The Question of Delocalization in "Anchored" Ions with Potential Trishomoaromatic Character. 2. The Tricyclo[4.2.1.$0^{3,9}$]nona-4,7-dien-2-yl Anion

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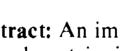
Abstract: An improved synthesis of 2,3-dihydrotriquinacen-2-one is described together with the conversion of this ketone to several nortriquinacene derivatives. The approach is based upon ring contraction of the α-diazocarbonyl system and subsequent degradation of the resulting carboxyl derivatives. All attempts to deprotonate nortriquinacene (**22**) were without success. This lack of acidity has been interpreted to mean that the transition state for exo H_2 abstraction does not experience significant stabilizing interaction with the proximate double bonds. Metal reduction studies also failed to provide evidence for formation of a stabilized carbanion. Spectroscopic measurements of Grignard derivatives have indicated an innate inability of the system to disperse charge. These findings receive additional support from MINDO/3 calculations on the carbanion. Various methylene nortriquinacenes were prepared and their spectra (^{1}H NMR, ^{13}C NMR, PES) determined. No important through-space interactions could be detected. The significance of these findings within the framework of homoaromaticity is discussed.

Our current appreciation of homocyclopentadienide character rests upon several significant experimental achievements: (a) demonstration of the exceptional facility with which bicyclo[3.2.1]octa-2,6-diene undergoes proton-deuterium exchange at C_4 to give **1**,[1] a property shared by its 6,7-benzolog[2] and related molecules;[3] (b) the ^{1}H NMR spectrum of **1**, the direct observation of which was made possible by Na-K alloy reduction of the *exo*-4-methoxy derivative;[4] (c) the entirely comparable properties of the bicyclo[3.2.2]nona-2,6-dienyl carbanion (**2**);[5] and (d) the extended interaction present in the hetero system **3**.[6] The unusual stability of **1**-**3** has been attributed to bishomoaromatic character, the topology necessary for interaction being maintained by the rather rigid geometry of these molecular frameworks.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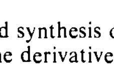
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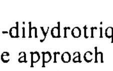
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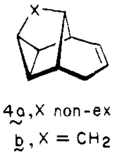
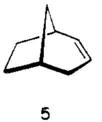
Conceptually, orbital interaction between an allyl anion and a proximate double bond should be capable of extension to mono- and trishomoaromatic systems. However, no monohomocyclopentadienides are yet known and Freeman and Hardy's attempt[7] to demonstrate trishomocyclopentadienide character in the anions of **4** was not realized. The exchange rates of **4a** and **4b** in KO-*t*-Bu/Me_2SO-d_6 were found to compare closely with that calculated for **5**[8] rather than **6**, an indication of the lack of homoaromatic overlap in **7**. Attempts to observe **8** by Na-K cleavage of the *exo*-4-methoxy derivative of **4a** also proved fruitless.[9]


4a, X non-existent
b, X = CH_2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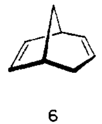
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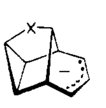
k^{exch}_{rel} 1,1   1 $10^{4.5}$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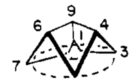
Although this lack of interaction of a cyclopropane σ bond with an allylic anion system is not in harmony with observations made on selected carbonium ions, the capacity for reasonable interaction with olefinic units having suitable topology is not precluded. In a continuation of our search for "anchored" trishomoaromatic character,[10,11] we herein consider the $2^02^01^-$ pericyclic topology defined by **9**. The constituent carbocyclic rings in this anion are now sufficiently small that the reduction in the gaps generated by the three homo bridges may lead to improved orbital overlap relative to higher homologues.[10,11] The particular connectivity embodied in **9** (six-electron system) is seen to be entirely favorable when viewed in standard Hückel terms (Table I);[12] furthermore, it suffers from no symmetry restraints when assessed by perturbation theory.[13] Such considerations implicate the possible existence of effective interaction at the termini of the three ribbons involved. The studies documented below were therefore conducted to determine if **9** is indeed a delocalized entity.



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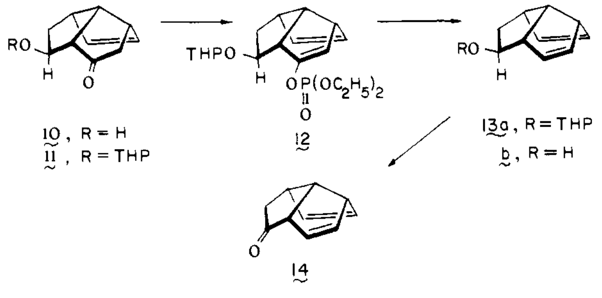
Synthetic Considerations. Because our synthetic plan required 2,3-dihydrotriquinacen-2-one (**14**)[14,15] as the key intermediate, attention was first given to the development of its large scale efficient synthesis. The method of choice involved conversion of the readily available β-hydroxy ketone **10** to its tetrahydropyranyl ether (**11**) and subsequent transformation of the carbonyl function to an enol phosphate[15] (Scheme I).

Scheme I



Reduction of **12** with lithium in liquid ammonia and tetrahydrofuran at −78 °C[16] routinely gave **13a** in 65% overall yield from **11**. The sequential reaction of **13a** with *p*-toluenesulfonic

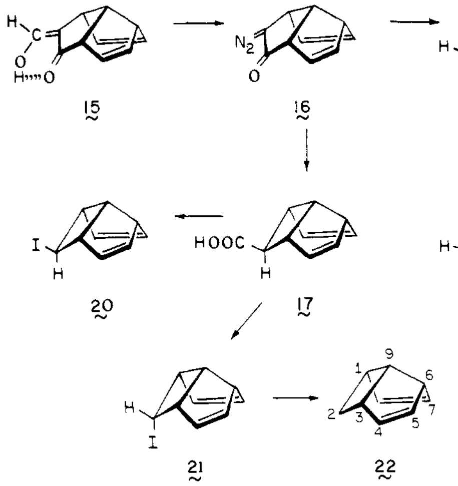
Table I. HMO Calculations for **9**

Case A: $\beta_{3,5} = \beta_{2,8} = \beta_{5,7}$					Case B: $\beta_{3,5} = \beta_{5,7}$; $\beta_{2,8} = 0$				
	E_π-6α	Negative charge				E_π-6α	Negative charge		
$\beta_{3,5}/\beta_0$	(β_0)	$C_{3,7}$	$C_{2,8}$	C_5	$\beta_{3,5}/\beta_0$	(β_0)	$C_{3,7}$	$C_{2,8}$	C_5
0.0	4.000	0.000	0.000	1.000					
0.3	4.264	0.021	0.084	0.789	0.0	4.172	0.000	0.076	0.847
0.5	4.740	0.071	0.161	0.536	0.5	4.448	0.000	0.167	0.667
0.75	5.542	0.141	0.201	0.318	0.75	4.916	0.000	0.265	0.471

acid in methanol at room temperature and the chromium trioxide-pyridine complex in methylene chloride solution afforded the desired ketone in 90% yield.

Suitable ring contraction of **14** required elaboration of α-diazo ketone **16** (Scheme II). This substance was prepared by α formylation[17] of **14**, followed by exposure of **15** to p-toluenesulfonyl azide and diethylamine.[18] Photolysis of **16** in methanol[19] produced a mixture of epimeric methyl esters, the endo isomer of which predominated by a factor of 7:3. Controlled saponification of this mixture afforded pure *exo*-carboxylic acid **17**. Its ^{1}H NMR spectrum shows the characteristic downfield broadened singlet for the carboxyl proton at δ 11.6, a doublet of doublets (J = 6 and 2 Hz) for one pair of olefinic protons at 6.02–6.11, and a broadened doublet having fine splitting for the other pair (5.60–5.85). Multiplets for the methine protons are positioned upfield at 3.31–4.08 (4 H) and 2.50 (1 H). Clearly, either the apical proton experiences shielding by the carboxyl group or endo H_2 is similarly affected by the double bonds. In confirmation of the assigned structure, the ^{13}C NMR spectrum of **17** exhibits seven signals.

Scheme II



endo-Carboxylic acid **18** was similarly prepared by irradiation of **16** in aqueous dioxane containing sodium bicarbonate.[20] Separation of the resulting mixture of **17** and **18** (3:7, NMR analysis) was accomplished by iodolactonization[21] giving **19** in 60% yield. With zinc in acetic acid,[21b,22] **19** yielded exclusively **18**, the ^{1}H NMR spectrum of which displays the carboxyl proton at δ 11.2, the olefinic protons as a broad multiplet between 5.6 and 6.2, and the remaining hydrogens in the 3.3–4.2 region.

