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An Aza-analogue of TTF[1]: 1,1';3,3'-Bistrimethylene-2,2'-diimidazolinylidine

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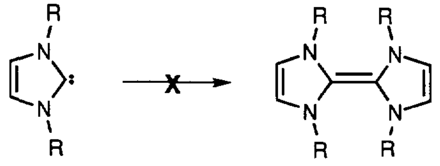
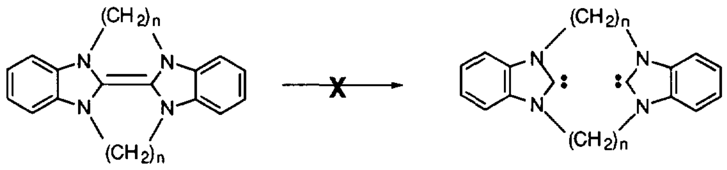
Abstract: Bulk electrolysis of 1,1';3,3'-bistrimethylene-2,2'-biimidazolium dibromide at -1.6 V in acetonitrile provides the air sensitive 1,1';3,3'-bistrimethylene-2,2'-diimidazolinylidine which was characterized by ^1H and ^{13}C NMR. The corresponding dinaphtho-fused species, prepared by deprotonation of a bis-trimethylene bridged bis-naphth[2,3]imidazolium dibromide, reacts readily with air to form a *syn*-ureaphane.

Arduengo and coworkers have reported the elegant preparation and characterization of stable imidazolidinyl carbenes *via* the deprotonation of N,N'-disubstituted imidazolium salts.[3] The desulfurization of imidazole-2(3H)-thiones similarly leads to imidazol-2-ylidenes[4] and a stable tris-1,3,5-imidazolylidenyl benzene has recently been reported.[5] The unusual stability of these carbenes has been the subject of considerable discussion[6] and their kinetic reactivity with respect to carbon monoxide has stimulated some recent debate.[7]



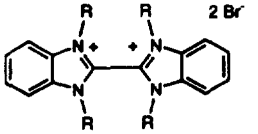
1 **2**

The apparent reluctance of imidazol-2-ylidene to undergo dimerization aroused our curiousity in light of the recent preparation of bridged dibenzimidazolinylidenes (3) which appeared to be quite stable and reluctant to undergo C=C bond cleavage.[8] This observation prompted us to reexamine the electrochemistry of a series of 3,3'-polymethylene bridged derivatives of 2,2-biimidazole which we had reported earlier.[9]



3 (n = 3,4) **4**

Figure 1 illustrates the cyclovoltammograms of the dibromide salts which would serve as potential precursors for the tetraaminoalkenes **2** and **3**. The bibenzimidazolium salts **5a,b** both show two reversible waves, implying two sequential one electron reductions, providing first the cation radical and then the alkene. Bulk electrolysis of the bibenzimidazolium salts under anaerobic conditions indeed does provide the alkenes **3**.[6] For the biimidazolium salts, on the other hand, the bis-trimethylene bridged system shows two closely spaced reversible waves and its behavior might be expected to mirror that of the bibenzimidazolium salts. The closely spaced waves signify a relatively unstable cation radical. The bis-tetramethylene bridged and tetramethyl species exhibit increasingly irreversible behavior and one can conclude that the species formed after reduction does not persist long enough to undergo reoxidation.



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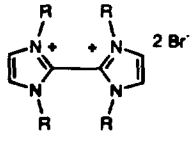

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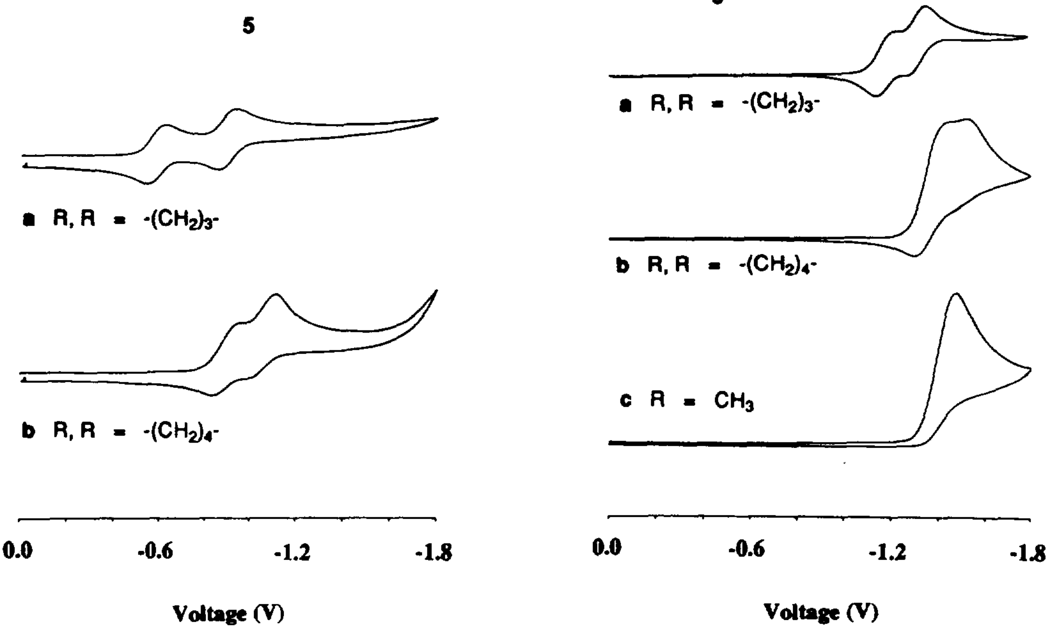
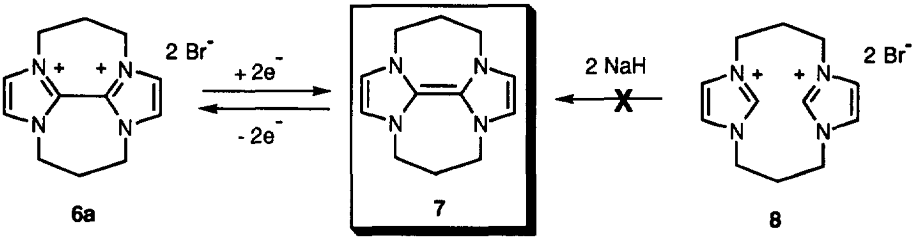


