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N-Heterocyclic Superelectrophiles and Evidence for Single Electron Transfer Chemistry

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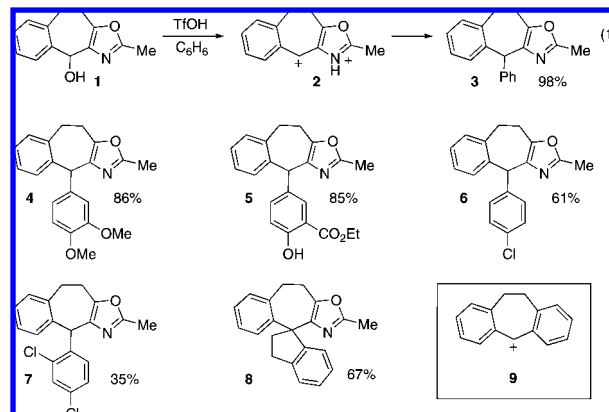
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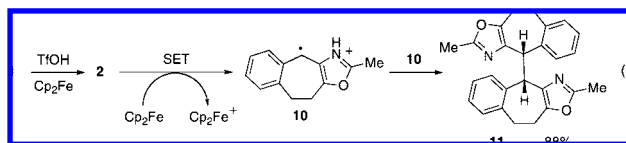
Since the pioneering work of Olah in the 1970s, superelectrophilic chemistry has been an active area of research.¹ Superelectrophiles have been the basis for many unusual synthetic transformations, for example leading to functionalized hydrocarbons,² heterocycles,³ and even polymers.⁴ Among the many superelectrophiles described in the literature, the protonitronium ion (HNO_2^{2+}) is typical.⁵ When nitronium ion (NO_2^+) salts are dissolved in excess Lewis acids or Brønsted superacids, the resulting species exhibit greatly enhanced electrophilic reactivities. In the case of Brønsted acids, this is considered to be the result of protosolvation of the nitronium ion (partial or complete proton transfer to the oxygen). As a result of protonation, the ion develops an increasing positive charge, and in the limiting case it may form the dicationic protonitronium ion. The superelectrophilic nitronium ion is capable of reacting with exceptionally weak nucleophiles, such as alkanes and strongly deactivated arenes.⁵ Besides synthetic studies, the protonitronium ion has been studied computationally,^{6a} and in accord with calculations, it has been observed as a kinetically stable species in gas-phase experiments.⁶

Computational studies have shown superelectrophiles to possess low-lying LUMOs, high electronegativities, and delocalized positive charges.⁷ These properties contribute to their high electrophilic reactivities. Interestingly, these same structural and electronic properties could also lead to efficient single electron transfer (SET) reaction pathways with suitable combinations of electron donors.⁸ Although the possibility of SET chemistry with superelectrophiles has been suggested previously,⁹ to the best of our knowledge no evidence has been reported to date confirming these types of reactions. In the following communication, we describe our studies of the chemistry of *N*-heterocyclic superelectrophiles and report examples of SET reactions involving these superelectrophiles.

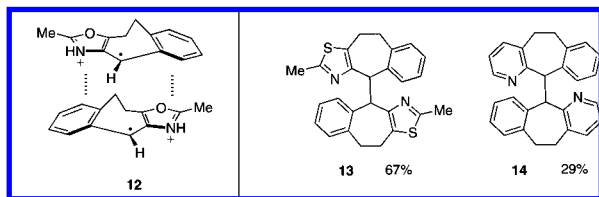
In work related to the synthesis of triarylmethane products, our studies began with reactions of 9,10-dihydro-2-methyl-4*H*-benzo[5,6]cyclohept[1,2-*d*]oxazol-4-ol (**1**) and arenes in the Brønsted superacid $\text{CF}_3\text{SO}_3\text{H}$ (triflic acid, TfOH, $H_0 = -14.1$).¹⁰ For example, compound **1** reacts with C_6H_6 in $\text{CF}_3\text{SO}_3\text{H}$ to give product **3** in high yield (eq 1). Ionization of **1** leads to formation of the superelectrophile **2**, which is capable of reacting with benzene. Other arenes also reacted and gave products **4**–**7**, including those from moderately deactivated arenes such as 1,3-dichlorobenzene. Intramolecular cyclizations were also accomplished, for example involving a phenylethyl derivative to produce **8**. In contrast to the high reactivity of the superelectrophile (**2**), the analogous monocationic species (**9**; generated from dibenzosuberol in $\text{CF}_3\text{SO}_3\text{H}$) does not react with benzene or 1,3-dichlorobenzene.