Iododecarboxylation of **17** with lead tetraacetate and iodine in carbon tetrachloride[23,24] produced a 68:32 mixture of **20** and **21**, the relatively large amount of endo isomer suggesting that the endo surface of the free-radical intermediate does not suffer from excessive steric hindrance. The iodides were conveniently separated by preparative VPC methods and identified on the basis of their spectral properties (see Experimental Section). Reduction of these iodides with tri-n-butyltin hydride in pentane or sodium in liquid ammonia afforded tricyclo[4.2.1.0^{3,9}]nona-4,7-diene (**22**). This hydrocarbon is characterized by a doublet of doublets (J = 5 and 2.5 Hz) between 5.94 and 6.19 due to H_5 and H_7, an eight-line pattern for H_4 and H_8 at 5.65–5.84, a broadened doublet (J = 6 Hz) centered at 3.94 attributable to H_6, a quartet (J = 6 Hz) at 3.63 for apical proton H_9, and a multiplet at 3.22 corresponding to the allylic protons (H_1, H_3). In addition, $H_{2\,\mathrm{exo}}$ appears at 1.22–1.64 as a doublet of triplets while $H_{2\,\mathrm{endo}}$ is seen as a broadened quartet between 2.13 and 2.70. Decoupling experiments have corroborated the structural and positional assignments (Experimental Section).

Attempted Deprotonation of 22. In order to gain a preliminary indication of possible trishomoaromatic stabilization in **9**, an investigation of the susceptibility of **22** to deprotonation was undertaken. Recourse was made to the technique of isotopic exchange[1,2,7,25] which, although not a measure of kinetic acidity independent of ground-state energy,[5] nevertheless provides a good reading on equilibrium acidity. Importantly, the proton to be abstracted in **22** (exo H_2) is bonded to an "insulated" sp^3-hybridized cyclobutyl carbon and as such differs intrinsically from the customary type of proton (allylic) for which reactivity data are available.[1-5,7,25] Although this dissimilarity in substrate structure does not allow for direct quantitative comparison with the molecules studied earlier (because development of allylic anion character is no longer a common trait), any errors introduced here are likely to be no worse than those given by any other available technique.

When a solution of **22** and freshly sublimed potassium *tert*-butoxide in anhydrous Me_2SO-d_6 was sealed in an NMR tube under a nitrogen atmosphere (vacuum line conditions) and heated at 50 °C for 49 h, there was observed no evidence for deuterium exchange. Nor was decomposition a complication. Mass spectral analysis of the recovered hydrocarbon confirmed the absence of significant isotopic exchange. Additional evidence for the total unresponsiveness of **22** to this base-solvent system was derived from comparable experiments where heating at 60 °C for 18 h, 80 °C for 105 h, and 90 °C for 89 h effected no observable spectroscopic change!

Although potassium amide in liquid ammonia has been successfully utilized in the deprotonation of several bicyclo[3.2.2]nona-2,6,8-trienes,[25] we were deterred from utilizing solvents such as NH_3 and cyclohexylamine[26] because of other experimental observations described herein which revealed that transient **9** generated otherwise was readily protonated by such solvents.

Accordingly, within the limits of such NMR measurements, any potential that **9** may have for trishomoaromatic delocalization is seen not to be reflected in increased acidity of the proton which would lead to its generation. This is to say that the transition state for exo H_2 abstraction evidently does not experience significant *stabilizing* interaction with the additional pair of double bonds. We emphasize that the data to this point do not demand that extended delocalization between the three bridges be ruled out, but simply that such interaction if present does not result in significant net stabilization.

Metal Reduction Studies. Exploratory studies were initially undertaken with iodides **20** and **21**. Treatment of cold (−78

Table II. ^{13}C NMR Data (22.6 MHz, $CDCl_3$ Solution, ppm)

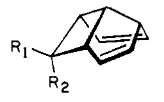
	Compd					
Carbons	**22**	**23c**	**24**	**28a**	**28b**	**36**
C_1, C_3	46.57	54.83	47.11	52.77	50.84	45.56
C_2	28.50	57.96[a]	48.30	149.02	131.59	161.78
C_4, C_3	134.03	130.20	133.06	130.78	130.89	33.40[a]
C_5, C_7	138.46	141.10	139.54	137.69	137.10	32.91[a]
C_6	58.71	58.28[a]	58.66	58.05	57.57	47.53[b]
C_9	41.50	43.07	45.60	44.35	43.65	44.92[b]
C_2 substituents				106.67	123.61 18.07	106.67

[a,b] Interchangeable assignments; see **22** for numbering scheme.

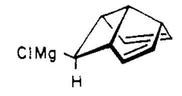
°C ND_3 solutions of these epimers with potassium metal under oxygen- and moisture-free conditions and subsequent transfer into NMR tubes with the aid of a specially designed vacuum line cell afforded solutions whose spectra gave no indication of anion formation. Rather, mixtures of monodeuterio derivatives **23a** (~80%) and **23b** (~20%) were formed. This observation provides convincing indication that the basicity of **9** is substantial.

In a second series of experiments, tetrahydrofuran-d_8 solutions of the iodides contained in NMR tubes were exposed to potassium mirrors at −20 to −5 °C (no observable reaction at −78 °C) while under an argon atmosphere. After several hours, no starting material remained within the limits of the spectroscopic measurements. However, the resulting spectra were identical with that of hydrocarbon **22** rather than representative of the anion. Essentially identical results were obtained when sodium-potassium alloy was employed as reducing agent. In both instances, careful quenching with CH_3OD and VPC isolation of **22** afforded material containing little if any deuterium. Similar observations by others have been regarded as puzzling and attributed to free-radical intervention followed by hydrogen atom abstraction from solvent (k_H/k_D necessarily $\geq$ 60!).[27] While this interpretation remains a distinct possibility, the likelihood that our observations may be the result of protonation by adventitious moisture cannot be summarily dismissed. Highly rigorous attempts were made to maintain strictly anhydrous conditions, but the amount of iodide (0.08 mmol) utilized per experiment would require merely 1–2 μL of water to quench all of the generatable anion. When similar difficulties were encountered in attempts to form Grignard reagents from **20** and **21**, likely due to complications from competing free-radical pathways,[28-30] attention was turned to chloride **23c**.

Available from the decarboxylation of **17** with lead tetraacetate in the presence of lithium chloride,[31] **23c** was found to react very slowly with triply sublimed magnesium in THF-d_8 containing some ethylene dibromide (18 h at 25 °C followed by 22 h at 60 °C). The ^1H NMR spectrum of the resulting Grignard reagent (**24**, stereochemical retention assumed) was



23 a, $R_1 = D, R_2 = H$
b, $R_1 = H, R_2 = D$
c, $R_1 = Cl, R_2 = H$



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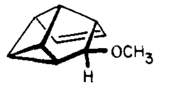

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characterized by moderate upfield shifts. The pairs of vinyl absorptions (formerly at δ 6.01 and 5.69) exhibited the most dramatic change by merging into one broad envelope centered at 5.69. The remaining multiplets originally seen for **23c** (δ 3.90, 3.70, and 3.39) now appeared at 3.77 (1 H), 3.60 (2 H), and 3.17 (2 H), respectively. Unfortunately, the signal due to the >C*H*MgCl proton could not be seen and was assumed to be masked by those absorptions emanating from the small levels of unlabeled or partially labeled THF present. Addition of D_2O to such solutions returned monodeuterated hydrocarbon.

The ^{13}C parameters of **24** are summarized in Table II. It is immediately apparent that C_2 in the organometallic is deshielded relative to the same carbon in **22**, suggesting that the C–Mg bond has significant covalency with little electron release from magnesium to carbon. The hybridization at C_2 is little perturbed as a result. Additionally, the chemical shifts for the olefinic carbons in **24** are seen to fall at positions intermediate between those of the parent hydrocarbon and chloride. This notable lack of variation in the ^{13}C parameters argues against any gain of electronic shielding at the "rear" of the molecule as expected from **9**.

