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THE RELATIVE MERITS OF 6π9C BISHOMOAROMATIC AND 10π13C LONGICYCLIC STABILIZATION

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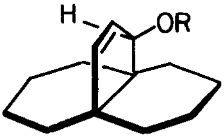
Summary The behavior of tricyclo[4.4.3.0^{1,6}]tridecapentaenyl and tricyclo[4.4.3.0^{1,6}]trideca-2,4,11-trienyl cations under short- and long-life conditions is described.

The concept of *two-dimensional* charge delocalization (homo-, bishomo-, and trishomoaromaticity)[2] and its more recent generalization to *three-dimensional* topologies (bicycloaromaticity)[3] have elicited high interest among physical-organic chemists. Although several homoaromatic cations have been well characterized, current opinion is unsupportive of comparable delocalization in neutral molecules[2c,4] and carbanionic systems.[5] The situation is much less clear-cut for bicycloaromatic ions.[6] Thus, additional studies are clearly warranted to gain proper perspective on the relationship between three-dimensional topology and beneficial or untoward charge delocalization.

In this connection, we have prepared the progressively unsaturated tricyclo[4.4.3.0^{1,6}]-



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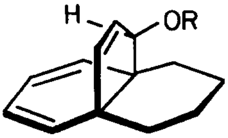

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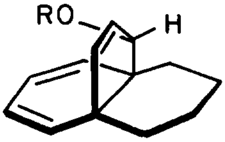

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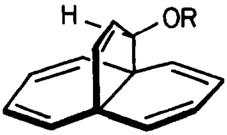
a, R = H ; **b**, R = $COC_6H_3(NO_2)_2$; **c**, R = CH_3



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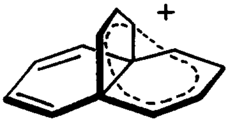

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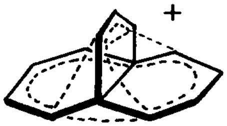

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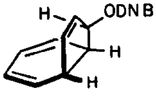
tridecanols **1a**-**4a** and carried out the solvolysis of their 3,5-dinitrobenzoates (**1b**-**4b**). Our interest in the ionization behavior of **4** stems from the possibility that the resulting cation may adopt bishomotropylium character (*cf.* **5**) or command interaction among all three bridges as in **6** in order to avail itself of bicycloaromatic stabilization. The carbocations resulting from **2** and **3** (and to a lesser extent **1**) were to serve as appropriate points of reference.

Titrimetric solvolysis rates, determined at four or more temperatures in 80% acetone-water by the aliquot method, showed good first-order behavior throughout. Since the infinity titers invariably agreed well with the calculated values, internal return to less reactive 3,5-dinitrobenzoates proved not to be a complication. While **1b** and **4b** were converted uniquely into **1a** and **4a**, respectively, under these conditions, **2b** and **3b** were transformed into an essentially identical 10:1 mixture of **2a** and **3a**. Solvolysis of **1b**-**4b** in methanol containing 2,6-lutidine gave only the methyl ethers (**2c**:**3c** = 85:15), the absence of alcohols signaling the exclusive operation of alkyl oxygen cleavage.

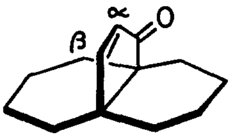
The rate data compiled in Table I reveal that neither **1b** nor **3b** react as fast as **7**[8] at 75 °C. On this basis, the presence of an added fused cyclohexane ring clearly exerts a small

Table I. Kinetic Data for 3,5-Dinitrobenzoate Solvolysis in 80% Aqueous Acetone

compd	$k \times 10^5$ sec^{-1}, 75°C	$\Delta H^{\ddagger}_{25°C}$, kcal/mol	$\Delta S^{\ddagger}_{25°C}$, eu	$\Delta G^{\ddagger}_{25°C}$, kcal/mol	k_{rel} 75°C
1b	0.95	27.8	+0.1	27.8	1
2b	37.4	25.4	-1.5	25.9	39
3b	0.39	30.5	+4.0	29.3	0.4
4b	7.40	24.6	-5.3	26.2	7.8
 **7**	3.42[a]				3.6

