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ELECTROCHEMISTRY OF HETEROSUBSTITUTED CYCLOPROPENYL CATIONS

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Previous electrochemistry of cyclopropenyl cations examined the effect of alkyl and aryl substituents on stability, reduction potentials and products, and pK_a's.[2] Heterosubstituted cyclopropeniums have not been examined electrochemically, but recent work indicates that tris-(dimethylamino)-cyclopropenium, 1a, and tris(thioethoxy)-cyclopropenium, 1b, differ markedly from the alkyl and aryl analogs.[3] For example, the observed substitution reactions of 1a and 1b are not typical for cyclopropenyl cations, and reflect an increased stability in the hetero-substituted cation. Calculations[3,4] show 1a to have a high energy HOMO and a high energy LUMO when compared to trialkyl cations which should result in more negative oxidation and reduction potentials for 1a. This is easily understood in terms of conjugation between the nitrogens and the ring. The perturbation by sulfur in 1b is difficult to predict due to the ability of sulfur to stabilize neighboring cations, anions, and radicals. Compared to alkyl cations, the sulfur should aid oxidation by stabilizing the additional positive charge in dication radical 2 (Scheme I), but the effect on reduction to radical 4 is ambiguous. The redox potentials of 1a and 1b should allow for a quantitative determination of these interactions.

Oxidation and reduction potentials for 1a and 1b are listed in Table 1 along with those for trimethylcyclopropenium,[5] 1c, and triphenylcyclopropenium,[6] 1d, for comparison. The reason for the differences in potential between platinum and mercury is not known, but maxima in the polarographic reduction waves suggest that adsorption effects are important.[7] The potentials were found to be reproducible using a.c. and second harmonic a.c. polarography.[8] The first oxidation wave of 1a was totally reversible with a peak separation for cyclic voltammetry of 61 mv,[9] but all other electrochemical processes showed irreversible behavior under our conditions.

The potentials for 1a are more negative than those for 1c and 1d, with oxidation shifted approximately 1.7 V (40 kcal) and reduction shifted approximately 1.5 V (35 kcal). The oxidation of 1a should be compared to that of tris(p-morpholinophenyl)-cyclopropenium, 1e, which oxidizes at +1.2 V vs. Ag/AgCl.[10] However, 1e oxidizes irreversibly in spite of being a larger, more delocalized system. The shifts for 1b are small, .5 V (12 kcal) for oxidation and a negligible shift for reduction. Thus, sulfur aids oxidation, but competitive stabilization by sulfur of cation 1b and radical 4b tends to cancel any shift for reduction.

One electron oxidation of 1 should give the dication radical 2 (Scheme I) which would oxidize further to trication 3, a heteroradialene derived from a conjugated ring containing no electrons. 1a does undergo two oxidations, both at easily accessible potentials. Since the first oxidation was reversible, preparative oxidation at +1.5 V using a platinum anode in acetonitrile containing .1 M tetrabutylammonium perchlorate (TBAP) gave a stable orange solution. An ESR spectrum of this solution was analogous to that obtained by Gerson et al.[4] for 1a in sulfuric acid and shows the first product to be the radical dication 2a. Therefore, the second oxidation represents formation of heteroradialene 3a. A stable salt of 2a has been isolated recently,[11] but 3a is too unstable for characterization as is 2b. One electron reduction of 1 should give radical 4 (Scheme I) which can dimerize to give biscyclopropenyl 5. Reduction of 4 to the anion is known, but a second reduction potential was not observed for either 1a or 1b. Preparative reduction of 1b led to intractible materials. However, reduction of 1a at -2.7 V at a mercury cathode in acetonitrile with .1 M TBAP afforded a 12% yield of hexakis-(dimethylamino)-benzene identified by the following data: mp 236° (lit.[12] 236°); pmr, singlet δ=2.72, ppm; cmr (vs. TMS), 44.88 ppm and 152.0 ppm; M^+ = 336. This product is analogous to that obtained from 1c which gives upon reduction hexamethyl benzene in 60% yield. We could also obtain 6a in 5% yield by reduction of 1a with sodium in HMPA or THF. The mechanism for the conversion of 5 to 6 is not clear.[13]