Any further interpretation of these data must conform to what is generally known about the structure of organomagnesium compounds. In ether solutions at concentrations below 0.1 M, chloride Grignard reagents are recognized to exist chiefly as dimers.[32] Higher degrees of association are indicated as concentration levels are increased, although tetrahydrofuran is capable of reversing this trend somewhat.[33] The Schlenck equilibrium is, of course, affected as well. Information on the extent to which the degree of ionic character in the C–Mg bond varies with the hydrocarbon moiety, solvation factors, and the like is also available, but to a more limited degree.[34,35] The numerous ^1H NMR studies of alkylmagnesium halides show convincingly that high covalency prevails. At the other extreme, x-ray crystal-structure analysis has shown the metal atom in the tetraethylethylenediamine solvate of cyclopentadienylmagnesium bromide (CpMgBr) to lie near the cyclopentadienide C_5 axis.[36] Further, gas-phase electron diffraction[37] and solid-phase x-ray diffraction[38] indicate dicyclopentadienylmagnesium (Cp_2Mg) to possess D_{5h} or D_{5d} symmetry. The IR and UV spectra of Cp_2Mg, CpMgCl, and CpMgBr in tetrahydrofuran solution also indicate that pentahapto structures exist in solution,[39] although it is possible that as much as 5–10% of h^1-CpMgX coexists in equilibrium.[40]

These findings give credence to the working hypothesis that for a given metal and solvent, the position of the molecule (RMgX) $\rightleftarrows$ ion pair (R^-Mg^+X) equilibrium should depend on the nature of R. When R is a simple alkyl or aryl group, the equilibrium might be expected to lie well on the side of the molecular species. However, as R becomes increasingly able to stabilize negative charge, the equilibrium should be displaced toward the ion-pair side. In this context, the spectral features of **24** clearly show the "anchored" trishomocyclopentadienide to lack the capability to disperse charge and to be rather closely allied in character to simple cyclobutyl Grignards.[35b]

In an effort to examine possible counterion effects, **23c** was reduced with Na-K alloy in anhydrous THF. There was produced a dark red solution whose ^{13}C NMR spectrum displayed absorptions at 138.7, 133.4, 64.6, 50.6, 48.1, and 43.2 ppm (compare Table II). After quenching with water, there was isolated a product having a spectrum rather different from that of **22**: 138.7, 133.4, 58.6, 50.7, 43.6, and 26.7 ppm. Its VPC retention time, mass spectral fragmentation behavior, and ^1H NMR spectrum [δ 6.09 (m, 4), 5.80 (m, 4), 3.99 (d, 2), 3.70 (q, 4), and 1.56 (t, 2)] indicated it to be dimeric. The structure of this material was not further investigated.

In yet another approach, reduction was not observed upon treatment of ether **25**[41a] with sodium-potassium alloy in THF-d_2 at temperatures up to 45 °C.

Because the above results demonstrate that the formation of **9** is not a particularly favorable process, we were led to carry out MINDO/3 calculations[42] on the carbanion. No constraints were placed on the molecular geometry, but the computer-generated minimum did compare closely to that adopted by triquinacene. The first findings were particularly interesting in that formulation **9** with an sp^2-hybridized center at C_2 was discovered not to be an energy minimum, nor even close to one. Rather MINDO/3 found the two hypothetical tetrahedral carbanion structures represented by **26** and **27** to be energy minima, with **27** giving indication of somewhat greater stability. Relevant features of their computed molecular geometries are collected in Table III together with the calculated heats of formation, ionization potentials, and dipole moment values. On the basis of this approximation, there seemingly exists a significant barrier to inversion between this pair of tetrahedral intermediates.

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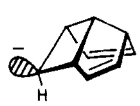

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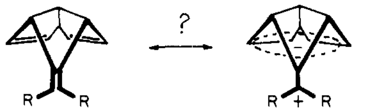
Orbital Interactions in 2-Methylenetricyclo[4.2.1.0^{3,9}]nona-4,7-diene Derivatives. Any suggestion that the tricyclo[4.2.1.0^{3,9}]nona-4,7-dien-2-yl anion might be capable of electron stabilization infers that "anchored" trishomoaromatic interaction may operate in neutral exo methylene hydrocarbons such as **28a** and **28b** in that direction which would deplete the exocyclic carbon of electron density to some degree (cf. **29**). Such polarization effects would be most readily recognized by ^{13}C chemical shifts which, although little affected by diamagnetic ring currents, are quite sensitive to changes in electron density. Although the parent monocyclic molecules pentafulvene and heptafulvene exhibit only relatively small dipole moments and marginal charge separation ($\Delta\delta$[43] = 29.2 and 34.7 ppm, respectively),[44] the terminal carbons in dimethylenecyclobutene **30** ($\Delta\delta$ = 63 ppm),[45] 7-methylenenorbornadiene (**31**, $\Delta\delta$ = 99 ppm),[46,47] and triene **32** ($\Delta\delta$ = 100 ppm)[46] are strongly shielded. This phenomenon has been attributed to an inherent tendency for development of ground-state cyclobutadiene dication, 7-norbornadienyl cation, and 1,4-bishomotropylium character, respectively.



28 **a**, R = H
b, R = CH_3

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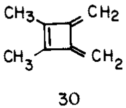

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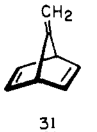

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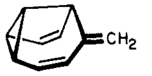

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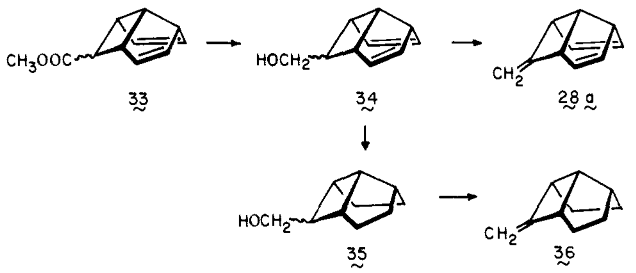
Table III. Calculated Molecular Geometries and Other Physical Data for **26**, **27**, and **28a**

Parameter	**26**	**27**	**28a**
Bond lengths, Å			
C_1C_2	1.535	1.526	1.541
C_1C_8	1.518	1.520	1.513
C_4C_5	1.353	1.351	1.350
C_5C_6	1.521	1.521	1.524
C_6C_9	1.581	1.578	1.579
C_1C_9	1.570	1.567	1.566
Nonbonded distances, Å			
C_2C_4	2.658	2.728	2.684
C_5C_7	2.610	2.589	2.579
Bond angles, deg			
$C_2C_1C_8$	120.92	126.30	123.29
$C_5C_6C_7$	118.19	116.62	115.59
Heat of formation (ΔH_f), kcal/mol	99.0	96.9	94.3
Ionization potential, eV	1.60	1.65	9.01, 9.19, 9.53
Dipole moment, D	12.53	12.79	

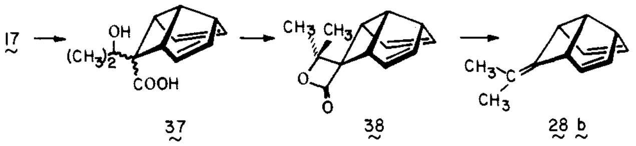
The preparation of **28a** involved sequential lithium aluminum hydride reduction of the epimeric esters **33**, reaction of primary alcohol **34** with sulfene, and base-promoted elimination of the mesylate mixture (Scheme III). The tetrahydro derivative **36**, required for reference purposes, was obtained by catalytic hydrogenation of **34** and entirely comparable dehydration of **35**.

Scheme III



The steps employed in elaboration of the isopropylidene group in **28b** are based on the procedure developed by Krapcho and Jahngen.[48] Treatment of carboxylic acid **17** with 2 equiv of lithium diethylamide gave the corresponding dianion, condensation of which with acetone led to hydroxy acid **37** in 93% yield. Cyclization to the β-lactone **38** was easily accomplished with benzenesulfonyl chloride in pyridine (92%). When heated to 120 °C for ca. 10 min, **38** underwent smooth decarboxylation to give **28b** (Scheme IV).

Scheme IV



The ^{13}C NMR spectrum of **28a** (Table II) is seen to exhibit a chemical-shift difference for the exocyclic methylene group carbons of 42 ppm, a value far smaller than the $\Delta\delta$ for **36** (55 ppm). Clearly, no contribution from zwitterionic form **29** is spectroscopically detectable in the ground state of this triene. The difference in the magnitudes of the $\Delta\delta$ values can be accounted for in terms of through-space shielding of C_2 by the additional pair of double bonds in **28a**. This conclusion is supported by the near identity of the C_9 chemical shifts in both compounds (44.35, 44.92) and the upfield position of C_2 in **28a** (149.02) relative to that in **36** (161.78).

