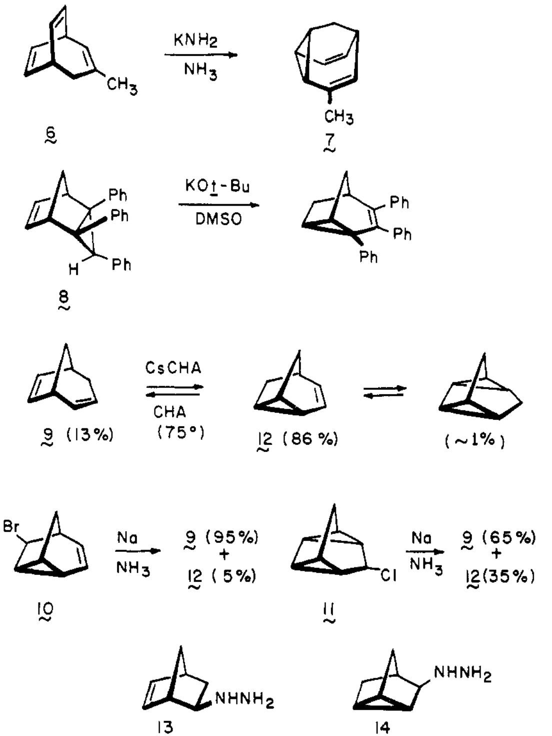
formations which satisfy all of the necessary criteria, the first being the barbaralyl-bicyclo[3.2.2]nonatrienyl example.[3] The preferred direction of positive charge control within $\mathbf{1}^+ \rightleftarrows \mathbf{5}^+$ is of course consistent with the cyclopropylcarbinyl cationic nature of $\mathbf{5}^+$. But do our experimental findings denote that the nortriquinacenyl anion is stabilized by homoaromatic delocalization or other homoconjugated interaction? Or is $\mathbf{1}^-$ favored simply because of greater electronic destabilization within $\mathbf{5}^-$. And to what extent does ring strain affect partitioning to products?

In this connection, work in other laboratories serves to emphasize that explicit definition of the energetic rewards of homoaromatic delocalization within simpler bicyclic carbanions has remained elusive. Thus, deprotonation of **6** with KNH_2 in liquid ammonia at 50 °C (3 h) gives rise exclusively to 3-methylbarbaralane (**7**)[8] despite the reputed homoaromatic stabilization of bicyclo[3.2.2]nonatrienyl anions.[8,9] The absence of bicyclo[3.2.1]octadiene products upon exposure of **8** to KO-*t*-Bu in Me_2SO is also noteworthy.[10] Winstein's investigation of **9–11** is equally revealing.[11] The alkaline oxidative cleavage (KIO_4, OH^-, H_2O) of hydrazines **13** and **14** to produce greater amounts of nortricyclene (56%) than norbornene (44%) can be understood in terms of preferential protonation of the cyclopropylcarbinyl anion intermediate.[12]



In the majority of these earlier examples, the results do not appear consistent with a single delocalized anion, but can be reasonably accommodated in terms of two or more equilibrating anions. In our view, the interconversions of $\mathbf{1}^-$ with $\mathbf{5}^-$ are governed analogously. Although there are several factors which contribute to the enhanced level of formation of hydrocarbon **2d** upon protonation, these do *not* include extended homoaromatic stabilization (trishomocyclopentadienide character). Through the application of reversible charge control, it is possible to gain valuable information on the *relative* energies of charged carbocyclic topologies. Finer inferences concerning the detailed structural features of the dominant ions are necessarily inappropriate on this basis alone.

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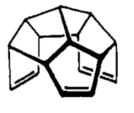
C_{16}-Hexaquinacene[1]

Sir:

The pentagonal dodecahedrane has recently become the object of intense synthetic[2-4] and theoretical pursuit.[5,6] Although no other structure can rival the unique I_h point group symmetry of this molecule, a number of related less complex hydrocarbons are notable in their own right. One of these, termed C_{16}-hexaquinacene (**1**) to distinguish it from a pair of equally unknown hexaquinacenes having 18 (**2**) and 17 (**3**) constituent carbon atoms,[7] possesses a highly convex topology with three mirror symmetry planes intersecting a threefold rotation axis. The sphericality of **1** is of sufficiently high order that trishapto coordination to suitable metal atoms will enclose a cavity of unprecedented construction. There is added interest in **1** from another viewpoint. The geometrical arrangement of its three pπ orbitals is such that the equilateral triangular array illustrated below may obtain. Should these orbitals adopt a suitable cant, cyclic six-electron pp-σ homoconjugative interaction could become significant.[8,9] The present study has been directed toward the development of an efficient synthesis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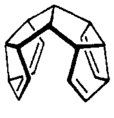
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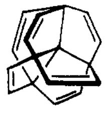
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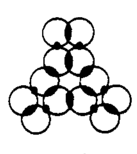

