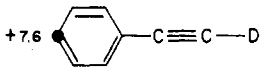
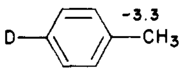
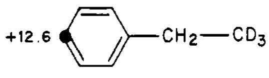
as well as in many others, the efficiency of coupling between certain vibrations of the intervening bond system plays a major role in determining the magnitude of the observed long-range effects. Thus, a more "linear" arrangement as in an *antiperiplanar* conformation is expected to yield the larger $^n\Delta$ values, if C–D and C–C stretching vibrations are considered. Support for this assumption comes from the large long-range isotope effects observed for molecules like **9**,[11] **10**,[12] and **11**.[11] In the present case it allows the rationalization of the results for $^3\Delta$ and $^4\Delta$, where the larger effects are found for those situations in which the intervening bond system can adopt an antiperiplanar conformation or a type of zig–zag arrangement. Spacial proximity of the resonating ^{13}C nucleus and the deuteration site obviously cannot be important here. Since vibrational coupling can also be effective for eclipsed bonds in a vicinal situation, as is well-known, for instance, for the C=O stretching vibration in cyclic α-diketones,[14] the large $^3\Delta$ values in bicyclic systems[4] may also result from vibrational coupling and thus would not be unexpected.



9



10



11

Experimental Section

The synthesis of the compounds followed published procedures (**1**, **2**, **3**, **4**,[15,16] **5**, **6**[17]) using suitably deuterated reagents ($NaBD_4$, CD_3I (Aldrich) and CHD_2I, CH_2DI (Merck, Sharp & Dohme)). ^{13}C NMR spectra were recorded at 100.61 MHz with a Bruker WH 400 spectrometer at 310 K using broad-band ^{1}H decoupling and a ^{2}H lock, 10-mm o.d. sample tubes, and $CDCl_3$ as solvent. The concentrations were 1.38 M (**1**, **2**), 2.3 M (**3**), 0.82 M (**4**), and 0.8 M (**5**, **6**), with a ratio of 3:1 for deuterated and non-deuterated material. The digital resolution was 0.037 Hz (**1**–**4**) and 0.01 Hz (**5**, **6**) which results in an experimental error of ca. ±0.5 ppb, if line-broadening is taken into account. Signal assignments were available from the literature (**1**–**4**,[10] **5**, **6**[18]) and the identification of isotope shifts was possible in all cases on the basis of the presence of ^{2}H, ^{13}C spin–spin coupling and/or the concentration difference for deuterated and nondeuterated material. For **1**, **2**, and **4** the following long-range ^{13}C,^{2}H coupling constants (in hertz) were measured: **1**, $^2J = 0.57$, $^3J = 0.29$; **2**, $^2J = 0.48$, $^3J = 1.25$; **4**, $^3J = 0.73$.

Acknowledgment. We are indebted to Prof. J. B. Stothers for his comments, to Dipl.-Chem. D. Moskau for assistance in some of the experiments, and to the Fonds der Chemischen Industrie for financial support. P.J.-N. thanks the DAAD for a travel grant.

Registry No. **1**, 53042-76-5; **2**, 17553-36-5; **3**, 30461-17-7; **4**, 30461-16-6; **5** (x = 2, y = 1), 91312-20-8; **5** (x = 1, y = 2), 91312-22-0; **5** (x = 0, y = 3), 91312-23-1; **6** (x = 2, y = 1), 91312-21-9; **6** (x = 1, y = 2), 91312-24-2; **6** (x = 0, y = 3), 91312-25-3; **7a**, 26168-37-6; **8a**, 1520-59-8; ^{13}C, 14762-74-4; D_2, 7782-39-0.

---

(14) Alder, K., Schäfer, H. K.; Esser, H.; Krieger, H.; Reubke, R. *Liebigs Ann. Chem.* **1955**, *593*, 23 ff.

(15) Wiseman, P. A. *J. Org. Chem.* **1975**, *40*, 112.

(16) Lansbury, P. T.; MacLeay, R. E. *J. Org. Chem.* **1963**, *28*, 1940. $NaBD_4$ was used for the reduction, and the isomer separation followed ref 9.