The dipole moment of **28a** as calculated by MINDO/3 is merely 0.17 D (Table III). Its first three ionization potentials are computed to occur at −9.01, −9.19, and −9.53 eV (C_2C_9), in quite close agreement with the experimentally determined values of −8.80, −9.23, and −9.63 eV.[49] By comparison, the photoelectron spectrum of **28b** consists of three bands at −8.31, −8.7, and −9.28 eV. The energy levels of the three π levels are so little different from their predicted positions in the absence of interaction that meaningful orbital overlap cannot be operative. It is therefore not surprising that chemical manifestations of trishomoaromatic character in nortriquinacenes have gone undetected.

Discussion

The current experimental results show that nortriquinacene (**22**) does not undergo base-catalyzed hydrogen–deuterium exchange at its methylene group and that this carbanion when formed by a less direct method is highly basic. Further revealed by our NMR analysis of Grignard derivatives of this ring system is its innate inability to disperse negative charge. The absence of homoaromatic interaction was also indicated by the spectral properties of the exo methylene derivatives **28a** and **28b**. These facts add up to an orbital profile showing that mixing of the constituent π levels with development of homoaromatic stabilization is simply not important. Such poor π overlap was similarly encountered previously with the tricyclo[5.3.1.$0^{4,11}$]undeca-2,5,8-trien-10-yl cation[11] and the tricyclo[5.4.1.$0^{4,12}$]dodeca-2,5,8,10-tetraenyl dianion.[10]

Our inability to uncover any hint of pericyclic stabilization in these ions stands in apparent contradiction to the conclusions reached by Goldstein and Hoffmann in their elegant theoretical analysis of ribbon topology.[13] It must be recalled however that the analysis of such cyclic stabilization as provided by these authors was founded upon a *qualitative evaluation* of the symmetry properties of component orbitals and their mutual geometric relationship. Allowance was not made for extraneous influences which could affect not only the coefficients in the constituent π orbitals, but also their relative energetic ordering. Hyperconjugative influences on possible through-space interactions were similarly not evaluated.

Because attention must now be paid specifically to such questions, a detailed theoretical assessment of electronic interactions in nortriquinacenes is planned. What is presently clear, however, is that distortions of π frameworks from mutual coplanarity with multiple interruption of continuous conjugation need not lead to a homoaromatic continuum, even when an orbital pattern conducive to interaction is seemingly available. In the cases cited above, the systems give no evidence of distorting to develop any stabilizing interaction. One might infer that the magnitude of the orbital overlap which might result would remain insufficient to offset any structural strain which may have developed. The implication here would be that the topological prerequisites for electronic stabilization are perhaps adequate, but that the inability of crucial HOMO-LUMO interactions to materialize (for whatever reasons) is at fault. This conclusion is presently not completely substantiated, but it does imply that stabilizing ribbon interactions are in reality difficult to predict in absolute terms on an a priori basis. Clearly, a detailed unraveling of the less than obvious contributions of these and other factors to the total electronic profile of several nortriquinacenes is warranted.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 137 and 467 spectrometers, whereas mass spectra were obtained with an AEI-MS9 instrument at an ionization potential of 70 eV. ^{1}H magnetic resonance spectra were recorded with Varian A-60A, Varian HA-100, and Jeolco MH-100 instruments; apparent splittings are given in all cases. ^{13}C spectra were taken on a Bruker 90 instrument. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The preparative VPC separations were accomplished on Varian Aerograph A90-P3 gas chromatographs equipped with thermal conductivity detectors.

Ketotetrahydropyranyl Ether 11.[50] A solution of **10**[14,15] (40 g, 0.24 mol), dry dihydropyran (40 mL), and *p*-toluenesulfonic acid (0.16 g) in dry ether (250 mL) was stirred under nitrogen at room temperature for 16 h. Concentration in vacuo produced an orange oil which was diluted with ether, washed with saturated sodium bicarbonate solution and water, dried, and concentrated. Chromatography on Florisil (elution 30% ether/pentane) yielded 48 g (80%) of **11** as a clear oil: $\nu_{\max}{}^{\text{film}}$ 1755, 1660, 1100, 1050, 1020, and 970 cm^{-1}; $\delta_{\text{Me}_4\text{Si}}{}^{\text{CDCl}_3}$ 5.50 (m, 2), 4.4-4.9 (m, 2), 4.08 (m, 1), 3.68 (m, 2), 3.40 (m, 3), 2.3-2.7 (m, 1), and 1.2-2.3 (m, 9).

This product was utilized without further purification.

Enol Phosphate 12. To dry tetrahydrofuran (100 mL) cooled to −78 °C was transferred *n*-butyllithium in hexane (21 mL of 2 M, 42 mmol) followed by diisopropylamine (4.2 g, 42 mmol). A solution of **11** (10.4 g, 42 mmol) in dry THF (100 mL) was added and the resulting mixture was stirred for several minutes before treatment with diethyl chlorophosphate (7.24 g, 6.22 mL, 42 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (40 mL). The solution was allowed to warm to room temperature and stirred for 2 h. After being quenched with saturated ammonium chloride solution, the mixture was poured into water (500 mL) and rapidly extracted three times with dichloromethane. The combined organic layers were dried and concentrated in vacuo to yield 18 g of a yellow oil, chromatography of which on silica gel (elution with 50% ether/pentane) yielded **12** (16 g, 91%): $\nu_{\max}{}^{\text{neat}}$ 2950, 1275, 1170, 1120, 1040, and 980 cm^{-1}.

This material was utilized without further purification.

***exo*-2,3-Dihydrotriquinacen-2-ol Tetrahydropyranyl Ether (13a).**[50] Into a dry three-necked 2-L round-bottomed flask charged with 240 mL of anhydrous ammonia was introduced lithium metal (2.03 g, 294 mg-atm) at −78 °C. The unpurified enol phosphate (16 g, 42 mmol) and *tert*-butyl alcohol (3.4 g, 46 mmol) in tetrahydrofuran (75 mL) was added dropwise under nitrogen and the mixture was stirred for 2.25 h at this temperature before being treated dropwise with water. After the ammonia was allowed to evaporate at room temperature, the mixture was poured into an ice water–ether mixture, and extracted three times with ether. The combined organic extracts were washed three times with water and twice with saturated sodium chloride solution before drying. Concentration in vacuo afforded a yellow oil which by chromatography on silica gel (elution with 15% ether/pentane) afforded 7.0 g (76%) of **13a**: $\nu_{\max}{}^{\text{CCl}_4}$ 3050, 1604, and 1025 cm^{-1}; $\delta_{\text{Me}_4\text{Si}}{}^{\text{CDCl}_3}$ 5.2-5.6 (m, 4), 4.58 (m, 1), 2.6-4.2 (m, 7), and 1.2-2.4 (m, 8).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.33; H, 8.78.

***exo*-2,3-Dihydrotriquinacen-2-ol (13b).** A solution of **13a** (8 g, 0.035 mmol) was stirred in methanol (75 mL) with *p*-toluenesulfonic acid (0.075 g) at room temperature for 12 h under nitrogen. The methanol was removed in vacuo and the residue was diluted with ether, washed three times with saturated sodium bicarbonate solution and twice with water, and dried. Concentration in vacuo afforded a yellow oil which after chromatography on silica gel (elution with 30% ether/pentane) yielded 5.2 g (100%) of **13a**.[15,51]

2,3-Dihydrotriquinacen-2-one (14). Into a 3-L three-necked round-bottomed flask equipped with an efficient mechanical stirrer was transferred 500 mL of dichloromethane (freshly distilled from barium oxide) and 66.5 mL of pyridine (previously dried over KOH). Chromium trioxide (41 g), which had been dried at 110 °C overnight at 70 °C (0.05 mm) for 18 h, was slowly added at 0 °C under nitrogen. After the vigorously stirred deep purple suspension was warmed to room temperature, **13b** (10 g, 0.0675 mol) dissolved in 500 mL of purified dichloromethane was added dropwise during 10 min and the resulting black suspension stirred for 30 min. The solution was decanted and concentrated to leave an oil. The original residue was extracted three times with ether and the washings combined with the previously concentrated oil. This organic solution was washed five times with 3% hydrochloric acid, five times with saturated sodium bicarbonate solution, and twice with water and brine, and dried. Concentration in vacuo and chromatography on Florisil (elution with 15% ether/pentane) afforded 9 g (91%) of **14**.[14,15]

