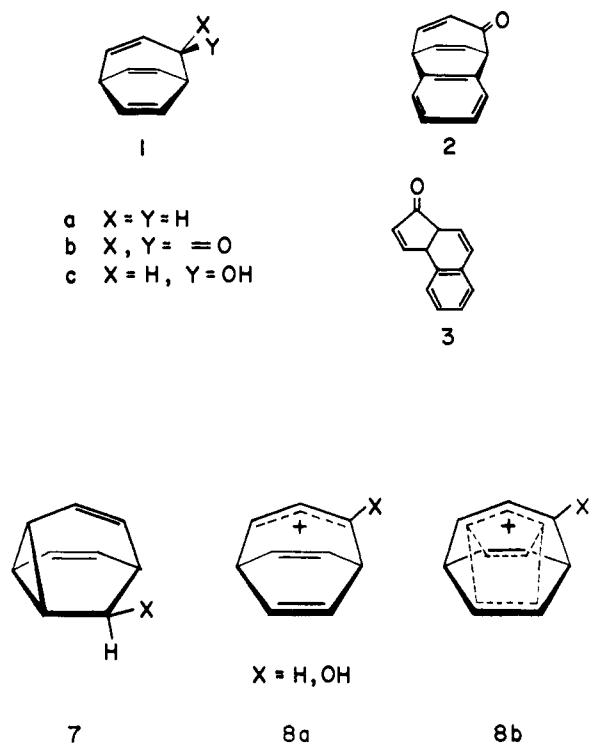


Rearrangements of Bicyclo[3.2.2]nonatrienes

Sir:

Only recently has bicyclo[3.2.2]nona-2,6,8-triene (**1a**) been obtained¹ and the first nontrivial chemical property, if of a derivative (the photochemical transformation of **2** to **3**), been reported.² We here supplement such, and previously obtained,^{3,4} knowledge with a rational and efficient synthesis of the parent ketone **1b** and alcohol **1c** and a preliminary outline of three distinguishable rearrangements of their carbon skeleton.



1b,⁵ bp 113–113.5° (10 mm), mp 44°, semicarbazone⁵ mp 214° dec, was isolated in 40% yield after treatment of the readily available cyclohepta-2,4,6-trienylacetyl chloride⁶ with triethylamine. Its spectroscopic properties⁷ closely resemble those of **2**; catalytic hydrogenation (3.1 equiv, Pt–EtOAc) to the known⁹ hexahydroketone,

(1) M. Jones, Jr., and S. D. Reich, *J. Am. Chem. Soc.*, **89**, 3935 (1967).

(2) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *ibid.*, **89**, 2778 (1967). We are grateful to Dr. Kende for providing us with a copy of this manuscript prior to publication.

(3) M. J. Goldstein and A. H. Gevartz, *Tetrahedron Letters*, 4413 (1965).

(4) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Am. Chem. Soc.*, **87**, 4007 (1965).

(5) Elemental analyses agreed with theory to within $\pm 0.3\%$.

(6) K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959); G. R. Jurch and T. G. Traylor, *ibid.*, **88**, 5228 (1966).

