was the corresponding hydrocarbon. In no case was the hydrocarbon formed quantitatively, a result which holds for the alkyldiazenes (eq 4). Data on product formation are included in Table I.

$$2RN{=}NH \longrightarrow RH + \text{other products} \qquad (4)$$

The alkyldiazenes so often postulated as intermediates can now be regarded as well-established, highly reactive compounds which have a significant and interesting chemistry. Further reports on monosubstituted diazenes will be made in due course.

(16) On leave from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Osaka, Japan.

(17) The authors are grateful for support from the National Institutes of Health, the Army Research Office (Durham), and the donors of the Petroleum Research Fund (PRF-3695-A1), administered by the American Chemical Society.

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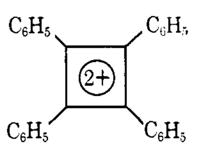
Received November 29, 1969

Stable Carbonium Ions. CI.[1] The Tetraphenylcyclobutadiene Dication[2]

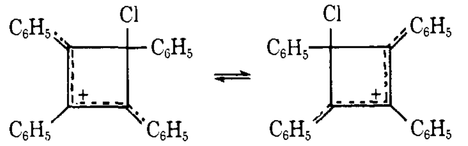
Sir:

We have recently reported the preparation and ^{1}H and ^{13}C nmr spectroscopic studies of the tetramethylcyclobutadiene dication,[3] the first well-defined four-membered ring (2 π electron) aromatic system.

Freedman reported previously the preparation of the tetraphenylcyclobutadiene dication **1** from 3,4-dibromotetraphenylcyclobutene and stannic bromide[4] but subsequently it was shown that only the monocation monodonor–acceptor complex **2** was obtained.[5–7]

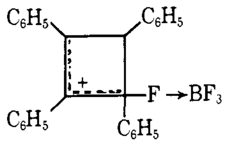


1



2

In continued work, Freedman and Young studied the metathetic reaction of 3,4-dibromotetraphenylcyclobutene with silver tetrafluoroborate[8] which indeed may have yielded the dication **1**. Unfortunately, with the exception of finding the expected 2 mol equiv of silver bromide eliminated in the reaction and observing the ^{19}F nmr of the tetrafluoroborate anion (from which, however, it may be difficult to differentiate the dication from a rapidly exchanging monofluoro cation–BF$_3$ system, **3**) no further characterization was given. Thus, until now, **1** was not satisfactorily characterized and we felt it of interest to extend our investigations to this ion.



3

We wish to report now the generation and characterization of the tetraphenylcyclobutadiene dication **1** by using the very strong SbF$_5$ and FSO$_3$H–SbF$_5$ acid systems as appropriate ionizing agents. When a saturated solution of antimony pentafluoride in sulfur dioxide was added with vigorous stirring at about −60° to a suspension of 3,4-dibromotetraphenylcyclobutene in sulfur dioxide, a dark red solution of **1** was obtained (it is uncertain whether the color is entirely due to the dication or to some possible impurities formed from the starting dibromide). The pmr spectrum of this solution (Figure 1a) shows a typical pattern of equivalent phenyl groups attached to a strong electron-withdrawing center: a doublet at δ 8.64 (*ortho*-), a triplet at δ 8.26 (*para*-), and a triplet at δ 7.87 (*meta*-hydrogen nuclei).[9] Further splitting of the main signals is due to long-range couplings. The best fitting nmr parameters were obtained from a computer-simulated spectrum[10] (Figure 1b): δ_o 8.644; δ_p 8.263; δ_m 7.868; $J_{om} = J_{o'm'} = 8.05$; $J_{op} = J_{o'p} = 1.15$; $J_{om'} = J_{o'm} = 0.30$; $J_{oo'} = 2.0$; $J_{mp} = J_{m'p} = 7.40$; $J_{mm'} = 0.80$ Hz. The proton deshielding in the *precursor* (δ 6.7–7.9),[11a] *monocation* (δ 7.5–8.3),[11b] *dication* (δ 7.9–8.7),[11c] sequence provides good evidence for the dication structure.

