π and n *vs.* σ electron-donor ability. The latter becomes more predominant when strongly electron-withdrawing groups or steric crowding decrease the otherwise dominant π-aromatic donor ability and allow the σ-donor single bonds to compete. Thus, protolytic cleavage of alkylbenzenes and substituted alkylbenzenes depends on the nature and availability of π-, σ-, and n-donor sites and the acid system used.

Acknowledgment. The support of our work by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Professor E. M. Arnett is thanked for samples of hexaisopropylbenzene and Professor M. S. Newman for samples of dineopentyltetramethylbenzenes.

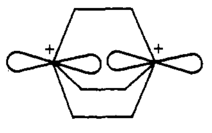
George A. Olah,* Y. K. Mo
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received February 9, 1973

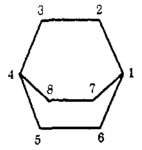
1,4-Bicyclo[2.2.2]octyl Dication, a Novel Pseudoaromatic System[1]

Sir:

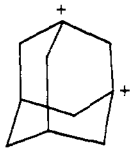
We have succeeded in preparing the 1,4-bicyclo[2.2.2]octyl dication **1** under stable ion conditions.



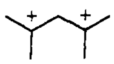
1



2



3
not observed

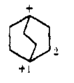
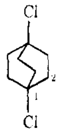
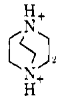
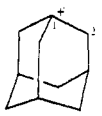
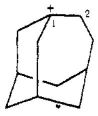
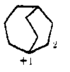
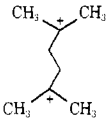
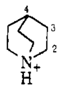
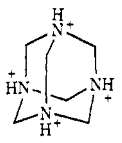


4
not observed

The close approach of charged atoms and of "vacant" orbitals makes this novel and unexpectedly stable dication an intriguing subject for study. The $C_1\cdots C_4$ nonbonded separation in bicyclo[2.2.2]octane (**2**) is only 2.6 Å; the $C_1^+\cdots C_4^+$ distance in dication **1** would be expected to be even shorter. Although a number of 1,4 dications are known,[2] none have positive centers held this closely together. Furthermore, alkyl-substituted 1,3 dications, which would have $C^+\cdots C^+$ separations comparable to **1**, have resisted attempts at preparation both in cage[3] (**3**) and in acyclic (**4**) systems.[3]

The 1,4-bicyclo[2.2.2]octyl dication **1** formed from 1,4-dichlorobicyclo[2.2.2]octane (**5**)[4] in SbF_5–SO_2ClF (SO_2) at $-78°$. Ion **1** was found to decompose gradually at temperatures above $-60°$. The dicarbenium ion nature of **1** is deduced from the following evidence. (1) The unrearranged dimethyl ether[5] is isolated on quenching the solution of ion **1** in MeOH–MeONa at $-78°$. (2) The pmr spectrum (60 MHz) of ion **1** at $-90°$ consists of a singlet at δ 3.45 (capillary Me_4Si). The Fourier transform (FT) ^{13}C nmr spectrum[6] of ion **1** shows two carbon resonances at $\delta_{^{13}C}$ -114.1 and $+149.3$ (*vs.* CS_2) assigned to the two equivalent bridgehead carbenium carbons and the six equivalent methy-

Table I. Proton (δ_H) and Carbon-13 ($\delta_{^{13}C}$) Parameters of the 1,4-Bicyclo[2.2.2]octyl Dication and Model Ions[a]

Dication	δ_H	$\delta_{^{13}C}$[b]
 1	3.45, s[c]	-114.1 (C_1) $+149.3$ (C_2)
 5	2.72, s[d]	$+128.6$ (C_1)[d] $+154.2$ (C_2)
	4.14, s[e] 7.38 (NH)	$+147.3$ (C_2)[e]
	4.19 (H_2)	-106.0 (C_1)[f] $+128.0$ (C_2)
	3.90 (H_2)	-110.9 (C_1)[f]
	4.20 (H_2)	-129.5 (C_1)[g]
 8	5.04 (CH_2) 4.24 (CH_3)	-137.8 (C^+) $+140.6$ (CH_2) $+146.2$ (CH_3)
	3.50 (H_2)[e] 2.20 (H_3, H_4) 7.73 (NH)	$+144.2$ (C_2)[e] $+169.7$ (C_3) $+173.4$ (C_4)
	5.85, s[e] 8.40 (NH)	$+121.1$[e]

