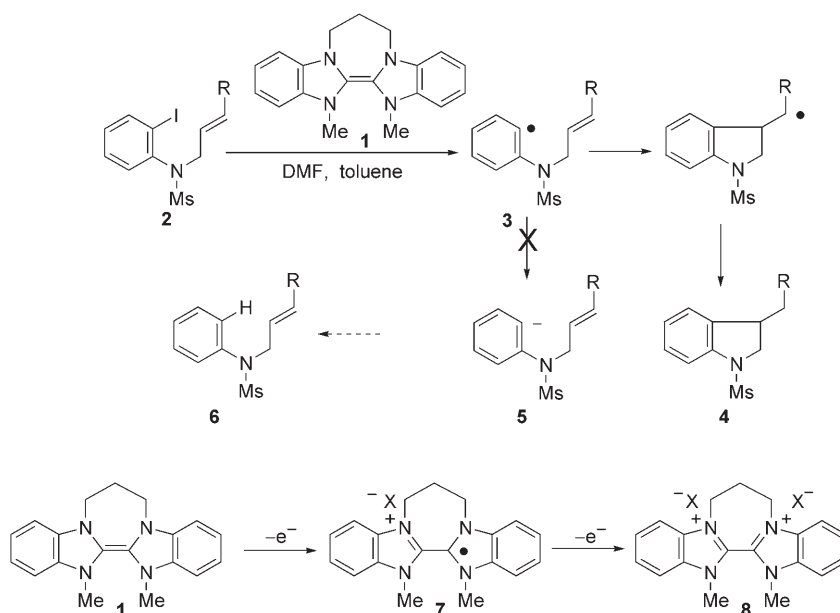


The Generation of Aryl Anions by Double Electron Transfer to Aryl Iodides from a Neutral Ground-State Organic Super-Electron Donor**

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Stabilized carbanions can be prepared by deprotonation of the corresponding carbon acids, but more reactive carbanions, such as aryl anions, are usually made by metal-halogen exchange or by electrochemical routes.^[1] Whereas the use of metals and organometallic compounds to form aryl anions is well established, the use of totally organic electron-transfer agents, in the absence of photochemical activation, is completely unknown.^[2] Herein we report the first neutral organic molecule to achieve this feat.

We recently reported^[3] the reactions of aryl halides with the fully characterized electron donor **1** (Scheme 1). Compound **1** is one of a series of compounds that had been prepared^[4] previously for the purpose of studying their electrochemical properties; their redox potentials had shown that they are strong reducing agents and that they can undergo sequential loss of two electrons^[4] (reduction potentials for the resulting dication **8** and radical cation **7** are $E_{1/2}(\text{DMF})^{[4a]} = -0.76$ and -0.82 V, respectively, versus the saturated calomel electrode (SCE)); thus they react spontaneously in air. However, their reactivity with organic molecules had not been tested previously.^[3] Treatment of donor **1** with aryl iodides **2** resulted in efficient cyclizations to indolines **4**, which is consistent with the intermediacy of aryl radicals **3**, and, therefore, with the



Scheme 1. Formation of radicals with benzimidazole-derived donor **1**. Ms = methanesulfonyl.

transfer of a single electron. Recent investigations^[5] have elucidated the standard reduction potential for the conversion of aryl radicals into aryl anions ($E^0 = +0.05$ V versus SCE for the parent phenyl case), and so we wondered whether aryl anions **5** could be formed under our conditions. Cyclization of aryl anions onto unactivated alkenes has been reported,^[6] but could anion **5** be contributing to the yields of indolines **4** in our reactions? The addition of aryl anions to unactivated alkenes is reported only to occur in systems where no alternative reactions, such as deprotonation of acidic sites or attack upon conventional electrophilic groups, are possible. In our case, aryl anions **5** would be expected to preferentially deprotonate the radical cation **7** or dication **8** to give arene **6**, or alternatively, undergo nucleophilic attack on these species or on the solvent (DMF). However, arene **6** was not observed, and no products from the nucleophilic attack by aryl anions **5** were seen. This finding suggested that anions were not formed from the reaction of donor **1** with aryl halides.