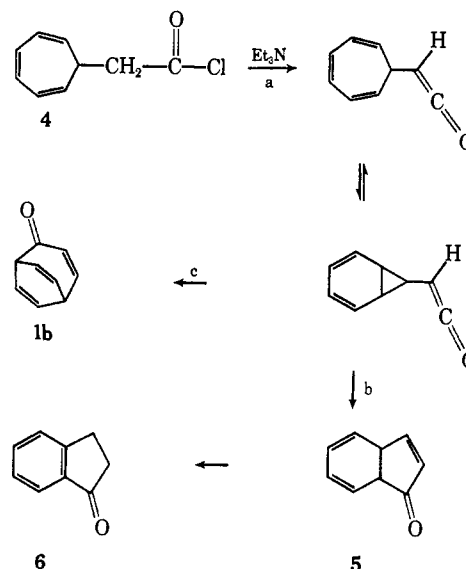
(7) m/e 132, 131 (base peak), 104, 103, 78, 77; metastable peaks at m/e 130, 81.5, 58; $\nu_{\text{max}}^{\text{C=O}}$ 3065, 3040, 2970, 1680, 1650, 1620, 1375, 1355, and 690 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ (e) 230 (3200), 283 (567), and 351 (92) $\text{m}\mu$; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (e) 228 (2075) (sh), 273 (539), 343 (52) (sh), 359 (69), 374 (65), and 395 (28) $\text{m}\mu$; τ^{CDCl_3} 2.98 (d, d, 11.0, 8.2), 3.28 (d, d, d, 7.5, 6.2, 1.6), 3.60 (d, d, d, 7.5, 6.6, 1.7), 4.97 (d, d, d, 11.0, 2.0, 0.9), 5.86 (t, q, 6.4, 1.8) and 6.22 ppm (m) of relative areas 4.9 (2.98 + 3.28 + 3.60):1 (4.97):1.8 (5.86 + 6.22).

(8) Abbreviated descriptions assuming first-order behavior followed by J (Hz); d, doublet; t, triplet; q, quartet; m, multiplet; d, d, doublet of doublets, etc.

(9) J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5019 (1964). An infrared spectrum, kindly provided by Professor Berson, proved to be adequately indistinguishable from the one obtained in this laboratory.

mp 154–156° (lit.⁹ 152.5–154.5°), completes the proof of structure.

Accompanying the production of **1b** was that of the dihydroindanone (**5**), characterized by its ultraviolet^{10a,c} and nmr¹⁰ spectra as well as by the melting point (240°)¹¹ and infrared spectrum^{10c} of its maleic anhydride adduct. Tautomerization of **5**, both accompanying its formation and subsequently, permitted the isolation of indanone (**6**) in 44% yield (based upon **4**). In support of the anticipated¹² reaction paths,



less than 2% of **5** or **6** could be detected when **1b** was resubjected to the reaction conditions. Similar (but less than optimal) preparative conditions permitted spectroscopic detection of the presumed aldoketene dimer.¹³

The transformation **1b** \rightarrow **6** could, however, be effected by sulfuric acid at 0°. In close analogy with **2**,² irradiation of a cyclohexane solution of **1b** through Pyrex provided **5**.¹⁴

The alcohol **1c**,⁵ mp 54–56°,¹⁵ was conventionally obtained from **1b** (LiAlH_4 , ether, -80° or NaBH_4 , methanol, 0°) and its structural assignment was assured by concordant spectroscopic properties and by reoxidation (MnO_2) to **1b**. It proved to be more labile than **1b**, both thermally and to Lewis acid catalysis. Thus, gas chromatographic conditions which permitted recovery of **1b**¹⁶ transformed **1c** into cyclohepta-2,4,6-trienylacetaldehyde (54%), a reaction most simply regarded as an “oxy-Cope” rearrangement.⁹

Ethereal AlCl_3 ,¹⁷ by contrast, isomerized **1c** to an

(10) (a) E. Vogel and E.-G. Wyes, *Chem. Ber.*, **98**, 3680 (1965); (b) J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966); (c) E. Baggolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta*, **50**, 297 (1967).

(11) Lit. mp 241° ,^{10a} 239–241°,^{10b} 239°.^{10c}
(12) (a) W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 108 (1946); (b) M. R. Wilcott and V. H. Cargle, *J. Am. Chem. Soc.*, **89**, 723 (1967); (c) J. M. Brown, *Chem. Commun.*, 638 (1967), ref 3, and further examples there cited.

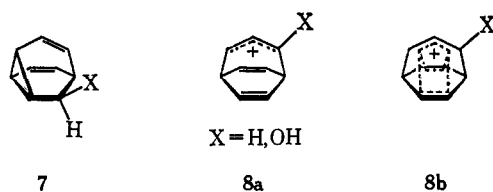
(13) $\nu_{\text{max}}^{\text{max}}$ 1870 and 1730 cm^{-1} ; τ^{CDCl_3} 3.29 (d, 6.5), 3.86 (m), 4.28 (m), 5.16 (m), 6.08 (d, 8.0), and 7.68 ppm (m) of relative areas 1.0:4.2:4.2:5.1:1:2.7.

