

saturation with exclusive production of the *cis*-isomer **4**, in conversions ranging from 7 to 68%, depending on the alkali metal used ($K > Na > Li$). This is to be contrasted with hydrogenations of **1** and its salts over heterogeneous palladium and platinum catalysts, which invariably lead to mixtures containing appreciable quantities of the *trans* isomer.⁸

We propose that these homogeneous reactions proceed by way of a complex resembling **3**, in which not only a solvent molecule but the anionic species as well, chloride in this instance, has been displaced. This corresponds closely to the type of complexing suggested to operate in reduction of certain acrylates and cinnamates.^{6a} We believe that the principles exemplified in the reduction of the salts of **1** offer valuable possibilities for haptophilic^{1b} stereochemical control of olefin reduction in a wide variety of chemical species and situations.

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(8) H. W. Thompson and E. McPherson, unpublished results.

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Novel Aromatic Systems. I. The Homocyclopropenyl Cation, the Simplest 2π Homoaromatic System

Sir:

In 1956 Applequist and Roberts^{1a} predicted the existence of the homocyclopropenyl cation, the simplest possible homoaromatic species, resembling in its aromatic stabilization the cyclopropenium ion, but involving cyclic electron delocalization of the 2π system through an intervening sp^3 hybridized carbon. Subsequently, homoaromatic systems including the homotropylium ion and related analogs were studied in detail, most notably by Winstein.^{1b} Although some information concerning the homoaromatic nature of cyclobutenyl cations has been provided over the past 2 decades through experimental study of substituted analogs^{2,3} showing some degree of 1,3-overlap, conclusive evidence for a truly homoaromatic cyclobutenyl cation, such as expected in the case of the parent homocyclopropenyl cation, has thus far not been obtained.

We now wish to report the preparation and characterization (by 1H and ^{13}C nmr) of the till now elusive parent cyclobutenyl cation **1** showing it to be the true homocyclopropenyl cation.

The homocyclopropenyl cation was prepared (after many inconclusive attempts) from 3-acetoxycyclo-

(1) (a) D. E. Applequist and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 4012 (1956); (b) For a review on homoaromaticity, see S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(2) (a) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964); (b) T. J. Katz, J. R. Hall, and W. C. Neikam, *ibid.*, **84**, 3199 (1962); (c) E. F. Kiefer and J. D. Roberts, *ibid.*, **84**, 784 (1962); (d) S. L. Manatt, M. Vogel, D. Knutson, and J. D. Roberts, *ibid.*, **86**, 2645 (1964); (e) I. A. Shleider, I. S. Isaer, and V. A. Koptuyug, *Zh. Org. Khim.*, **8**, 1337 (1972).

(3) G. A. Olah, P. R. Clifford, Y. Halpern, and R. G. Johanson, *J. Amer. Chem. Soc.*, **93**, 4219 (1971), and references therein.

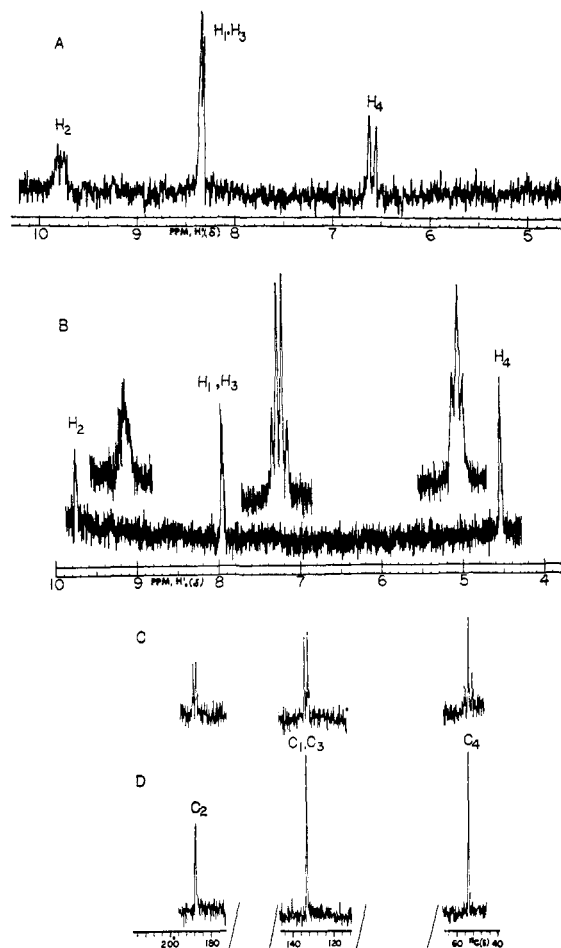
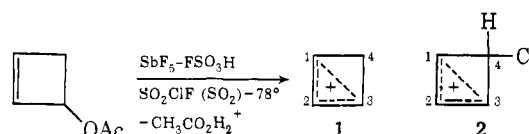