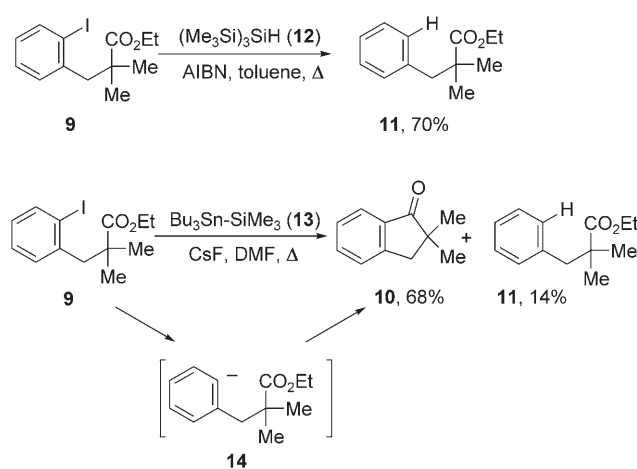
Nevertheless, to be clear on this point and also prior to testing for the formation of aryl anions with other electron donors, a diagnostic test was needed for aryl anions. A reaction therefore needed to be identified that would unambiguously distinguish aryl anions from aryl radicals. It is well known that reactive anions, such as aryl anions, attack esters, while carbon radicals do not.^[7] Hence, the iodoester **9**

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Supporting information for this article (experimental details) is available on the WWW under <http://www.angewandte.org> or from the author.

was selected as a test substrate (Scheme 2). This system was tested firstly with a known procedure for forming aryl radicals. Heating **9** in the presence of tris(trimethylsilyl)silane (**12**) and the radical initiator azobisisobutyronitrile (AIBN) in

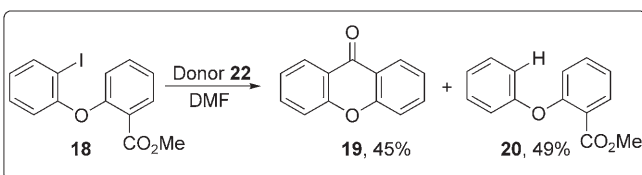
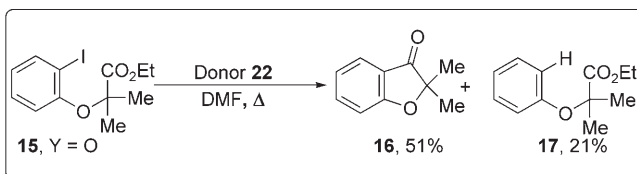
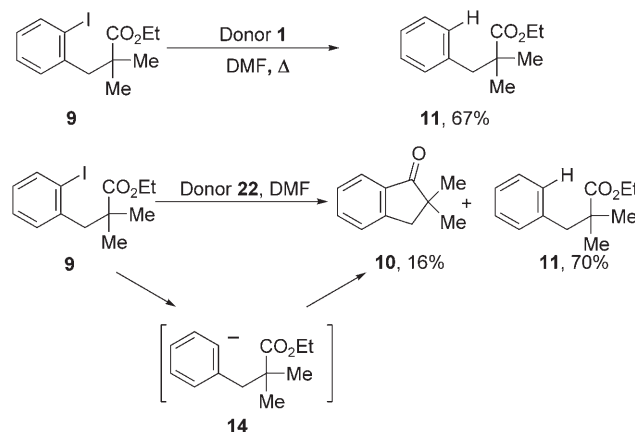


Scheme 2. Different outcomes of aryl anion and aryl radical reactions derived from iodide **9**.

toluene, gave exclusively the reduced product **11** (70% yield). No trace of indanone **10** was observed; this result is totally consistent with the expected intermediacy of aryl radicals. Iodoester **9** was then tested with a known method for the formation of aryl anions. Reaction of trimethyl(tributylstannyl)silane (**13**) with fluoride ions^[8] (CsF) in the presence of **9** led to the formation of the indanone **10** (68%) together with the reduced compound **11** (14%). The presence of the indanone clearly indicated that formation of an aryl anion had occurred. Formation of **11** likely also arose from the aryl anion, with quenching of the anion resulting from minute traces of water in the dried reagents, solvents, or glassware. These two reactions therefore establish the validity of using **9** for illustrating the presence of aryl anions; the formation of indanone product **10** gives unambiguous evidence of the presence of aryl anions in any test reaction that we performed.

