the elimination of an alcoholate and the formation of a styrene product; however, in no case was such a fragmentation observed. It could be argued that the reagent has the intrinsic electron-donating power to form anions, but that the radical cyclization of these substrates occurred more rapidly than anion formation. To test further for the possibility of formation of alkyl anions, we studied the substrates **51** and **56**. Iodide **51** afforded the indoline **55** in 90% yield, presumably through quenching of radical **52**. Again, there is no evidence for formation of anion **53**, which should lead to rapid elimination to form alkene **54**. Substrate **56** also showed evidence of formation of radicals but not anions. Thus, the directly reduced product **57** was formed in 18% yield, but the major product was the ether **58**, which results from a neophyl rearrangement through radicals **59** and **60** followed by quenching.



Scheme 5. Thoughts on the mechanism of S.E.T. (single electron transfer) reactions of tetraazaalkene **16**.

In summary, the first reductions of unactivated aryl and alkyl iodides by a neutral ground-state organic molecule have been described. The reducing agent is formed in two steps from *N*-methylbenzimidazole using very simple chemistry: 1) alkylation with 1,3-diiodopropane to form a stable crystalline salt and 2) treatment of this salt with base to form the reactive reducing agent. Considerable variation of these super S.E.T. (single electron transfer) structures is now possible to afford reducing agents of greater power or to tailor reductions to particular substrates. Applications in synthesis and materials chemistry are likely to arise from this discovery.

Experimental Section

Exemplary procedures for the cyclization of aromatic and aliphatic iodide substrates are mentioned below. See Supporting Information for details of the synthesis and characterization of other compounds prepared during this research.

Cyclization of aromatic substrates: 1-Methanesulfonyl-3-ethyl-2,3-dihydro-1*H*-indole (**28**):[21] A solution of salt **20** (202 mg, 0.36 mmol) in toluene (10 mL) and DMF (5 mL) under argon was purged with argon for 0.5 h at room temperature. Potassium bis(trimethylsilyl)amide (1.44 mL of 0.5 M solution in toluene, 0.72 mmol) was added dropwise to the mixture, and the resulting yellow solution was stirred for 1 h under argon. A solution of *N*-but-2-enyl-*N*-(2-iodophenyl)methanesulfonamide (**25**; 0.105 g, 0.3 mmol) in toluene (5 mL) was added, and the reaction mixture was heated and maintained at reflux for 18 h under Ar. The reaction mixture was then cooled and poured into diethyl ether (50 mL) and water (50 mL). The organic phase was further washed with water (3 × 50 mL) and then a saturated solution of NaCl (50 mL). The organic extract was dried over anhydrous sodium sulfate, filtered, and evaporated, and the residue was purified by column chromatography (ethyl acetate/petroleum ether 10:90) to afford the title compound as a colorless liquid (0.059 g, 88 %). FT-IR (disc): $\tilde{\nu}$ = 3016, 2963, 2930, 1599, 1478, 1342, 1232, 1161, 1051 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.07 (3 H, t, J = 7.3, CH_3) 1.66 (1 H, m, CH_2), 1.90 (1 H, m, CH_2), 2.93 (3 H, s, SO_2CH_3), 3.38 (1 H, m, CH), 3.69 (1 H, dd, J = 10.2, 6.4, CH_2), 4.13 (1 H, dd, J = 10.2, 9.2, CH_2), 7.11 (1 H, dd, J = 7.5, 7.5, ArH), 7.27 (2 H, m, ArH), 7.46 ppm (1 H, d, J = 7.9, ArH); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 11.3 (CH_3), 27.5 (CH_2), 34.3 (CH_3), 41.4 (CH), 55.9 (CH_2), 113.4 (CH), 123.6 (CH), 124.7 (CH), 128.1 (CH), 135.0 (C), 141.8 ppm (C); *m*/*z* (EI): 225 (M^+, 45 %), 196 (50), 146 (78), 130 (79), 118 (100), 91 (35); HRMS (ESI) *m*/*z*: Calcd for $C_{11}H_{15}NO_2S$: 243.1167 ($M + NH_4^+$); found: 243.1169 ($M + NH_4^+$).

Cyclization of aliphatic substrates: 2-(4-Methoxyphenyl)octahydrobenzofuran (**45**):[22] A suspension of salt **20** (0.672 g, 1.20 mmol, 4.00 equiv) in dry THF (20 mL) was degassed by purging with argon at room temperature. Potassium bis(trimethylsilyl)amide (4.5 mL of 0.5 M solution in toluene, 2.25 mmol, 7.50 equiv) was added to this white suspension—the reaction mixture immediately turned bright yellow and was allowed to stir under Ar for 1 h. The solution was concentrated in vacuo, then 1-[1-(cyclohex-2-enyloxy)-2-iodo-ethyl]-4-methoxybenzene (**44**; 0.108 g, 0.30 mmol, 1.00 equiv) in dry toluene (20 mL) was added by cannula under an argon atmosphere. The reaction mixture was heated to 110 °C under Ar and was maintained at reflux for 15 h before cooling to room temperature and concentrating under reduced pressure. The residue was dissolved in diethyl ether (75 mL), and the solution was extracted with deionized water (75 mL). The aqueous phase was further extracted with diethyl ether (2 × 25 mL). The combined organic extracts were washed with a solution of brine (3 × 100 mL), separated, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness in vacuo to yield a yellow-orange semi-solid. This residue was purified by flash chromatography (diethyl ether/petroleum ether 15:85) to afford the title compound **45** as a colorless oil as a mixture of diastereoisomers (5:8) that could not be separated (0.061 g, 88 %). FT-IR (neat): $\tilde{\nu}$ = 2931, 2854, 1613, 1513, 1458, 1443, 1302, 1246, 1172, 1036, 995, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21–2.42 (11 H, m, CH and 5 × CH_2), 3.81 (3 H, minor, s, OCH_3), 3.82 (3 H, major, s, OCH_3), 4.02 (1 H, major, dd, J = 9.5, 4.8, OCH), 4.25 (1 H, minor, dd, J = 7.5, 3.5, OCH), 4.93 (1 H, major, t, J = 7.8, OCHAr), 5.15 (1 H, minor, t, J = 7.8, OCHAr), 6.85–6.93 (2 H, m, ArH), 7.21–7.30 (1 H, m, ArH), 7.32–7.40 ppm (1 H, m, ArH); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 21.1 (CH_2), 22.0 (CH_2), 24.3 (CH_2), 24.6 (CH_2), 27.9 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.5 (CH_2), 38.7 (CH), 39.2 (CH), 41.0 (CH_2), 42.5 (CH_2), 55.8 (CH_3), 78.4 (CH), 79.1 (CH), 79.8 (CH), 114.1 (CH), 114.2 (CH), 127.2 (CH), 127.4 (CH), 136.8 (C), 137.8 (C), 159.1 (C), 159.1 ppm (C); *m*/*z* (CI): 250 ($[M + NH_4]^+$, 91 %), 233 (100). HRMS (ESI) *m*/*z*: Calcd for $C_{15}H_{20}O_2$: 233.1536 (MH^+); found: 233.1536 (MH^+).

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