Methanolysis of solutions of **1** in the presence of sodium methoxide at −78° gave a mixture of dimethoxytetraphenylcyclobutenes (identified by nmr but not further studied relative to isomer distribution).

Carbon-13 magnetic resonance measurements strongly support the structure **1**. Using the indor technique we have found a ^{13}C chemical shift of +17.6 ppm (upfield from ^{13}CS$_2$) for the four-membered ring carbon atoms; the aromatic ^{13}C atoms gave two broad absorptions at 50 and 74 ppm, tentatively assigned to the *ortho* and *para*, and α and *meta* positions, respectively.

Comparing the δ ^{13}C +17.6 ppm value obtained for the tetraphenylcyclobutadiene dication to that (−14.4 ppm) reported for the tetramethylcyclobutadiene dication[3] suggests a significant participation of the phenyl rings in charge delocalization.

Using the simple HMO method (the size of the molecule did not allow use of extended Hückel or SCF

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(1) Part C: G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Lui, *J. Amer. Chem. Soc.*, in press.

(2) Reported in part at the 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969.

(3) G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3667 (1969).

(4) H. H. Freedman and A. M. Frantz, *ibid.*, **84**, 4165 (1962).

(5) D. G. Farnum and B. Webster, *ibid.*, **85**, 3502 (1963).

(6) R. F. Bryan, *ibid.*, **86**, 733 (1964).

(7) H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964).

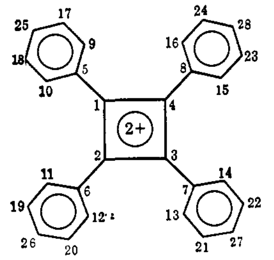
(8) A method found effective to produce carbonium ions under acid-free conditions [G. A. Olah, A. E. Pavlath, and J. A. Olah, *ibid.*, **80**, 6540 (1958)].

(9) The same pattern is obtained with a FSO$_3$H–SbF$_5$–SO$_2$ solution, however, with some loss of resolution and a downfield shift (*ca.* 0.4 ppm) of the lines. Resolution is further impaired in the SbF$_5$–SO$_2$ClF solution.

(10) Program, LAOCOON III (A. A. Bothner-By and S. Castellano); computer, Univac 1108; recorder, CALCOMP 663 (California Computer Prod., Inc.).

(11) Actually the deshielding is probably larger in the monocation–dication step, since we have made no solvent-shift correction (in SO$_2$ signals would appear at a higher field); (a) in SO$_2$ solution at −60°; (b) methylene chloride solution, reported by Freedman;[4] (c) SbF$_5$–SO$_2$ solution, present work.

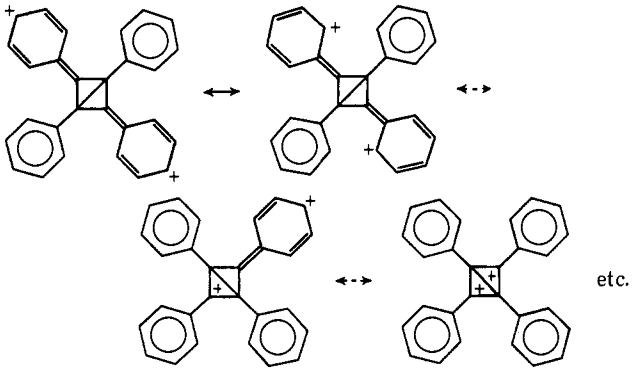
Table I. Electron Density and Bond Order in Tetraphenylcyclobutadiene Dication



$q_{1,2,3,4} = 0.714$
$q_{5,6,7,8} = 1.000$
$q_{9,10,11,12,13,14,15,16} = 0.928$
$q_{17,18,19,20,21,22,23,24} = 1.000$
$q_{25,26,27,28} = 0.928$