Interestingly, attempts to access ketone **10** through other reactions that should afford aryl anions, by using the reagents *t*BuLi (acting as a nucleophile on the I–Ar bond) as well as sodium naphthenide or magnesium metal (both as electron donors), were all unsuccessful, and afforded complex mixtures of products that included, at best, minute traces of indanone **10**. In effect, these reagents are too reactive; indeed the reaction of *t*BuLi with indanone has already been reported.^[9] Furthermore, cyclic voltammetry indicated that ketone **10** ($E_{1/2}(\text{DMF}) = -2.02$ V versus SCE) is more easily reduced than iodoester **9** ($E_p(\text{DMF}) = -2.14$ V versus SCE (see the Supporting information; the Ag/AgCl electrode potential is 0.04 V negative of SCE), and hence it is not surprising that the ketone was not stable in the presence of such strong electron donors as sodium naphthenide ($E^0 = -2.47$ V versus SCE)^[10] and magnesium metal (known to produce pinacol reduction of ketones).^[11]

Substrate **9** was then tested with donor **1** (2.5 equiv) in DMF (Scheme 3). No indanone **10** was produced, but the reduced compound **11** was isolated (67%). The absence of indanone indicated that aryl anions had not been formed.

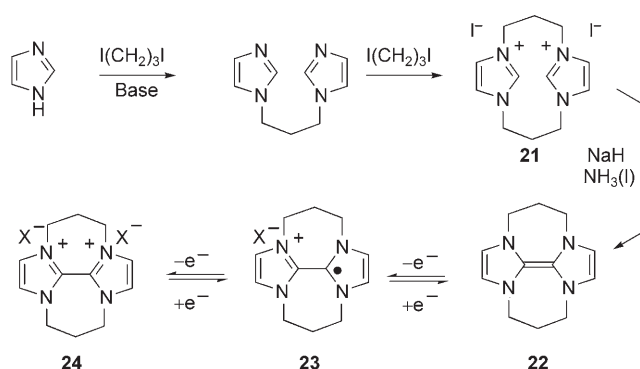


Scheme 3. Reactions of iodoaryl esters with donors **1** and **22**.

Thus, despite the experimentally determined redox potentials for **1** ($E_{1/2} = -0.76, -0.82$ V versus SCE, as stated above) being much more negative than the standard potential for the reduction of an aryl radical ($E^0 = +0.05$ V versus SCE for the phenyl radical), the reaction does not proceed. This finding can be attributed to the difference between the standard potential and the actual potential for the reduction of an aryl radical to an aryl anion under our experimental conditions; Andrieux and Pinson saw the peak attributed to this reduction at -0.64 V versus SCE under the conditions used in their experiments.^[5] Under our conditions, we assume that the actual potential may be even more negative. To check this, we selected a more powerful reducing agent from the same class of organic donors as **1**.

Electrochemical reduction of dication **24** ($X = \text{Br}$)^[4a,b,c] affords **22** (Scheme 4), which is one of the more powerful electron donors in this class (reduction of **24** ($X = \text{Br}$): $E_{1/2}(\text{MeCN})^{[4a]} = -1.18$ V and -1.37 V (ir) versus SCE, where “ir” represents an irreversible process; $E_{1/2}(\text{DMF})^{[4a]} = -1.20$ V versus SCE; and $E_{1/2}(\text{MeCN})^{[4b]} = -1.12$ V and -1.28 V (ir) versus SCE).

Since our work would require significant quantities of **22**, a direct synthetic route to it was required, and none was



Scheme 4. Preparation of imidazole-derived donor **22**.

available, although a scheme for such a transformation was reported by Taton and Chen,^[4c] while Shi et al.^[12] refer to failed attempts to generate **22** from the dibromide analogue of **21**.

