

an environment (MeOH, 95°, 8 hr) which irreversibly transforms **1a** to an ester, presumably methyl (4*Z*)-(7'-cyclohepta-2',4',6'-triényl)but-3-(and/or 2-enoate,¹⁶ in 85% yield.

The synthetic implications of mechanism **e** are apparent: **2**, but not **1a**, should also be accessible by an independent synthesis of **4**, e.g., through the readily available 7-vinylcycloheptatrienes.^{12a,17}

Mechanistically more instructive is the apparent need of a two-step sequence to break and to form precisely those same bonds as would otherwise be achieved by the one-step mechanism **b**.¹⁸ The subsequent choice of eight-electron (**e**) rather than six-electron (**d**) cycloaddition recalls the exclusively four-electron *intermolecular* cycloadditions of ketenes¹³ and the otherwise unexpected thermal stability of barbaralene.¹⁹ More diverse are the previous reports of *intramolecular* thermal ketene cycloadditions. Examples of *apparent* six-electron,^{12a,b} as well as four-^{12a,20} and/or eight-electron^{12a,c} processes suggest opportunities for closer scrutiny.

Finally, we note the illustration of a more general suggestion. Symmetry-forbidden processes (such as **a**) ought to be regarded with some skepticism until the full scope of symmetry-allowed processes has been considered, much less excluded by experiment.

Acknowledgment. Financial support was provided by Public Health Service Research Grant No. 10495 from the National Cancer Institute.

(16) Ir (CCl₄) 3000, 2905, 1730, 1602, 1428, 1240, 1190, 1165, and 700 cm⁻¹ but *not* at 960–970 cm⁻¹; pmr (CCl₄) τ 3.38 (2 H, tt), 3.70–4.53 (4 H, m), 4.93 (2 H, dd), 6.38 (3 H, s), 7.05 (2 H, d), 7.66 (1 H, m).

(17) J. Daub and P. v. R. Schleyer, *Angew. Chem.*, **80**, 446 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 468 (1968).

(18) Cf., J. E. Baldwin and M. S. Kaplan, *J. Amer. Chem. Soc.*, **93**, 3969 (1971); **94**, 4696 (1972).

(19) T. Mukai and K. Kurabayashi, *ibid.*, **92**, 4493 (1970).

(20) P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 2493 (1968); H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, **93**, 6266 (1971).

M. J. Goldstein,* S.-H. Dai

Department of Chemistry, Cornell University
Ithaca, New York 14850

Received July 12, 1972

A C₁₁H₁₁ Cation of Unusual Structure¹

Sir:

The modal description of the isomeric C₁₁H₁₁ longicyclic cations (**1a–c**) is uniformly (2,2,0).² All should therefore be stabilized. The further adjective, "bicycloaromatic," compares these with their isoconjugate homoantiaromatic pericyclics (**2a–d**) in a way that disparages potential isomerization, at least into the latter topology. We now report that conventional low-temperature FSO₃H extraction of the immediate alcohol precursor of **1b**³ in fact provides *none* of these.

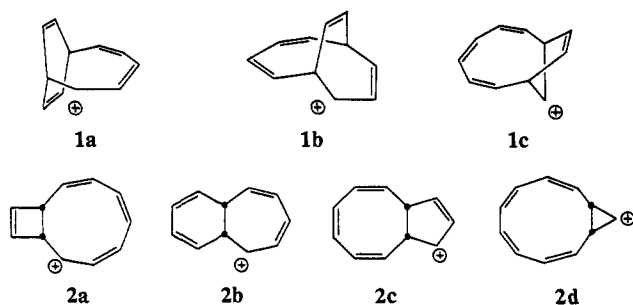
The observed pmr spectrum,⁴ τ_A 1.91 (d, $J = 7.0$ Hz,

(1) Taken in part from the Ph.D. Thesis of S. A. Kline, Cornell University, 1972.

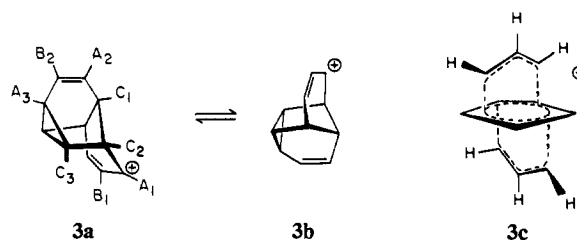
(2) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(3) The unambiguous synthesis and structure proof of *syn*- (to diene) bicyclo[4.3.2]undeca-2,4,8,10-tetraen-7-ol is described elsewhere: M. J. Goldstein and S. A. Kline, submitted for publication to *Tetrahedron Lett.*

(4) FSO₃H–CD₂Cl₂ solutions also containing SO₂, SO₂ClF, and/or SO₂F₂ at 60 and 90 MHz for protons, at 22.62 MHz with proton decoupled Fourier transform accumulation for ¹³C.