$p_{1,2;\ 2,3;\ 3,4;\ 1,4} = 0.454$
$p_{1,5;\ 2,6;\ 3,7;\ 4,8} = 0.473$
$p_{6,9;\ 5,10;\ 6,11;\ 6,12;\ 7,13;\ 7,14;\ 8,15;\ 8,16} = 0.577$
$p_{9,17;\ 10,18;\ 11,19;\ 12,20;\ 13,21;\ 14,22;\ 15,23;\ 16,24} = 0.689$
$p_{17,25;\ 18,25;\ 19,26;\ 20,26;\ 21,27;\ 22,27;\ 23,28;\ 24,28} = 0.649$
$p_{1,3} = 0.285$

calculations) we have computed the charge distribution and bond-order pattern in the tetraphenylcyclobutadiene dication (see Table I) which is in good agreement with the experimental results. The calculated bond-order values indicate that the exocyclic C–C bonds have more double bond character than those of the four-membered ring; 1–3 interaction is also predicted. Significant contribution of canonical forms like the ones depicted to the mesomeric structure of the ion is therefore suggested.



It is interesting to compare the experimental and theoretical data obtained so far with the cyclobutadiene dications and cyclopropenium cations. Taking triphenylmethanol as a "suitable model compound," Ray, Colter, and Kurland[12] have estimated that in the triphenylcyclopropenium cation[13] the net amount of charge apparently withdrawn from the cyclopropenium ring is small, as predicted by Hückel molecular orbital calculations.[14] Recent extended Hückel calculation by Hoffmann[15] shows that in arylcyclopropenium systems, charge is delocalized even if the effect on energy is not significant (especially in the case of phenylcyclopropenium ion). However, a progression in stability with phenyl substitution seems to be indicative of a conjugative interaction.

We have measured the ^{13}C chemical shift of the unsubstituted cyclopropenium cation[16] and found it at +17.8 ppm. Comparison with the corresponding value (+38.8 ppm) reported for the triphenyl derivative[12] clearly reveals phenyl participation in charge delocalization.

The validity of the Spiesecke–Schneider correlation of ^{13}C shifts and aromatic π-electron densities[17] can now be extended to the 2 π electron systems (Figure 2).

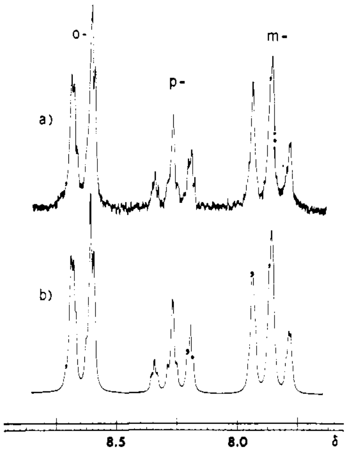


Figure 1. The 100-MHz proton magnetic resonance spectrum of **1** in SbF_5-SO_2 at −40° (a) and the computer simulated spectrum (b).

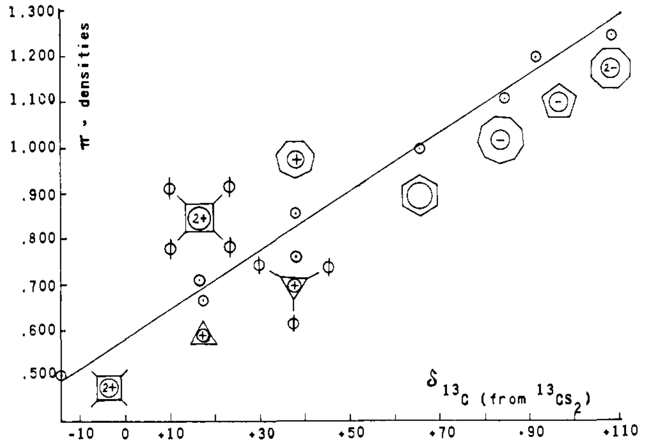


Figure 2. Correlation of ^{13}C chemical shift and π-electron density in aromatic systems.

