Stereoelectronic Control of 2-Nortriquinacenylamine Deaminations. Relevance of Geometry and Proximity to Long-Range Orbital Interaction and Charge Stabilization in Cup-Shaped Molecules

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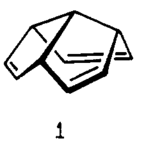
Received May 8, 1978

Deamination of *exo*-2-nortriquinacenylamine (**10**) leads exclusively to *exo*-tetracyclo$[4.2.1.0^{3,5}.0^{4,9}]$non-7-en-2-ol (**15**). Comparable treatment of endo epimer **13** affords *cis*-*exo*-dihydroindenyl acetate (**18a**, 48%), its derived alcohol (**18b**, 37%), and lesser amounts of the unrearranged acetate **19a** (12%) and alcohol **19b** (4%). No convergence to a common cation is seen. The overwhelming tendency for neighboring double-bond participation during the deamination of **10** is not shared by *exo*-dihydrotriquinacenyl tosylate during solvolysis. In the diazonium ion derived from **13**, the principal nitrogen extrusion pathway involves participation by one of two identical antiplanar σ bonds. The consequences of stereoelectronic alignment and proximity are discussed, and key thermodynamic considerations are placed on a firm basis by investigation of the complete reversible charge control spectrum. Whereas the tetracyclo$[4.2.1.0^{3,5}.0^{4,9}]$nonenyl cation is thermodynamically favored over the nortriquinacenyl cation, the reverse is true for the carbanions. The preference for one carbon skeleton over the other appears to be dictated chiefly by the cyclopropylcarbinyl character of the tetracyclic species. In our estimation, the observed chemical behavior is made possible by the rather compressed cup-shaped geometry of the nortriquinacene framework.

The expectation that the conformational rigidity and unique three-dimensional features of triquinacene (1)[2] might lead to homoconjugative interaction between its three π-bond segments has not been realized. A recent X-ray crystal structure analysis of 1[3] has revealed that the cant which is structurally enforced upon its pπ orbitals is not conducive to favorable through-space interaction within the molecular interior.[4] Photoelectron spectroscopic studies have provided further confirmatory assessment of the almost complete lack of neutral homoaromatic character despite the high molecular puckering.[5,6]



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Homoconjugation has been encountered more frequently in charged species because cations and anions generally share a heightened driving force for dissipation of their charge.[7] Notwithstanding, Paquette and his co-workers have uncovered no evidence for extended delocalization in the systems **2**–**4**.[8–10] Nuclear magnetic resonance and photoelectron spectroscopy,[6,11] as well as calculations, are in agreement with the absence of detectable charge dispersal in the three ions.

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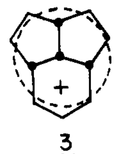

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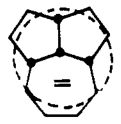

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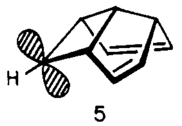
The nortriquinacene structure from which **2** is derived has evoked additional interest in this laboratory for several reasons. Firstly, the excision of a peripheral carbon from triquinacene can be seen with molecular models to result in greater accentuation of the cup-shaped nature of the carbon framework. Should sp^2 hybridization be attained at its C$_2$ center (cf. **5**), the internal lobes of the five pπ orbitals form a more tightly knit cluster on the concave underside of the molecule. Is such an arrangement conducive to stabilization? When a negative charge is present, the answer is clearly no. In fact, MINDO/3 calculations reveal 5^- not to be an energy minimum at all, nor even close to one.[9] Rather, the tetrahedral structures 6^- and 7^- are computed to possess the greatest stability. A significant barrier to the interconversion of 6^- and 7^- has also been found. Since the requisite attainment of sp^2 character at C$_2$ in carbanion **2** apparently is thermodynamically destabilized, the inability to detect homoconjugative interaction becomes more comprehensible.



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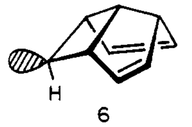

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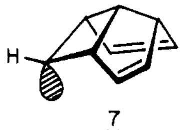

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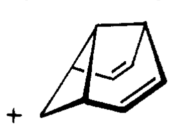
The properties of the corresponding cation had yet to be closely scrutinized.[12] Since C$_2$ of nortriquinacene can be specifically functionalized with both exo and endo stereochemistry, the consequence of leaving group geometry can be directly assessed. Phenomenologically, 5^+ constitutes a new $[CH]_9^+$ species[13] and joins other unusually behaved isomeric cations of which the homocubyl,[14] 9-pentacyclo$[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]$nonyl,[15] bicyclo[3.2.2]nona-3,6,8-trien-2-yl,[16] barbaralyl,[16] and *exo*-tricyclo$[4.2.1.0^{2,5}]$nona-3,7-dien-9-yl systems[17] are exemplary. When drawn as illustrated by **8**, the nortriquinacenyl cation may also be classified as a homosemibullvalenyl derivative, where the additional carbon has been inserted into an edge cyclopropane bond. The possible "anchored" trishomocyclopentadienylium character of this cation should likewise not be overlooked.



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Results

The method selected herein for carbocation generation consisted of the formation of epimeric diazonium ions and their in situ decomposition. This choice was dictated in part by synthetic considerations and in part because the lower activation energies normally required to eject nitrogen from diazonium intermediates was expected to maximize differences in chemical response between the exo and endo isomers, if such existed. Amines **10** and **13** were obtained by modified Curtius rearrangement of carboxylic acids **9** and **12**, respectively.[9] Upon treatment of **9** with diphenylphosphoryl azide, *tert*-butyl alcohol, and triethylamine in benzene at 50–55 °C for 8 h,[18] followed by hydrolysis of the resulting urethane in 3% hydrochloric acid, exo amine **10** was isolated in near

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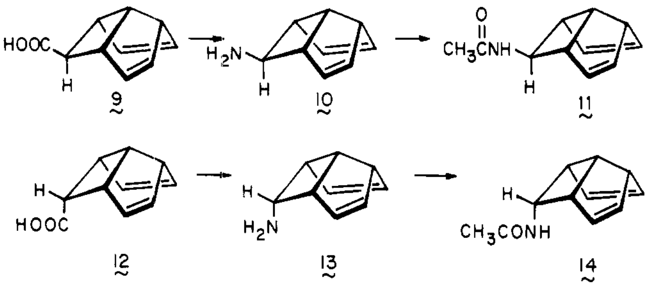
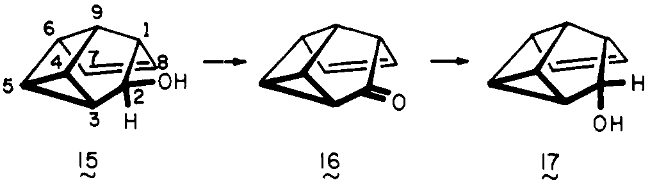


quantitative yield. Endo amine **13** was obtained (77% yield) by application of somewhat more severe conditions. Thus, succcessful Curtius rearrangement with diphenylphosphoryl azide was achieved only upon heating the benzene solution overnight at the reflux temperature,[19] followed by acidic hydrolysis at 90–95 °C for 1 h. The two amines were converted to their respective crystalline acetamides **11** and **14** for characterization.