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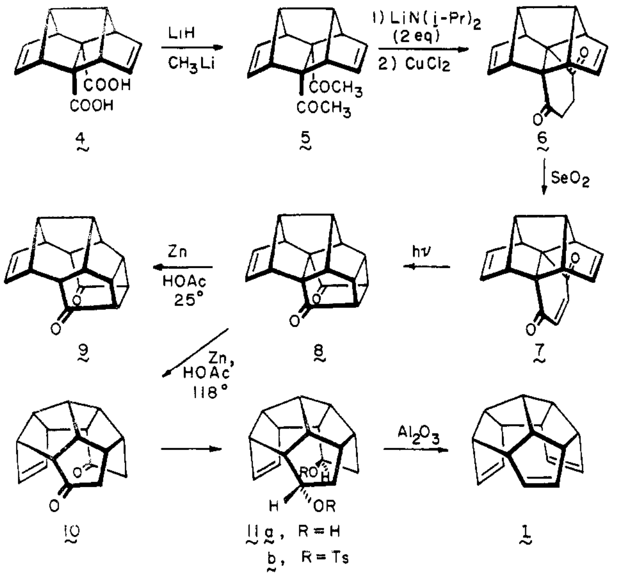
of **1** and we now report its successful elaboration in nine steps from sodium cyclopentadienide.

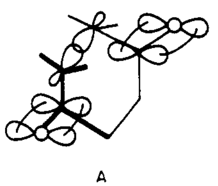
Dicarboxylic acid **4** can be obtained directly by cycloaddition of dimethyl acetylenedicarboxylate to 9,10-dihydrofulvalene,[10,11] generated in situ by oxidative coupling of cyclopentadienide anion with iodine in tetrahydrofuran at −78 °C.[12] Although **4** is hexacyclic, its six five-membered rings are clearly not properly arrayed relative to those present in **1** and extensive structural reorganization is therefore required. Furthermore, as **4** is only a C_{14} system, our strategy called for the incorporation of two additional carbon atoms. To this end, **4** was converted to diketone **5** (94% yield) by sequential treatment with lithium hydride and methyllithium in THF, followed by dropwise addition to cold dilute hydrochloric acid with vigorous stirring: mp 113 °C; IR (KBr) 1682 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 6.10 (m, 4), 3.31 (m, 4), 2.58 (m, 2), and 2.02 (s, 6); ^{13}C NMR ($\mathrm{CDCl_3}$) 207.24, 132.96, 77.19, 65.12, 59.47, and 28.95 ppm.[13]



To construct the 1,4-cyclohexanedione part structure of **6** while at the same time circumventing the possible serious complication of aldolization, **5** was treated with 2 equiv of lithium diisopropylamide in THF-hexane at −78 °C and the resulting dienolate anion solution was added *inversely* to anhydrous cupric chloride dissolved in DMF-THF (7:1). This adaptation of Saegusa's oxidative coupling procedure[14] afforded maximized yields (58%) of **6**, mp 214-215 °C. The six lines comprising its ^{13}C NMR spectrum ($\mathrm{CDCl_3}$; 210.22, 133.21, 69.30, 67.12, 61.29, and 39.02 ppm) provide unequivocal evidence that C_{2v} symmetry had been maintained during the cyclization.

Subsequently, **6** was heated with selenium dioxide and potassium dihydrogen phosphate in dioxane solution to introduce a third double bond as in **7** (60%). This step elaborates a molecule which can be considered to be a multiple cycloaddition product of the elusive benzoquinonyne[15] and 9,10-dihydrofulvalene. Expectedly, **7** is somewhat labile at more elevated temperatures, perhaps because it experiences retrograde [4 + 2] π Diels-Alder fragmentation and polymerization. However, this has not proven to be a serious problem and **7** can be efficiently photocyclized ($\mathrm{C_6H_6}$, 3500 Å, 87%) to its highly strained cage isomer **8**: ^{1}H NMR $\mathrm{CDCl_3}$) δ 6.05 (t, J = 1.5 Hz, 2) and 3.5-2.6 (br m, 10 H); ^{13}C NMR ($\mathrm{CDCl_3}$) 209.00, 128.47, 76.56, 70.15, 63.27, 52.46, 48.73, 48.52, and 38.20 ppm.