2,3-Dihydro-3-hydroxymethylenetriquinacen-2-one (15). Into a three-necked 500-mL round-bottomed flask was transferred 1.46 g (33 mmol) of a mineral oil suspension of sodium hydride (50%). After three washings with pentane, the sodium hydride was dried in vacuo and slurried in ether (150 mL). To this mechanically stirred suspension was added a solution of **14** (2.4 g, 16 mmol) and dry ethyl formate (1.9 g, 26 mmol) in ether (50 mL). The reaction was initiated with methanol (0.1 mL). After 6 h, methanol and ice water were added to the cooled reaction mixture. The layers were separated and the organic phase was extracted four times with 1 N sodium hydroxide solution. The combined aqueous extracts were acidified in the cold with 3 M hydrochloric acid and extracted four times with dichloromethane. The combined organic layers were washed with saturated sodium chloride solution, dried, and concentrated to give 2.5 g (89%) of **15** as a light brown solid. Sublimation [100 °C (0.05 mm)] and recrystallization from ether/pentane afforded colorless crystals: mp 109-110 °C; $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 11.0 (br s, 1), 7.4 (s, 1), 5.5-6.0 (m, 4), and 3.6-4.0 (m, 4).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.74; H, 5.87.

3-Diazo-2,3-dihydrotriquinacen-2-one (16). A solution of **15** (3.8 g, 0.022 mol) and *p*-toluenesulfonyl azide (4.55 g, 0.023 mol) in dry tetrahydrofuran (200 mL) was treated under nitrogen at 0 °C with diethylamine (3.22 g, 4.6 mL, 0.044 mol) and stirred at room temperature for 4 h. The mixture was diluted with water and extracted five times with dichloromethane. The combined organic extracts were dried and concentrated in vacuo. Chromatography on Florisil (elution with 25% ether/pentane) yielded 4.0 g of **16** as an orange oil: $\nu_{\max}^{\mathrm{neat}}$ 3050, 2900, 2070, 1660, and 1315 cm^{-1}; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 303 (ϵ 3000) and 253 nm (7500); $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 5.8-6.1 (m, 2), 5.5-5.8 (m, 2), 4.2-4.4 (m, 1), 3.8-4.1 (m, 1), and 3.6-3.8 (m, 2).

This material was employed directly in the ring contraction experiments.

***exo*-Tricyclo[4.2.1.0^{3,9}]nona-4,7-diene-2-carboxylic Acid (17).** A solution of **16** (4 g, 23 mmol) in methanol (600 mL) was irradiated with a 450-W Hanovia lamp through a Pyrex filter for 4 h. The solvent was removed in vacuo and the crude oil was dissolved in ether (125 mL), washed with water (2 × 30 mL), and dried. The concentrated ether layer was chromatographed on Florisil (elution with 15% ether/pentane) to give 2.8 g (68%) of epimeric methyl esters; the ^{1}H NMR spectrum indicating the presence of a 70:30 mixture with the endo isomer predominating: $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 5.52-6.08 (m, 4), 3.2-4.1 (m, 4.7), 3.60 (s, 0.9), 3.50 (s, 2.1), and 2.36 (m, 0.3). A solution of this ester mixture (2.8 g) in methanol (100 mL) was treated with sodium methoxide in methanol (prepared by dissolving 1.3 g of sodium in 100 mL of methanol) and heated for 15 h at 50 °C. Water (5 mL) was then added and the mixture was refluxed for an additional 3 h under nitrogen. The cooled solution was treated with water (5 mL) and concentrated in vacuo to afford an oil which was diluted with water (100 mL) and washed with ether (3 × 50 mL). The aqueous layer was acidified before extraction with dichloromethane (4 × 75 mL). The combined organic phases were washed with water and dried. The concentrated oil crystallized to afford 2.2 g of crude exo acid. Sublimation [70 °C (0.05 mm)] yielded 1.7 g (46%) of **17** as a white solid. Recrystallization (ether/pentane) gave analytically pure material: mp 106-107 °C; $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 11.5 (br s, 1, COO*H*), 6.02-6.21 (d of d, J = 6 and 2 Hz, 2, olefinic), 5.60-5.85 (d with fine splitting, J = 6 Hz, 2, olefinic), 3.31-4.08 (m, 4), and 2.50 (m, 1); ^{13}C NMR ($CDCl_3$) (ppm) 44.24, 44.73, 45.27, 58.22, 132.13, 139.79, and 181.82.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.88; H, 6.24.

Iodolactone 19. A solution of **16** (5.0 g, 0.029 mol) and sodium bicarbonate (6 g, 0.071 mol) in dioxane (150 mL) and water (350 mL) was irradiated with a 450-W Hanovia lamp filtered through Pyrex for 4 h. The solution was acidified with 3 M hydrochloric acid and extracted three times with dichloromethane. The combined organic layers were concentrated in vacuo to yield a red oil which was taken up in ether and extracted three times with 1 N sodium hydroxide solution. The combined alkaline layers were acidified with 3 M hydrochloric acid and extracted four times with dichloromethane. The combined organic phases were washed with brine, dried, and concentrated in vacuo to yield, after chromatography, 2.2 g (47%) of epimeric carboxylic acids.

This mixture (2.2 g, 13.6 mmol) in 110 mL of 0.5 N sodium bicarbonate solution was treated dropwise under nitrogen and in the dark with iodine (3.45 g, 27.2 mmol) and potassium iodide (8.3 g, 68 mmol) in water (100 mL) at room temperature. After 2 h the resulting suspension was extracted four times with dichloromethane and the combined organic layers were washed with 5% sodium thiosulfate solution and water before drying and concentration in vacuo. Sublimation (60 °C and 0.05 mm) of the residue gave 2.34 g (60%) of **19**. The original basic layer was acidified with 3 M hydrochloric acid and extracted with dichloromethane. The combined organic layers were washed with 5% sodium thiosulfate solution and otherwise similarly processed to afford a crude residue which when sublimed yielded 0.6 g (27%) of **17**. A sample of **19** was recrystallized (ether/pentane) to produce a white solid: mp 128-129 °C; $\nu_{\max}^{\mathrm{CHCl_3}}$ 2980, 1760, 1150, and 992 cm^{-1}; $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 6.02-6.23 (d of d, B part of AB, J = 6.5 and 2.5 Hz, 1), 5.73-5.94 (d with fine coupling, A part of AB, J = 6.5 Hz, 1), 5.30-5.49 (d with fine coupling, J = 6 Hz, 1), 4.50 (s, 1), and 3.32-4.11 (m, 5).

Anal. Calcd for $C_{10}H_9IO_2$: C, 41.69; H, 3.15. Found: C, 41.63; H, 3.16.

***endo*-Tricyclo[4.2.1.0^{3,9}]nona-4,7-diene-2-carboxylic Acid (18).** Iodolactone **19** (2.3 g, 0.008 mol) was dissolved in 150 mL of glacial acetic acid and cooled to the freezing point. Zinc dust (10.1 g, 0.154 mol) was added in one portion, the mixture was vigorously shaken as a slush for 20 min, and the solids were removed by rapid filtration through a Celite pad. Acetic acid was removed in vacuo and the residue was diluted with dichloromethane (50 mL) and extracted with 10% sodium hydroxide solution (100 mL). The alkaline layer was acidified with 3 M hydrochloric acid solution and extracted with dichloromethane (4 × 50 mL). The combined organic layers were dried and concentrated to leave a light brown material which was sublimed (70 °C and 0.01 mm). There was obtained 1.3 g (100%) of **18** as a white solid: mp 118.5-119.5 °C (from ether/pentane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 2900 and 1680 cm^{-1}; $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 11.2 (br s, 1, COO*H*), 5.6-6.2 (m, 4, olefinic), and 3.3-4.2 (m, 5, methine).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.95; H, 6.27.