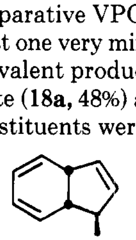
Deamination of the Exo Isomer. When treated with sodium nitrite in 2 N perchloric acid,[20] **10** was observed to undergo clean conversion to a single alcohol which was identified as **15** on spectral and chemical grounds. Pseudocontact shifting studies with Eu(fod)$_3$ furnished the following experimentally determined ΔEu values:[21] 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. Further, the ^{13}C NMR spectrum exhibited chemical shifts indicating the presence of a cyclopropane ring (see Experimental Section).

Oxidation of **15** with Collins reagent provided ketone **16**,

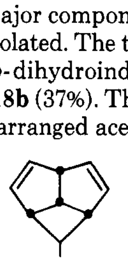


the infrared spectrum of which displays an intense carbonyl stretching frequency at 1705 cm^{-1}. Double irradiation ^{1}H NMR studies were likewise in full accord with the given assignment. In addition, lithium aluminum hydride reduction of **16** gave **17**, the availability of which made it possible to establish that this substance was not present within detectable limits (>2%) in the original deamination reaction mixture.

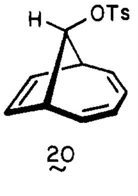
Deamination of the Endo Isomer. When **13** was diluted with water, acidified to pH 3.5 with 2 N perchloric acid, and treated with sodium nitrite at 5 °C as before, only a very slow reaction was observed even at room temperature. Therefore, an alternate procedure[22] was employed in which **13** was caused to react with sodium nitrite in acetic acid–water (1:1). Under these circumstances, rapid evolution of nitrogen was noted at −5 to −10 °C. The subsequent isolation of products by preparative VPC furnished four pure major components. At least one very minor substance was not isolated. The two most prevalent products proved to be *cis-exo*-dihydroindenyl acetate (**18a**, 48%) and its derived alcohol **18b** (37%). The minor constituents were characterized as unrearranged acetate **19a** (12%) and alcohol **19b** (4%). In a second deamination experiment conducted in acetic acid-water (4:1) as solvent, the relative composition of the same four products was found to be 44:17:24:14 (VPC analysis). This multicomponent mixture was directly hydrolyzed to permit isolation of **18b** (58%) and **19b** (33%). Unknown constituents totaled 9% in this case.



18a, R = COCH$_3$
b, R = H



19a, R = COCH$_3$
b, R = H



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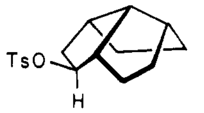
Principal acetate **18a** proved to be identical with a known sample prepared by acetolysis of tosylate **20**.[23] The hydrolysis of **18a** in methanol containing suspended potassium carbonate afforded **18b**, the ^{1}H NMR spectrum of which unequivocally established the stereochemistry of its hydroxyl group as cis-exo.[24]

Since control experiments established the stability of all four products to the deamination conditions, the alcohols do not result from hydrolysis of the acetates. The stereochemistry of the oxygenated functionality in **19a** and **19b** was not established because the small amounts of material available from deamination did not permit chemical interconversions to be made. Furthermore, we have been frustrated to this time in our attempts to prepare the derived ketone efficiently by other methods.[25]

Discussion

The pertinent features of our results can best be appreciated by considering Kelly's earlier investigation[26] of the acetolysis of the dihydro- and tetrahydrotriquinacenyl tosylates **21–24**



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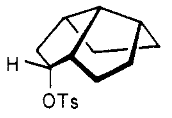
$k_{25°} = 1.7 \times 10^{-7}\ \mathrm{sec}^{-1}$



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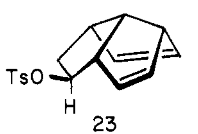
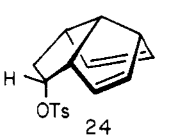
$k_{25°} = 7.8 \times 10^{-8}\ \mathrm{sec}^{-1}$



23

$k_{25°} = 1.8 \times 10^{-8}\ \mathrm{sec}^{-1}$



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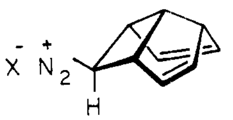
$k_{25°} = 3.9 \times 10^{-9}\ \mathrm{sec}^{-1}$

and contrasting the mechanistic demands of solvolysis and deamination. When heated in acetic acid, **21–24** experience liberation of *p*-toluenesulfonic acid at rates which indicate enhanced reactivity for the saturated series. No rearrangement products were found; rather, only those substances presumably derived from localized carbonium ions were determined to be present. The lower reactivity of **23** and **24** can be attributed to adverse inductive effects contributed by the π bonds. Anchimeric assistance arising because of the close proximity of at least one double bond to the reaction center was notably absent.

It is generally agreed that solvolytic processes usually occur by way of late transition states and provide conditions well suited to the relocation of atomic nuclei so as to achieve maximum stabilization of the transient cation intermediate ("nonvertical" ionization). Stated differently, the endothermicity of such reactions is considered to be particularly conducive to neighboring group participation and strong interaction with solvent dipoles.

Deaminations, on the other hand, are viewed as starting from more highly energetic diazonium ions, passing through earlier transition states, and involving much less distortion of nuclear positions ("vertical" ionization).[27,28] The activation energy required to eject molecular nitrogen is low. Two theories have evolved concerning the role of neighboring group participation in such transition states. The first proposal considers the involvement of a neighboring group neither necessary nor possible because of the small positive charge localized on the carbon atom bearing the diazonium group.[27b,28a] The second hypothesis is diametrically opposite, espousing pronounced participation by neighboring groups to assist in the expulsion of nitrogen.[27a] Examples can be found to support either contention. Moreover, solvolysis and deamination have given rise to identical results in a number of situations. We have previously stated that generalizations cannot be transferred from system to system without adequate consideration of geometric factors.[29] In actuality, a good correlation exists between the nature and reactivity of product-forming intermediates and the three-dimensional structural features of their reactants.

