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Stable Carbonium Ions. LXXXIX.[1]
The Tetramethylcyclobutenium Dication, an Aromatic 2 π-Electron System

Sir:

Simple molecular orbital theory predicts that the cyclobutenium dication should have aromatic resonance stabilization because it is a planar, monocyclic system containing $4n + 2$ ($n = 0$) π electrons.[2] A number of investigators have tried to prepare this dication or its derivatives but were unsuccessful.[3,4] The tetraphenylcyclobutenium dication was reported by Freedman, but X-ray crystallographic studies on an isolated crystalline salt showed the monocation mono-donor–acceptor structure.[5,6] There is now the serious possibility that exchange phenomena involving the monocation monodonor–acceptor complex and not the dication are responsible for the observed apparent equivalence of the phenyl groups in pmr studies in solution.[5]

The preparation of the tetramethylchlorocyclobutenium cation **2** from tetramethylcyclobutenyl dichloride **1** and silver hexafluoroantimonate has been reported by Katz.[7] He and others have reported the preparation of other derivatives of this monocation.[8] Since the work of Breslow on cyclopropenium cations indicates that alkyl groups make an aromatic cation thermodynamically more stable than aryl groups[9] (the kinetic stability might, however, be decreased), we felt that the tetramethylcyclobutenium dication might be stable in $SbF_5–SO_2$ solution.

We wish now to report our success in preparing the tetramethylcyclobutenium dication, the first well-defined cyclobutenyl dication. When **1**[10] was added to $SbF_5–SO_2$ at −78°, a very pale yellow solution was formed whose nmr spectrum was identical with that

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

(2) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, p 122. This book contains many other relevant references, and a complete discussion of cyclobutenium dications is recorded in Chapter 3.

(3) D. G. Farnum, M. A. T. Heybey, and B. Webster, *J. Amer. Chem. Soc.*, **86**, 673 (1964); *Tetrahedron Lett.*, 307 (1963).

(4) The 1,3-dihydroxydiphenylcyclobutenium dication (D. G. Farnum and B. Webster, *J. Am. Chem. Soc.*, **85**, 3502 (1963)) is apparently accepted as a cyclobutenium dication. However, G. A. Olah and A. M. White (*ibid.*, **87**, 4752 (1967)) have suggested that diprotonated squaric acid is better represented as a diprotonated diketone rather than as tetrahydroxycyclobutenium dication, based on the chemical shift of the protons on oxygen. A ¹³C nmr study should, however, clarify this point.

(5) R. F. Bryan, *J. Amer. Chem. Soc.*, **86**, 733 (1964); H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

(6) H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964); H. H. Freedman, personal communication, Feb 1969.

(7) T. J. Katz and E. G. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964); T. J. Katz, J. R. Hall, and W. C. Neikam, *ibid.*, **84**, 3199 (1962).

(8) E. H. Gold and T. J. Katz, *J. Org. Chem.*, **31**, 372 (1966); C. F. Wilcox, Jr., and D. L. Nealy, *ibid.*, **39**, 3668 (1964); **28**, 3446 (1963).

(9) R. Breslow, H. Höver, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

(10) R. Criegee and A. Moschel, *Chem. Ber.*, **92**, 2181 (1959).
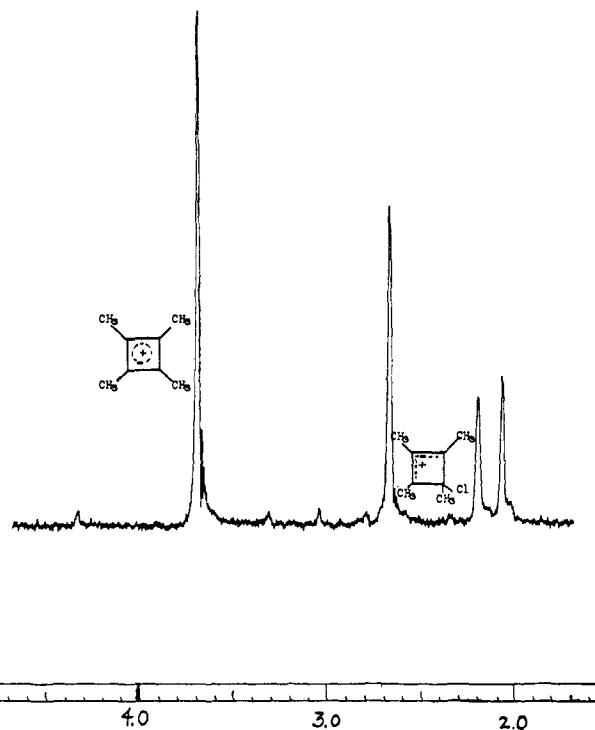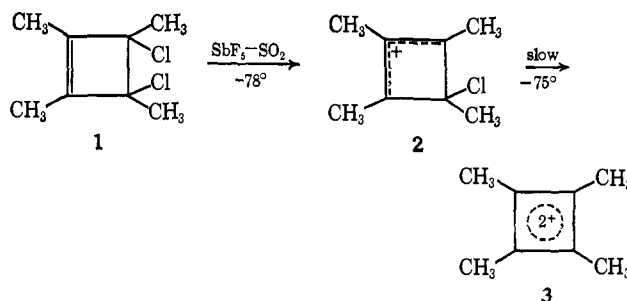