Now, it becomes appropriate to consider a stereoelectronic question central to our synthetic plan. The structural factors prevailing in **6** enforce an essentially orthogonal relationship between the carbonyl pπ orbitals and the central σ bond (see A). This specifically means that reductive cleavage of this 1,4-dicarbonyl system should not be possible and, in accord with theory,[16] **6** has been found to be stable to the most forcing reducing agents. The entire situation changes when we progress to **8** for in this diketone both 1,4-dicarbonyl subunits are now ideally aligned for maximum through bond interaction (see B). In model systems closely related to the caged part structure in **8**, [17] simple treatment with zinc in acetic acid at room temperature has proven adequate for cleavage of the internal cyclobutane bond. In contrast, comparable reduction of **8** leads exclusively to fission of the central norbornyl-like bond to deliver **9**: mp >360 °C; IR (KBr) 1719 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 5.83 (s, 2), 4.00-3.20 (m, 8), and 3.20-2.74 (m, 4); ^{13}C NMR ($\mathrm{CDCl_3}$) 219.71 (s), 131.08 (d), 61.38 (d), 60.35 (d), 60.17 (d), 59.14 (d), 58.11 (d), 44.79 (d), and 44.57 (d) ppm. This result provides mute but convincing testimony to the level of strain prevailing at this site in diketone **8**. Once this bond is ruptured, the structure adopts a more spherical contour and begins its more advanced evolution toward **1**.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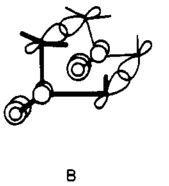
B

Although this conformational realignment does detract from the original ideality of the overlap between the carbonyl groups and the internal cyclobutane bond, the second-stage reduction can be accomplished without difficulty by merely raising the reaction temperature to 118 °C. Under these conditions, both **8** and **9** are converted to the beautifully crystalline diketone **10**. The relative simplicity of the ^{1}H (($\mathrm{CDCl_3}$) δ 5.70 (s, 2), 3.61 (m, 6), 3.01 (m, 4), and 2.19 (m, 4)) and ^{13}C NMR spectra (($\mathrm{CDCl_3}$) 219.93, 132.57, 60.38, 59.17, 58.71, 57.65, 56.07, 43.82, and 42.44 ppm) of this tetrahydro hexaquinacenedione conform to the presence in **10** of a molecular plane of symmetry.

Completion of the C_{16}-hexaquinacene synthesis requires replacement of the two identical carbonyl groups by double bonds. This was accomplished by sequential reduction with lithium aluminum hydride, esterification with *p*-toluenesulfonyl chloride in pyridine, and basic alumina promoted elimination of 2 equiv of sulfonic acid.[4a,b,18] The hydrocarbon so produced (mp 231.5-235 °C)[13] clearly has C_{3v} symmetry: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 5.36 (s, 6) and 3.76-3.20 (br m, 10); ^{13}C NMR ($\mathrm{CDCl_3}$) 131.57, 60.15, 54.91, and 53.06 ppm. The infrared spectrum of **1** (KBr) is characterized by six moderately intense bands at 3048, 2953, 2920, 1362, 752, and 730 cm^{-1} in addition to an approximately equal number of weaker absorptions.

Quantification[8] of the extent of homoconjugation in **1**, if any, awaits completion of photoelectron spectroscopic and three-dimensional x-ray crystal structure analyses. Such studies are in progress, as are efforts to transform **10** and **11** into dodecahedrane by proper introduction of four additional carbon atoms in a manner suitable for closing the sphere.

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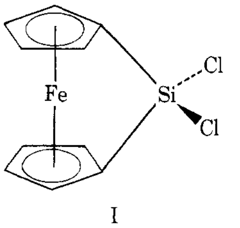
Design and Study of a Photosensitive Interface: A Derivatized n-Type Silicon Photoelectrode

Sir:

We have found that the photoanodic decomposition of n-type Si can be suppressed by the competitive oxidation of ferrocene in EtOH solution with $[n\text{-Bu}_4\text{N}]\text{ClO}_4$ as the supporting electrolyte.[1] Such studies[1-4] have led us to suspect a strong interaction of the stabilized photoanode with the reductant added to the solution. We now report the covalent attachment of a photoelectrochemically active ferrocene derivative to the surface of n-type Si which passivates the electrode to decomposition (SiO_2 formation). This study opens a new avenue for the stabilization of semiconductor/liquid junction photocells.

