

properties of which are in good accord with those reported by Huffman¹¹ and his associates.

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

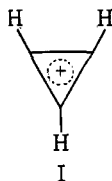
(11) We thank Professor Huffman for sending a copy of the infrared spectrum of desethylgogamine.

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

Cyclopropenyl Cation

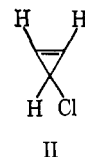
Sir:

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.



We have previously reported⁴ 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 ΔH^\ddagger for this process must be quite small since the spectrum is unresolved from -40 to +40°.

- (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. Sadd, 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).



II

On mixing solutions of II and SbCl_5 in CH_2Cl_2 , cyclopropenyl hexachloroantimonate (I-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 spectrum⁵ (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) ¹³C satellites ($J_{\text{C-H}} = 265$ cps). The ¹³C coupling constant is larger than those⁴ for cyclopropenes or cyclopropenone, as in the case of other⁶ 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-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

(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

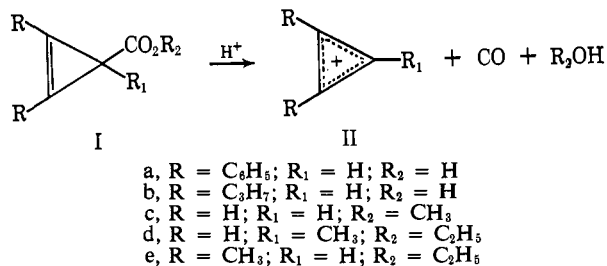
Ester Decarbonylation as a Route to Cyclopropenium Ion and Its Mono- and Dimethyl Derivatives

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).

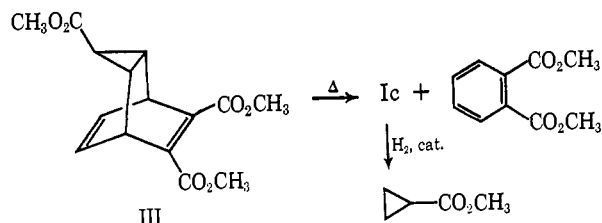
Breslow² demonstrated the further value of the reaction. We now show that a yet simpler and more powerful modification of the decarbonylation conditions permits the preparation of the parent cyclopropenium ion IIc and its mono- (IId) and dimethyl (IIe) derivatives from the corresponding esters Ic-e.



Solution of ethyl 1,2-dimethylcyclopropene-3-carboxylate (IIe)³ in 25% sulfur trioxide in sulfuric acid or, more simply, in chlorosulfonic or fluorosulfonic acid at room temperature, proceeded with gas evolution and the formation of dimethylcyclopropenium ion in solution in near-quantitative yield as judged from the appearance of characteristic peaks at τ 6.96 (singlet, area 6.0) and -0.04 (singlet, area 1.0).⁴ The ion could be precipitated in low yield from chlorosulfonic acid as the hexachloroantimonate by the addition of 10% antimony pentachloride in acetyl chloride followed by dilution with ether. The colorless crystalline salt thus obtained ($\lambda_{\text{max}}^{\text{Nujol}}$ 3.20, 5.55 μ . Anal. Found: C, 15.01; H, 1.76; Cl, 51.96) was identical with that obtained in 75% yield by reaction of 1,2-dimethylcyclopropene-3-carboxylic acid (mp 76.5–77.5°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ 2.9–4.0, 5.25, 5.95 μ . Anal. Found: C, 64.30; H, 7.18) with 10% antimony pentachloride in acetyl chloride at 0° (cf. ref 1). The salt was converted to the ether by shaking it with aqueous sodium bicarbonate and ether. When the ethereal solution thus obtained was extracted with sulfuric acid, the strong peaks characteristic of dimethylcyclopropenium ion appeared in the nmr spectrum of the acid solution.

When a solution of ethyl 3-methylcyclopropene-3-carboxylate⁵ in methylene chloride was added to cold, well-stirred chlorosulfonic acid, gas evolution was evident. The nmr spectrum of the resultant solution exhibited strong peaks at τ -0.58 and 6.87^4 in area ratio 2.0:3.0 for the methylcyclopropenium ion IIId. The rest of the spectrum was quite clean, exhibiting only multiplets for the ethyl group at τ 5.4 and 8.5 in addition to solvent peaks.