(17) DePuy, C. H.; King, R. W. *J. Am. Chem. Soc.* **1961**, *83*, 2743.

(18) Senda, Y.; Ishiyama, J.; Imaizumi, S. *Tetrahedron* **1975**, *31*, 1601; cited from Breitmaier E., Haas, G. Voelter, W. "Atlas of ^{13}C NMR Data", Vol. 2, Heyden: London 1976.

3-Fluorocyclopropene

Norman C. Craig,* Kevin L. Sloan, Julian R. Sprague, and
Philip S. Stevens

*Department of Chemistry, Oberlin College,
Oberlin, Ohio 44074*

Received April 3, 1984

As an extension of the use of 3,3-difluorocyclopropene and 1,3,3-trifluorocyclopropene as precursors of the monofluoro- and difluorocyclopropenyl cations,[1,2] we sought 3-fluorocyclopropene (**1**) as a source of the cyclopropenyl cation itself. However, when finally made, **1** proved to be too labile for use in most chemistry, including preparation of colorless cation solutions in sulfur dioxide at low temperature for use in Raman spectroscopy.

Dehydrohalogenation of halocyclopropanes has been a useful way to prepare other fluorocyclopropenes, including 3,3-difluorocyclopropene,[3] 1,3,3-trifluorocyclopropene,[2] and perfluorocyclopropene.[4] Accordingly, the cis and trans isomers of 1-chloro-2-fluorocyclopropane were synthesized and treated with a variety of strong bases, including Ascarite (sodium hydroxide on asbestos) coated with a crown ether, in unsuccessful attempts to prepare **1**.

Ultimately, 3-chlorocyclopropene (**2**), which was prepared by the method of Breslow and co-workers,[5] was converted into **1** by passing gaseous **2** through a column containing a rigorously dry mixture of silver difluoride and potassium fluoride.[6] This fluorination reaction, which is presumed to go through a cation intermediate under mild conditions, goes in high yield in the cyclopropene system. The purity of the **1** product, which is too labile for chemical or gas chromatographic purification, depends on careful prior purification of **2**. **1** does not survive passage through an Ascarite-packed column, which explains the failure of the dehydrohalogenation method of preparation. Even in the gas phase **1** has a limited lifetime in an infrared cell. Localized dark deposits formed in a decomposition process. Hydrogen fluoride, silicon tetrafluoride, and acetylene were volatile products of this composition in glass cells. Good-purity samples of **1** sealed in melting point capillaries made of borosilicate glass could be studied in Raman experiments for hours at −50 °C. Such samples could be stored for months at liquid nitrogen temperature.

Proton and ^{19}F NMR spectra at −50 °C confirmed the identity of **1**. The proton spectrum consisted of a doublet of doublets ($J_{HF} = 3.2$ Hz, $J_{HH} = 1.5$ Hz) at 7.7 ppm relative to Me_4Si due to the HC=CH protons and a doublet of triplets ($J_{HF}^{gem} = 110$ Hz, $J_{HH} = 1.5$ Hz) at 5.0 ppm due to the CFH proton. The ^{19}F spectrum was a doublet of triplets ($J_{HF}^{gem} = 110$ Hz, $J_{HF} = 3.2$ Hz) at a chemical shift of −145 ppm (upfield) relative to $CFCl_3$. At temperatures above −20 °C most of the fine structure had collapsed. The geminal HF coupling constant of 110 Hz is exceptionally large. In 1-fluoroethylene $J_{HF}^{gem} \approx 80$ Hz.[7] In 1-fluoro-

---

(1) Craig, N. C.; Lai, R. K.-Y.; Matus, L. G.; Miller, J. H.; Palfrey, S. L. *J. Am. Chem. Soc.* **1980**, *102*, 38–46.

(2) Craig, N. C.; Lai, R. K.-Y.; Penfield, K. W.; Levin, I. W. *J. Phys. Chem.* **1980**, *84*, 899–906.

(3) Craig, N. C.; MacPhail, R. A.; Spiegel, D. A. *J. Phys. Chem.* **1978**, *82*, 1056–1070.