We also examined the oxidation of 6a, a peraminobenzene. 6a undergoes irreversible oxidation at +.32 V vs. Ag/AgCl in CH_2Cl_2 containing .1 M TBAP. This value should be compared with those for 1,3,5-tripyrrolidinobenzene[14] (+.32 V, irrev), N,N,N',N'-tetramethyl-p-phenylenediamine (+.10 V, rev), and N,N-dimethylaniline (+.76 V, irrev), which were obtained under identical conditions. These values should be compared with those of Zweig for alkoxy and alkylamino benzenes.[15] The oxidation potential for 6a is more positive than one would predict because steric hindrance prevents conjugation of the nitrogens with the aromatic ring. A crystal structure has shown that steric hindrance does not prevent conjugation in 1a.[3]

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Scheme I

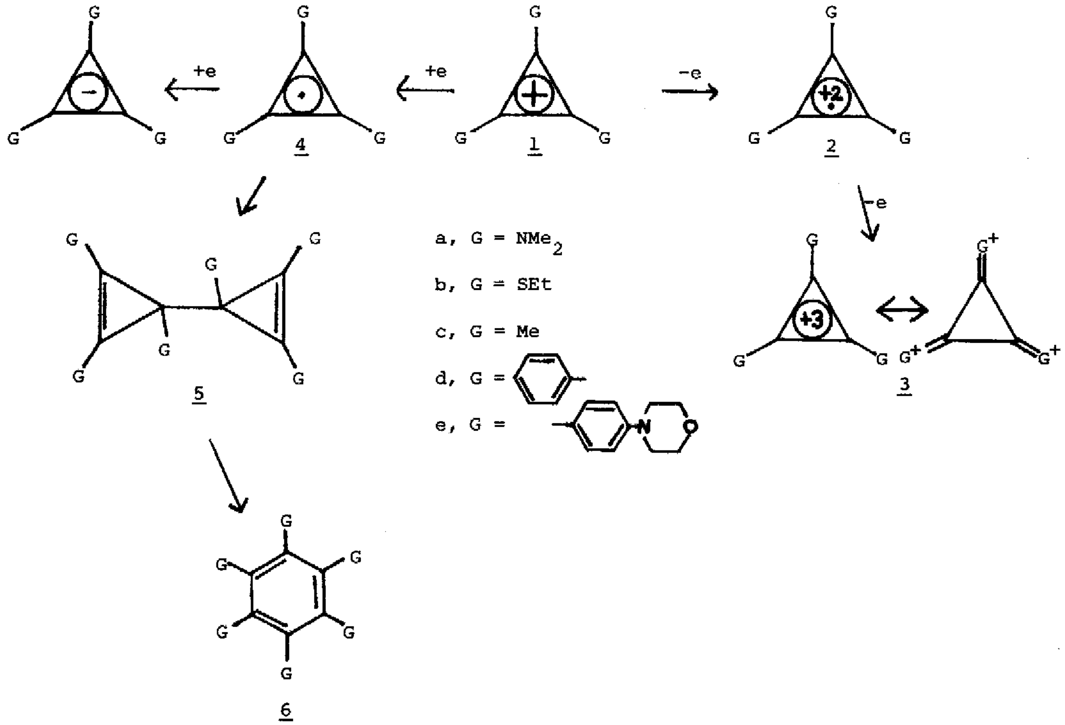

Table 1[a]

Redox Potentials for 1

	−e	+e	
	Pt[b]	Pt[b]	Hg[c]
1a	+1.12, +2.1	<−3.0	−2.60
1b	+2.3	−1.40	−.80
1c	>+2.8	−1.22	−1.50
1d	+2.7	−.84	−.62

a. All potentials vs. saturated calomel electrode in acetonitrile with .1 M tetra-n-butylammonium perchlorate.

b. E at 85% of peak current from cyclic voltammetry with 0.5 V/sec scan rate.[9]

c. $E_{1/2}$ from polarography at a d.m.e.

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