In this context, we see the inability of exo tosylate **23** to utilize one or more neighboring double bonds to delocalize positive charge as a striking contrast to the efficient involvement of one double bond during the deamination of exo amine **10**. These results may reflect the following: (a) an improved geometry of the relevant orbitals in diazonium ion **25** relative to those present in **23**, such that kinetically controlled anchimeric assistance now becomes fully dominant; (b) a greater thermodynamic preference for carbocation **26** which is not shared by **27** despite their comparable cyclopropylcarbinyl character; (c) a frustration of thermodynamics, the lesser stable **26** resulting because of some need for increased molecular distortion to achieve stabilization of the positive charge under vertical ionization conditions; and/or (d) the differing nucleophilicities of the solvents employed in tosylate solvolysis (HOAc) and deamination (H_2O).



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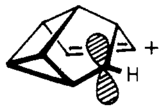
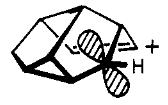


26



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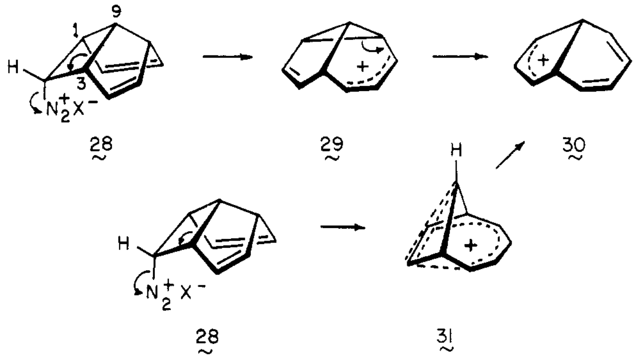
We view possible differences due to solvent to be of minimal importance in this instance. The far greater nucleophilicity of water should lead to carbonium ion interception at earlier stages and provide a product distribution where less structural changes are observed. This is contrary to our findings.

Nor is the conclusion that **15** is formed as a consequence of the frustration of thermodynamics supported by experimental fact. As will be demonstrated below, cation **26** actually enjoys greater stabilization than 5^+. Unfortunately, reversible charge control criteria do not provide us with finer inferences on the detailed structure of "open" cation 5^+.

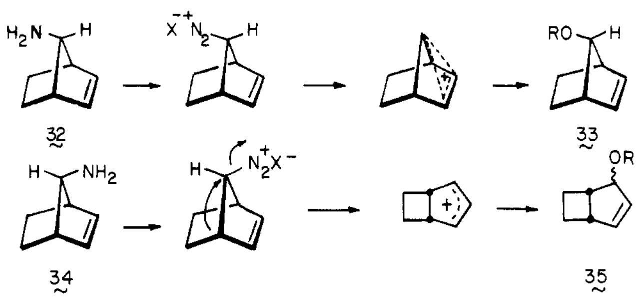
Since deamination of endo amine **13** produces no detectable quantities of **15**, the deaminations of the epimeric 2-nortriquinacenylamines clearly do not converge to a common cation. Rather, **13** is transformed to a diazonium ion whose geometry precludes double-bond participation. Available evidence suggests that the unstable diazo hydroxides formed on deamination frequently decay to products through ion pair intermediates.[27] But the timing of C–N and N–O heterolytic bond cleavages is markedly dependent upon structure.[30] In those instances where the diazonium ion is long lived, solvent exchange occurs extensively and the product structure is largely that of solvent capture (e.g., acetate ester in acetic acid). Conversely, when loss of nitrogen from the diazonium ion leads to a very stable carbocation, its formation is believed[30] to be coincident with breaking of the N–O bond or shortly following it. The observable consequence of this timing is substantial capture by the geminate hydroxide ion to give alcohol, often with substantial stereochemical retention in the alcohol.[28,31] A number of investigators have also observed the alternative course of direct displacement of nucleophiles upon diazonium ions.[32]

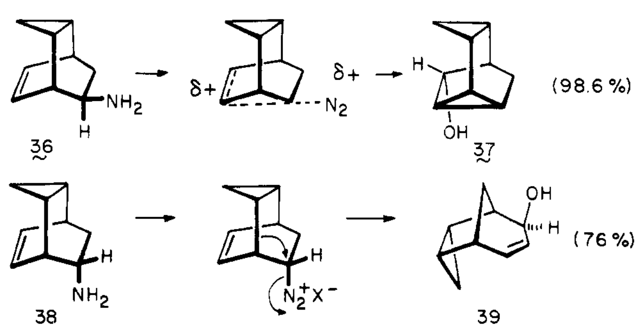
The results with **13** suggest that its diazonium ion is probably of medium longevity. Thus, in HOAc–H_2O (1:1), a 3:1 ratio of **19a** to **19b** was noted, a value which decreased to 1.7:1 in the less aqueous 4:1 solvent combination. Although ion pair exchange with solvent becomes less prevalent as the proportion of water is decreased (due to "tighter" ion pairs), the data accommodate the conclusion that equilibration of the diazonium hydroxide with solvent is occurring prior to covalent C–O bond formation.

Significantly, the principal nitrogen extrusion pathway from the endo diazonium ion is participation by one of two identical adjacent σ bonds (C_2,C_9 or C_3,C_9) possessing the most favorable stereoelectronic alignment (see **28**). Such assistance may give rise initially to carbonium ion **29**, which has previously been shown to be especially prone to conversion to the dihydroindenyl cation **30**.[33,34] Alternatively, the bicyclo[4.2.1]nona-2,4,7-trien-9-yl cation (**31**) may intervene prior to generation of **30**.[28b,35,36]



Equally dramatic differences in the reactivity of epimeric amines have been encountered on earlier occasions. For example, Tanida and his co-workers observed the conversion of *anti*-7-norbornenylamine (**32**) to **33** with retention both of structure and stereochemistry, in contrast to the nearly exclusive formation of bicyclo[3.2.0]hept-2-en-4-yl derivatives (**35**) from the syn isomer.[37] In the first instance, loss of nitrogen presumably is facilitated by double-bond participation and intervention of a bishomocyclopropenium cation which captures solvent without loss of configuration. In the diazonium ion corresponding to **34**, σ-bond participation occurs to deliver the allylic cation precursor to **35**.





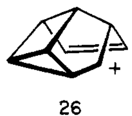
Kirmse and Wahl have reported that the deaminations of **36** and **38** result predominantly in the formation of rearranged products.[20] Neighboring double-bond assistance plays a dominant role in the case of the exo isomer, while Wagner-

Meerwein shift of the antiplanar σ bond is most prevalent within the diazonium ion generated from **38**.

