

Clearly, the ready availability and good thermal stability of **1** (recoverable after heating in dichlorobenzene at 180 °C for several days) are key factors in the broad application of this vinyl sulfoxide as an acetylene synthon. A significant feature of this scheme is the in situ thermal elimination of phenylsulfenic acid. While this by-product is not always innocuous (see above), it is frequently so. Consequently, its formation and likely subsequent disproportionation present little problem. Optimistically, the addition of tertiary amine bases will reduce any future potential complications to nil (work in progress).²⁷

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- National Health Service Postdoctoral Fellow, 1975–1977.

Leo A. Paquette,* Rudi E. Moerck²⁸
Bijan Harirchian, Phillip D. Magnus*

Evans Chemical Laboratories, The Ohio State University
Columbus, Ohio 43210

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Reversible Charge Control of Nortriquinacenyl-Tetracyclo[4.2.1.0^{3,5}.0^{4,9}]nonenyl Isomerizations

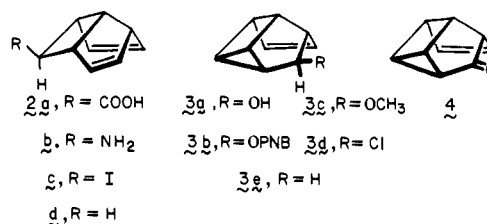
Sir:

As part of a study of "anchored" trishomoaromatic ions,¹ we previously established by classical methods that the nor-



triquinacenyl anion (**1**⁻) lacks the ability to stabilize its negative charge.^{1b} This result was subsequently corroborated by MINDO/3 calculations^{1b} and photoelectron spectral analysis of selected derivatives.² However, no experimental information was available concerning the thermodynamic stability of **1**⁻ relative to other (CH)₉⁻ isomers. Here we report on this question and describe in addition the full complement of reversible charge control criteria³ for this ring system which necessarily include pericyclic transforms of the related cation **1**⁺.

For systematic reasons, the present investigation began with the deamination of **2b** which can be readily prepared by Curtius rearrangement of acid **2a**^{1b} with diphenylphosphoryl azide.⁴ Upon treatment with sodium nitrite in 2 N perchloric acid,⁵ **2b** was cleanly transformed into **3a**, the structural as-

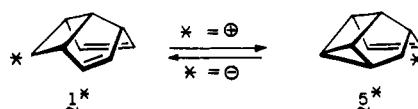


ignment to which was substantiated by Eu(fod)₃ shifting of the ¹H NMR spectrum,⁶ oxidation with Collins' reagent to ketone **4** (ν 1705 cm⁻¹), and hydride reduction of **4** to produce the endo alcohol. With the availability of the endo epimer, it was possible to establish that this substance was not present within detectable limits (>2%) in the original reaction mixture. Quantitatively similar results were realized when iodide **2c**^{1b} was exposed to a threefold excess of silver perchlorate in 25% aqueous acetone at room temperature for 2.5 h in the dark.

To establish that the tetracyclic cation is capable of retaining its structural integrity under more diverse conditions, *p*-nitrobenzoate **3b** (mp 94.5–96.0 °C)⁷ was prepared and subjected to methanolysis (100 °C, 48 h). There was uniquely produced a 7:1 mixture of **3c** and the unrearranged endo-methyl ether. Quite clearly, a proclivity for skeletal rearrangement to **1**⁺ or other topologically isomeric cations is not operational.