Figure 1. Cyclovoltammograms for 2,2'-bibenzimidazolium dibromides (left) and 2,2'-biimidazolium dibromides (right) recorded in CH_3CN containing 0.1 M tetrabutylammonium perchlorate at 25 °C with a sweep rate of 200 mV/sec.

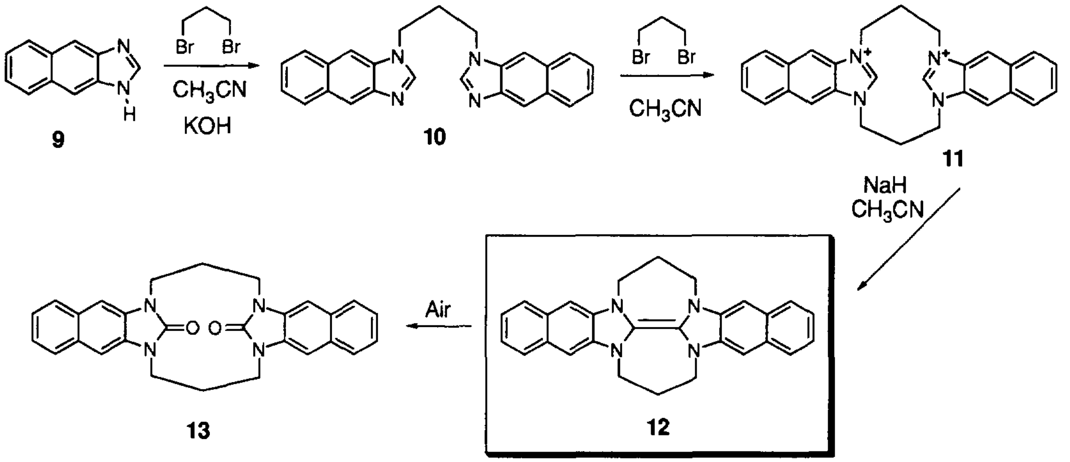
We then carried out bulk electrolyses on the three biimidazolium salts **6a-c** under the identical conditions used to generate **3**. Electrolysis of **6a** in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) at -1.6 V led initially to a bright orange color which was presumed to be the intermediate cation radical. The color eventually faded as the current decreased to zero. The resulting solution was evaporated to dryness and the residue was extracted with benzene. Evaporation of the benzene extracts provided a yellow, air sensitive solid. The 300 MHz ^{1}H NMR showed three characteristic peaks: a sharp singlet (4H) at 5.47 ppm, a triplet (8H) at 2.42 ppm, and a multiplet (4H) at 1.39 ppm. The proton-decoupled ^{13}C NMR showed four lines at δ127.0 (C4,5), 119.7 (C2), 53.8 (α-C), and 30.9 (β-C). Both spectra indicated some contamination by TBAP but these TBAP resonances did not interfere with **7** and could readily be subtracted.



In an effort to avoid the involvement of TBAP, we attempted to generate **7** by the deprotonation of an appropriately tethered bis-imidazolium species. The bis-imidazolium salt **8** was synthesized by carefully bridging imidazole with dibomopropane under high dilution conditions. Treatment of this salt with sodium hydride in acetonitrile did not, however, lead to the desired **7**.

The bulk electrolysis of **6b** and **6c** under identical conditions, using a potential which would insure complete reduction, did not provide the tetraazafulvalene derivatives analogous to **7**. This was especially disappointing in the case of **6c** since we expected that formation of a species such as **2** might in turn lead to the stable carbene **1** (R = CH_3).

The failure of **8** to generate the neutral species **7** prompted us to examine the corresponding naphtho-fused system. The alkylation of naph[2,3]imidazole[10] with 1,3-dibromopropane was carried out in a stepwise fashion, the first N,N'-bridge being installed in 65% yield under basic conditions. The second bridge required high



dilution and neutral conditons, being formed in 30% yield. Deprotonation of **11** with sodium hydride in dry acetonitrile under argon led to the formation of **12** as a red, highly air sensitive precipitate whose IR spectrum was quite similar to that of **3** (n = 3).[11] Poor solubility precluded analysis by NMR.

When **12** is exposed to air it emits a brilliant blue-purple chemiluminescence which eventually fades to afford the ureaphane **13** as a pale white solid. Chemiluminescent behavior is typical of tetraaminoethylenes[12] and is also observed for **3**. The ureaphane **13** shows a strong C=O absorption at 1720 cm^{-1} in the IR. The ^{1}H NMR shows aromatic multiplets at 7.24 (4H) and 6.91 (4H) and a singlet at 6.79 ppm (4H) as well as aliphatic multiplets at 4.78 (4H), 3.89 (4H), 3.34 (4H), and 2.02 ppm(4H), indicating that the geminal methylene protons are non-equivalent and the molecule exists in a rigid *syn* conformation with its carbonyl groups oriented in the same direction. This oxidative cleavage is directly analogous to what is observed for the benzo-fused derivative **3**.

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