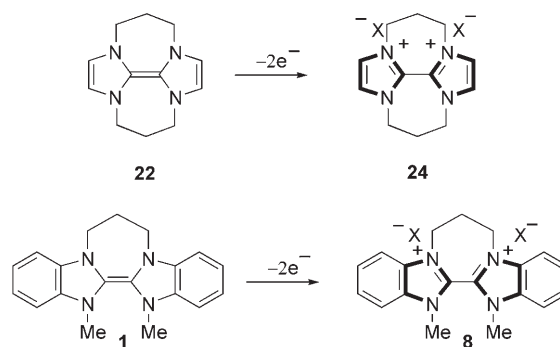
We conveniently prepared diiodide **21** (Scheme 4) from imidazole and diiodopropane. In this case, the desired donor **22** was formed from **21** using NaH as a base with liquid ammonia as the solvent. Liquid ammonia was selected as it affords a way to generate pure donor **22**. Thus, following the generation of the donor **22**, evaporation of the ammonia afforded a solid residue that was easily extracted with diethyl ether, thereby affording donor **22** (98 %) as an air-sensitive pure yellow solid. However, it is not necessary to use this route to prepare **22**; it can alternatively be prepared in situ from **21** using DMF as the solvent. This procedure was used for the reactions shown in Scheme 6.

Reaction of the substrate **9** with donor **22** (Scheme 3) afforded two products, the indanone **10** (16 %) and the reduced compound **11** (70 %). The indanone **10** provides the required positive proof of the intermediacy of an aryl anion for the first time in these reactions, and so **22** is the first neutral organic reagent to achieve such a transformation, the hallmark of the super-electron donor (SED) sought by us and others in recent years. The isolation of the reduced compound **11** could reflect the intermediacy of aryl anion **14** and/or the corresponding aryl radical. The aryl anion could abstract a proton from the radical-cation **23** or dication **24** while the putative aryl radical could abstract a hydrogen atom from the same sites. The formation of the indanone **10** in 16 % yield thus reflects a minimum amount of aryl anion formed in this reaction.

If the aryl anion **14** derived from substrate **9** affords the reduced product **11**, then this protonation reaction is in competition with the cyclization to form indanone **10**. Two further ester substrates, **15** and **18**, were therefore selected that might lead to faster cyclizations, and hence to a more accurate picture of the percentage of aryl anion formed in these reactions with aryl halides. The reaction of **15** and **18** with donor **22** again afforded cyclization in both cases: **15** yielded ketone **16** (51 %) as well as reduced product **17** (21 %) as an inseparable mixture, with yields determined by calibrated ¹H NMR spectroscopy, while iodide **18** led to the isolation of xanthone (**19**, 45 %) and reduced product **20** (49 %). These results confirm the generation of aryl anions by

electron transfer from donor **22**, and indicate that 51 % and 45 % represent minimum percentages for the formation of the anion.

The difference in the reactivity of **1** and **22** merits some comment. The simplest observation is that the corresponding dications **8** and **24**, which result from the loss of two electrons, feature two new heterocyclic aromatic rings (shown in bold in Scheme 5). The aromatic stabilization energy, which is fully



Scheme 5. The aromaticity of dications **8** and **24**.

present only in the dications, explains why the loss of the second electron from **1** and **22** is not much more difficult than the first. In the case of the dication **8**, the new aromatic heterocyclic rings are fused with existing benzene rings, whereas for dication **24** the new imidazolium rings are not fused, and, as such, impart greater aromatic stabilization energy to that dication.

We were keen to compare the equilibrium geometries of the relevant dications at a deeper level (Figure 1). The NMR spectra of dications **8** and **24** were notably different: the NCH₂ protons of the trimethylene bridge in dication **8** were diastereotopic ($\delta = 4.52\text{--}4.61$ (2H, m, CH₂), $5.25\text{--}5.32$ ppm (2H, m, CH₂)), indicative of a rigid helical twist, whereas the NCH₂ protons for the dication of **22** were a simple triplet ($\delta = 4.61$ ppm (8H, t, $J = 6.0$, $4 \times \text{CH}_2$)), thus indicating a freely moving segment and no helicity. As shown below, this is borne out by computational studies (for full details of the optimization procedure see the Supporting Information).