Figure 1. Nmr spectrum of tetramethylcyclobutene dichloride in $SbF_5–SO_2$ solution at −65°.

previously reported by Katz for ion **2** in SO_2 solution.

After several minutes at −75°, a single new absorption appeared as a sharp singlet at δ 3.68. The rate of appearance of the species giving this singlet increased with increasing temperature and was apparently formed irreversibly. In order to generate a maximum concentration of this ion (which we believe to be **3**) in SO_2 the temperature was maintained at or below about −65° because at higher temperatures absorptions characteristic of **2** disappeared but were not proportionately replaced by the single line of **3**. About 60% of **2** could be converted to **3** before appreciable decomposition took place at −65°. Figure 1 is a typical spectrum.

Solutions of ion **2** in $FSO_3H–SO_2$ are completely stable at −78° for at least 2 weeks. Solutions of **2** in $SbF_5–SO_2$ show a maximum concentration of **3** at −78° after approximately 24 hr, and, thereafter, decomposition takes place to another species whose structure we have been unable to determine. Solutions of **2** in 1:1 $HFSO_3–SbF_5$ in SO_2 are more than 80% decomposed after only 6 hr at −78°. Decomposition of these solutions can take place through the reaction of the dication **3** with the monocation **2**. The dimeric species can be quenched in methanol–sodium methoxide at −78° to a white crystalline solid containing chlorine but no methoxyl groups.[11] We have not yet been able to assign a

structure to this material. When **1** was dissolved in SbF_5–SO_2ClF at $-78°$, no absorptions characteristic of **2** could be observed. Instead only the single line, somewhat viscosity broadened, characteristic of the dication **3**, appeared at δ 4.11. The dication was considerably more stable in this medium. It showed no decomposition after 24 hr at $-78°$ and showed no detectable decomposition after 15 min at $-40°$.[12,13]

We believe the species giving rise to the singlet absorption in these solutions is the tetramethylcyclobutenium dication **3** for the following reasons: (1) The chemical shift of the methyl protons and singlet nature of the absorption are consistent with this structure. We have estimated a chemical shift of δ 3.2 in SbF_5–SO_2 solution (the estimate would be δ 3.5 in SbF_5–SO_2ClF) for **3** assuming the same amount of deshielding for the second ionization as observed for the first ionization yielding **2**. This suggests that the observed shift is a reasonable one for the dication **3**. (2) None of this species is formed in FSO_3H–SO_2, although ionization to the monocation **2** is complete. In 1:1 FSO_3H–SbF_5 diluted with SO_2, the singlet producing species is also incompletely formed and is less stable chemically than in SbF_5 media. (3) Methanolysis of solutions containing a maximum concentration of **3** in SO_2 in the presence of sodium methoxide at $-78°$ gave in 75–80% yields a mixture of cis- and trans-3,4-dimethoxytetramethylcyclobutene-1 (the relative amounts were 55 and 45%, but we did not assign the stereochemistry). When **2** was solvolyzed under identical conditions, a similar result was obtained, but the proportions of the isomers changed to 15 and 85%.[14] When the dichloride itself was treated with sodium methoxide in methanol at room temperature, the ethers were obtained in the proportion of 3 and 97%. (4) The ^{13}C chemical shift of the ring carbon atoms is consistent with the dication formulation, but inconsistent with other formulations. The ^{13}C chemical shift of the ring carbon atom in the dication was obtained in natural abundance using the indor method.[15] The three-bond carbon–hydrogen coupling constant was found to be 4.0 Hz and the ^{13}C chemical shift in SbF_5–SO_2 solution at $-70°$ to be -14.4 ppm (from CS_2). In SbF_5–SO_2ClF solution this shift was -15.8 ppm. Spiesecke and Schneider[16] have measured the ^{13}C shifts for