***exo*- and *endo*-2-Iodotricyclo[4.2.1.0^{3,9}]nona-4,7-dienes (20 and 21).** A solution of **17** (200 mg, 1.23 mmol) and anhydrous lead tetraacetate (540 mg, 1.23 mmol) in dry carbon tetrachloride (50 mL) was heated at reflux with concomitant irradiation from a 600-W Sylvania DYD projector bulb while a mixture of iodine (316 mg, 1.23 mmol) in carbon tetrachloride (10 mL) was added dropwise until a pink color persisted. The cooled suspension was filtered and the filtrate was washed with 10% sodium thiosulfate solution, 1 N sodium hydroxide solution, and water before drying. Concentration in vacuo afforded a yellow oil (290 mg), which upon molecular distillation (40 °C and 0.1 mm) afforded 178 mg (60%) of epimeric iodides. The ^{1}H NMR spectrum indicates the mixture to consist of 68% exo and 32% endo isomers: $\nu_{\max}^{\mathrm{neat}}$ 3050, 2950, 1350, 1300, 1130, 863, and 805 cm^{-1}. The mass spectrum displays a very weak molecular ion at *m/e* 244 and a more intense m − 1 at *m/e* 243. The isomers were separated by preparative gas chromatography (6 ft × 0.25 in. column packed with 12% Carbowax 20M on Chromosorb W, 150 °C).

For **20**: $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 6.10 (d of d, J = 6 and 2 Hz, 2), 5.68 (d, with fine coupling, J = 6 Hz, 2), and 3.50-4.08 (m, 5).

Anal. Calcd for C_9H_9I: C, 44.29; H, 3.72. Found: C, 44.30; H, 3.77.

For **21**: $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 6.18 (d with fine coupling, J = 6 Hz, 2), 5.28 (d of d, J = 6 and 2 Hz, 2), 4.98 (m, 1), and 3.45-3.95 (m, 4).

Anal. Calcd for C_9H_9I: C, 44.29; H, 3.72. Found: C, 44.37; H, 3.88.

Tricyclo[4.2.1.0^{3,9}]nona-4,7-diene (22). (a) Tri-*n*-butyltin Hydride Reduction. A solution of the iodide mixture (52 mg, 0.21 mmol), tri-*n*-butyltin hydride (100 mg, 0.35 mmol), and a trace of azobisisobutyronitrile in pentane (0.2 mL) was stirred at room temperature for 12 h under nitrogen. Purification by preparative gas chromatography (12% Carbowax 20M on Chromosorb W, 150 °C) afforded 18 mg (73%) of **22**: $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 5.94-6.19 (d of d, $J_{4,5}$ = 5 Hz, $J_{5,6}$ = 2 Hz, H_5 and H_7), 5.56-5.84 (octet, $J_{1,8}$ = 3 Hz, $J_{4,6} \simeq$ 1 Hz, 2, H_4 and H_8), 3.94 (br d, $J_{6,9}$ = 6 Hz, 1, H_6), 3.63 (q, $J_{1,9}$ = 6 Hz, H_9), 3.22 (m, 2, H_1 and H_3), 2.13-2.70 (q, $J_{2\,\mathrm{exo},\,\mathrm{endo}} \simeq J_{2\,\mathrm{endo},\,3}$ = 10 Hz, $H_{2\,\mathrm{endo}}$), and 1.22-1.64 (d of t, $J_{2\,\mathrm{exo},\,3}$ = 4 Hz, 1, $H_{2\,\mathrm{exo}}$). Saturation of the region 5.56-5.84 (H_4,H_8) caused resonances for H_6 to collapse to a doublet of triplets, for H_1,H_3 to simplify to a sextet, and for H_5,H_7 to become a doublet. Decoupling of H_6 left H_5,H_7 as a doublet and H_4,H_8 as a doublet of doublets ($J_{4,5}$ = 5 Hz, $J_{1,8}$ = 3 Hz). Saturation of H_1,H_3 resulted in the appearance of H_5,H_7 as a quartet, and the transformation of H_4 and H_8 signals to a doublet of doublets ($J_{4,6} \simeq$ 1 Hz); the signals for $H_{2\,\mathrm{endo}}$ and $H_{2\,\mathrm{exo}}$ remain a pair of doublets: calcd *m/e* 118.07824, found 118.07845.

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.68; H, 8.56.

(b) Sodium in Liquid Ammonia Reduction. To a dark solution of sodium metal (420 mg) in 420 mL of liquid ammonia cooled to −78 °C was added dropwise a solution of **20** and **21** (750 mg, 3.08 mmol) in 3 mL of ether. After 60 min at −78 °C, the mixture was allowed to warm to −33 °C for 30 min and quenched by addition of saturated ammonium chloride solution. The resulting solution was carefully poured into 100 mL of cold water and extracted with pentane (4×). The combined organic extracts were dried, filtered, and carefully concentrated by distillation through a 6-in. Vigreux column. The residue was purified by preparative VPC as before to give 77 mg (21.2%) of **22**.

General Procedure for Attempted *tert*-Butoxide Promoted H/D Exchange in 22. Into a dry NMR tube was placed 10 mg of purified **22**, 15 mg of freshly sublimed potassium *tert*-butoxide, and 0.4 mL of anhydrous dimethyl-d_6 sulfoxide. The contents were immediately blanketed with dry nitrogen, cooled to −78 °C, and sealed under high vacuum. The spectrum was recorded and several peaks of **22** were integrated relative to that of the incompletely D-labeled solvent. The tube was then heated at 60 °C for 18 h and examined periodically for H/D exchange or decomposition. Neither was evident from the relative peak areas. Nor was change noted upon subsequent heating for 49 h at 50 °C, 105 h at 80 °C, and finally 89 h at 90 °C. The cooled tube was opened, the solution was poured into water, and the hydrocarbon was recovered by pentane extraction. Its mass spectrum (*m/e* 118.0782) revealed the absence of deuterium incorporation.

***exo*- and *endo*-2-Chlorotricyclo[4.2.1.0^{3,9}]nona-4,7-dienes (23c).** Lead tetraacetate (274 mg, 0.617 mmol) was added to a solution of **17** (100 mg, 0.617 mmol) and 148 mg (2.47 mmol) of acetic acid in 10 mL of dry benzene which had been thoroughly flushed with nitrogen. The mixture was stirred at room temperature until a light yellow homogeneous solution was observed. Lithium chloride (26 mg, 0.617 mmol) was added and the mixture was again flushed with nitrogen. After 3 h at 80 °C, the reaction mixture was cooled, quickly washed with cold 1 N perchloric acid and sodium carbonate solutions, and dried. Evaporation of solvent left 79 mg of a pale yellow oil which was chromatographed rapidly through 3 g of neutral alumina (activity I) with ether (2%) in pentane elution to give 40.3 g (43%) of **23c** as a clear oil. VPC analysis on a 12% Carbowax 20M column (120 °C) showed two peaks in a 9:1 ratio. These products were isolated and shown to be the exo and endo isomers, respectively.

For **23c**: $\delta_{\mathrm{Me_4Si}}{}^{\mathrm{CDCl_3}}$ 6.01 (m, 2), 5.69 (m, 2), 3.90 (m, 1), 3.70 (m, 2), and 3.39 (m, 2); calcd *m/e* 152.0393, found 152.0395.

For the endo chloride: $\delta_{\mathrm{Me_4Si}}{}^{\mathrm{CDCl_3}}$ 6.17 (m, 2), 5.50 (m, 2), 4.70 (m, 1), 3.90 (d, J = 3.5 Hz, 1), and 3.55 (m, 3).

Vacuum Line Experiments. (a) Reduction of Iodides 20 and 21 in ND_3. Approximately 0.5 mL of ND_3 was vacuum transferred to a small reaction vessel equipped with a miniaturized glass-encased magnetic stirring bar. Freshly cut potassium metal (ca. 2 g-atoms equiv) was introduced into the reaction vessel after removal of the serum cap under a positive pressure of dry nitrogen. In practice, nitrogen was simply allowed to flow over the surface of the solid ND_3 during this operation. The cap was replaced and the ND_3 was slowly allowed to thaw by gradual removal of the liquid nitrogen cooling bath and replacement with a dry ice–isopropyl alcohol bath. The iodide mixture was injected by syringe into the resulting dark blue solution with simultaneous frequent agitation of the reaction mixture by means of an external magnet. When the reduction was complete, the mixture was frozen in the liquid nitrogen bath and the serum cap removed under nitrogen and replaced with an NMR tube side arm containing a plug of glass wool in the upper portion. After regaining partial vacuum (40 mm), the reaction vessel was inverted by rotation about the standard taper $^{10}/_{30}$ joint and the tube rapidly cooled to −78 °C. Upon thawing, the contents of the reaction vessel collected above the glass wool plug. Filtration through the plug was achieved by rapidly removing the dry ice–isopropyl alcohol bath and replacing it with the liquid nitrogen bath. The tube was sealed in vacuo in the customary fashion after degassing the sample and the solid in the tube was carefully thawed by swabbing with cold dry ice–isopropyl alcohol solution. The spectrum was then recorded in a precalibrated cold probe and found to comprise a mixture of **23a** and **23b** in the approximate ratio of 80/20 on the basis of the relative intensities of the 2.13–2.70 and 1.22–1.64 absorptions.