These systems share with **10** and **13** a predilection for electronic relocation under vertical ionization conditions, which is very striking. One can arrive at the plausible conclusion that the observed intramolecular neighboring group interactions gain importance because minimal geometric distortion is necessary to maximize stereoelectronic overlap from behind the $>C-N_2^+$ bond. To gain additional specific information on this point in the nortriquinacenyl series, the complete spectrum of interrelated reversible charge control phenomena was studied.

Reversible Charge Control of Nortriquinacenyl–Tetracyclo[4.2.1.0^{3,5}.0^{4,9}]nonenyl Isomerization.[12] Two additional experimental criteria were employed to establish the relative thermodynamic stabilities of cations **40** and **26**. In the first, exo iodide **41**[9] was treated in the dark with a threefold excess of silver perchlorate in 25% aqueous acetone at room temperature for 2.5 h. Clean conversion to *exo*-tetracyclononenol **15** was observed, the result being quantitatively similar to that realized from the deamination of **10**. To establish that the tetracyclic cation is capable of retaining its structural integrity under more diverse conditions, *p*-nitrobenzoate **42a** was prepared and subjected to methanolysis at 100 °C for 48 h. There resulted a mixture of unrearranged methyl ether **42b** and its endo isomer **43** in a 7:1 ratio.


40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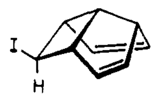
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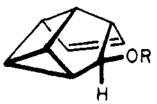
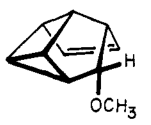

42 a, R = PNB
b, R = CH$_3$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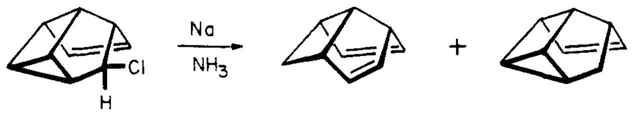
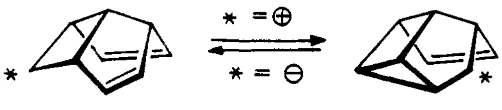
Quite clearly, therefore, there exists no proclivity for skeletal rearrangement to **40**, structural isomer **26** being the more stable cation.

The preferred direction of this transformation is the reverse of that realized under anionic conditions. It has previously been established that reduction of iodide **41** under a variety of conditions provides nortriquinacene (**45**) as the exclusive hydrocarbon product.[9] The last of the four requisite experimental criteria materialized in the form of chloride **44**, which when comparably reduced produced both **45** and **46**. Serious limitations on the quantity of **44** precluded execution of a wide range of experiments. Nevertheless, it proved possible to establish that reactions conducted in liquid ammonia at −78 and −33 °C exhibited only a small temperature effect on the ratio of **45** to **46** (1.3–1.4:1).



44 45 46

The predescribed evidence demonstrates that the nortriquinacen-2-yl and tetracyclo[4.2.1.0^{3,5}.0^{4,9}]non-7-en-2-yl carbon skeletons are interconvertible by merely controlling the formal charge (*) on the system. The present example represents only the second complete set of experimental transformations which has explicitly examined the four requisite criteria, the first being the barbaralyl–bicyclo[3.2.2]-nonatrienyl pair.[38]

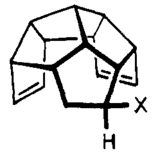


Conclusion

The preferred direction of positive charge control within **40** and **26** is of course consistent with the cyclopropylcarbinyl cationic nature of **26**. The possibility that **27** differs intrinsically from **26** in not being more thermodynamically stable than its tricyclic dihydrotriquinacen-2-yl cation isomer appears somewhat remote. However, this point remains to be experimentally established. If both **26** and **27** were thermodynamically favored, then the conversion of amine **10** and iodide **41** to **15** and the singular inability of **23** to undergo bond relocation would argue for favorable operation of long-range orbital interaction only in the nortriquinacenyl systems. As alluded to earlier, the increased accentuation of the cup-shaped nature of the nortriquinacene framework does result in greater potential pπ proximity and more favorable pπ orbital alignment.

The molecular geometry prevailing prior to rearrangement is known to markedly influence transition state energies in ways that need not necessarily be revealed by static enthalpy consideration. However, in the case of nortriquinacenes, such effects can also be made apparent by reversible charge control techniques.

The divergent chemical consequences associated with the dihydrotriquinacene–nortriquinacene structural change are dramatic, and one can only conjecture at this time as to the nature of the effects which might be encountered during ionization of more highly spherical C$_{16}$-dihydrohexaquinacenyl (**47**) and norhexaquinacenyl (**48**) derivatives. Our recent successful efficient synthesis of the parent hydrocarbon **49**[39] now permits an experimental assessment of these questions to be made.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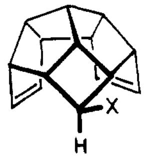
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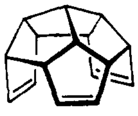
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Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^1H NMR spectra were determined with Varian T-60, Varian A-60A, and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C spectra were also obtained with the Bruker spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative scale VPC separations were performed on a Varian Aerograph Model A-90-P3 instrument equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***exo*-2-Aminotricyclo[4.2.1.0^{3,9}]nona-4,7-diene (10).** A solution of **9**[9] (1.37 g, 8.5 mmol), diphenylphosphoryl azide (2.40 g, 8.5 mmol), triethylamine (0.94 g, 9.4 mmol), and dry *tert*-butyl alcohol (0.63 g, 8.5 mmol) in dry benzene (125 mL) was heated at 60–65 °C for 9 h under nitrogen. The cooled reaction mixture was washed with 5% citric acid solution, concentrated, and diluted with 3% hydrochloric acid (100 mL). After being heated at 50–55 °C under nitrogen for 2 h, the solution was cooled and washed twice with dichloromethane. The aqueous layer was basified in an ice bath with 10% sodium hydroxide solution and extracted with dichloromethane (5 × 50 mL). Concentration in vacuo afforded **10** (1.0 g, 99%) as an oil which crystallized at 0 °C: ^1H NMR (CDCl$_3$) δ_{Me_4Si} 6.10 (dd, J = 5 and 2 Hz, 2, olefinic), 5.78 (d with fine coupling, J = 5 Hz, 2, olefinic), 3.78 (m, 2, methine), 2.88 (m, 3, methine), and 2.18 (s, 2, NH$_2$).