Loss of two electrons from **22** results in the more planar structure **24**. The central C–C bond is increased in length from 1.36 to 1.44 Å, which indicates the formation of a resonance-stabilized structure. The donor molecule **1** also experiences the formation of a resonance-stabilized structure with a similar increase in bond length. However, in contrast to **22**, the overall structure of **1** becomes increasingly less planar as electrons are removed. The angle τ between the planes of the benzimidazole rings increases from 16° in **1** to 42° in **8** (the dication derived from **1**) whereas in **22** the angle τ between the planes of the imidazole rings is decreased from 10° to 1.5° on formation of the dication **24** (Figure 1). The larger changes observed in the structure of **1** indicate that the electronic structure of the neutral species is unable to easily accommodate the formation of positive charge, which in turn suggests larger reorganization energies for this molecule. To test this theory, we have calculated the internal reorganization

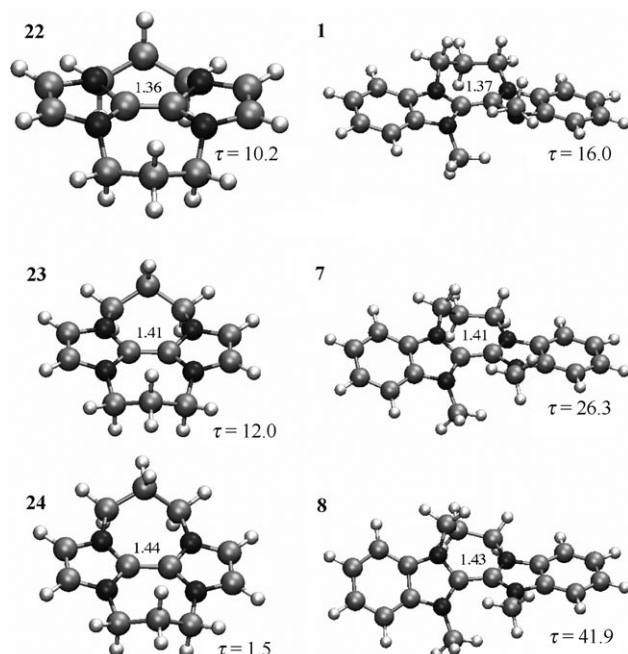


Figure 1. Optimized structures of donor molecules **22**, **23**, **24**, **1**, **7**, and **8**. The central C–C bond length is given in Å. τ is the angle between the planes formed by the imidazole/benzimidazole rings in degrees.

energies of **1** and **22** for the radical cation and dication of each compound.

The internal reorganization energy was calculated using Equations (1)–(4), where iodobenzene (IB) was used as a model acceptor compound:



The internal reorganization energy is calculated as, for example, in Equation (1), with Equations (5) and (6):

$$\lambda_i(\mathbf{22}) = \frac{\lambda_i(\mathbf{22}) + \lambda_i(\text{IB})}{2} \quad (5)$$

where:

$$\lambda_i(\mathbf{22}) = (E_N(R_C) - E_N(R_N)) + (E_C(R_N) - E_C(R_C)) \quad (6)$$

$E_N(R_C)$ is the energy of the neutral species in the geometry of the radical cation; $E_N(R_N)$ is the energy of the neutral species in its optimized geometry; $E_C(R_N)$ is the energy of the cationic species in the geometry of the neutral compound; and $E_C(R_C)$ is the energy of the cationic species in its optimized geometry. The analogous process is used to calculate $\lambda_i(\text{IB})$ (Table 1). This procedure, with similar methodology to that employed here, has previously been shown to provide reliable results for the calculation of reorganization energies.^[13–15]

Table 1: The component reorganization energies and the half-reaction free energies ΔG_c for the donor (D) and anion (A) compounds.^[a] Energies are in kcal mol^{−1}.

	$\text{DA} \rightarrow \text{D}^{+\cdot} + \text{A}^{-\cdot}$		$\text{D}^{+\cdot} + \text{A}^{-\cdot} \rightarrow \text{D}^{2+} + \text{A}^{2-}$	
	λ_i	ΔG_c	λ_i	ΔG_c
A = IB	66.1	−66.9	52.7	−85.5
D = 1	17.4	79.0	11.8	93.8
D = 22	23.6	69.1	12.5	83.0

[a] The half-reactions are $\text{D} \rightarrow \text{D}^{+\cdot}$; $\text{D}^{+\cdot} \rightarrow \text{D}^{2+}$; $\text{A} \rightarrow \text{A}^{-\cdot}$; $\text{A}^{-\cdot} \rightarrow \text{A}^{2-}$.