(4) Sargeant, P. B.; Krespan, C. G. *J. Am. Chem. Soc.* **1969**, *91*, 415–419.

(5) Breslow, R.; Ryan, G.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 988–993.

(6) Conversion of chlorocyclobutane into fluorocyclobutane. Kim, H.; Gwinn, W. D. *J. Chem. Phys.* **1966**, *44*, 865. Wiberg, K. B.; Barth, D. F.; Pratt, W. E. *J. Am. Chem. Soc.* **1976**, *98*, 4286.

(7) Becker, E. D. "High Resolution NMR. Theory and Chemical Applications", 2nd ed.; Academic Press: New York, 1980; p 100.

0022-3263/84/1949-3847$01.50/0

allene it is 84 Hz.[8] In various fluorocyclopropanes $J_{HF}^{gem} \approx 60$ Hz,[9] and in fluoromethanes $J_{HF} \approx 45$ Hz.[7] The large value of J_{HF}^{gem} in 1 suggests an unusually large CFH bond angle.

The gas-phase infrared spectrum of 1 had the following principal features (band center in cm^{-1}, intensity, band shape): 3161, w, A; 3032, m, C; 1622, m, A; 1327, m, ?; 1200, s, A; 1060, m, B; 956, vs, A; 876, m, B; 660, s, C; and 456, m, A. The band at 3161 cm^{-1} and the less distinct feature to somewhat lower frequency are due to stretching of the CH bonds attached to the double bond. The 3032-cm^{-1} frequency is due to stretching of the methylene CH bond. The band at 1622 cm^{-1} is largely C=C stretching, and the intense band at 956 cm^{-1} is largely CF stretching. Thus, the infrared spectrum is also consistent with 1 being 3-fluorocyclopropene. In a separate paper we will present a complete vibrational assignment of 1 and its d_3 isotopomer based on Raman as well as infrared spectra.

We attempted to prepare the cyclopropenyl cation for Raman spectroscopy by reaction of 1 with BF_3 in liquid SO_2 at low temperature.[1] However, this reaction could not be controlled. In the first attempt the mixture glowed red and charred upon partial thawing. In another attempt the depth of color gave overwhelming fluorescence in Raman spectroscopy. However, a controlled reaction of 1 with BF_3 was achieved on a CsI crystal at low temperature to give $C_3H_3^+BF_4^-$ for use in infrared spectroscopy.[1] Frequencies of bands due to the $C_3H_3^+$ ion were in satisfactory agreement with the ones reported previously for the spectra of crystalline $C_3H_3^+SbCl_6^-$ and $C_3H_3^+AlCl_4^-$ in hydrocarbon mulls.[5]

Experimental Section

Warning: *Breslow and co-workers have noted the hazardous nature of chlorocyclopropenes.[5] Fluorocyclopropene is likely to be more hazardous due to its greater instability and the well-known toxicity of compounds containing monofluoro-substituted carbon atoms. We handled these materials other than the perchlorocyclopropene starting material in small amounts in enclosed systems.*

3-Chlorocyclopropene (2). Perchlorocyclopropene (3 g) (Aldrich Chemical Co.) was reduced to 2 with 17 g of tributyltin hydride (Alfa Products, Morton Thiokol, Inc.).[5] It is essential to remove residual diethyl ether from the tributyltin hydride by distillation in vacuo at room temperature before using this material in the reaction. 2 was separated from the reaction products by gas chromatography[5] and passed through a column packed with 2 cm of 3-Å molecular sieves, which had been dried at 100 °C under vacuum for 12 h. Passage through the molecular sieves removed water and reduced the amount of hydrogen chloride, which had formed during chromatography. Partial vaporization during slow warmup of the sample removed impurity acetylene and some more of the residual HCl. 2 was confirmed by its proton NMR spectrum (7.5_5 ppm, intensity 2; 4.2_5 ppm, intensity 1 at room temperature), although the reported splitting patterns in CCl_4 solution were not observed in $CFCl_3$ solution, even at temperatures as low as -90 °C.[10] Principal infrared bands of 2 in the gas phase were (band center in cm^{-1}, intensity, band shape): 3170, w, A.; 3139, w, B; 3028, m, C; 1631, s, A; 1265, s, A; 1179, m, A; 1140, s, A; 1033, s, B; 912, m, C; 867, m, B; 839, m, B; 713, vs, A; 590, s, C; and 348, s, B. Agreement with the frequencies of the reported spectrum of 2 in solution in CCl_4 in solution was only fair,[5] even when the frequencies of the liquid-phase Raman spectrum were compared.