When the oxazole derivative **1** is reacted with ferrocene in $\text{CF}_3\text{SO}_3\text{H}$, the product from electrophilic aromatic substitution is not obtained, but rather a dimerization product (**11**) is generated in good yield (eq 2). Gas chromatography–mass spectral analysis indicates that two isomeric dimers are produced (ca. 20:1 ratio) in the reaction. The minor component of the product mixture could not be isolated, but the major component was isolated and a single crystal X-ray diffraction structure was determined (see Supporting Information). Compound **11** crystallizes as a mixture of the two enantiomers. Decamethyl ferrocene also reacts with **1** in superacid to give a high yield of product **11**.



We propose that dimer **11** is the result of a SET reaction between the superelectrophilic dication (**2**) and ferrocene, a good single electron donor (eq 2).¹¹ The SET reaction produces the radical cation **10**, which then dimerizes to give **11** as a racemate.¹² The strong preference for the racemate over the meso product suggests that the dimerization step occurs by stacking the cationic ring over the neutral ring (**12**). Similar dimerization products (**13**, **14**) were formed in reactions of a thiazole-based alcohol and a pyridine-based alcohol. In products **13** and **14**, the stereochemistry of the bridging carbons has not yet been determined. The dimer **11** is not formed in reactions of **1** with other arenes in $\text{CF}_3\text{SO}_3\text{H}$ (i.e., benzene or 1,2-dimethoxybenzene), nor is it formed in the absence of ferrocene. This suggests that 2-electron reactions are occurring with these arenes, by a conventional Friedel–Crafts mechanism. If the SET reaction



does take place, then it requires the rapid collapse of the two radical cations (i.e., **10** and the radical cation of benzene).

The chemistry of the oxazole-based superelectrophile (**2**) was also examined by calculations.¹³ Energies of LUMOs and HOMOs of dication **2** and two analogous monocations **9** and **15** were estimated at the HF/6-31G(d) level (Figure 1). As expected, oxazole-based superelectrophile **2** is characterized by a low-lying LUMO, one significantly lower than the LUMOs of the monocations. From calculations at the B3LYP/6-311G(d,p) level, gas-phase single electron reduction energies (ΔE_{RED}) of the ions were estimated by comparing their ZPE-corrected DFT model energies with those of the respective radical or radical cation reduction products (Figure 1). All three exhibit strongly exothermic ΔE_{RED} values; however, reduction of superelectrophile **2** releases 90 kcal/mol more energy than for either monocation. This large energy of one-electron reduction suggests a certain measure of stability for the product radical cation (**10**), as back electron transfer (from **10** to the ferrocenium cation) should be highly unfavorable.

	2	9	15
E_{LUMO}	-8.1	-4.1	-3.7
E_{HOMO}	-16.8	-12.7	-12.3
ΔE_{RED}	-237.6	-146.0	-140.3

Figure 1. Calculated E_{HOMO} and E_{LUMO} levels (eV; HF/6-31G(d) level) and energetics of single electron reduction (kcal/mol; B3LYP/6-311G(d,p) level) involving dication **2** and monocations **9** and **15**.

In summary, we have found evidence for SET chemistry involving superelectrophilic species. The SET chemistry occurs in reactions of ferrocene with oxazole, thiazole, and pyridine-based superelectrophiles. Both low-lying LUMOs and energetically favorable single-electron reductions are considered important to the success of this SET chemistry. The approximate coplanarity of two aryl-rings may also be a critical structural feature, as this can be expected to stabilize the new radical center. Besides the SET chemistry, oxazole-based superelectrophile **2** exhibits high electrophilic reactivities with weak nucleophiles (nonactivated and moderately deactivated arenes).

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Supporting Information Available: Complete ref 13; NMR spectra of new compounds, representative experimental procedures, crystallographic data, computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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