***exo*-2-Acetamidotricyclo[4.2.1.0^{3,9}]nona-4,7-diene (11).** To **10** (60 mg, 0.45 mmol) dissolved in 25 mL of 3% hydrochloric acid was added 10% sodium hydroxide solution until cloudly and 3% hydrochloric acid until clear again. The mixture was cooled with a few added chips of ice, followed by 0.5 mL of acetic anhydride, stirred for 4 h, and stored overnight in a refrigerator. The solution was then poured into 100 mL of water, basified with 10% sodium hydroxide solution, and extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with water and dried. Concentration produced 65 mg (81%) of crude material. Purification by preparative TLC (silica gel, ether) and sublimation (70 °C, 0.05 mm) yielded 21 mg of **11** which was recrystallized (ether–pentane) to give a white solid: mp 142–143 °C; ^{1}H NMR (CDCl$_3$) $\delta_{\mathrm{Me_4Si}}$ 6.6 (br s, 1, >NH), 6.2–5.5 (m, 4, olefinic), 4.3–2.8 (m, 5, methine), and 2.0 (s, 3, methyl); MS calcd, *m/e* 175.0997; MS found, *m/e* 175.0999.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.36; H, 7.48; N, 8.01.

***endo*-2-Aminotricyclo[4.2.1.0^{3,9}]nona-4,7-diene (13).** Endo acid **12**[9] (500 mg, 3.1 mmol) and diphenylphosphoryl azide (850 mg, 3.1 mmol) dissolved in benzene were treated with triethylamine (345 mg, 3.4 mmol), and the solution was heated at the reflux temperature for 8.5 h under nitrogen. The cooled solution was washed with 5% nitric acid solution and concentrated in vacuo to afford a yellow oil which was diluted with 3% hydrochloric acid (15 mL) and heated at 85 °C for 1 h. The cooled solution was extracted with dichloromethane. The organic layer was discarded, and the acidic layer was basified with 10% sodium hydroxide solution and reextracted four times with dichloromethane. These organic layers were dried and concentrated under reduced pressure to give 320 mg (77%) of **13**: IR (CHCl$_3$) $\nu_{\max}$ 3370, 3180, 2920, 1700, 1570, 1453, 1380, and 1265 cm^{-1}; ^{1}H NMR (CDCl$_3$) $\delta_{\mathrm{Me_4Si}}$ 6.20–5.95 (dd, *J* = 6 and 2.5 Hz, 2, olefinic), 5.60–5.40 (d with fine splitting, *J* = 6 Hz, 2, olefinic), 4.08–3.77 (m, 1, methine, 3.65–2.97 (m, 4, methine), and 1.61 (s, 2, NH$_2$).

***endo*-2-Acetamidotricyclo[4.2.1.0^{3,9}]nona-4,7-diene (14).** To **13** (80 mg, 0.6 mmol) dissolved in 10 mL of 3% hydrochloric acid was added 10% sodium hydroxide solution until cloudy and 3% hydrochloric acid until clear again. The mixture was cooled with a few added chips of ice, followed by 0.5 mL of acetic anhydride, stirred for 4 h, and stored in a refrigerator overnight. The reaction mixture was poured into 100 mL of water, basified with 10% sodium hydroxide solution, and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with water, dried, and concentrated to afford 75 mg (44%) of a yellow solid which was chromatographed, sublimed, and recrystallized (ether–pentane) to give **14** as a white solid: mp 97–98 °C; IR (CHCl$_3$) $\nu_{\max}$ 3422, 1655, 1490, and 1230 cm^{-1}; MS calcd, *m/e* 175.0997; MS found, *m/e* 175.1000.

Anal. Calcd for $C_{11}H_{13}ON$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.21; H, 7.67; N, 7.81.

Deamination of 10. *exo*-Tetracyclo[4.2.1.0^{3,5}.0^{4,9}]non-7-en-2-ol (15). A solution of **10** (110 mg, 8.3 mmol) in water was cooled to 0 °C, acidified with 2 N perchloric acid to pH 3.5, treated with sodium nitrite (620 mg, 9.0 mmol), and allowed to warm to room temperature. After being stirred for 7 h, the mixture was extracted with dichloromethane (5 × 30 mL), and the combined organic phases were washed with brine and dried. The concentration oil (620 mg) was chromatographed on Florisil (5 g; elution with 25% ether–pentane) to yield **15** as a slightly yellow oil (500 mg, 45%). This single product was isolated in analytically pure form by preparative gas chromatography (6 ft 12% Carbowax 20M on Chromosorb W at 135 °C).

The original acidic layer was basified with 10% sodium hydroxide solution and extracted with dichloromethane (4 × 30 mL). The combined organic extracts were washed, dried, and concentrated to return **10** (300 mg, 28%).

For **15**: IR (film) $\nu_{\max}$ 3320, 2940, 1260, 1190, and 1025 cm^{-1}; ^{1}H NMR (CDCl$_3$) $\delta_{\mathrm{Me_4Si}}$ 6.13–5.85 (dd, *J* = 6 and 3.5 Hz, 1, H$_8$), 5.74–5.52 (dd, *J* = 6 and 2 Hz, 1, H$_7$), 3.96 (br s, 1, H$_2$), 3.35–2.64 (m, 3, H$_1$, H$_6$, and H$_9$), 2.47 (m, 1, H$_3$), 1.98 (br s, 1, OH), and 1.96–1.38 (m, 2, H$_4$ and H$_5$); ^{13}C NMR (CDCl$_3$) 19.21, 22.82, 32.75, 42.51, 48.18, 57.19, 75.59, 134.18, and 140.22 ppm; MS calcd, *m/e* 134.0732; MS found, *m/e* 134.0733.

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: 80.44; H, 7.59.