Perhaps surprisingly, the sum of the component internal reorganization energies for the reactions involving **22** are greater than those involving **1** (that is, $\lambda_i[\text{Eq. (1)}] = 44.8$ kcal mol^{−1}; $\lambda_i[\text{Eq. (2)}] = 32.6$ kcal mol^{−1}; $\lambda_i[\text{Eq. (3)}] = 41.7$ kcal mol^{−1}; and $\lambda_i[\text{Eq. (4)}] = 32.3$ kcal mol^{−1}). However, the formation of the positive charge in **1** is approximately 10 kcal mol^{−1} less favorable than in **22**, and as such the reactions involving **1** are more endergonic (Table 2).

Table 2: Activation and reaction free energies for the reactions described in Equations (1)–(4). All energies are in kcal mol^{−1}.

Equation	ΔG^*	ΔG_R
(1)	12.3	2.2
(2)	6.9	−2.5
(3)	17.4	12.1
(4)	12.8	8.3

As a first approximation,^[16] the activation energy can be calculated from Marcus theory [Eq. (7)] using the internal reorganization energies and the reaction free energies.

$$\Delta G^* = \frac{\lambda_i}{4} \left(1 + \frac{\Delta G_R}{\lambda_i} \right)^2 \quad (7)$$

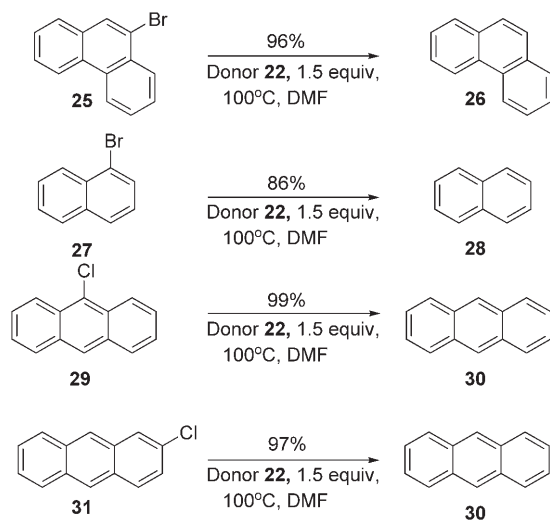
The activation energies for Equations (1) and (2) (Table 2) are both sufficiently low to explain the experimentally observed activity. In the overall reaction of $\mathbf{22} + \text{IB} \rightarrow \mathbf{24}^{2+} + \text{IB}^{2-}$, the first electron transfer is the rate-limiting step and the reaction is mildly exergonic. Thus, with **22** the electron transfer is both thermodynamically and kinetically viable.

The electron-transfer reactions involving **1** are less favorable. The initial electron transfer encounters a larger energy barrier, relative to that in **22**; however, under our experimental conditions this transfer could occur. A comparison of Equations (1) and (2) relating to **22** with Equations (3) and (4) relating to **1**, shows that both the energy barriers to reaction and the free energy changes are more favorable with donor **22**, which is in line with our experimental findings.

The maintenance of planarity during electron loss from **22** may be a factor assisting its ability to act as a very strong two-electron donor. The flat structure would be able to interact closely with the π system of the acceptor arene and assist with stabilization through formation of an intimate complex. Given that the reduction potential of aryl iodides is about

−2.2 V versus SCE, the stabilization achieved through such complexes is expected to be crucial.

The above differences between donors **1** and **22** should also be evident in other aspects of reactivity, and we were keen to compare the donors in their reactions with a range of challenging substrates (Scheme 6). Reaction of **1** with 9-



Scheme 6. Reactions of aryl bromides and chlorides with donor **22**.

bromophenanthrene (**25**) in DMF at 100°C gave very poor conversion. Even when 5 equivalents of donor were used, only 7% of phenanthrene (**26**) was produced. However, phenanthrene (**26**) was formed in 96% yield when 1.5 equivalents of donor **22** were used in DMF at 100°C. Similarly, **1** was completely ineffective in reducing 1-bromonaphthalene (**27**) to naphthalene (**28**; 0% yield). In contrast, **22** gave an 86% yield of naphthalene from this substrate. The chlorides 9-chloroanthracene (**29**) and 2-chloroanthracene (**31**) were also reduced to anthracene (**30**; 99% and 97%, respectively) by **22** under these conditions.