Figure 1. (A) The 60-MHz pmr spectrum of **2** at -60° . (B) The 100-MHz pmr spectrum of **1** at -40° . (C) and (D) off-resonance and noise decoupled cmr spectra of **1** at -60° .

butene⁴ in FSO_3H-SbF_5 (Magic Acid)- SO_2ClF (or SO_2) solution at -78° .⁵ The pmr spectrum (100 MHz) of the solution of ion **1** at -60° (Figure 1B) shows three



absorptions at δ 4.53, 7.95, and 9.72 with relative peak intensities of 2:2:1 (Table I), respectively. The pmr spectrum of **1** remained unchanged upon warming the solution to 20° . Below -60° ion **1** shows temperature-dependent behavior. Within the temperature range studied (-60 to -110°) the two most deshielded absorptions remained unchanged, while the more shielded methylene signal gradually became broadened and finally merged into the baseline as the temperature was lowered to -110° . The process is reversible and raising the temperature of the sample to -60° regenerated the original spectrum. We attribute this temperature-

(4) K. B. Wiberg, V. Z. Williams, Jr., and N. E. Friedrich, *J. Amer. Chem. Soc.*, **92**, 564 (1970).

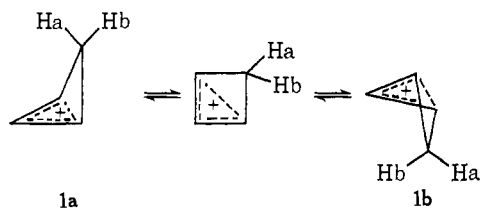
(5) Ionization of 3-acetoxycyclobutene gives, beside the formation of **1**, also protonated acetic acid, acetylium ion, some polymeric material, protonated crotonaldehyde, and fluorosulfonates. The formation of crotonaldehyde is believed to result from the ring opening protolysis of 3-acetoxycyclobutene. Attempts to ionize 3-acetoxycyclobutene at -120° did not eliminate the formation of protonated crotonaldehyde.

Table I. Proton and Carbon-13 Nmr Parameters of Cycloalkenyl Cations^a

	Proton					Carbon-13					
	H ₁ ,H ₃	H ₂	H ₄	H ₅	J _{1,2} (Hz)	Δ ₁ ^b	C ₁ ,C ₃	C ₂	C ₄	Δ ₂ ^b	
	11.1 (s) ^c						175.9	(d, 265) ^c			
	7.95 ^d	9.72	4.53		1.60	-1.77	130.0 (d, 211.2)	187.6 (d, 236.3)	54.0 (t, 167.1)	-57.6	
	8.38 ^e	9.80	6.62		1.60	-1.42	141.6 (d, 224.3)	178.7 (d, 230.6)	63.7 (d, 220.0)	-37.1	
							191.5 ^f	174.4	76.0	+17.1	
	11.26	8.65	4.23		4.20	+2.61	234.7	145.7	48.7	+89.0	
	10.25	8.32	3.81	2.40	8.00	+1.93	217.7	136.7	33.2	+81.0	
	10.18	8.34	4.19	2.38	9.80	+1.84	205.8	151.4	42.8	+54.4	