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(12) G. J. Ray, A. K. Colter, and R. J. Kurland, *Chem. Phys. Lett.*, **2**, 324 (1968).

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(15) R. Hoffmann, R. Bissel, and D. G. Farnum, *J. Phys. Chem.*, **73**, 1789 (1969).

(16) R. Breslow, T. J. Groves, and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 5048 (1967). We thank Professor Breslow for a sample of cyclopropenyl chloride.

(17) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

Acknowledgment. We are grateful to Dr. H. H. Freedman for a sample of 3,4-dibromotetraphenylcyclobutene. Partial support of the work by the National Science Foundation and the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged.

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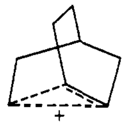
Stable Carbonium Ions. CII.[1]

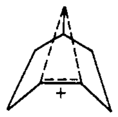
The Bicyclo[3.3.0]-1-octyl Cation and Its Preferential Formation from Bicyclo[3.2.1]- and -[2.2.2]octyl Systems under Long-Lived Ion Conditions

Sir:

Solvolytic carbonium ion reactions of bicyclo[2.2.2]-2-octyl derivatives yield both bicyclo[2.2.2]- and -[3.2.1]-octyl products, the result of rearrangements of the initially formed bicyclo[2.2.2]-2-octyl cation.[2,3] Further rearrangements are necessary to produce bicyclo[3.3.0]-octyl cations, but apparently solvent capture occurs before this can proceed. However, when initial rearrangement can produce these ions, bicyclo[3.3.0]octyl products are dominant, as in the case of solvolysis of *exo*- and *endo*-bicyclo[3.2.1]octyl 8-tosylates.[4] Solvolysis of bicyclo[3.3.0]-2-octyl derivatives give mainly unrearranged products[5] or the rearranged bicyclo-[3.3.0]-1-octyl and -8-octyl derivatives. Bicyclo[3.3.0]-octyl products have also been observed upon the treatment of decalin with aluminum chloride,[7] or cyclooctene oxide with lithium diethylamide,[8] and from a variety of unsaturated precursors, *e.g.*, cyclooct-4-en-1-ly tosylate,[6] *cis,cis*-1,5-cyclooctadiene,[9,10] octamethyltricyclooctadienes,[11] benzobicyclo[2.2.2]octadienol,[12] and cyclooctadienyllithium.[13]

Barrett and Linstead reported the conversion of the [3.3.0]octane to the [3.2.1] isomer with aluminum chloride.[14] Schleyer and coworkers have equilibrated all three hydrocarbons with aluminum bromide at 23–72° and have shown the order of stability of the ring systems to be [3.2.1] > [3.3.0] > [2.2.2].[15] Although bicyclo[3.3.0]octane is more strained (1.9 kcal/mol)[16] than either of the other two isomers, its high entropy indicates it should be the most stable of the isomers above 378 °K.[15]


1


2

Although the carbonium ions in solvolysis reactions of bicyclo[2.2.2]- and -[3.2.1]octyl derivatives have been ascribed nonclassical character, as in **1** and **2**, respectively,[2] we wish to report that, under long-lived ion conditions in superacid media, all bicyclooctyl systems rearrange to the more stable tertiary bridgehead bicyclo-[3.3.0]-1-octyl cation **14**. This ion is produced by ionization, hydride abstraction, or protonation from a variety of precursors as shown in Scheme I.