[a] Data taken from reference 8 for the *p*-nitrobenzoate and adjusted on the basis of the relationship k_{ONDB}/k_{OPNB} = 6 [Schleyer, P. von R.; van Dine, G. W. *J. Am. Chem. Soc.* 1966, ***88***, 2321, footnote *i* of Table I].

rate-retarding effect upon ionization. More enlightening with regard to the development of long-range delocalization are the solvolysis results for the epimeric pair **2b**/**3b**. The *ca.*



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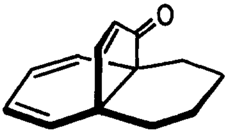

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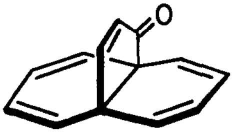

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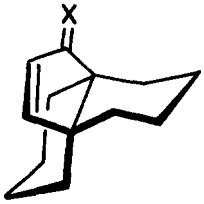

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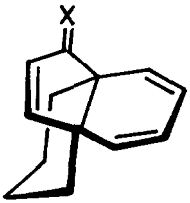

B

100-fold relative rate acceleration observed for 2b indicates substantial participation in the rate-determining step This value, which can be compared to the significantly smaller exo/endo rate ratio of 12 for the dihydroindenyl derivatives (7 and its epimer)[8] corresponds to a substantial difference in the barrier to ionization. *The greater reactivity of 2b is suitably in line with the development of bishomotropylium cation character in the transition state.*

The kinetic response of 4b is 5 times slower than that of 2b These results suggest that bishomotropylium ion 5 and not the bicycloaromatic species 6 is being generated under short-lived conditions The relative rate of 4b correlates well with that of 2b after proper allowance for the adverse inductive effect of the second 1,3-cyclohexadiene moiety and the increased conformational rigidity which it imposes (see below).

Since 2b and 3b give rise to identical product distributions within experimental error, the syn isomer likely experiences an allyl → bishomotropylium electronic reorganization after rate-determining ionization In an attempt to observe such cations under long-life conditions, 1a-4a were examined in superacid media Unfortunately, 2a-4a proved exceptionally prone to polymerization under such conditions

Alternatively, a distinction between cations of type 5 and 6 *under ground-state circumstances* was sought through protonation studies on 8-10 Their 300 MHz ^{1}H NMR spectra were recorded in FSO_3H-SO_2ClF-CD_2Cl_2 solution at -80°C. The data reflect the incursion of a large electronic change in progressing from 8-H$^+$ (H_α, δ 6.72; H_β, δ 9 02) to 9-H$^+$ (H_α, δ 7.20, H_β, δ 8.63), in complete agreement with the development of 6π9C charge delocalization The distinction between 9-H$^+$ and 10-H$^+$ (H_α, δ 7 43, H_β, δ 8 76) is much smaller (note downfield shift of

H_B') and congently interpretable in terms of appreciably altered inductive and conformational influences

Our failure to observe longicyclic stabilization in the cations derived from **4b** (short-life) and **10** (long-life) likely arises from the need to tilt the three-carbon bridge toward that cyclohexadiene ring with which through-space interaction occurs in order to maximize bishomoconjugative orbital overlap[9] The consequence of this geometrical distortion away from C_{2v} in **5** is simply to isolate the second set of diene fragment orbitals

In these terms, one can appreciate that the more negative entropy requirements encountered in the ionization of **4b** arise in large part because of the higher level of structural constraint present in its ground state and the added resistance encountered in flexing one cyclohexadienyl bridge toward the incipient cationic center in the activated complex (a difference also encountered with **2b** and **7**) Due to the highly varied conformational degrees of freedom in **1**-**4**, therefore, direct comparison of $\Delta H^{\ddagger}$ (**3b** - **1b**) versus $\Delta H^{\ddagger}$ (**4b** - **2b**) as a possible measure of cyclohexadienyl inductive effects is inappropriate

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(7) The details of our synthetic work will be presented in the full paper

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