^a Both ¹H and ¹³C nmr chemical shifts are in parts per million from external TMS (capillary). ^b Δ₁ = δ_{H1} - δ_{H2}; Δ₂ = δ¹³C₁ - δ¹³C₂. ^c Multiplicities and coupling constants J_{CH} (Hz) are given in parentheses. ^d J_{2,4} = 0.4 Hz; J_{1,4} = 1.6 Hz. ^e J_{2,4} = 4.0 Hz. ^f We have obtained slightly different carbon-13 shifts for this ion using the Varian XL-100 instrument from the previously reported indor values. See ref 3.

dependent behavior to be the result of a slow ring-inversion process (**1a** ⇌ **1b**) via the planar cyclobutenyl



cation.⁶ A similar process has been observed previously in the case of the homotropylium ion.^{6b,c}

Although we were able to observe the described reversible coalescence of the methylene absorption, we have been unable thus far to observe the methylene protons under conditions of their magnetic nonequivalence, presumably due to the low intensity of the observable spectrum and obstruction of the regions of interest by overlapping absorptions of polymeric by-products formed in the ionization process⁵ and/or failure to decrease the rate of the ring-inversion process relative to the nmr time scale sufficiently to resolve the absorptions.⁷

For comparison, we have also prepared the 4-chlorohomocyclopropenyl cation **2** from *cis*-3,4-dichlorocyclobutene⁸ in SbF₅-SO₂ClF at -78°. Ion **2** is also

(6) (a) Former theoretical treatments of the cyclobutenyl cation have only included planar geometries (*i.e.*, stabilization via resonance only). The present experimental investigation of the ion clearly indicates that nonplanar geometries must be considered. (b) S. Winstein, H. D. Kaesz, G. T. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, **87**, 3267 (1965); (c) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966).

(7) Lowering the temperature below -110° resulted in the freezing of the sample. Attempted freezing point depression of the sample by dilution with SO₂F₂ resulted in decreased solubility of the ion that did not allow studies at lower temperatures.

stable to 20° and its 60-MHz pmr spectrum (Figure 1A) is not temperature dependent in the temperature range studied (20 to -120°). Although the spectra of **1** and **2** show considerable similarity, the latter does not readily undergo ring-inversion presumably because of the presence of the heavy chlorine atom which substantially raises the energy barrier.⁹

The homoaromatic nature of **1** and **2** is evident from their proton and carbon-13 nmr spectra (Figure 1C and D). The nmr parameters of the ions are summarized in Table I along with those of model allylic systems. In the case of the previously reported allylic cycloalkenyl cations,¹⁰ the terminal protons in the allylic fragment are always more deshielded than the central proton indicating heavy delocalization of positive charge onto the terminal positions with correspondingly little charge placement at the central carbon. Table I reveals the striking reversal of proton chemical shifts observed in both **1** and **2** indicating the presence of strong 1,3-orbital interaction which localizes substantial amounts of positive charge onto the central allylic position. In the FT ¹³C nmr spectra of **1** and **2**, C₁ and C₃ are (57.6 and 37.1 ppm, respectively) less deshielded than C₂. The order of deshielding is also reversed from that of larger ring cycloalkenyl cations (Table I). In the 4-chlorotetramethylcyclobutenyl cation, C₂ is still found to be less deshielded (by about

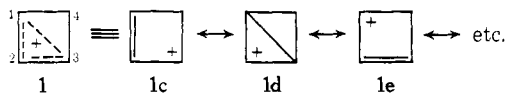
(8) M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marica, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 372 (1964).

(9) A referee has suggested that a rapid ring inversion in **2** would probably be undetectable by nmr, even if it became slow enough to freeze out at low temperatures, if one of the conformers were as little as 1.5 kcal mol more stable than the other as this would result in a population range of 93-99% for the major conformer over the temperature range studied.