[a] δ_H and $\delta_{^{13}C}$ are in parts per million from external Me_4Si and CS_2, respectively. [b] Obtained by Fourier transform ^{13}C nmr method unless otherise indicated. [c] s, singlet. [d] In $CDCl_3$. [e] In FSO_3H–SO_2, $-60°$. [f] G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 194 (1973). [g] Obtained by the indor ^{13}C nmr method: G. A. Olah, G. Liang, J. R. Wiseman, and J. A. Chong, *J. Amer. Chem. Soc.*, **94**, 4927 (1972).

---

[1] (a) Stable Carbocations. CLXII. (b) Taken in part from the Ph.D. Thesis of G. Liang, Case Western Reserve University, Cleveland, Ohio, 1973.

[2] J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 156 (1967).

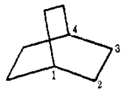
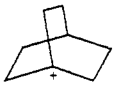
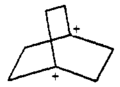
[3] Unpublished observations of G. A. Olah, *et al.*

[4] 1,4-Dichlorobicyclo[2.2.2]octane was provided by Dr. J. C. Kauer. See J. C. Kauer, U. S. Patent 3,255,254 (June 7, 1966); *cf. Chem. Abstr.*, **65**, 15249*g* (1966).

[5] When the solution of **1** was added to NaOMe-MeOH at $-78°$, 1,4-dimethoxybicyclo[2.2.2]octane was obtained in 45% yield (in addition to some unidentifiable materials): pmr ($CDCl_3$, capillary Me_4Si) δ 2.60 (s, CH_2) and 3.05 (s, CH_2O) in a ratio of 2:1.

[6] Carbon-13 nuclear magnetic resonance spectra were obtained by the Fourier transform method using a Varian XL-100 nmr spectrometer equipped with a variable temperature probe. Carbon shifts are reported in parts per million from capillary CS_2.

Table II. Calculations on the Bicyclo[2.2.2]octyl System

	 2		 6		 1		
	Molecular mechanics	MINDO/3	Molecular mechanics	MINDO/3	Molecular mechanics I[b]	Molecular mechanics II[c]	MINDO/3
$\Delta H_f°$ [a]	-22.2[d]	-10.1[d]	184.9[e]	191.2	395.7[e]	543.0[e]	511.2
C_1–C_2, Å	1.535	1.549	1.481	1.498	1.490	1.494	1.515
C_2–C_3, Å	1.539	1.531	1.544	1.544	1.553	1.576	1.561
C_1–C_4, Å	2.594	2.593	2.359	2.348	2.163	2.337	1.990
$\angle C_6C_1C_2$, deg	108.8	108.9	116.6	117.1	115.9	113.8	118.1
$\angle C_1C_2C_3$, deg	110.1	110.0	100.7	99.3	101.8	104.7	98.1

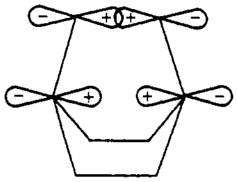
[a] Kcal/mol. [b] No electrostatic interaction included. [c] Electrostatic repulsion between two full positive charges included. [d] Experimental $\Delta H_f° = -23.7$ kcal/mol: R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany, and D. McNally, *J. Phys. Chem.*, **75**, 1264 (1971). [e] Heat of formation based on group increment for tertiary cation, corrected for the number of α branches (192.8 kcal/mol), derived from experimental data of the heats of formation of simple cations.

lene carbons, respectively. The latter on off-resonance determination shows a triplet, while the signal due to the carbenium carbon remains as a singlet. (3) Both pmr and ^{13}C nmr parameters, when compared with those for **5** and model mono- and dication systems (see Table I), appear to be consistent with the proposed dication structure **1**. In particular, the $\delta_{^{13}C}$ bridgehead value of -114.1 appears to exclude the possibility of rapid equilibration between **1** and a significant concentration of a 4-chlorobicyclo[2.2.2]octyl monocation. Although the -114.1 value is less shielded than that typically observed for tertiary acyclic cations (*e.g.*, **8**), chemical shifts of nonplanar carbenium ions at bridgehead positions are found in a comparable range (Table I).