In summary, donor **22** shows unprecedented reactivity for a neutral, ground-state organic electron donor, which reduces aryl halides to aryl anions. The formation of cyclic ketones **10**, **16**, and **19** demonstrates that aryl iodides are reduced to aryl anions by **22** at room temperature. Aryl bromides and chlorides are reduced by **22** at higher temperature. The very different behavior of **22** and **1** demonstrates a sharp demarcation between the reductive capabilities of these reagents with aryl halides.

Interestingly, our finding that potentials more negative than −1.0 V are needed for the formation of aryl anions is mirrored in a recent report by Otero et al.^[17] These reductions do not of course reflect the conditions that lead to the estimation of standard potentials. However, this illustrates that the use of reduction potentials, determined from electrochemical procedures, to determine the feasibility of chemical reactions, can be misleading. Thus, **22** should be too weak a donor, by about 1 V, to reduce iodoarenes ($E_p = -2.2$ V), and yet reduces these substrates very easily. On the other hand, the reduction of ketones, such as indanone **10**, should be

slightly easier ($E_{1/2} = -2.02$ V versus SCE), and yet is not observed. This phenomenon is commonly encountered in mediated electrochemistry,^[10] but is perhaps not well recognized in other areas of synthetic chemistry. Organic and inorganic mediators can facilitate redox events such as the reduction of aryl halides in solution; this arises through formation of intimate complexes and through ion pairing, which is not readily available at electrodes. Thus, for example, indirect electrochemical reduction of aryl halides such as chlorobenzene ($E^0 = -2.78$ V) can be achieved in benzonitrile ($E^0 = -2.44$ V) as the solvent by use of appropriate mediators.^[18] A key feature of such reactions is that they feature an easily and irreversibly cleavable bond (for example, C–X, where X = halogen).

Unlike sodium naphthenide ($E^0 = -2.46$ V versus SCE) and magnesium, donor **22**, ($E_{1/2} = -1.20$ V versus SCE) does not reduce ketones, and this selectivity may later be used to advantage in synthetic chemistry. The easy availability and tunability of donors such as **22** opens the door for the design of highly selective but powerful electron-transfer reagents. We are currently exploring the possibility of related donors partaking in a catalytic cycle.

Experimental Section

22: 1,1':3,3'-Bis(trimethylene)bis(imidazolium) diiodide (**21**; 10 g, 21.184 mmol, 1.0 equiv) was placed in a Schlenk flask under argon and dried in vacuo at 100°C for 2 h. After cooling the mixture to RT, it was purged with argon gas, and then sodium hydride (6.779 g of 60% dispersion of NaH in mineral oil, 169.47 mmol, 8.0 equiv) added. The mixture was washed with dry hexane (3 × 80 mL) in an argon atmosphere, and a dry-ice condenser was attached to the flask. The residual hexane in the reaction mixture was removed under vacuum and the system was back-filled with argon gas. Ammonia (150 mL) was condensed into the flask while a steady flow of argon gas was maintained at all times during the course of the reaction. The stirred suspension turned yellow as the ammonia was refluxed at RT for 2 h; the ammonia was then evaporated slowly, and the flask transported into a glove box under nitrogen. The yellow solid residue was then extracted with deoxygenated dry diethyl ether (3 × 80 mL). The yellow suspension was filtered and the filtrate was evaporated to afford a yellow solid. This was dried in vacuo to obtain **22** (4.47 g, 98%) as a yellow solid which was stored at RT under nitrogen. ¹H NMR (400 MHz, C₆D₆): δ = 1.38–1.43 (4H, m, 2 × CH₂), 2.43–2.45 (8H, m, 4 × CH₂), 5.48 ppm (4H, s, 4 × C=CH); ¹³C NMR (100 MHz, C₆D₆): δ = 31.49 (CH₂), 54.37 (CH₂), 120.37 (C), 127.62 ppm (CH).^[10] Atomic absorption (AAS) analysis: 0.005 mg of Na in 100.0 mg of tetraazafulvalene **22** (0.047 mol %). $E_{1/2}(\text{DMF}) = -1.1072$ V (0.1632 V) versus Ag/AgCl/KCl(sat.), averaged over 5 runs; conditions: **22** (10.463 mM), Bu₄NPF₆ (49.917 mM), Pt working and counter electrodes, 50 mV s^{−1}.