(b) Reduction of 20 and 21 with a Potassium Mirror and Na–K Alloy in Tetrahydrofuran-d_8. For the potassium mirror experiments, a 3-mg sample of the iodide was placed in the NMR tube of an apparatus similar to the above but modified somewhat in design. Dry THF-d_8 (ca. 350 μL) was vacuum transferred from Na–K alloy into this tube and the resulting solution was degassed and then frozen in a liquid nitrogen bath. Small pieces of freshly cut, clean potassium metal (ca. 200 mg) were placed in the adjacent reactor vessel by temporary transfer through an opening previously closed by a rubber septum but now permanently sealed. The total system was pumped down to 10^{-6} Torr and the potassium metal was just melted to remove trapped gases and finally vaporized into the NMR tube in small amounts. The metal condensate was carefully moved downward into the tube by continued heating at the top leading edge of the mirror with the Bunsen flame (overheating should be avoided as the glass will tarnish). The entire process generally required 20–30 min. The tube is then sealed off under argon and inverted to permit chemical reaction. No reaction occurred at −78 °C, but at somewhat warmer temperatures (−20 to −5 °C), the spectrum of the iodide was replaced by that of the saturated hydrocarbon. When this reaction was repeated on a larger scale (15 mg of **20**) to enable isolation of the product (collected by VPC, 2–3 mg) Fourier ^1H analysis showed it to be fully identical with **22**.

For the Na–K alloy experiments, the NMR tube was initially fitted with a loose plug of glass wool at its midpoint. After preparation of the iodide solution by vacuum transfer in the predescribed manner, a pea of Na–K alloy (ratio 1:5, ca. 25 mg) was inserted above the plug and the tube was sealed under argon after thorough degassing. In these experiments, the solution was conducted through the plug by suitable cooling of either end of the tube. Essentially identical results were obtained.

When tubes from either experiment were opened, treated with one drop of CH_3OD, and processed to furnish hydrocarbon product, mass spectral analysis of the oily samples showed them to contain little, if any, deuterium.

(c) Na–K Reduction of 23c for ^{13}C NMR Studies. The same procedure as above was employed except for the fact that a 10-mm tube was now necessary and larger quantities of the chloride (e.g., 80 mg) were required. After recording of the spectrum, the reaction mixture was poured into water and extracted into pentane. The dried organic extracts were dried and carefully concentrated. Preparative VPC isolation on a 5 ft × 0.25 in. 5% Carbowax 20M on Chromosorb G column at 147 °C showed a single component to be present: $\delta_{\mathrm{Me_4Si}}{}^{\mathrm{CDCl_3}}$ 6.09 (m, 4), 5.80 (m, 4), 3.99 (d, 2), 3.70 (q, 4), and 1.56 (t, 2); ^{13}C ($CDCl_3$) 138.7, 133.4, 58.6, 50.7, 43.6, and 26.7 ppm; *m/e* 117 (base peak); no molecular ion seen. The structure of this apparently dimeric hydrocarbon was not further investigated.

Grignard Preparation. The chloride dissolved in ~0.5 mL of THF-d_8 was added to 4 mg-atoms equiv of triply sublimed magnesium. This mixture was then sealed in an NMR tube (along with a small amount of ethylene dibromide as initiator) under vacuum in such a way that the metal is separated from the solution by a plug of glass wool. Reaction was allowed to proceed by heating the inverted tube. To examine the solution spectroscopically (NMR), the liquid phase was filtered through the glass wool plug. The spectral data are given in the text.

2-Hydroxymethyltricyclo[4.2.1.0^{3,9}]nona-4,7-diene (34). A solution of ester **33** (1.00 g, 5.68 mmol) in dry ether (30 mL) was added dropwise to a stirred suspension of lithium aluminum hydride (216 mg, 5.68 mmol) in 60 mL of dry ether under a nitrogen atmosphere. After 4 h at room temperature, the mixture was cooled to 0 °C, treated dropwise with 3 mL of water, 3 mL of 10% sodium hydroxide solution, and 6 mL of water, and poured into a separatory funnel. The organic layer was washed with water and the aqueous phase reextracted with ether. The combined organic layers were dried, filtered, and evaporated to leave 490 mg (58%) of **34**: $\nu_{\max}{}^{\mathrm{neat}}$ 3330, 3021, 2899, 1603, 1333, 1163, and 1025 cm^{-1}; $\delta_{\mathrm{Me_4Si}}{}^{\mathrm{CDCl_3}}$ 5.89 (m, 2), 5.55 (m, 2), 3.89 (m, 1), 3.73–3.02 (br m, 5), 2.78 (m, 1), and 2.31 (br s, 1); calcd *m/e* 148.0888, found 148.0890.

2-Methylenetricyclo[4.2.1.0^{3,9}]nona-4,7-diene (28a). A cold (0 °C) solution of **34** (240 mg, 1.62 mmol) and triethylamine (226 mg, 2.23 mmol) in dichloromethane (4 mL) was treated dropwise with methanesulfonyl chloride (232 mg, 2.03 mmol). After 1.5 h at 5 °C, cold 10% hydrochloric acid was added and the organic layer separated. Prior to drying, the dichloromethane solution was washed with saturated sodium bicarbonate solution and water. Evaporation left 316 mg (86%) of the mesylate as a pale yellow oil: $\nu_{\max}{}^{\mathrm{neat}}$ 3130, 2940, 1430, 1310, 1160, and 945 cm^{-1}; $\delta_{\mathrm{Me_4Si}}{}^{\mathrm{CDCl_3}}$ 6.09–5.81 (d of d, J =

5 and 2 Hz, 2), 5.70–5.34 (m, 2), 3.92 (d, J = 7.5 Hz, 2), 3.55–3.15 (m, 3), 3.10–2.75 (m, 2), and 2.87 (s, 3).

The unpurified mesylate (308 mg, 1.36 mmol) dissolved in freshly distilled dimethyl sulfoxide (5 mL) was treated with potassium *tert*-butoxide (229 mg, 2.04 mmol) and stirred under nitrogen at room temperature for 24 h. After the addition of water (5 mL), the mixture was poured into water (100 mL) and extracted four times with pentane. The combined organic layers were washed with water, dried, and carefully concentrated by distillation through a Vigreux column. The residue was purified by preparative VPC (6 ft × 0.25 in. 5% Carbowax 20M on Chromosorb W, 68 °C) to give 25 mg (14%) of **28a:** $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 5.96 (d of d, J = 5 and 2 Hz, 2), 5.66 (m, 2), 4.70 (s, 2), 4.01 (br d, 1), 3.73 (m, 2), and 3.48 (q, J = 5 Hz, 1); calcd *m/e* 130.0785, found 130.0785.

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.86; H, 7.89.

2-Hydroxymethyltricyclo[4.2.1.0^{3,9}]nonane (35). A solution of **34** (200 mg, 1.35 mmol) in dry ethyl acetate (40 mL) containing 100 mg of 10% palladium on charcoal catalyst was shaken overnight under 50 psig of hydrogen. Filtration through a Celite pad followed by solvent evaporation afforded 205 mg (99.8%) of **35:** $\nu_{\max}^{\text{neat}}$ 3279, 2890, 1460, and 1284 cm^{-1}; $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 4.32 (m, 1), 3.62 (m, 1), 2.76 (m, 2), 2.20 (br s, 2), 1.60 (br s, 6), 1.28 (br s, 2), and 1.89 (m, 2).

2-Methylenetricyclo[4.2.1.0^{3,9}]nonane (36). Treatment of **35** as described above and isolation of the olefin by preparative VPC (6 ft × 0.25 in. 12% Carbowax 20M on Chromosorb W, 110 °C) furnished 44 mg (24%) of **36:** $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 4.72 (s, 2), 3.05 (m, 3), 2.56 (m, 1), and 1.71 (br m, 8): calcd *m/e* 134.1095, found 134.1099.