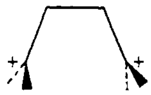
The reasons for the surprising stability of **1** were probed by molecular mechanical[7] and MINDO/3[8] calculations (Table II). Both methods give remarkably similar predictions concerning the structures of **2** and the 1-bicyclo[2.2.2]octyl cation **6**.[9] The unmodified molecular mechanics force field (Table II, column 6) does not take the strong electrostatic repulsion in **1** into account; a $C_1 \cdots C_4$ distance of 2.16 Å is predicted on this basis. Inclusion of a classical electrostatic repulsion term (Table II, column 7) raises the energy appreciably but the rigid molecular framework prevents more than a modest lengthening of the $C_1 \cdots C_4$ distance to 2.34 Å. Remarkably, the MINDO/3 method finds the $C_1 \cdots C_4$ distance (1.99 Å) to be significantly *shorter* than that predicted by the molecular mechanics force field even in the *absence* of any electrostatic repulsion (Table II). Furthermore, MINDO/3 predicts a $C_1 \cdots C_4$ shortening of 0.245 Å in going from **2** to **6**, but even greater contraction (0.358 Å) in going from **6** to **1**. Despite the two positive charges, the bridgehead carbons come closer together! What is the reason for this unexpected behavior?

The calculated bond orders suggest that the small 1,4 distance in **1** is due to the hyperconjugative transfer of electron density to the cationic centers which then participate in symmetry-allowed 1,4 bonding. This can be represented pictorially in **7**.[10]

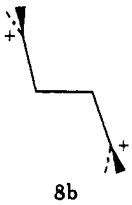
The existence of this interaction does not imply that 1,4 dications will prefer the cis orientation. MINDO/3 calculations for **8** in the cis and trans geometries **8a** and **8b** indicate that **8b** is more stable than **8a** but only by 11 kcal/mol, after correction for a difference in ground-state energies.



7



8a



8b

Apparently, when a 1,4 dication is locked in a cis geometry as in **1**, the 1,4-bonding interaction which develops helps to overcome the unfavorable electrostatic repulsion. This may account for the surprising stability of **1**.[10] Based on the calculations in Table II, the delocalized MINDO/3 structure for **1** is about 44 kcal/mol more stable than the molecular mechanics estimate with electrostatic repulsion. The interaction between each pair of peripheral 2p atomic orbitals in **1** (*e.g.*, ϕ_1 and ϕ_4 in **9**) and the central 2p atomic orbitals (ϕ_7 and ϕ_8) is topologically equivalent to, or isoconjugate with, those between the 2p atomic orbitals in the ρ molecular orbitals of cyclobutadiene.[11] Indeed, the situation is the same as in the transition state for cyclodimerization of ethylene.[11] In **9** there are, of course, three pairs of peripheral 2p atomic orbitals. Since, however, **1** has a threefold axis of symmetry, these must be replaced (*cf.* the Walsh orbitals of cyclopropane) by three linear combinations, *i.e.*

$$\psi_1 = (1/\sqrt{3})(\phi_1 + \phi_2 + \phi_3); \quad \psi_2 = (1/\sqrt{2})(\phi_2 - \phi_3);$$
$$\psi_3 = (1/\sqrt{6})(2\phi_1 - \phi_2 - \phi_3)$$
$$\psi_4 = (1/\sqrt{3})(\phi_4 + \phi_5 + \phi_6); \quad \psi_5 = (1/\sqrt{2})(\phi_5 - \phi_6);$$
$$\psi_6 = (1/\sqrt{6})(2\phi_4 - \phi_5 - \phi_6)$$

Only the symmetric combinations ψ_1 and ψ_4 can interact with ϕ_7 and ϕ_8 and the resulting four-orbital system is

---

(7) Calculations were carried out using a force field similar to that described by J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 4628 (1972).