(14) Further insight is provided by the report that photolysis of **5** in methanolic solution affords methyl cyclohepta-2,4,6-trienylacetate.^{10c}

(15) Purification achieved by Mr. S. Natowsky.
(16) “On-column” injection, 5 ft \times $\frac{3}{8}$ in. column packed with 8% Carbowax M on 60–80 mesh Chromosorb P, 140°.

(17) Otherwise identical treatment of **1b** with ethereal AlCl_3 permitted 90% recovery of a 9:1 mixture of **1b** and **6**.

alcohol (58% yield) whose room-temperature nmr spectrum is uniquely consistent with that of fluxional tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-ol (barbaralol, **7**, X = OH).^{18,19} Correspondingly, LiAlH₄-AlCl₃ reduction²⁰ of **1b** provided barbaralol (**7**, X = OH, 30%), indan (13%),¹⁷ and barbaralane (**7**, X = H, 30%).²¹ **1a** could not be detected.



These facile cationic rearrangements are difficult to reconcile with any hope that the six- π -electron bicyclo[3.2.2]nonatrienyl cation (**8a**) might enjoy the unusual stability suggested by its alternative formulation as a "bicyclopentadienyl" ion (**8b**), for if one chooses to rationalize these results by invoking an unusually selective nucleophilic capture of a stable **8b**, one is then compelled to predict correspondingly unusual high solvolytic rates for appropriate derivatives of **7**.²³ Since acetolysis of barbaryl tosylate (**7**, X = OTs) is, in fact, a remarkably sluggish reaction,¹⁹ one is led to favor the simpler alternative: **8** possesses *no* unusual stability. In the accompanying communication,²⁴ any suggestion to the contrary is shown to be incompatible with the theoretical prediction that **8** be "antibicyclic-aromatic."

Acknowledgment. Financial support was in part provided by Public Health Service Research Grant No. 10495-01 (National Cancer Institute).

(18) τ_{CDCl_3} 4.12 (t, 7.5), 4.45 (t, 7.5), 5.92 (m), 6.02 (m), 6.38 (t, 3.5), 7.55 (m), and 8.03 ppm (broad singlet vanishing upon D₂O treatment) of relative areas 0.9:0.9:4.5 (5.92 + 6.02):1:2.1:1.1. Lit.¹⁹ τ 4.00 (t), 4.35 (t), 6.02 (d), 6.48 (t), 7.57 (m), and 8.62 ppm (m).

(19) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967). We are grateful to Professor Doering for providing a copy of this manuscript prior to publication.

(20) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967).

(21) $\nu_{\text{max}}^{\text{CDCl}_3}$ 3045, 2950, 2920, 2860, and 1615 cm⁻¹; τ_{CDCl_3} 4.32 (t, 8.7.5), 5.97 (t, 7.5), 7.63 (m), and 8.93 ppm (t, 2.5), of relative areas 2:4:1:2.8:2.5. Lit.¹⁹ ν_{max} 3045, 2952, 2920, 2862, and 1618 cm⁻¹; τ 4.38 (t, 7.3), 6.10 (t, 7.1), 7.73 (m), and 8.97 ppm (t, 2.5). Lit.²² 4.37 (t, 7.5), 6.03 (t, 7.5), 7.67 (m), and 8.94 ppm (t, 2.5).

(22) V. Buthan, H. Klusacek, and H. Musso, *Angew. Chem.*, **79**, 152 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 176 (1967).

(23) A. Diaz, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3133 (1966).