4.1), τ_B 2.41 (t, $J = 7.0$ Hz, 2.1), and τ_C 7.31 (s, 4.8) ppm with unresolved fine splitting (J_{AC}), suggests **3a** \rightleftharpoons **3b** as a first approximation to the structure of the (presumably more stable) cation.⁵ Each such step, the corner alkylation of cyclopropane by an allyl cation, corresponds in stereochemistry both to that of the *exo*-deltacycyl cation,⁶ where it leads to twofold degeneracy, and of the cyclopropylcarbanyl cation,⁷ where the degeneracy becomes threefold. The fivefold degeneracy of **3** is attained by a double circumambulatory



process, one that has previously been anticipated but never heretofore achieved.^{8,9}

The barrier to such rotation must be lower than that of any single cationic circumambulation that we know;^{8e,10} nmr spectra remain unchanged between -20° and the lowest easily accessible temperatures (-150° for pmr, -60° for cmr). At this level of approximation, the *transition state* **3c**—two mutually perpendicular 1,3-dehydroallyl cationic ligands, above and below the plane of a cyclopentadienyl anion—provides an attractive rationale. Such a geometry, accurately either C₂ (as shown) or C_s but approximately D_{2a}, permits stabilization to follow from mixing one of the vacant cyclopentadienyl π orbitals with the a₂ combination of allyl ψ_2 . It requires both a negligible rotational barrier and an incomplete transfer of negative charge to the ligands.

Can such stabilization suffice to make **3c**, instead, the

(5) The role of **1a** and **1b**, as potential intermediates in the formation of **3**, will be described separately.

(6) P. K. Freeman, D. M. Balls, and J. N. Blazeovich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970).

(7) K. B. Wilberg and G. Szeimies, *ibid.*, **92**, 571 (1970); Z. Majerski and P. v. R. Schleyer, *ibid.*, **93**, 665 (1971).

(8) (a) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1613 (1965); (b) P. v. R. Schleyer and R. E. Leone, *ibid.*, **90**, 4164 (1968); (c) G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, **87**, 1053 (1968); (d) J. J. Gajewski and C. N. Shih, *Tetrahedron Lett.*, 2967 (1970); (e) For a comprehensive review, cf. R. E. Leone and P. v. R. Schleyer, *Angew. Chem.*, **82**, 79 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

(9) A topologically analogous process, however, provides an alternative interpretation of results observed in more complicated environments: (a) H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, **93**, 6264 (1971); (b) H. Hart and M. Kuzuya, *ibid.*, **94**, 8958 (1972).

(10) (a) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971); J. A. Berson and J. A. Jenkins, *ibid.*, **94**, 8907 (1972); W. J. Hehre, *ibid.*, **94**, 8908 (1972). (b) For two recently reported exceptions, cf. S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *ibid.*, **94**, 8936 (1972), and ref 9b.

structure of the cation itself? If so, **3** would become the first entirely organic sandwich compound.

In the absence of crystallographic data, cmr chemical shifts now appear to provide the most reliable criterion for achieving so subtle a distinction.¹¹ In Table I,

Table I. Estimated and Observed Nmr Chemical Shifts of **3**^a

Nu- cle- us	As- signed loca- tion	Model estimates		Mean		Obsd ^b	
		5-Ring	6-Ring	5-Ring	6-Ring		
¹ H	A ₁	-1.26 ^{c,d}	-0.25 ^c	2.29	2.80	1.91	
	A ₂	4.35 ^e	4.00 ^d				
	A ₃	7.69 ^d	7.69 ^d				
	B ₁	1.35 ^{c,e}	1.68 ^c	2.53	2.69	2.41	
		B ₂	3.71 ^d				3.71 ^d
	C ₁	7.30 ^d	7.30 ^d	6.98	7.17	7.31	
		C ₂	5.77 ^{c,e}				6.19 ^c
		C ₃	8.05 ^d				8.05 ^d
	¹³ C	A ₁	-24 ^c	-41 ^c	50	42	-4
A ₂		63 ^e	66 ^e				
A ₃		184 ^f	184 ^f				
B ₁		57 ^c	48 ^c	55	62	40	
		B ₂	63 ^e				66 ^e
C ₁		165 ^f	165 ^f	165	171	105	
		C ₂	145 ^c				160 ^e
		C ₃	184 ^f				184 ^f

^a Pmr shifts follow the τ scale; positive cmr shifts are upfield from CS₂. ^b Internal references: τ (CDHCl₂) 4.70, δ (CH₂Cl₂) 103. ^c Cyclopentenyl and cyclohexenyl cations relative to external Me₄Si: G. A. Olah, G. Liang, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3544 (1972). ^d Ketone **4**, Table II. ^e Cyclopentene and cyclohexenes: D. E. Dorman, M. J. Joutelet, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971). ^f Nortricyclane: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3955 (1969). ^g Unimportant differences in the 5-ring means (2.51, 2.62, 7.02) result from the cyclopentenyl τ values of M. Saunders and R. Berger, *ibid.*, **94**, 4049 (1972).

those of **3** are compared with fluxional averages derived from reasonable models for **3a** \rightleftharpoons **3b**. The disagreement appears to be significant. (As expected, pmr shifts are less decisive.) Although suitable models for **3c** are more difficult to find, we note that δ_A is appropriate for an extensively delocalized trivalent cation (e.g., benzhydryl, -5.6 ppm);¹² δ_C falls between that of the cyclopentadienyl anion (90 ppm) and of ferrocene (123 ppm).¹³

Whether **3c** be indeed regarded as the structure of **3** or as that of its low-energy transition state, a new generic term seems appropriate. We suggest *armilene* (from the resemblance to an armillary sphere) and a numerical homologative specification. **3** is then called the [3.5.3]armilenium cation. It remains to be seen what significance might be drawn from previous failures to observe the [2.5.2]armilenium cation and related species.⁸

Least ambiguous of all is the gross structure of **3**. Aqueous quenching, followed by MnO₂ or CrO₃-

(11) Cf. G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

(12) G. A. Olah, *ibid.*, **94**, 808 (1972), and references there cited.