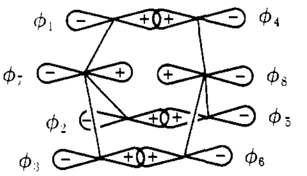
(8) R. C. Bingham, D. H. Lo, and M. J. S. Dewar, to be submitted for publication.

(9) Cation **6** has not been observed experimentally since it rearranges to the 1-bicyclo[3.3.0]octyl cation: G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **93**, 6873 (1971).

(10) The interesting 1,4-bicyclo[2.2.2]octyl diradical, which corresponds to the 1,4-bicyclo[2.2.2]octyl dication **1**, has recently been discussed by R. Hoffmann, *et al.* See R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971); R. Hoffmann and W-D. Stohrer, *J. Amer. Chem. Soc.*, **94**, 779 (1972). We also thank Professor R. Hoffmann for discussions and his interest in this work.

(11) See M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

again entirely equivalent to that in cyclobutadiene. Thus, since **1** is isoconjugate with the cyclobutadiene, dication $(CH)_4^{2+}$ should be aromatic. Whereas the parent cyclobutadiene dication was not yet observed under stable ion conditions, the tetramethylcyclobutadiene dication **10**[12a] as well as the tetraphenyl dication **11**[12b] were reported as stable 2π-aromatic systems. The lesser stability of **8a** can then be attributed to the overlap of the "empty" 2p atomic orbitals being less efficient than that of ϕ_7 and ϕ_8 in **9** (in addition, of course, to the adverse steric effect in **8a**) and the lesser stability of **3** to the absence of aromaticity. In order to relieve the unfavorable electrostatic repulsion between positive charges in **1**, MINDO/3 indicates that more than half of the charge is delocalized to the 12 hydrogen atoms with the charge at the cation centers, comparable to that found for the monocation **6**. Calculations seem to indicate that dication **1** thus approximates a doubly charged sphere with the positive charge distributed over its surface.[13]



9

Acknowledgment. Support of this work by the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Air Force Office of Scientific Research is gratefully acknowledged.

(12) (a) G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3667 (1969); (b) G. A. Olah and Gh. D. Mateescu, *ibid.*, **92**, 1430 (1970).

(13) An interesting report on bridgehead halide exchange appeared in which the dichloride **5** had been converted at room temperature to the corresponding diiodide. The mechanism, however, of this halogen exchange is still unclear. See, J. W. McKinley, R. E. Pincock, and W. B. Scott, *J. Amer. Chem. Soc.*, **95**, 2030 (1973).

