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ELECTROPHILIC ADDITION TO SEMIBULLVALENE.
EVIDENCE FOR ANTIAROMATIC BEHAVIOR IN A 4n SYSTEM

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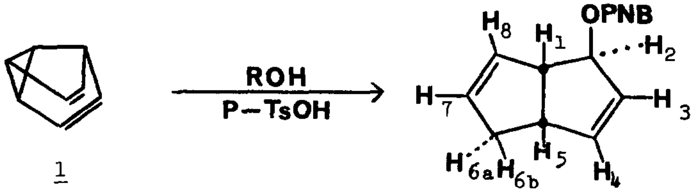
We find that acid-catalysed addition of protic solvents to semibullvalene[1a,b,c] proceeds as indicated below (1→2a-d) in 80% yield.[2] A stereospecific 1,4 addition upon the vinylcyclopropyl system present in 1 accounts for the formation of 2a-d and parallels the analogous addition reactions of bullvalene.[3]



1

2 80%

a: R = H
b: R = $COCH_3$
c: R = CH_3
d: R = $COCF_3$

The basic structure of the series 2a-d was proven by catalytic reduction of 2a to exo-cis bicyclo[3.3.0]octan-2-ol (3).[4] Reduction and saponification of 2b gives 3. The position of the double bonds was demonstrated by means of nmr analysis using $Eu(DPM)_3$ induced shifts upon the p-nitrobenzoate derivatives of 2a, namely, 2e, m.p. 88-89°. The spectral parameters are listed in Table 1. The coupling constants and chemical shifts accord uniquely with the proposed structure and exclude conceivable alternatives such as the 2-substituted bicyclo[3.3.0]oct-3,6-dienyl system or the 8-substituted bicyclo[3.2.1]oct-2,6-dienyl structure.[5] Thus irradiation of either bridgehead proton affects only one vinyl system and the coupling constants of the proton bound to carbon bearing the OPNB group indicates that this group cannot be at the 8-position of a bicyclo[3.2.1]octyl system.

TABLE I

Spectral Parameters for 2e

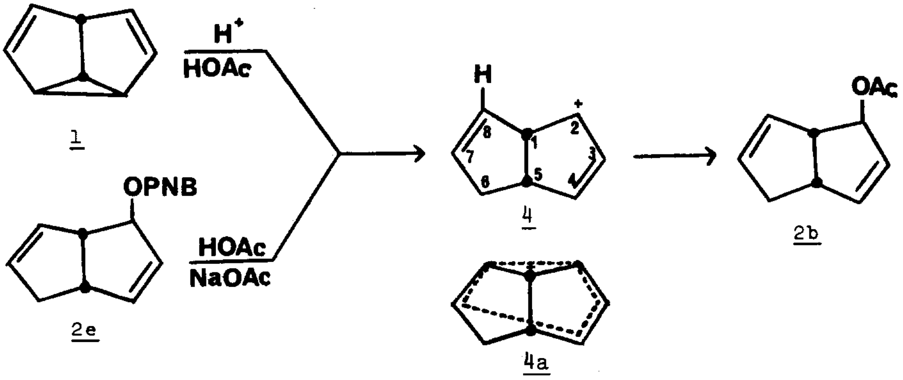
Chemical Shift ppm	Chemical Shifts Eu $(DPM)_3$ added
H_1 - 3.65	4.05
H_5 - 3.50	3.60
H_{6a} - 2.05-2.92	1.90 (2.51)
H_{6b}	2.51 (1.90)
H_8 - 6.05	5.60
H_7 - 5.75	5.32
H_4 - 5.63	6.35
H_3 - 5.55	5.85
H_2 - 5.42	7.36

Coupling Constant

JHz

$H_1 - H_8 = 2.0$
$H_7 - H_8 = 5.4$
$H_7 - H_{6a}$ and $H_{6b} = 2.3$
$H_5 - H_4 = 2.0$
$H_4 - H_3 = 5.6$
$H_3 - H_2 = 2.3$
$H_1 - H_2 = 4.0$
$H_1 - H_5 = 7.2$

The exo configuration of the C_2 substituent is reasonable in terms of the preferred mode of exo attack upon 4. Acid-catalysed addition of acetic acid to 3,5-cyclocholest-6-ene yields chloesteryl acetate as the product of kinetic control in close analogy with the behavior of 1 under these conditions.[8]



Absence of product derived from attack at C_4 in ion 4 could be due to a steric factor. The C_2 position in 4 is less hindered by interaction with the one *peri* vinyl hydrogen relative to the C_4 position which incurs a more destabilizing steric interaction with the two *peri* methylene hydrogens at C_6.

In order to gain further information on the product forming ion, its synthesis from the acetolysis of 2e was studied under conditions of kinetic control using buffered acetic acid. The same product, 2b, in the same yield as found in the acid-catalysed addition of acetic acid to 1 was obtained.

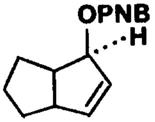
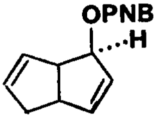
This may suggest that the same intermediary carbonium ion occurs in both the acid-catalysed addition as well as the acetolysis under kinetic control.

A fully homoconjugated cyclic action such as 4a would be a $4n\pi$ system and, therefore, destabilized with respect to the 2π system. In this sense it would be antiaromatic or "antibicycloaromatic."[9] With a view towards learning whether this might be evidenced kinetically relative rates of acetolysis of 2e and the allylic derivative 5 (Table 2) were studied. The homoallylic double bond in 2e is rate retarding by about a factor of ten. This corresponds to a negative inductive effect with no compensatory delocalization. Ion 4 might be characterized as a homoallylically destabilized allylic ion. This is the first example

TABLE 2

First Order Rate Constants for Acetolysis

of Bicyclo[3.3.0]octenyl p-Nitrobenzoates

	k_{80°	1.03×10^{-4} sec^{-1}
	$k_{89.8^\circ}$	2.42×10^{-4} sec^{-1}
	k_{100°	7.08×10^{-4} sec^{-1}
	k_{80°	1.13×10^{-5} sec^{-1}
	$k_{89.8^\circ}$	2.40×10^{-5} sec^{-1}
	k_{100°	1.08×10^{-4} sec^{-1}

of such an effect in the bicyclo[3.3.0]octadienyl system. Cations derived from the bicyclo[3.2.1]octadienyl system are similarly destabilized relative to their monoene analogs,[7,10] as is the bishomotropylium ion.[11] A related system, namely, the bicyclo[3.2.0]heptadienyl cation has been studied.[12]

Acknowledgement. The valuable help of our colleague, Dr. K. C. Ramey, Arco Chemical Company, Glenolden, Pennsylvania, on the nmr studies carried out on these compounds is gratefully acknowledged.

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2. Derivatives 2a-c gave correct microanalyses and consonant ir and ms spectra.

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