Tetracyclo[4.2.1.0^{3,5}.0^{4,9}]non-7-en-2-one (16). A solution of **15** (500 mg, 3.7 mmol) in dichloromethane (50 mL) was added dropwise to a stirred mixture of dry chromium trioxide (2.5 g, 25 mmol) and dry pyridine (4.0 g, 50 mmol) in dichloromethane (50 mL). After the brown suspension had been stirred at room temperature for 30 min, the dichloromethane was separated by decantation and concentrated to leave an oil. The residue in the reaction flask was rinsed with ether, and this solution was added to the oil before washing with 3% hydrochloric acid, saturated sodium bicarbonate solution, and water. The dried ether extracts were concentrated, and the oily residue was chromatographed on Florisil (5 g) to afford 415 mg (85%) of **16**. VPC purification on a 6 ft column of 5% SE-30 on Chromosorb G (130 °C) yielded analytically pure **16**: IR (film) $\nu_{\max}$ 2980, 2870, 1705, and 1105 cm^{-1}; ^{1}H NMR (CDCl$_3$) $\delta_{\mathrm{Me_4Si}}$ 6.13 (dd, *J* = 5.5 and 3.0 Hz, 1, H$_7$), 5.97 (dd, *J* = 5.5 and 1.5 Hz, H$_8$), 3.55 (m, 2, H$_1$ and H$_9$), 3.01 (m, 2, H$_3$ and H$_6$), 2.29 (m, 1, H$_4$), and 1.85 (m, 1, H$_5$). In double resonance studies, irradiation of those resonances due to H$_3$ and H$_6$ (see **15** for numbering) collapsed the signals at δ 1.85 due to H$_5$ ($J_{4,5}$ = 6.6 Hz) and at δ 6.13 due to H$_7$ to doublets. Saturation of the absorptions for H$_1$ and H$_9$ resulted in the appearance of H$_8$ as a doublet with little change elsewhere. Simultaneous irradiation of the H$_1$, H$_3$, H$_6$, and H$_9$ resonances brought about collapse of the H$_4$,H$_5$ and H$_7$,H$_8$ pairs to individual pairs of doublets.

Anal. Calcd for C_9H_8O: 81.79; H, 6.10. Found: C, 81.66; H, 6.12.

***endo*-Tetracyclo[4.2.1.0^{3,5}.0^{4,9}]non-7-en-2-ol (17).** A solution of **16** (315 mg, 2.4 mmol) in anhydrous ether (8 mL) was added dropwise to a suspension of lithium aluminum hydride (46 mg, 1.2 mmol) in ether (10 mL). The mixture was heated at reflux for 2 h under nitrogen, stirred at room temperature for 1 h, and hydrolyzed by the addition of water (0.5 mL), 10% sodium hydroxide solution (0.5 mL), and water (0.5 mL). The slurry was filtered, and the lithium and aluminum salts were washed several times with ether. The ether filtrate was dried and concentrated to give 320 mg of crude oil which was quickly filtered through Florisil (2 g; elution with 25% ether–pentane) to afford 315 mg (98%) of **17**. VPC purification on a 6 ft column of 12% Carbowax 20M on Chromosorb W (160 °C) afforded analytically pure **17**: IR (film) $\nu_{\max}$ 3350, 2980, and 1060 cm^{-1}; ^{1}H NMR (CDCl$_3$) $\delta_{\mathrm{Me_4Si}}$ 6.01–5.77 (m, 2, H$_7$ and H$_8$), 4.63 (br s, 1, H$_2$), 3.32–2.62 (m, 3, H$_1$, H$_6$, and H$_9$), 2.17 (m, 1, H$_4$), 1.92–1.15 (m, 3, H$_3$, H$_5$, and OH).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.56; H, 7.54.

Deamination of 13. A solution of **13** (578 mg, 4.35 mmol) in acetic acid (8 mL) and water (2 mL) cooled to −5 to −10 °C was treated with sodium nitrite (620 mg, 9.0 mmol) in one portion and stirred at −5 °C for 40 min. The orange solution was poured into water (10 mL) and extracted with ether (2 × 30 mL) and dichloromethane (2 × 30 mL). The ether extracts were washed with saturated sodium bicarbonate solution and water, dried, and concentrated at atmospheric pressure. Analysis (VPC) at 90 °C on a 6 ft SE-30 column packed with Chromosorb G indicated no detectable indene. The dichloromethane extracts were washed with saturated sodium bicarbonate solution and water, dried, and concentrated to afford an oil which was combined with the ether concentrate. The remaining solvent was removed in vacuo, and the residual oil was subjected to VPC analysis (6 ft column containing 12% Carbowax 20M on Chromosorb W, 160 °C). The four major components were identified as **18a** (44%), **19a** (24%), **18b** (17%), and **19b** (14%). An unidentified component (1%) was also present. The crude oil was chromatographed on Florisil (elution with 25% ether–pentane) to give 320 mg of crude product mixture with the same component ratio (VPC analysis).

The original acidic extract was basified with 10% sodium hydroxide solution and extracted with dichloromethane. The organic layer was dried and concentrated to yield 90 mg of slightly impure **13**.

The crude alcohol-acetate mixture (320 mg) was dissolved in methanol (8 mL), treated with potassium carbonate (600 mg, 4.3 mmol), and stirred for 3.25 h under nitrogen. The methanol was evaporated, and the residue was diluted with water (50 mL) and extracted with dichloromethane (5 × 30 mL). The combined organic layers were washed twice with water, dried, and concentrated. Chromatography on Florisil (2 g; elution with 25% ether–pentane) yielded an impure mixture (140 mg, 29%). The alcohol components were separated by preparative gas chromatography (6 ft column packed with 12% Carbowax 20M on Chromosorb W, 160 °C) to afford 26 mg (57.7%) of **18b**, 15 mg (33.3%) of **19b**, and 9 mg (9%) of unknown constituents.

For **19a**: ^{1}H NMR (CDCl$_3$) $\delta_{\mathrm{Me_4Si}}$ 6.2–5.5 (m, 4, olefinic, 4.3–3.0 (m, 5, methine), and 2.08 (s, 3, methyl).

For **18a**: IR (film) $\nu_{\max}$ 3040, 1730, and 1235 cm^{-1}; ^{1}H NMR (CDCl$_3$) $\delta_{\mathrm{Me_4Si}}$ 6.1–5.5 (m, 7, olefinic and >CHOAc), 3.7 (br d, 1, bridgehead), 3.0 (br d, 1, bridgehead), and 2.0 (s, 3, methyl).

For **18b**: IR (film) $\nu_{\max}$ 3310, 3040, 2890, 1588, and 1020 cm^{-1}; ^{1}H NMR (CDCl$_3$) $\delta_{\mathrm{Me_4Si}}$ 6.1–5.5 (m, 6, olefinic), 4.74 (m, 1, >CHOH), 3.7 (m, 1, bridgehead), 2.9 (m, 1 , bridgehead), and 1.86 (br s, 1, OH); MS calcd, *m/e* 134.07315; MS found, *m/e* 134.07333.

For **19b**: ^{1}H NMR (CDCl$_3$) $\delta_{\mathrm{Me_4Si}}$ 6.10–5.95 (dd, *J* = 6 and 2.3 Hz, 2, olefinic), 5.75–5.57 (octet, 2, olefinic), 3.92 (d with fine splitting, *J* = 8 Hz, bisallylic), 3.9–3.5 (m, superimposed on q, *J* = 7.5 Hz, 2, >CHOH and apical), 3.1–2.9 (m, 2, allylic), and 2.0 (br s, 1, OH); MS calcd, *m/e* 134.07315; MS found, *m/e* 134.07333.