(10) (a) G. A. Olah, G. Liang, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3544 (1972); (b) G. A. Olah and G. Liang, *ibid.*, **94**, 6434 (1972).

17 ppm) than C_1 and C_3 , although the magnitude of the shift difference is substantially reduced as the result of imposed geometric constraints making 1,3-orbital-interaction more favorable. The reversal of shifts again indicates that a considerable amount of positive charge has been delocalized onto C_2 in the cyclobutenyl cations **1** and **2**, *via* a strong 1,3-interaction. In addition, the one-bond $^{13}\text{C-H}$ coupling constants observed in the allylic fragment of these ions are unusually large (on the order of 230 Hz).¹¹ For example, the $J_{^{13}\text{C-H}}$'s for C_1 and C_3 (211.2 and 224.3 Hz for **1** and **2**, respectively) are larger than those of bridgehead positions in bicyclo[1.1.0]butane (205 Hz)¹² and the $J_{^{13}\text{C-H}}$'s for C_2 (236.3 and 230.6 Hz, respectively) are found to approach those of the recently reported cyclopropenium ion.¹³ The $J_{^{13}\text{C-H}}$ of **1** is found to be substantially smaller than that of **2** and is not unexpected as increasing geminal substituent electronegativity has been demonstrated to result in increased $J_{^{13}\text{C-H}}$'s.¹²

Although the unusual deshielding at C_2 and shielding at C_1 , C_3 alone would indicate that structure **1d** is a significant contributor to **1**, the unusually large $J_{^{13}\text{C-H}}$'s and temperature-dependent pmr spectra for **1** indicate that the cyclobutenyl cation (*planar*) approaches the truly homocyclopropenyl-type geometry (*nonplanar*) **1a** (or **1b**) with the $C_1-C_2-C_3$ angle intermediate between 60 and 90°. Vicinal, *cis* vinylic

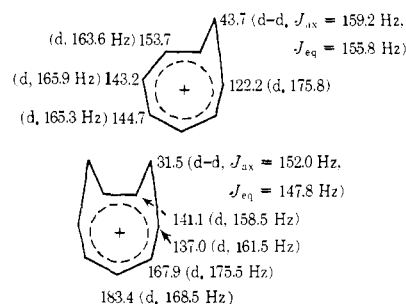


proton coupling constants have been shown to depend on ring size, the magnitude decreasing monotonically with reduction of ring size.^{12d} In the pmr spectra of **1** and **2**, $J_{1,2}$ (1.60 Hz) is much smaller than that observed in cyclobutene systems ($J_{1,2} = 2.5\text{--}3.7$ Hz) and approaches that of a cyclopropenyl system ($J_{1,2} = 0.5\text{--}1.5$ Hz). In addition, the $J_{^{13}\text{C-H}}$'s observed for C_1 , C_2 , and C_3 in **1** and **2** bear a good resemblance to that observed in the cyclopropenyl cation.¹³ Increasing $J_{^{13}\text{C-H}}$ values for small-ring compounds have been shown to correlate at least qualitatively with increased ring strain¹² (according to decreasing ring size). For example, the $J_{^{13}\text{C-H}}$'s for the vinylic carbons in cyclopropene and cyclobutene are 220 and 170 Hz, respectively.¹² Moreover, the pentamethyl- and 1,2,3,4-tetramethylcyclobutenyl cations reported by Katz^{2a,b} have been shown to be allylic ions with an unusually significant 1,3-orbital interaction, which, because of the geometric constraints of the four-membered ring, render the 1,3-distance unusually small. In the unsubstituted, parent cyclobutenyl cation **1**, and the 4-