G. A. Olah,* G. Liang
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

P. v. R. Schleyer, E. M. Engler
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

M. J. S. Dewar, R. C. Bingham
Department of Chemistry, University of Texas
Austin, Texas 87812

Received May 19, 1973

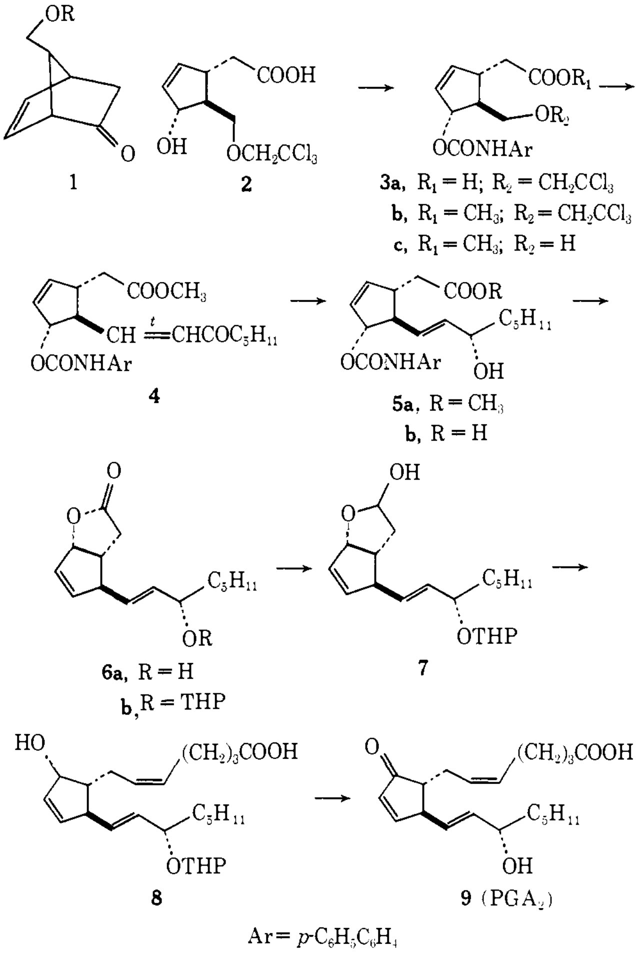
Direct, Stereocontrolled Synthesis of A Prostaglandins Using the Bicyclo[2.2.1]heptene Approach

Sir:

Earlier papers from this laboratory have described general and direct syntheses of all the primary (F_α and E) prostaglandins from a common intermediate.[1] We report here a novel modification of the general scheme which leads *directly* to A prostaglandins with stereochemical control. This route is of special practical value for the synthesis of analogs of A prostaglandins, currently of considerable interest in regard to medical treatment of hypertension. Further, since a stereocontrolled and efficient route from A prostaglandins to primary prostaglandins is now available,[2] this approach can even be applied to the generation of E and F type structures.[3]

The ketone **1** is available from thallous cyclopentadienide and bromomethyl 2,2,2-trichloroethyl ether without isolation of intermediates in 92% overall yield.[1c,e] Reaction of **1** either with peracid followed by aqueous base or with alkaline hydrogen peroxide[4] affords the hydroxy acid **2** in >95% yield (Scheme I). For storage, the acid labile **2** was converted to the crystalline ammonium salt by reaction in ether with ammonia gas. This ammonium salt was converted quantitatively to the *tert*-butyldimethylsilyl ester by stirring for 5 hr at 25° with an equivalent of *tert*-butyldimethylsilyl chloride, and the resulting ester was treated with *p*-phenylphenyl

Scheme I



---

(1) See (a) E. J. Corey, T. K. Schaaf, W. Huber, U. Koelliker, and N. M. Weinschenker, *J. Amer. Chem. Soc.*, **92**, 397 (1970); (b) E. J. Corey, R. Noyori, and T. K. Schaaf, *ibid.*, **92**, 2586 (1970); (c) E. J. Corey, S. M. Albonico, U. Koelliker, T. K. Schaaf, and R. K. Varma, *ibid.*, **93**, 1491 (1971); (d) E. J. Corey, H. Shirahama, H. Yamamoto, S. Terashima, A. Venkateswarlu, and T. K. Schaaf, *ibid.*, **93**, 1490 (1971); (e) E. J. Corey, T. Ravindranathan, and S. Terashima, *ibid.*, **93**, 4326 (1971); (f) E. J. Corey and R. K. Varma, *ibid.*, **93**, 7319 (1971); (g) E. J. Corey, K. B. Becker, and R. K. Varma, *ibid.*, **94**, 8616 (1972); (h) E. J. Corey and T. K. Schaaf, *J. Org. Chem.*, 37, 2921 (1972); (i) E. J. Corey, *Ann. N. Y. Acad. Sci.*, **180**, 24 (1971).

(2) E. J. Corey and H. E. Ensley, *J. Org. Chem.*, **38**, 3187 (1973).

(3) For a different and complimentary stereocontrolled synthesis of A prostaglandins see E. J. Corey and J. Mann, *J. Amer. Chem. Soc.*, **95**, 6832 (1973).

(4) N. M. Weinschenker and R. Stephenson, *J. Org. Chem.*, **37**, 3741 (1972).