species like $C_5H_5^-$, C_6H_6, $C_7H_7^+$, and $C_8H_8^{2-}$ for which the π-electron densities are taken as known (i.e., benzene = 1, tropylium ion = 0.86, etc.) and obtained a linear relationship with a dependence of 160 ppm per π electron. In the cyclobutenium dication, the π-electron density is 0.5, giving a chemical shift relative to benzene of 80.0 ppm or -14.4 ppm from CS_2, a value identical with that obtained for the tetramethylcyclobutenium dication in SO_2 solution. The effect of the methyl groups on the ^{13}C shift will be small and will be similar to the 4.6 ppm observed on comparing hexamethylbenzene with benzene,[17] and thus the observed chemical shift provides convincing evidence for the proposed dication structure of the ion. The observed chemical shift rules out the alternate possibility that the ion has the rapidly exchanging monocation mono-donor–acceptor complex structure. The predicted shift for such a species can be estimated from shifts observed in the precursor to the ion and the t-butyl cation. The ^{13}C data for the precursor (together with dication **3**) are summarized in Table I, and using these values

Chart I. Nmr Chemical Shifts and Coupling Constants for Tetramethylcyclobutenyl Dichloride[a] and the Tetramethylcyclobutenium Dication

δ_{H_A}1.15; δ_{H_B}1.26

δ_{C_1}, δ_{C_4}+52.2; δ_{C_2}, δ_{C_3}+115.6

J_{HC-C_2} = J_{HC-C_1} = 6.0 Hz

$J_{HC_2-C\,H}$ = $J_{HC_1-C_2-H}$ = 0.0 Hz

$J_{H-C_1-C_4-H}$ = 1.3 Hz

δ_H 3.68 (SbF_5–SO_2)

4.11 (SbF_5–SO_2ClF)

δ_C -14.4 (SbF_5–SO_2)

-15.7 (SbF_5–$SOClF$)

J_{CCH} = 4.0 Hz

[a] Proton shifts (δ in ppm from internal TMS) and ^{13}C shifts (δ in ppm from $^{13}CS_2$) were obtained in CCl_4 solutions at room temperature.

gives an averaged, estimated shift of $+20$ ppm. If bridging of the chlorine occurs, this estimated shift would be increased to 55 ppm (using the tetramethylethylenechloronium ion as a model). Our previous experience in ^{13}C studies of equilibrating carbonium ions has shown that the maximum error involved in predicting shifts using this approach is 10 ppm, and we thus regard the observed shift as being incompatible with a monocation formulation of the stable ion.

In conclusion, the ^1H and ^{13}C nmr spectral data presented provide strong evidence for the observation of the tetramethylcyclobutenium dication, a 2 π-electron aromatic system similar to Breslow's cyclopropenium cation.[18]

(11) This crystalline solid has a wide melting range (75–100°) after recrystallization and sublimation. This suggests a mixture of stereoisomers. Its nmr spectrum shows one methyl on saturated carbon at δ 1.56, two methyls on double bonds coupled by 1.1 Hz at δ 1.63 and 1.69, and a two-proton AB quartet, J_{AB} = 13.6 Hz, at δ 3.12 and 3.34 (CCl_4 from internal TMS).