chloro-substituted analog **2**, the much stronger 1,3-interaction should make the 1,3-distances even shorter and consequently result in the bending of the molecule necessitated to relieve ring strain. A related, well-known example is that of the homotropylium cation in which strong 1,7-orbital overlap (intermediate between σ and π) renders the ion *nonplanar*.¹⁵ The magnetic nonequivalence of the methylene protons in the homotropylium cation allows measurement of the rate of the ring-inversion process. The strong 1,3-orbital interaction in the cyclobutenyl cations **1** and **2** should also involve overlap intermediate between σ - and π -bonding nature, resulting in the nonplanarity of these ions.¹⁸ We, therefore, conclude that the presently studied cyclobutenyl cations **1** and **2** should indeed be considered as monohomocyclopropenyl cations with ring deformation. The homoaromaticity predicted for the homocyclopropenyl cation is thus explicitly established. Ion **1** is the homoaromatic analog of Breslow's cyclopropenyl cation,¹³ and thus the simplest possible homoaromatic system.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

(15) We have previously reported the carbon shifts for both the mono- and bishomotropylium ions.¹⁶ We have now also obtained the carbon-hydrogen coupling constants for these ions from the proton



coupled CFT spectra. Although a recently published explanation for homoaromatic stability proposes that homotropylium ions might be stabilized through a Möbius structural arrangement (eight electrons) rather than a Hückeloid type (six electrons),¹⁷ the observed coupling constants indicate no appreciable cyclopropane ring formation.

(16) G. A. Olah, G. Liang, L. A. Paquette, M. J. Broadhurst, and P. Warner, *J. Amer. Chem. Soc.*, **95**, 3386 (1973).

(17) W. J. Hehre, *J. Amer. Chem. Soc.*, **95**, 5807 (1973).

(18) Recently Lodder and Buck, *et al.*, reported a series of aryl substituted cyclobutenyl cations and they also have found, in one case, that 1,3-interaction, induced by unfavorable steric crowding, became important in 1,3-diphenyl-2-*tert*-butylcyclobutenyl cation, which showed a deshielded C_2 shift. See A. E. Lodder, J. W. Haan, L. J. M. Ven, and H. M. Buck, *Rec. Trav. Chim. Pays-Bas*, **92**, 1040 (1973).

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Chromium Carbonyl Photocatalyzed 1,4-Hydrosilation of 1,3-Dienes. A Synthesis of Allylsilanes

Sir:

We recently communicated¹ some characteristics of the $\text{Cr}(\text{CO})_6$ photocatalyzed hydrogenation of 1,3-dienes which may have synthetic utility. The reports²⁻⁴ that

(1) M. Wrighton and M. A. Schroeder, *J. Amer. Chem. Soc.*, **95**, 5764 (1973).

(2) W. Jetz and W. A. G. Graham, *Inorg. Chem.*, **10**, 4 (1971).

(3) A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **10**, 1 (1971).

(4) J. K. Hoyano and W. A. G. Graham, *Inorg. Chem.*, **11**, 1265 (1972).

(11) Long range carbon-hydrogen coupling constants in **2** are $J_{C_1H_4} = J_{C_2H_4} = 6.5$ Hz, $J_{C_1H_2} = J_{C_2H_2} = 6.5$ Hz, $J_{C_2H_1} = J_{C_3H_3} = 7.2$ Hz, and $J_{C_4H_1} = J_{C_4H_3} = 6.5$ Hz.

(12) (a) K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 194 (1968); (b) J. B. Stothers, "Carbon-13 Nmr Spectroscopy," Academic Press, New York, N. Y., 1972; (c) G. C. Levy and G. L. Nelson, "Carbon-13 Nmr for Organic Chemists," Wiley, New York, N. Y., 1973; (d) L. M. Jackman and S. Sternhell, "Applications of Nmr Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, Tables 4-2-8, p 303.

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

(14) Recent MINDO/2 and *ab initio* (4-31G) calculations have predicted the homocyclopropenyl cation to be nonplanar. (a) W. W. Schoeller and G. E. Schenck, *Tetrahedron*, **29**, 425 (1973); (b) A. J. P. Devaquet and W. J. Hehre, *J. Amer. Chem. Soc.*, **96**, 3644 (1974).