A number of interesting papers have been published recently concerning derivatized electrodes,[5-16] and attachment of electroactive groups to electrodes via surface oxide and hydroxide groups has proven fruitful. We have carried out initial derivatization of n-type Si with the ferrocene derivative (1,1′-ferrocenediyl)dichlorosilane (I) prepared by slow addition of 1,1′-dilithioferrocene to neat $SiCl_4$. The red-orange solid I is purified by sublimation. The mass spectrum shows a parent peak region characteristic of a molecule bearing two Cl atoms. The ^1H NMR shows a pair of multiplets centered at δ 4.02 and 4.29, respectively, in dry C_6D_6, characteristic of a disubstituted ferrocene.[17,18] The elemental analysis (Galbraith) is satisfactory [calcd (found): C, 42.43 (42.44); H, 2.83 (2.90); Cl, 25.07 (25.30); Si, 9.93 (10.22)]. Such a complex has precedence from the reaction of Ph_2SiCl_2 with 1,1′-dilithioferrocene which yields the diphenyl analogue of I.[18] Complex I is hydrolytically unstable (fumes in moist air), and this is the basis of its attachment to the Si surface.



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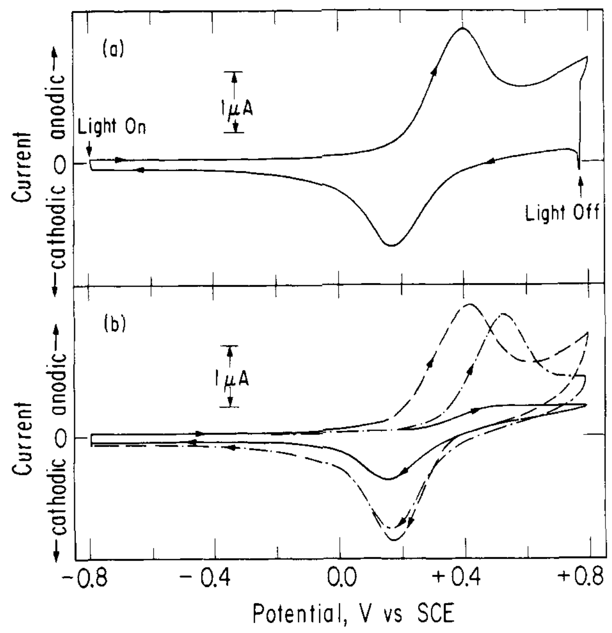

Figure 1. Cyclic voltammograms (100 mV/s) of derivatized n-type Si electrode in 0.1 M $[n\text{-Bu}_4\text{N}]\text{ClO}_4$ in CH_3CN under Ar at 298 K. (a) Scan begins at −0.8 V with 632.8-nm He-Ne laser irradiation (3 mW, 6× beam expanded); at the anodic limit the light is switched off. (b) Scans with 632.8-nm He-Ne laser irradiation (- - -), room light irradiation (· · · ·), and in the dark (—).

n-Type Si (3–5Ω cm) electrode material was single-crystal with ~0.1 cm^2 of a 100 face exposed. Contact was made by rubbing Ga–In eutectic onto the back of the Si, and a copper wire lead was attached with Ag-epoxy. The assembly was encased in a glass tube for secure mounting and insulated with ordinary epoxy to expose only the Si surface. The electrode was etched for 10 s at 298 K in concentrated HF immediately prior to use. The electrode surface was pretreated by dipping into 10 M NaOH for 60 s at 298 K, presumably introducing surface groups which could react with I to form SiOSi bonds. The electrode was washed with H_2O and with acetone and dried in air at 298 K. Attachment of I was accomplished by dipping the electrode into a dry isooctane solution of I under Ar. The reaction was carried out at 298 K for a typical time of 45 min. The electrode was washed with isooctane and finally with CH_3CN.

Derivatized n-type Si was characterized by cyclic voltammetry in 0.1 M $[n\text{-Bu}_4\text{N}]\text{ClO}_4$ in CH_3CN solvent at 298 K under Ar. The electrolyte solution contained no deliberately added electroactive species. Figure 1 shows the cyclic voltammograms for derivatized n-type Si. The first noteworthy point is that we find cyclic waves at all. Integration of the cyclic waves typically shows $\sim 2 \times 10^{-10}$ mol/cm^2 of surface attached electroactive material. Nonderivatized electrodes show a photoanodic current which corresponds to the buildup of SiO_2, but there is no reduction peak in the potential range scanned; with such cycling the oxide layer builds and the current declines to essentially nothing after 4–10 scans. By way of contrast, the derivatized electrodes show persistent cyclic waves (oxidation and reduction); e.g., the data shown in Figure 1 are after ~50 scans.

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