Fluorinated Cyclopropenyl Methyl Ethers. New Stable Cyclopropenium Cations

Bruce E. Smart

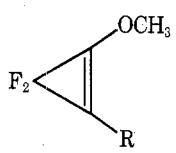
Contribution No. 2354 from the Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Received February 20, 1976

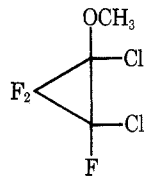
The first fluorinated cyclopropenyl ethers, 1-methoxytrifluorocyclopropene, 1-methoxy-2-chlorodifluorocyclopropene, and 1,2-dimethoxydifluorocyclopropene, have been synthesized. These ethers are exceedingly reactive and much less stable than homologous polyfluorocycloalkenyl ethers, but they react with antimony pentafluoride to give unusually stable cyclopropenium hexafluoroantimonate salts.

The reaction of nucleophiles, especially alkoxides, with perfluoroalkenes and perfluorocycloalkenes (having four, five, and six carbons) has received considerable mechanistic and synthetic attention.[1,2] However, similar studies on polyfluorocyclopropenes generally have been limited and often unsuccessful. West and co-workers[3] described the synthesis of various fluorinated cyclopropenes where polyhalocyclopropenes were treated with fluoride ion. Sargeant and Krespan[4] reported that perfluorocyclopropene reacted, often uncontrollably, with amines to give extensive degradation products. Polyfluorocyclopropenes are reported here to react with methoxide ion to give the first examples of polyfluorocyclopropenyl ethers.

Preparation and Properties of Cyclopropenyl Ethers. 1-Methoxytrifluorocyclopropene (**1a**), bp 67–68 °C, and 1,2-dimethoxydifluorocyclopropene (**1b**), bp 74 °C (80 mm),



1a, R = F
b, R = OCH_3
c, R = Cl



2

were prepared by cautiously adding perfluorocyclopropene to a slurry of 1 or 2 equiv of sodium methoxide in dry diglyme at −78 °C. The products were flash distilled from the reaction mixture at room temperature and purified by fractional distillation. 1-Methoxy-2-chlorodifluorocyclopropene (**1c**), bp 61–62 °C (150 mm), was similarly prepared from 1,2-dichlorodifluorocyclopropene.

It is essential in these syntheses that the cyclopropene be added to the alkoxide suspension while keeping the reaction temperature below −60 °C. In some cases the reaction mixture has ignited when sodium methoxide powder was added to perfluorocyclopropene in diglyme at low temperature. Methanol solvent must be avoided in these reactions (vide infra).

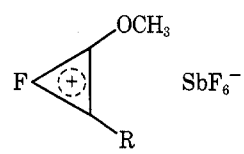
Caution: The cyclopropenes **1a–c** *are exceedingly reactive molecules and should be handled with great care. They must be prepared under anhydrous conditions as directed, purified immediately, and stored at −78 °C in an inert atmosphere.*

The cyclopropenyl ether structures were readily confirmed by ir (Table I), NMR (Table II), and mass spectral data. The cyclopropenes **1a** and **1b** could not be combustion analyzed owing to their instability. 1-Methoxytrifluorocyclopropene (**1a**) is unusually volatile and flashes into a black mushroom cloud when placed near an open flame. Cyclopropane **2** was prepared in 47% yield when **1a** was treated with molecular chlorine.

Cyclopropenes (**1a–c**) are hydrolytically very unstable. For example, **1b** splatters when added to water, and a sealed vial containing **1a** and water or methanol exploded after standing at room temperature. Under controlled conditions, **1a** reacts with methanol to give methyl *cis*-2,3-dimethoxyacrylate, $CH_3OCH{=}C(OCH_3)CO_2CH_3$.

The cyclopropenyl ether reactivity is in marked contrast with the behavior of homologous 1-alkoxyperfluorocycloalkenes. For example, the 1-methoxy- or 1,2-dimethoxyperfluorocyclobutenes do not appreciably react with water at room temperature; in fact, these derivatives are routinely prepared in methanol solvent followed by aqueous workup.[5–7] The well-known hydrolysis of 1,2-diethoxytetrafluorocyclobutene to squaric acid requires prolonged heating at 100 °C in 50% sulfuric acid.[8]

Fluorocyclopropenium Cations. The cyclopropenes **1a–c** readily react with SbF_5 in SO_2 at −78 °C to give the cyclopropenium hexafluoroantimonates **3a–c**. At room tempera-



3a, R = F
b, R = OCH_3
c, R = Cl

ture, **1a–c** react explosively with SbF_5. This contrasts with the 1-methoxypolyfluorocyclobutenes which smoothly react with neat SbF_5 at room temperature.[9]