(12) The acidity of the medium is not decreased as much on dilution with SO_2ClF as it is with SO_2 because the nucleophilicity of this solvent is considerably less than that of SO_2. This effect is evidenced indirectly in that acid media diluted with SO_2ClF are better hydride abstracters than when diluted with SO_2. However, resolution of the spectra is generally poorer, and it is usual to observe the chemical shifts of cations about 0.3 to 0.4 ppm to lower field than the same ions in SO_2; cf. G. A. Olah and J. Lukas, J. Amer. Chem. Soc., **89**, 4739 (1967).
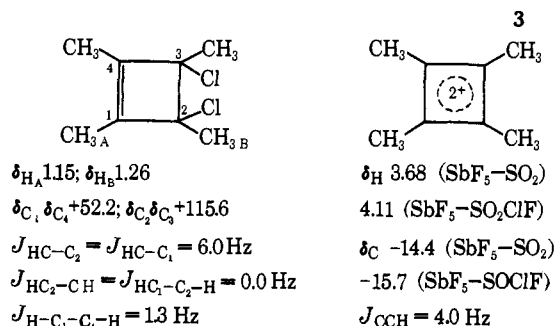
(13) As another possible route to this dication, we added (tetramethylcyclobutadiene)nickel dichloride (R. Criegee and G. Schröder, Ann., **623**, 1 (1959)) to SbF_5–SO_2. An orange solution developed whose nmr spectrum at $-60°$ showed a broadened singlet at δ 1.45. This may be the (tetramethylcyclobutadiene)nickel(II) ion.

(14) Methanolysis of the SO_2ClF solutions was performed at $-90°$ since this reaction is considerably more vigorous than quenching SO_2 solutions, and yields of the dimethyl ethers varied between 55 and 60%. Identification of the materials isolated from the various quenching experiments was made on the basis of nmr and ir spectral comparison with material prepared according to I. V. Smirnov-Smakov (Dokl. Akad. Nauk SSSR **83**, 869 (1952); Chem. Abstr., **47**, 2711h (1953)) by reaction of sodium methoxide with **1**.

(15) A. M. White and G. A. Olah, J. Amer. Chem. Soc., **91**, 2943 (1969).

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

(17) P. C. Lauterbur, J. Amer. Chem. Soc., **83**, 1838 (1961).

(18) NOTE ADDED IN PROOF. We have now obtained (with Gh. D. Mateescu) the ^{13}C nmr shift of Breslow's cyclopropenium cation (R. Breslow, T. J. Groves, and G. Ryan, ibid., **89**, 5048 (1967)) which we prepared from cyclopropenyl chloride in SbF–SO_2 solution at $-60°$. The experimental $\delta_{^{13}C}$ = $+17.8$ ppm (J_{CH} = 262 Hz) compares well with a value of $+12.3$ ppm calculated using a shift dependence of 160 ppm per π electron. This agreement provides further confimation of the validity of the relation of ^{13}C shifts and aromatic π-electron densities for 2 π electron systems. We are indebted to Professor R. Breslow for a sample of cyclopropenyl chloride.

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Solvent Effects on the Iodine–Pyridine Charge-Transfer Complex

Sir:

Some recent results obtained by various physical-chemical techniques indicate that the formation constant of a molecular complex is strongly solvent dependent.[1–6] However, no direct comparison has been made between values of the formation constant and physical properties of the solvents. In the present communication, we wish to present our results for the iodine–pyridine complex in various solvents, since the variation of the equilibrium constant with solvent-interaction force is significant. We shall then interpret our results on the basis of a theory developed recently by Buchowski, *et al.*[7] Finally, we shall present
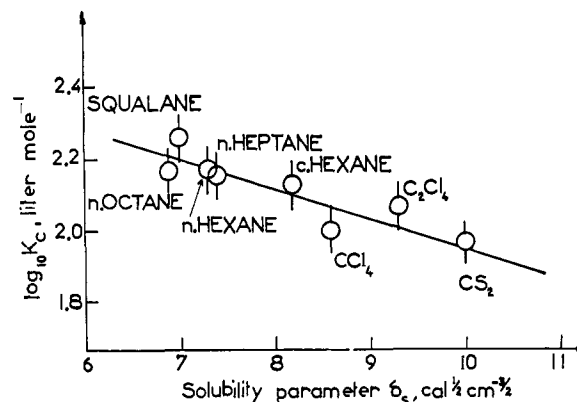

Figure 1. Plot of the logarithm of the equilibrium constant of the iodine–pyridine complex *vs.* the solubility parameter of the solvents.

pyridine varied between 6.2×10^{-4} and 0.25 mole/l. The equilibrium constant K_c expressed in l./mole (Table I) was determined[11,12] by following both the decrease in intensity of the free iodine band and the increase in intensity of the complexed iodine band with increasing pyridine concentration. All the solvents chosen are nonpolar. Nevertheless, it is possible to