(24) M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

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Received September 15, 1967

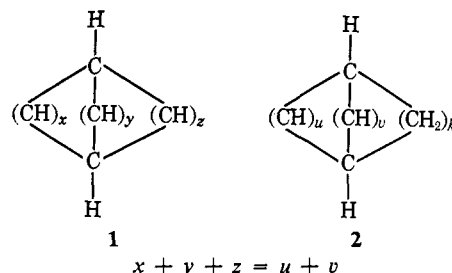
Bicyclicaromaticity. The $4m + 2, 4n$ Rule

Sir:

The elaboration of π MO theory, and of Hückel's rule in particular, requires a prior segregation of σ and π orbitals. This, in turn, is rigorously permitted only by a planar geometry. It is less clear that experimental manifestations of aromaticity demand this geometry as a prerequisite. With this in mind and stimulated by recent preparative achievements,¹ the author here out-

lines a π MO treatment of C_mH_m bicyclic hydrocarbons which leads to a simple theoretical rule for anticipating aromaticity, if only when m is odd (cations and anions).

π bicyclicaromaticity is first defined as the enhanced thermodynamic stability (measured or predicted) of the hydrocarbon **1** in comparison with an appropriate reference compound, one that possesses the same number of trigonal carbons and π electrons. The latter, **2**, is a bicyclic representative of Winstein's bishomocon-



jugated series² chosen such that $u + v = x + y + z$. k , the number of methylene groups in **2**, is an experimental parameter wisely adjusted so as to minimize differences between the σ -bond interactions of **1** and **2**.

Following a well-explored sequence of approximations,³ one recognizes that odd systems (odd z in **1**, odd v in **2**, all other bridges even) permit the neglect of all bridge-bridge interactions except for that one between the NBMO⁴ of (CH)_z or (CH)_v and the HBMO or LABMO of the even bridges. Only one of these latter two can possess the same symmetry as does the NBMO (symmetric (S) or antisymmetric (A) with respect to the plane bisecting the bridgehead-bridgehead axis). Its interaction then lowers the lower energy MO of the interacting pair while raising that of the higher one somewhat more.⁵

Bishomoconjugation. As illustration, if $v = 1$, $5 \dots 4q + 1$, the S-NBMO of (CH)_v in **2** must mix with the S-HBMO of (CH)_u whenever $u = 2, 6 \dots 4r + 2$. The $(u + v - 1)$ π electrons of the cation are then accommodated within $2(q + r) + 1$ BMO's, the highest of which has now been stabilized. The $(u + v + 1)$ π electrons of the corresponding anion must in addition now occupy a (formally antibonding) destabilized MO. Alternatively, if $v = 3, 7 \dots 4q + 3$, the A-NBMO

(1) (a) T. S. Cantrell and H. Schechter, *J. Am. Chem. Soc.*, **87**, 3300 (1965); (b) W. Grimme, *Chem. Ber.*, **100**, 113 (1967); (c) L. G. Cannell, *Tetrahedron Letters*, 5967 (1966); (d) M. Jones, Jr., and S. D. Reich, *J. Am. Chem. Soc.*, **89**, 3935 (1967); (f) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *ibid.*, **89**, 3656 (1967); (g) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967); (h) J. M. Brown, *Chem. Commun.*, 638 (1967).

(2) (a) Footnote 4 in ref 1f. (b) The otherwise convenient term "bishomoaromatic" is here avoided only because the pertinent reference system has not yet been defined. E.g., the computed delocalization energy of 0.386β for the 7-norbornenyl cation²⁰ refers to the isolated π bridges. It becomes -0.342β or -0.432β if referred to the allyl or the cyclopropenyl cation. (c) R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, **2**, 423 (1963).

(3) (a) M. J. S. Dewar, *Proc. Cambridge Phil. Soc.*, **45**, 639 (1949); (b) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341, 3345 (1952); (c) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966); (d) K. Fukui, "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p 525; (e) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511, 4388, 4389 (1965).

(4) Abbreviation used: NBMO, nonbonding molecular orbital; HBMO, highest bonding molecular orbital; LABMO, lowest antibonding molecular orbital.

(5) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 75, eq 5 with $S > 0$.