When bicyclo[2.2.2]-1-octyl chloride (**3**) is ionized in $FSO_3H-SbF_5-SO_2ClF$ at −70°, the tertiary ion formed (**7**) must undergo a 1,2-hydride shift to give the secondary ion **8**, also produced by ionization of the secondary derivatives **4** and **5**, or by hydride abstraction (in SbF_5-SO_2ClF) from the hydrocarbon **6**. A Wagner–Meerwein shift would then yield ion **10**, also obtained directly by ionization of bicyclo[3.2.1]-2-octanol (**9**). Hydride shifts and a second rearrangement would give the secondary [3.3.0] ion **15**, also obtained directly by ionization of *endo-cis*-bicyclo[3.3.0]-2-octanol (**17**) or bicyclo[3.-3.0]octane (**18**) or by protonation and ring opening of the tricyclic hydrocarbon **16** in $FSO_3H-SbF_5-SO_2ClF$. A final 1,2-hydride shift would give the observed tertiary [3.3.0] ion **14** (Figure 1), which on quenching in either KOH–ice or MeOH–MeONa suspensions at low temperature gives *cis*-bicyclo[3.3.0]-1-octanol or its methyl ether, respectively, as shown by nmr and glpc comparisons with authentic materials.[17] That the [3.3.0] ion **14** is formed in preference to the other possible tertiary ions may be due simply to the fact that in the latter cases (*i.e.*, the [2.2.2]- and [3.2.1]-1-octyl cations) the carbonium ion center is at the bridgehead and cannot become planar.[18] Secondary ions require stabilization by σ delocalization (**1** and **2**) and are obviously less favorable than a classical planar tertiary ion.[19]

As we observed that cyclodecanol undergoes a transannular reaction in $FSO_3H-SbF_5-SO_2ClF$ to give the bicyclo[4.4.0]decyl cation,[20] we were interested in whether cyclooctanol would give the [3.3.0] ion **14** under the same conditions. No evidence of *cis*-1-methoxybicyclo[3.3.0]octane[21] was found in the meth-

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(1) Part CI: G. A. Olah and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 1430 (1970).

(2) J. Berson in "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 213–226; H. Kwart and J. L. Irvine, *J. Amer. Chem. Soc.*, **91**, 5541 (1969).

(3) Solvolysis of bicyclo[3.2.1]-2-octyl tosylate also gives some bicyclo[2.2.2]octyl products: H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2848, 2856, 2862 (1968).

(4) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

(5) H. C. Brown and W. J. Hammar, *J. Amer. Chem. Soc.*, **89**, 6378 (1967). Small amounts (~8%) of bicyclo[3.3.0]-1-octyl and -[3.2.1]-8-octyl acetates were observed by Closson and Kwiatkowski.[6]

(6) W. D. Closson and G. T. Kwiatkowski, *Tetrahedron Lett.*, 6345 (1966); A. C. Cope, J. M. Grisar, and P. E. Peterson, *J. Amer. Chem. Soc.*, 82, 4299 (1960); A. C. Cope and P. E. Peterson, *ibid.*, 81, 1643 (1959).

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(8) A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2849 (1958).

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(12) A. C. Gray, T. Kakihana, P. M. Collins, and H. Hart, *ibid.*, **89**, 4556 (1967).

(13) R. B. Bates and D. A. McCombs, *Tetrahedron Lett.*, 977 (1967).

(14) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936).

(15) P. von R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Amer. Chem. Soc.*, 85, 1358 (1963).

(16) This value is somewhat less than that calculated (5.6 kcal/mol) by N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968).

(17) We are indebted to Professor R. Fort for a sample of *cis*-bicyclo-[3.3.0]octan-1-ol (nmr δ 2.05 (m), 1.79 (m)), from which we prepared the methyl ether by a modification (refluxing THF for 2 days) of the method of C. H. Hurd and W. H. Saunders, *ibid.*, **74**, 5324 (1952); nmr δ ($CDCl_3$) 3.2 (s, 3 H, OMe), 2.1–1.0 (m, 13 H); ir ν_{C-O} 1090 cm^{-1}.

(18) R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 284 (1967); G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

(19) This is not the case in the bicyclo[2.2.1]heptyl system, however, since the corresponding tertiary [3.2.0] ion could not become planar.

(20) To be published.

(21) Less than 1% of quenched material with the same retention time as an authentic sample.