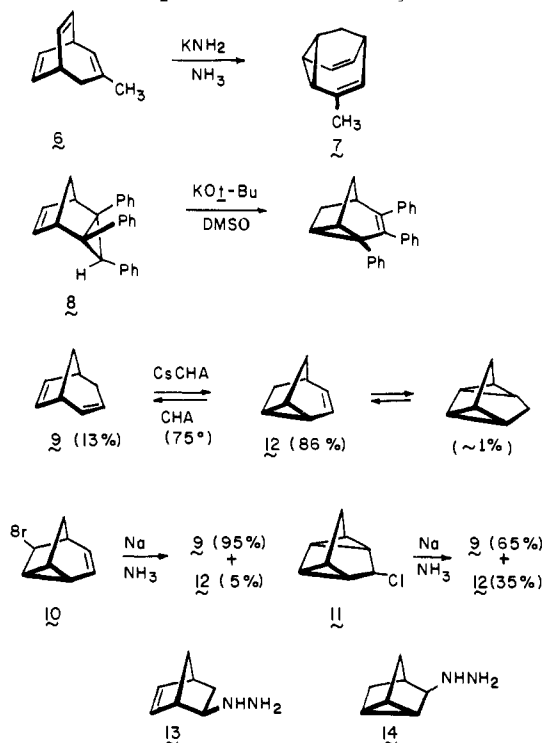
Experiments intended to permit recognition of the relative thermodynamic stabilities of the related anions began with the reduction of iodide **2c** using sodium in liquid ammonia. This reaction provides nortriquinacene (**2d**) as the exclusive hydrocarbon product. When chloride **3d**, obtained from the corresponding alcohol with thionyl chloride in pyridine, was comparably reduced, nortriquinacene was again produced although contamination with significant amounts of hydrocarbon **3e** was easily diagnosed (VPC analysis). Despite the fact that serious limitations on the quantity of **3d** precluded execution of a wide range of experiments, we were able to establish that reactions conducted at -78 and -33 °C exhibited only a small temperature effect on the ratio of **2d** to **3e** (1.3–1.4:1).

The prescribed evidence demonstrates that carbon skeletons **1**^{*} and **5**^{*} are interconvertible by merely controlling the formal charge (*) on the system. As such, this example constitutes only the second complete set of experimental trans-



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 $1^+ \rightleftharpoons 5^+$ is of course consistent with the cyclopropylcarbinyl cationic nature of 5^+ . But do our experimental findings denote that the nortriquinaceny anion is stabilized by homoaromatic delocalization or other homoconjugated interaction? Or is 1^- favored simply because of greater electronic destabilization within 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 $\text{KO}-t\text{-Bu}$ in Me_2SO is also noteworthy.¹⁰ Winstein's in-



vestigation of **9-11** is equally revealing.¹¹ The alkaline oxidative cleavage ($\text{KIO}_4, \text{OH}^-, \text{H}_2\text{O}$) 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 1^- with 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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- (6) $\delta_{\text{Me}_2\text{SO}}$ 6.13-5.85 (dd, $J = 6$ and 3.5 Hz, H_9), 5.74-5.52 (dd, $J = 6$ and 2 Hz, H_7), 3.96 (br s, H_2), 3.35-2.64 (m, $\text{H}_1, \text{H}_6, \text{H}_9$), 2.47 (m, H_3), 1.98 (br s, -OH), and 1.96-1.38 (m, H_4, H_5); ^{13}C NMR 140.22, 134.18, 75.59, 57.19, 48.18, 42.51, 32.75, 22.82, and 19.21 ppm. The following ΔE_i values (P. V. Demarco, T. K. Elzey, R. B. Lewis and E. Wenkert, *J. Am. Chem. Soc.*, **92**, 6335 (1970)) were experimentally determined: H_9 , -10.29; H_8 , -5.14; H_7 , -4.19; H_6 , -6.86; H_5 , -7.20; H_4 , -14.92; H_3 , -19.32; H_2 , -34.47; H_1 , -23.58; -OH, -142.6.
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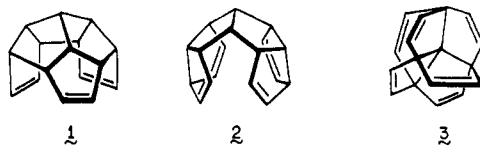
Leo A. Paquette,* Charles R. Degenhardt,¹³ Howard C. Berk
Evans Chemical Laboratories, The Ohio State University
Columbus, Ohio 43210

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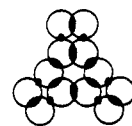
C_{16} -Hexaquinacene¹

Sir:

The pentagonal dodecahedrane has recently become the object of intense synthetic²⁻⁴ 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 sphericity 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 $p\pi$ orbitals is such that the equilateral triangular array illustrated below may obtain. Should these orbitals adopt a suitable cant, cyclic six-electron $pp\text{-}\sigma$ homoconjugative interaction could become significant.^{8,9} The present study has been directed toward the development of an efficient synthesis