Cyclization with 22: A solution of methyl 2-(2-iodophenoxy)-benzoate (**18**; 0.0992 g, 0.28 mmol, 1.0 equiv) dissolved in dry DMF (15 mL, deoxygenated) was treated with tetraazafulvalene **22** (0.097 g, 0.448 mmol, 1.6 equiv) at RT for 18 h inside a glove box in a nitrogen atmosphere. The reaction was stopped by the addition of hydrochloric acid (20 mL, 2M) and the mixture was extracted with diethyl ether (3 × 20 mL). The combined organic phases were further washed with hydrochloric acid (4 × 20 mL, 2M), followed by a mixture of brine (20 mL) and hydrochloric acid (10 mL, 2M) solution. The ethereal layer was separated, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The residue was purified by column chromatography on silica gel (eluant: toluene/dichloromethane/petroleum ether 1:1:3) to give methyl 2-phenoxybenzoate^[19]

(**20**) as a colorless liquid (32 mg, 49 %) and xanthone^[20] (**19**) as a white solid (25 mg, 45 %). **20**: HRMS (ESI): m/z 229.0859 [$M+H$]⁺; C₁₄H₁₂O₃ requires: [$M+H$]⁺ 229.0859; IR (neat film, NaCl): $\tilde{\nu}$ = 3068, 3039, 2951, 1732, 1603, 1483 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 3.89 (3H, s, CH₃), 7.04–7.09 (3H, m, ArH), 7.09–7.19 (1H, m, ArH), 7.27 (1H, ddd, J = 7.6, 7.6, 1.1 Hz, ArH), 7.39–7.43 (2H, m, ArH), 7.52–7.57 (1H, m, ArH), 8.01 ppm (1H, dd, J = 7.8, 1.8 Hz, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 52.3 (CH₃), 118.4 (CH), 121.1 (CH), 123.3 (CH), 123.4 (C), 123.7 (CH), 129.9 (CH), 132.0 (CH), 133.8 (CH), 156.4 (C), 157.8 (C), 166.4 ppm (C); EIMS: m/z 228 (M^+ , 76 %), 197 (100), 168 (28), 108 (57), 77 (78). **19**: m.p. 168–170 °C (lit.^[20] m.p. 172–173 °C); HRMS (ESI): found: 197.0596 [$M+H$]⁺, C₁₃H₈O₂ requires: 197.0597 [$M+H$]⁺; IR (KBr): $\tilde{\nu}$ = 3054, 2987, 1655, 1609 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.38–7.42 (2H, m, ArH), 7.51 (2H, d, J = 8.3 Hz, ArH), 7.72–7.76 (2H, m, ArH), 8.36 ppm (2H, dd, J = 7.9, 1.6 Hz, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 118.2 (CH), 122.1 (C), 124.1 (CH), 127.0 (CH), 135.0 (CH), 156.5 (C), 177.5 (C); EIMS: m/z 196 (M^+ , 100 %), 168 (59), 139 (53), 92 (11), 74 (17), 63 (25).

Computational methods: Structures were optimized with the gradient-corrected BP86 functional.^[21] Systems involving the iodine atom employed a large-core, quasi-relativistic, effective core potential^[22] with the associated (16s11p6d)/[9s6p1d] valence basis set; all other atoms were described with the def2-TZVP basis set.^[23] Single-point solvent-phase calculations of the gas-phase-optimized structures were performed using the polarizable continuum model^[24] with a dielectric constant of 38.3 for DMF. For the single-point calculations the B3LYP functional^[21a–b,25] was used in conjunction with the 6-311 + G(d,p) basis set.^[26]

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