***exo-cis*-Dihydroindenyl Alcohol (18b).** To **18a** (150 mg, 0.85 mmol) in methanol (8 mL)–water (1.5 mL) was added potassium carbonate (600 mg, 4.3 mmol), and the resulting suspension was stirred under nitrogen for 3.75 h. The methanol was evaporated, and the residue was diluted with water and extracted four times with dichloromethane. The organic layer was washed with water and dried.

Concentration afforded 102 mg (89%) of **18b** as a dark oil. A pure sample of **18b** was obtained by preparative gas chromatography (6 ft column packed with 5% SE-30 on Chromosorb G, 130 °C) and was identical in all respects with **18b** isolated above.

Silver Ion Assisted Solvolysis of 41. A solution of **41**[9] (120 mg, 0.50 mmol) and dry silver perchlorate (320 mg, 1.55 mmol) in acetone (2 mL) and water (1 mL) was stirred in the dark for 2.5 h under nitrogen. Brine was then added and the precipitate removed by filtration. The filtrate was extracted four times with ether, and the combined organic layers were washed with brine and dried. Solvent evaporation produced a light yellow oil which was subjected to preparative gas chromatography (6 ft 5% SE-30 on Chromosorb G, 140 °C). There was isolated 50 mg (75%) of a single component which was identified as **15** on the basis of its spectra.

Tetracyclo[4.2.1.$0^{3,5}$.$0^{4,9}$]non-7-en-2-yl *p*-Nitrobenzoate (42a). A solution of **15** (99.4 mg, 0.741 mmol) in dry pyridine (5 mL) was cooled to 0 °C, treated with 275 mg (1.48 mmol) of *p*-nitrobenzoyl chloride, and stored in a refrigerator overnight at 0 °C. The dark brown mixture was poured onto ice water and extracted twice with ether. The combined organic layers were washed with ice-cold 12% hydrochloric acid, saturated sodium bicarbonate solution, and water prior to drying. Evaporation of solvent under high vacuum left 191 mg (91%) of solid **42a**. Recrystallization from ether-pentane gave colorless crystals: mp 94.5–96.0 °C; ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 8.30 (s, 4, aromatic), 6.22–6.02 (dd, *J* = 5 and 2 Hz, 1, olefinic), 5.86–5.64 (dd, *J* = 6 and 2 Hz, 1, olefinic), 5.24 (s, 1, >CHO–), 3.43–3.12 (m, 1, methine), 3.12–2.84 (m, 2, methine), 2.66–2.40 (m, 1, cyclopropyl), and 2.00–1.53 (m, 2, cyclopropyl); MS *m/e* 283 (M$^+$).

Methanolysis of 42a. A degassed solution of **42a** (45.7 mg, 0.161 mmol) in dry methanol (8 mL) was sealed in a thick walled glass tube under vacuum and placed in an oil both heated to 100 °C for 50 h. The contents of the cooled tube were poured onto water and extracted with ether (four times). The combined organic layers were washed with saturated sodium bicarbonate solution and water prior to drying. Solvent removal left 22.7 mg (95%) of product. ^{1}H NMR analysis showed the mixture to consist of unreacted **42a** (11%), **43** (11%), and **42b** (78%). The ethers were isolated by preparative VPC (6 ft 12% Carbowax 20M on Chromosorb W, 130 °C) and identified by spectral comparison with the authentic samples prepared as described below.

***exo*-2-Methoxytetracyclo[4.2.1.$0^{3,5}$.$0^{4,9}$]non-7-ene (42b).** A solution of **15** (500 mg, 3.73 mmol) in ether (10 mL) was added dropwise to a suspension of potassium hydride (450 mg, 11.19 mmol) in ether (20 mL) under nitrogen at 0 °C, and the mixture was stirred at room temperature for 15 min. Methyl iodide (2 mL) was added and the resulting suspension stirred for 4 h. The mixture was quenched with methanol and then water at 0 °C, and the ether layer was separated. The aqueous layer was extracted with ether, and the combined organic extracts were washed with water, dried, and concentrated to give a yellow oil (525 mg, 95%). Purification by preparative VPC on a Carbowax 20M column at 160 °C afforded analytically pure **42b**: IR (film) ν_{max} 2980, 2940, 2880, 1199, 1095, 1088, and 802 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 6.11–5.88 (dd, *J* = 6 and 2.5 Hz, 1, olefinic), 5.82–5.57 (dd, *J* = 6 and 2.5 Hz, 1, olefinic), 3.63 (s, 1, >CHOCH$_3$), 3.33 (s, 3, methoxyl), 3.53–2.76 (m, 3), 2.48 (m, 1), and 1.68 (m, 2); MS calcd, *m/e* 148.0888; MS found, *m/e* 148.0891.

***endo*-2-Methoxytetracyclo[4.2.1.$0^{3,5}$.$0^{4,9}$]non-7-ene (43).** A solution of **17** (220 mg, 1.64 mmol) in ether (10 mL) was added dropwise to a suspension of potassium hydride (400 mg, 10 mmol) in ether (10 mL) at 0 °C under nitrogen, and the mixture was stirred at room temperature for 1 h. Methyl iodide (2 mL) was added and the resultant mixture stirred for 7 h. The suspension was quenched with methanol and then water, and the ether layer was separated. The water layer was extracted with ether, and the combined organic extracts were washed with water, dried, and concentrated. Purification by preparative VPC (Carbowax 20M column, 160 °C) yielded analytically pure **43**: IR (film) ν_{max} 3000, 2930, 1453, and 1115 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 5.90 (dd, *J* = 6 and 3 Hz, 1, olefinic), 5.68 (d with fine splittings, *J* = 6 Hz, 1, olefinic), 4.23 (m, 1, >CHOCH$_3$), 3.40 (s, 3, methoxyl), 3.16 (m, 2), 2.86 (m, 1), 2.21 (m, 1), and 1.62 (m, 2).

Anal. Calcd for C$_{10}$H$_{12}$O: C, 81.05; H, 8.16. Found: C, 80.81; H, 8.34.