(13) P. S. Pregosin and E. W. Randall in "Determination of Organic Structures by Physical Methods," Vol. 4, F. C. Nachod and J. J. Zuckerman Ed., Academic Press, New York, N. Y., 1971, p 263.

pyridine oxidation, provides a ketone¹⁴ whose pmr spectrum (Table II) and ozonolytic degradation to **5**¹⁶ are consistent only with **4**.

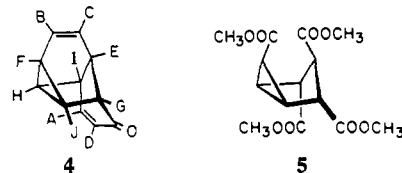


Table II. Pmr Spectrum of Ketone **4**^a

Assign- ment	A ^b	τ	s^c	Appearance ^d
H _A	1.13	2.41	-9.2	dd ($J = 9.8, 6.6$)
H _B	1.01	3.71	-4.8	ddd ($J = 8.0, 7.0, 1.5$)
H _C	0.91	4.00	-3.2	ddd ($J = 8.0, 8.0, 1.6$)
H _D	1.12	4.08	-32.8	dd ($J = 9.8, 1.7$)
H _E	0.95	7.30	-15.3	d ($J = 8.0$)
H _F	0.93	7.69	-6.4	dtd ($J = 7.0, 6.0, 1.6$)
H _G	0.97	8.03	-32.4	s
H _H	1.07	8.05	-12.3	t ($J = 6.0$)
H _I	0.90	8.23	-8.0	d ($J = 6.6$)
H _J	1.05	8.51	-18.7	t ($J = 6.0$)

^a In CDCl₃ at 90 MHz. ^b Areas normalized to ten protons at optimal [Eu(fod)₃]. ^c Slope of τ vs. molar ratio [Eu(fod)₃]/[substrate]. ^d Reported J (Hz) are first-order splittings as observed at appropriate [Pr(fod)₃].

Acknowledgment. We are greatly indebted to M. A. Battiste, R. Hoffmann, P. v. R. Schleyer, and G. Schröder for their critical comments, to D. E. Goldstein, H. Caplan, and E. A. Matzner for linguistic suggestions, and to Public Health Service Research Grant No. 10495 (National Cancer Institute) for partial financial support.

(14) m/e 158; ir (CCl₄) 5990, 4450 ($\epsilon(4450)/\epsilon(5990) = 2.4$),¹⁵ 3048, 3032, 2950, 2925, 2312 (w?), 1680, 1617, and 1598 cm⁻¹; Raman (CCl₄) 3064, 3048, 2950, 1680, 1617, and 1598 cm⁻¹; uv max (isooctane) and ϵ 248 (3300), 304 (80), and 326 (117) nm. *Anal.* Found: C, 83.23; H, 6.68.

(15) Cf. H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964).

(16) τ (C₆D₆) 4.83 (t, $J = 7.3$ Hz, 0.95), 5.83 (d, $J = 7.3$ Hz, 2.12), 6.38 (s, 2.93), 6.40 (s, 6.09), 6.54 (s, 2.89), 7.89 (d, $J = 8.7$ Hz, 1.91), and 8.26 (t, $J = 8.7$ Hz, 1.11) ppm.

(17) U. S. Public Health Service Fellow, 1967-1970, and Trainee, 1970-1971.

M. J. Goldstein,* Stanley A. Kline¹⁷

Department of Chemistry, Cornell University
Ithaca, New York 14850

Received August 2, 1972

Effect of Divalent Metal Ions on the Intramolecular Nucleophilic Catalysis of Phosphate Diester Hydrolysis

Sir:

Recent investigations^{1,2} have demonstrated that remarkable rate enhancements may be obtained in the hydrolysis of phosphate diesters by suitably positioning nucleophilic groups within the reacting molecule. Moreover, these reactions are thought to proceed *via* metastable pentacovalent intermediates owing to the magnitude of the rate enhancements (10^4 - 10^6), high sensitivity to changes in leaving group pK_a ($\beta = -1.2$),

(1) K. J. Schray and S. J. Benkovic, *J. Amer. Chem. Soc.*, **93**, 2532 (1971).

(2) (a) S. A. Khan, *et al.*, *J. Chem. Soc. B*, 1182 (1970); (b) D. M. Brown and D. A. Usher, *J. Chem. Soc.*, 6558 (1965).