Table I. Solvent Effects on the Equilibrium Constant of the Iodine–Pyridine Complex on the Iodine Bands and on the Charge-Transfer Band

Solvent	$\delta_s{}^a$	V_s, cm^3	K_c (25°), l. mole^{-1}	Log K_c	Free I$_2$ band, Å	Complexed I$_2$ band, Å	C–T band, Å
$C_{30}H_{64}{}^b$	7.0		185 ± 12	2.26	5230 ± 5	4235 ± 10	2325 ± 5
i-C$_8$H$_{18}$	6.9	166	150 ± 9	2.17	5220 ± 5	4230 ± 10	2342 ± 2
n-C$_6$H$_{14}$	7.3	132	148 ± 8	2.17	5225 ± 5	4235 ± 10	2346 ± 2
n-C$_7$H$_{16}$	7.4	149	142 ± 8	2.15	5230 ± 5	4235 ± 10	2347 ± 2
c-C$_6$H$_{12}$	8.2	109	135 ± 8	2.13	5235 ± 5	4230 ± 10	2365 ± 3
CCl$_4$	8.6	97	102 ± 6	2.00	5175 ± 5	4170 ± 10	2425 ± 10
C$_2$Cl$_4$	9.3	103	119 ± 7	2.07	5180 ± 5	4175 ± 10	
CS$_2$	10.0	61	95 ± 6	1.97	5195 ± 5	4190 ± 10	
Pyridine	10.7						2450^c

^{a} Solubility parameter of the solvent, expressed in cal$^{1/2}$ cm$^{-3/2}$ (ref 13). ^{b} Squalane or 2,6,10,15,19,23-hexamethyltetracosane; its solubility parameter $\delta_s = 7.0 \pm 0.5$ was evaluated from its evaporation temperatures at several temperature. ^{c} From ref 8.

our analysis of solvent effects on the frequencies of free and complexed iodine absorption bands and on the energy of the charge transfer.

The absorption spectrum of the iodine–pyridine complex has already been examined by numerous authors.[8–10] Although the equilibrium constant of this complex in three solvents has been determined, the values were reported by three different authors and hence cannot be directly compared.

We have determined the equilibrium constant of the iodine–pyridine complex in a series of nonpolar solvents at 25° using a Cary 14 spectrophotometer. The initial concentration of iodine was 10^{-4} mole/l. while that of

(1) M. Kroll, *J. Am. Chem. Soc.*, **90**, 1097 (1968).
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(3) J. Prochorow and A. Tramer, *J. Chem. Phys.*, **44**, 4545 (1967).
(4) R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *J. Am. Chem. Soc.*, **88**, 2717 (1966).
(5) E. M. Voigt, *J. Phys. Chem.*, **70**, 598 (1966).
(6) J. Grundnes and S. D. Christian, *J. Am. Chem. Soc.*, **90**, 2239 (1968).
(7) H. Buchowski, J. Devaure, P. V. Huong, and J. Lascombe, *Bull. Soc. Chim. Fr.*, 2532 (1966).
(8) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3871 (1954).
(9) A. G. Maki and E. K. Plyler, *J. Phys. Chem.*, **66**, 766 (1962).
(10) A. I. Popov and R. H. Rygg, *J. Am. Chem. Soc.*, **79**, 4622 (1957).

detect significant variations of the equilibrium constant, which decreases when the interaction with the solvent increases.

According to the calculation of Buchowski, *et al.*,[7] which is based on Hildebrand–Scott theories of solutions,[13] the equilibrium constant K_c of a donor–acceptor complex can be related to the solubility parameter[13] δ_s of the solvent by the relation

$$\log K_c = a + b\delta_s$$

where a and b depend only on the properties of the donor and acceptor. In the case of the iodine–pyridine complex, the experimental results can be interpreted on the basis of this relation, as shown in Figure 1, where b is positive. When the equilibrium constant of a molecular complex increases with the solvent interaction as in the case of the trimethylamine–sulfur dioxide complex considered by Grundnes and Christian,[6] the coefficient b should have an opposite sign.

(11) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).
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(13) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Dover Publications, New York, N. Y., 1964.