***exo*-2-Chlorotetracyclo[4.2.1.$0^{3,5}$.$0^{4,9}$]non-7-ene (44).** A solution of **15** (77.1 mg, 0.575 mmol) in dry benzene (10 mL) was cooled to 0 °C and treated with 160 mg (2.92 mmol) of pyridine followed by 206 mg (1.73 mmol) of thionyl chloride (via syringe). The mixture was stirred at 0 °C for 35 min, and water (5 mL) was introduced. Benzene (15 mL) was added. The organic layer was separated and washed twice with cold 10% hydrochloric acid, twice with saturated sodium bicarbonate solution, and with water prior to drying. The solvent was removed to leave 71.2 mg (83.6%) of **44** as a light yellow oil: ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 5.96 (dd, *J* = 6 and 3 Hz, 1, olefinic), 5.66 (dd, *J* = 6 and 3 Hz, 1, olefinic), 4.25 (s, 1, >CHCl), 3.37 (m, 2, methine), 2.96 (m, 1, methine), 2.57 (m, 1, cyclopropyl), and 1.78 (m, 2, cyclopropyl).

This chloride was utilized in the subsequent experiments without further purification.

Reductive Dehalogenation of 44. A three-neck 100-mL flask containing 27 mg (1.18 mg-atom) of sodium was charged with 30 mL of liquid ammonia (freshly distilled from sodium). Chloride **44** (30 mg, 0.196 mmol) dissolved in 3 mL of ether was added dropwise at −78 °C. After 1 h at this temperature, the mixture was allowed to warm to −33 °C for 30 min. The solution was again cooled to −78 °C and quenched with saturated ammonium chloride solution. The resultant mixture was slowly poured onto 100 mL of ice water and extracted four times with ether. The combined organic layers were dried, filtered, and carefully concentrated by slow distillation through a 6 in. Vigreux column. Preparative VPC isolation of the two hydrocarbon components of the concentrate (6 ft 10% SE-96 on Chromosorb W, 75 °C) afforded 3.2 mg of **45** and 2.0 mg of **46**. An analytical VPC trace of the concentrate showed these compounds to be present in a 1.3.:1 ratio.

For **45**: the ^{1}H NMR spectrum proved to be identical with that of an authentic sample.[9]

For **46**: ^{1}H NMR (CDCl$_3$) δ_{Me_4Si} 6.13–5.96 (dd, *J* = 7 and 3 Hz, 1, olefinic), 5.61–5.46 (dd, *J* = 8 and 3 Hz, 1, olefinic), 3.31–3.04 (m, 1), 3.01–2.70 (m, 2), 2.30–2.02 (m, 2), 2.02–1.72 (m, 2), and 1.50–1.22 (m, 2); MS calcd, *m/e* 118.0782; MS found, *m/e* 118.0786.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for their financial support of this research.

Registry No.—**9**, 64096-66-8; **10**, 66337-88-0; **11**, 67584-28-5; **12**, 64130-41-2; **13**, 67650-26-4; **14**, 67650-27-5; **15**, 66470-25-5; **16**, 67612-72-0; **17**, 67650-28-6; **18a**, 54288-22-1; **18b**, 38694-39-2; **19a**, 67584-29-6; **19b**, 67584-30-9; **41**, 64096-68-0; **42a**, 66337-89-1; **42b**, 66337-90-4; **43**, 66429-04-7; **44**, 66470-26-6; **45**, 58913-91-0; **46**, 50345-67-0; diphenylphosphoryl azide, 4129-17-3; *p*-nitrobenzoyl chloride, 122-04-3; methyl iodide, 74-88-4; thionyl chloride, 7719-09-7.

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Cycloaddition Reactions of Triazolinediones to Tricyclo[4.1.0.0^{2,7}]hept-3-enes. Consequences of Charge Control as Compared to Frontier Orbital Control

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Received June 2, 1978

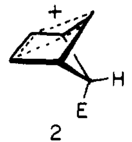
Tricyclo[4.1.0.0^{2,7}]hept-3-enes substituted with methyl groups at C_1, C_1–C_7, C_6, and C_1–C_6–C_7 react with *N*-phenyltriazolinedione to yield 2,4,6-triazapentacyclo[5.4.1.0^{2,6}.0^{8,10}.0^{9,12}]dodecane-3,5-diones. The cycloaddition proceeds with skeletal rearrangement of the strained hydrocarbon system. Through deuterium labeling, it was established that the C_1–C_6–C_7 cyclopropyl triad maintains its integrity. The regiospecificity of the reaction is believed to be a manifestation of charge control, with the triazolinedione attacking olefinic carbon C_4 and presumably generating a dipolar 7-norbornenyl intermediate. This reaction mode differs from that followed by H^+ or D^+, which attack an edge bicyclobutane bond under frontier orbital (HOMO–LUMO) control. The title reaction is somewhat sensitive to the locus and extent of alkyl substitution. Both 1,6-dialkyl derivatives examined suffered prior rearrangement to the related 1,2-disubstituted cycloheptatriene. Various mechanistic factors are considered.

One of the continuing and persistent questions in mechanistic organic chemistry concerns a priori knowledge of when perturbation HMO theory might apply to a chemical reaction and when it does not. The highly successful utilization of frontier orbital analysis in rationalizing the regioselectivity of Diels–Alder reactions,[2] 1,3-dipolar cycloadditions,[3] and a variety of other processes[4] attests to the impressive predictive powers of this theory. Such HOMO–LUMO control of reactivity is seemingly made feasible because of the reactant-like nature of the activated complex which precedes bond formation. When this condition does not apply and the original reactant structures become so greatly altered in the transition state that they no longer represent suitable models of the prevailing interactions, then some other factor, typically charge control, can be expected to gain importance. [2 + 2] cycloadditions, which customarily proceed with the endothermic production of zwitterions in late transition states, appear representative of this latter mechanistic category.[5]

Given the elegant studies alluded to above, there has been little attention directed to assessing the possible multifaceted reactivity of a *single* structural type. Molecules which we consider ideal for the evaluation of a crossover from orbital-controlled to charge-controlled behavior are those which have at least two sites of potential reactivity. An additional criterion necessary to the recognition of the desired mechanistic divergency is an abrupt change in regiospecificity (preferred) or regioselectivity with alteration in the governing reaction mode.

In the particular case of benzvalene (1),[6,7] whose geometry (microwave spectroscopy[8]) and electronic character (PE measurements[9,10] and theoretical calculations[10–12]) have recently become available, there is seen a strikingly intense interaction between the $b_2(\pi)$ orbital of its double bond and the $b_2(\sigma)$ orbital of the neighboring bicyclobutane ring. Since the HOMO is predominantly π in character, those electrophilic reactions which proceed under frontier orbital control should occur at the double bond. The ground-state polarization does induce some measure of negative charge on the bicyclobutane moiety in 1. Accordingly, when other factors are discounted,


1



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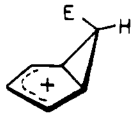

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