Although the very unstable methylcyclopropene-3-carboxylate Ie has not been reported as isolated in pure form, Doering⁶ has obtained evidence for its presence in the pyrolysate of Diels–Alder adduct III by low-temperature hydrogenation to the methylcyclopropanecarboxylate. Passage of the effluent vapors from pyrolysis of III in a helium stream into cold (-40 to -70°)



chlorosulfonic or fluorosulfonic acid gave clear solutions which evolved gas on warming. The nmr spectra of these solutions were quite complicated, but in addition to peaks characteristic of solvents and dimethyl phthalate, a persistent sharp singlet at τ -0.80 appeared. Blank solutions containing either adduct III or dimethyl phthalate in the acids gave no gas evolution on warming and gave no nmr resonance near τ -0.80 .

The species responsible for this peak was very stable in chlorosulfonic acid, since the solutions could be evaporated by heating under vacuum to a syrup with re-appearance of the nmr peak upon dilution to the fluid stage. The chemical consistency of our results as well as the agreement of the resonance peak at τ -0.80 with that observed by Breslow for solutions of cyclopropenium hexachloroantimonate in fluorosulfonic acid (τ -0.87)⁷ suggest that this species is the cyclopropenium ion (IIc).

Acknowledgments. We are pleased to acknowledge support of this work by the Petroleum Research Fund administered by the American Chemical Society under Grant 742-A-4 and the National Science Foundation under Grant GP 6378. We also appreciate valuable early discussions with Professor M. J. Goldstein.

(7) R. Breslow, J. T. Groves, and G. Ryan, *J. Am. Chem. Soc.*, **89**, 5048 (1967).

(8) Fellow of the Alfred P. Sloan Foundation 1962–1965. Address correspondence to Department of Chemistry, Michigan State University, East Lansing, Mich. 48823.

D. G. Farnum,⁸ G. Mehta, R. G. Silberman

Department of Chemistry, Cornell University
Ithaca, New York 14850

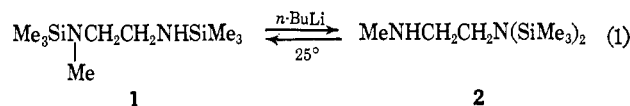
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

Received July 31, 1967

New Anionic Rearrangements. VI.¹ Condensation of Organosilylethylenediamines to Silaimidazolidines²

Sir:

A new condensation reaction has been discovered in experiments designed to extend our studies of the 1,2-anionic rearrangement of organosilylhydrazines^{1,3} to 1,4 systems. We treated N,N'-bis(trimethylsilyl)-N-methylethylenediamine⁴ (1) with *n*-butyllithium, ex-



(1) Previous paper in this series: R. West and M. Ishikawa, *J. Am. Chem. Soc.*, **89**, 4981 (1967).

(2) Research sponsored by Air Force Office of Scientific Research (SRC), O.A.R., U.A.S.F. Grant No. AF-AFOSR 1061-66.

(3) R. E. Bailey and R. West, *J. Am. Chem. Soc.*, **86**, 5369 (1964); R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966); **89**, 4068, 4072 (1967).

(4) Satisfactory elemental analyses for C, H, Si, and N were obtained for all compounds described in this communication.

(2) R. Breslow and H. Höver, *J. Am. Chem. Soc.*, **82**, 2644 (1960).

(3) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960); R. G. Silberman, M.S. Thesis, Cornell University, 1963.

(4) Nmr spectra are referenced to internal tetramethylammonium tetrafluoroborate taken as τ 6.87.

(5) M. J. Jorgensen and C. H. Heathcock, *J. Am. Chem. Soc.*, **87**, 5264 (1965). We are grateful to Dr. Jorgensen for a sample of the ester.

(6) W. von E. Doering, G. Laber, R. Bonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956); R. Gevirtz, Ph.D. Thesis, Cornell University, 1965.