3-Fluorocyclopropene (1). About 1 mmol of 2 as a gas was passed through a 2-cm length of a 1.3 g:1 g mixture of silver difluoride (Alfa Products) and potassium fluoride to give 1. The potassium fluoride was material that had been dried by heating at 175 °C under vacuum for 3 h. Glass wool plugs (20 cm) held the loosely packed solid mixture in place. The column was packed in a dry bag and then heated to 130 °C under vacuum for 12 h. During the heating some lighter color developed in the dark brown AgF_2. Typically, to achieve nearly quantitative conversion a sample was passed six times through the column by allowing material to vaporize in one tube while being condensed at liquid nitrogen temperature in another.

For successful gas-phase infrared spectroscopy in a demountable 10-cm minigas cell (Wilmad Glass Co.), it was essential to scrub all of the interior glass surfaces with a detergent and to use Krytox grease. Krytox, a Dupont product, is a polymer of perfluoropropylene oxide that is thickened with Teflon powder. Silicone grease, which is thickened with silica powder, is not a good grease for prolonged contact with 1. However, silicone grease, which darkens upon contact with 1, suffices for the vacuum system.

A good vacuum system was used for all of the sample handling after the synthesis of 2. The detector for the gas chromatography system was a thermal conductivity cell, which may have caused the HCl formation.

Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer Model 580B spectrometer. NMR spectra were obtained on a Perkin-Elmer Model R12B instrument. NMR samples were prepared in sealed tubes with Me_4Si as proton reference and with $CFCl_3$ as the solvent and ^{19}F reference.

Acknowledgment. This research was supported by a Cottrell grant from Research Corporation and by National Science Foundation College Research Instrumentation grants (PRM-7911202 and PRM-8115415). The synthesis, characterization, and exploration of dehydrohalogenation of *cis-* and *trans*-1-chloro-2-fluorocyclopropane were done by Kenneth Felz and David S. Phillips. We are grateful for their contributions.

Registry No. 1, 72507-66-5; 2, 17336-56-0; $C_3H_3^+BF_4^-$, 12294-37-0; *cis*-1-chloro-2-fluorocyclopropane, 91444-06-3; *trans*-1-chloro-2-fluorocyclopropane, 91444-07-4.

---

[8] As measured by us on a sample obtained by flash vacuum pyrolysis of *cis*-1-chloro-2-fluorocyclopropane. This material had the same infrared spectrum as was reported for 1-fluoroallene by Durig, J. R.; Li, Y. S.; Witt, J. D.; Zens, A. P.; Ellis, P. D. *Spectrochim. Acta* 1977, *33A*, 529–544.

[9] Agopovich, J. W.; Craig, N. C.; Gillies, C. W., unpublished.

[10] **Note added in proof**: The expected splitting pattern of a doublet and a triplet has now been observed for a sample, low in HCl impurity, in CCl_4 solution at -30 °C.

Studies on the Flash Vacuum Pyrolysis and Anomalous Course of Alkali Metal Promoted Reductions of 8-Methylenepentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-11-one

Goverdhan Mehta* and Kotha Sambasiva Rao

School of Chemistry, University of Hyderabad, Central University P.O., Hyderbad 500 134, India

Alan P. Marchand* and Riza Kaya

Department of Chemistry, North Texas State University, Denton, Texas 76203

Received March 28, 1984

Thermal [2 + 2] cycloreversions of substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diones 1 have been studied extensively as a simple, general method for the synthesis of tricyclo[6.3.0.0^{2,6}]undecanes (i.e., linearly fused