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.57; H, 10.51.

Hydroxy Acid 37. To a solution of lithium diisopropylamide in tetrahydrofuran [prepared from 206 mg (2.04 mmol) of the amine in 3 mL of solvent and 850 μL (2.04 mmol) of 2.4 M *n*-butyllithium in hexane] cooled to −78 °C was added a solution of **17** (150 mg, 0.925 mmol) in 2 mL of the same solvent. The mixture was allowed to warm to room temperature and then heated at 50 °C for 2 h. After cooling to −78 °C, the reaction mixture was treated with acetone (54 mg, 0.925 mmol) via syringe technique, kept at −23 °C for 2 h and at room temperature for 30 min, before being poured onto ice (40 g). The mixture was extracted four times with ether, acidified with 3 N hydrochloric acid, and reextracted with ether (4 × 25 mL). The latter extracts were combined, dried, and evaporated to give 190 mg (95%) of **37** as a viscous yellowish oil which was used without further purification: $\nu_{\max}^{\text{neat}}$ 3500–2400 and 1700 cm^{-1}; $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 7.54 (br s, 2), 6.16–5.80 (m, 2), 5.80–5.52 (m, 2), 4.04–3.18 (m, 4), 1.40 and 1.30 (s, 6 total); calcd *m/e* 220.1099, found 220.1103.

2-Isopropylidenetricyclo[4.2.1.0^{3,9}]nona-4,7-diene (28b). A cold (−5 °C) solution of **37** (190 mg, 0.862 mmol) in dry pyridine (9 mL) was treated with benzenesulfonyl chloride (609 mg, 3.45 mmol) and stored at 0 °C for 23 h. The mixture was poured onto ice (40 g) and extracted with ether (5 × 25 mL). The combined organic layers were washed with saturated sodium bicarbonate solution, dried, and concentrated. Residual pyridine was removed at 0.5 mm. There was obtained 160 mg (92%) of **38** as a light brown crystalline solid: mp 74–77 °C; $\nu_{\max}^{\text{KBr}}$ 3020, 2900, 1810, and 1770 cm^{-1}; $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 6.22–5.77 (m, 2), 5.77–5.34 (m, 2), 4.05–3.17 (m, 4), 1.47 (s with fine structure, 6); calcd *m/e* 202.0994, found 202.0996.

The unpurified lactone was heated to 120 °C in a 50-mL round-bottomed flask fitted with a short-path condenser and maintained at this temperature for 10 min. NMR analysis indicated approximately 80% reaction. The material was vacuum transferred and subjected to preparative VPC purification (6 ft × 0.25 in. 12% Carbowax 20M, 110 °C). There was obtained 48.6 mg (42%) of **28a** as a colorless liquid: $\delta_{\mathrm{Me_4Si}}^{\mathrm{CDCl_3}}$ 6.07–5.88 (m, 2), 5.88–5.64 (m, 2), 4.15–3.34 (m, 4), and 1.63 (t, J = 1 Hz, 6); calcd *m/e* 158.1095, found 158.1098.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.15; H, 8.97.

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study and a more detailed analysis of the nortriquinacene system will appear elsewhere.

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Catalysis of Transimination Through Trapping by Acids and Bases[1]

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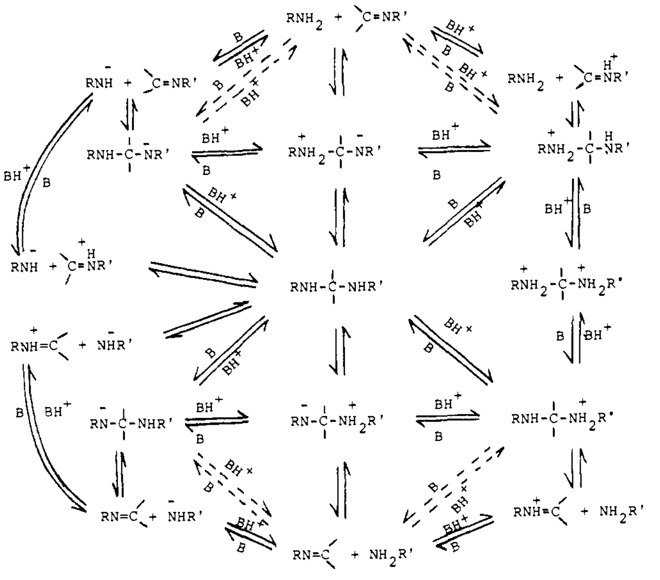
Abstract: Catalysis of the transimination reaction of *N*-*p*-methoxybenzylidenepyrrolidinium cation and hydroxylamine by buffer acids and bases and by the proton exhibits a sharp rate increase followed by a leveling off to a pH-independent rate at high catalyst concentrations. This is evidence for a change in rate-determining step and an intermediate in a stepwise reaction mechanism. Catalytic constants, k_{HA}, for cacodylic and carboxylic acids show a small or no increase with increasing acidity, but k_{HA} for the proton is 57 times larger and k_{HA} for hydroxylammonium ion is more than ten times smaller than k_{HA} for cacodylic and acetic acids. Catalytic constants for buffer bases drop sharply for catalysts of pK_a < 4.6. The reaction with *N*-methylhydroxylamine shows similar behavior in acetate buffers, but exhibits approximately tenfold slower rates, presumably because of steric hindrance. The observed catalysis by acids and bases is attributed to trapping of the initially formed cationic addition intermediate by proton transfer. Catalysis by cacodylic and carboxylic acids and by water is attributed to a bifunctional, proton switch mechanism.

Transimination (eq 1), such as occurs in the reaction of an amino acid with the imine formed from pyridoxal phosphate and the lysine ε-amino group of an enzyme, is an apparently

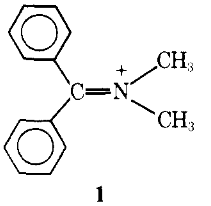
$$R_1NH_2 + {>}C{=}NR_2 \rightleftharpoons R_1N{=}C{<} + R_2NH_2 \qquad (1)$$

simple reaction that is made complicated by the requirement that two protons be removed from the attacking amine and added to the leaving amine. An oversimplified summary of the possible mechanisms for transimination, which omits all transport (diffusion) steps, is shown in Scheme I. Although the role of the gem diamine in the center of Scheme I as an intermediate has been questioned,[2] a recent temperature-jump study of the reaction of pyridoxal phosphate with ethylenediamine has not only identified this species, but has shown that it is formed rapidly enough to be kinetically competent as an intermediate in the nonenzymic transimination reaction and also in enzymic reactions, if the enzyme can bring together the reacting groups as effectively as in the model reaction.[3]

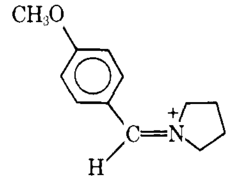
Scheme I



It was shown by Cordes and co-workers[4] that the transimination reaction of benzhydrylidenedimethylammonium ion (**1**) and hydroxylamine is subject to general base catalysis



1



2

according to the rate law

$$v = k_1[\mathrm{HONH_2}][{>}C{=}N^{+}{<}] + k_B[\mathrm{HONH_2}][{>}C{=}N^{+}{<}][B] \qquad (2)$$

Some of the possible kinetically ambiguous mechanisms of catalysis in the upper right corner of Scheme I are eliminated by this result because the *N*-dimethyliminium ion is cationic initially, so that catalysis cannot involve the addition of a proton to the neutral imine. The experiments described here were initiated in an attempt to utilize the converse of this technique, in which a (fixed) methyl group serves as a model for a (mobile) proton. Catalysis of the reaction of **1** with hydroxylamine and with *N*-methylhydroxylamine was compared in an attempt to determine whether removal of the second proton from hydroxylamine in one of the steps shown in the lower half of Scheme I is involved in the catalysis. If this proton removal is important for the hydroxylamine reaction no such catalysis should be seen for the reaction with *N*-methylhydroxylamine, in which this proton removal is not possible. A series of preliminary experiments carried out by Moore and Reenstra showed that the terms k_1 and k_B in the rate law of eq 1 are 300 and 1600 times smaller, respectively, for the reaction of *N*-methylhydroxylamine than of hydroxylamine with **1**.[5] This result could be interpreted in terms of the catalytic mechanism or could simply reflect an unexpectedly large unfavorable steric effect from the methyl group of *N*-methylhydroxylamine.