properties of which are in good accord with those reported by Huffman[11] and his associates.

Acknowledgment. We wish to thank Mr. M. Murakami for his technical assistance.

---

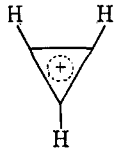
[11] We thank Professor Huffman for sending a copy of the infrared spectrum of desethyligogamine.

Wataru Nagata, Shoichi Hirai, Kyozo Kawata, Tamotsu Okumura
Shionogi Research Laboratory, Shionogi & Co., Ltd.
Fukushima-ku, Osaka, Japan
Received July 6, 1967

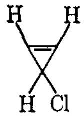
Cyclopropenyl Cation

Sir:

Following the synthesis of triphenylcyclopropenyl cation,[1] a number of other derivatives of this simplest aromatic system have been prepared.[2] The properties of these species, particularly in comparison with related compounds,[3] show clearly that the two π-electron cyclopropenyl cation is strongly stabilized by conjugation and meets other criteria of aromaticity. However, the properties of the parent cyclopropenyl cation (I) are still of considerable interest. We wish to report the synthesis of this cation as an isolable salt and some evidence on its stability.


I

We have previously reported[4] that the reduction of tetrachlorocyclopropene with tri-*n*-butyltin hydride affords a mixture of mono-, di-, and trichlorocyclopropenes; the dichlorocyclopropenes were converted to cyclopropenone.[4] Under appropriate conditions one can produce a mixture of mono- and dichlorocyclopropenes from which 3-chlorocyclopropene (II) is isolated by preparative glpc (5-ft 3% SE-30 on Chromosorb G at 22°) in 22% over-all yield. The mass spectrum shows the parent ion at m/e 74 (and 76), chlorocyclopropenyl cation at m/e 73 (and 75), and a very strong peak (85% of total intensity) for cyclopropenyl cation at m/e 39. The infrared spectrum (CCl_4 solution) has bands at 3080, 2970, 1615, 1245, 1155, 1120, 1025, and 865 cm^{-1}. In the nmr, II (in CCl_4 at 40°) shows a two-proton doublet at δ 7.57 and a one-proton triplet at δ 4.23 (J = 1.5 cps). In SO_2 (−40°) the chlorine rapidly moves from one carbon to another, presumably by reversible ionization to I, and a single sharp nmr line appears at δ 6.72, the weighted average position. In acetonitrile solution, the exchange rate is intermediate and lines from II are broadened beyond detection; the $\Delta H^{\neq}$ for this process must be quite small since the spectrum is unresolved from −40 to +40°.


II

On mixing solutions of II and $SbCl_5$ in CH_2Cl_2, cyclopropenyl hexachloroantimonate ($I\text{-}SbCl_6^-$) is precipitated as a white solid in quantitative yield and almost analytical purity (*Anal.* Found: C, 10.37; H, 1.42). The compound is stable for long periods at −20° and for several hours at room temperature, but on heating it darkens with no well-defined decomposition (or melting) point. Exposure to atmospheric moisture causes rapid blackening. The infrared spectrum[5] (mulls in Nujol or in CCl_4) shows only four bands in the usual region: 3105, 1276, 908, and 738 cm^{-1}. The first and third are C–H stretching and bending frequencies, while the second and fourth correspond to the two skeletal E′ bands reported[2e] for trichlorocyclopropenyl cation in this region. The nmr spectrum (in CH_3CN with $SbCl_5$) shows a single peak at δ 11.1 with singlet (half-width 0.75 cps) ^{13}C satellites ($J_{^{13}C-H}$ = 265 cps). The ^{13}C coupling constant is larger than those[4] for cyclopropenes or cyclopropenone, as in the case of other[6] carbonium ions. The satellites should be triplets, but the H–H coupling constant is expected to be small. In FSO_3H this salt has its signal at δ 10.87.[7] When II is treated with $AgBF_4$ in CH_3CN or SO_2 at −40°, AgCl precipitates and solutions of $I\text{-}BF_4^-$ are produced identical in nmr with the above.

The observations on the stability of I, and in particular the fact that it is readily prepared but that II is covalent even in SO_2, are consistent with our previous[2b] extrapolations from substituted derivatives. Further work will be required to determine thermodynamic quantities of interest for I, and these must be interpreted[2a,d] in terms of both the conjugative and the strain factors which are involved. However, the fact that a salt of I can be prepared under such mild conditions is further evidence for the aromatic character of this system.[8]

---

[1] R. Breslow, *J. Am. Chem. Soc.*, **79**, 5318 (1957).

[2] (a) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961); (b) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961); (c) D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960); (d) R. Breslow, H. Höver, and H. W. Chang, *ibid.*, **84**, 3168 (1962); (e) R. West, A. Sadô, and S. Tobey, *ibid.*, **88**, 2488 (1966); (f) for a review see A. W. Krebs, *Angew. Chem. Intern. Ed. Engl.*, 4, 10 (1965).

[3] R. Breslow, W. Bahary, and W. Reinmuth, *J. Am. Chem. Soc.*, **83**, 1763 (1961); R. Breslow and P. Dowd, *ibid.*, **85**, 2729 (1963).

[4] R. Breslow and G. Ryan, *ibid.*, **89**, 3073 (1967).

[5] These bands disappear on exposure to atmospheric moisture in favor of a complex new spectrum.

[6] *Cf.* G. Olah, E. Baker, J. Evans, W. Tolgyesi, J. McIntyre, and I. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

[7] *Cf.* D. G. Farnum, G. Mehta, and R. S. Silberman, *ibid.*, **89**, 5048 (1967).

[8] This work was supported by the National Institutes of Health, through GM-13651 and a predoctoral fellowship for J. T. G.

Ronald Breslow, John T. Groves, Gordon Ryan
Department of Chemistry, Columbia University
New York, New York 10027
Received July 31, 1967

Ester Decarbonylation as a Route to Cyclopropenium Ion and Its Mono- and Dimethyl Derivatives

Sir:

Some years ago we reported the decarbonylation of 1,2-diphenylcyclopropene-3-carboxylic acid (Ia) in perchloric acid to give diphenylcyclopropenium ion (IIa).[1] The simultaneous application of this technique to the synthesis of dipropylcyclopropenium ion (IIb) by

---

[1] D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, **82**, 2651 (1960).