The hexafluoroantimonates **3a–c** can be isolated as colorless, crystalline solids which are indefinitely stable at room temperature if moisture is rigorously excluded. Furthermore, the isolated salts can be heated to ca. 90 °C for several minutes (liquefied), and the solid cation salts are recovered unchanged on cooling. Salts **3a–c** are therefore more thermally stable than the previously reported fluorinated cyclopropenium hexafluoroantimonates which decompose at 80 °C or less.[3,4]

The ^{19}F and ^{1}H NMR spectral data for **3a–c** and related cations are shown in Table III. In all cases, a singlet in the ^{19}F NMR spectra is observed. The ^{1}H and ^{19}F NMR spectra are unchanged in the −78 to 80 °C temperature range. The allyl and vinyl fluorines of the precursor cyclopropenes are deshielded by 35 ± 1 and 61–82 ppm, respectively, on ionization to **4a–c**. However, in **3a** the fluorines are deshielded by only 8.4 ppm from the allyl fluorines and 69.9 ppm from the vinyl fluorines in **1a**. In **3c**, the deshielding is 18.2 ppm from the allyl fluorines, and in **3b** the fluorine atom is shielded 9.4 ppm from the allyl fluorines in **1b**.

These results suggest that there is important conjugative interaction of the oxygen lone pair electrons which diminishes the electron density at the carbon atom bound to fluorine, i.e.,

Table I. Cyclopropene Carbon–Carbon Double Bond Vibrational Stretching Frequencies

Cyclopropene	νC=C, cm⁻¹	Cyclopropene	νC=C, cm⁻¹
	1641[a,d]		1945[a,f]
	1810[a,e]	 (1a)	1907[b]
	c,e	 (1b)	1895[b,g]
	1860[a,e]	 (1c)	1832[b]

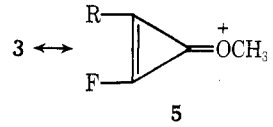
[a] Gas phase. [b] Neat liquid phase. [c] Inactive C=C ir, 1760 cm⁻¹ (Raman). [d] Reference 14. [e] Reference 3. [f] Reference 4. [g] Exceedingly weak.

Table II. NMR Data for Fluorocyclopropenes[a]

Cyclopropene	Chemical shift (multiplicity) C_1	C_2	C_3	J_{FF}, Hz
	−145.1 (d)		−96.7 (t)	43.5
		−127.8 (t)	−98.5 (d)	41.4
			−99.8	
	3.68	−154.6 (t)	−93.1 (d)	48.2
		3.84	−93.5	
	3.97		−99.1	

[a] All chemical shifts in parts per million relative to tetramethylsilane (¹H) or trichlorofluoromethane (¹⁹F); multiplicities are singlets unless noted; d = doublet, t = triplet. [b] Reference 4. [c] Reference 3.

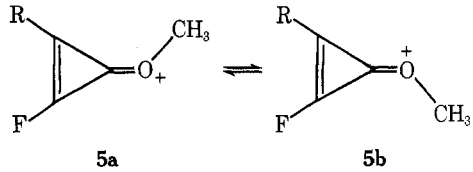
resonance hybrid **5** is an important contribution. The 0.46–0.81-ppm downfield shift of the methyl protons in **3** further indicates delocalization of electrons from oxygen into the ring.



5

In **3b**, positive charge can be equally delocalized onto both methoxy groups, and the fluorine in **3b** has more vinyl character compared with the fluorines in **3a** and **3c**.

It should be pointed out that hybrid **5** can exist in two isomeric forms (R ≠ F), **5a** and **5b**. The magnitude of the methoxy group rotational barriers will depend upon the contribution of hybrid **5** to the cation. If hybrid **5** is unimportant, the rotational activation barrier will be approximately that in dimethyl ether, 2.7 kcal/mol.[10] Assuming no ring charge delocalization, the **5a** ⇌ **5b** barrier can be estimated to be greater than 17 kcal/mol.[11] The inability to observe temperature-dependent ¹H NMR or ¹⁹F NMR spectra is strong evidence that cations **3b,c** have relatively low methoxy group rotational barriers[12] and they retain a substantial degree of their delocalized, two π electron aromatic character.



5a **5b**

The unusual reactivity of **1a–c** is due to the lability of their allyl fluorines. Solvolysis of these derivatives most likely proceeds through stabilized cyclopropenium cations or cyclopropenones. Dehmlow[13] has reported products analogous to the methanolysis product of **1a** or **1b** in the ethanolysis of 1,2-diethoxycyclopropenone or trialkoxycyclopropenium cations.

Table III. NMR Data for Cyclopropenium Cations

Cation[a]	Chemical shift, ppm[b] ¹⁹F	¹H
$C_3F_3^+$ (4a)	−63.1	
$C_3Cl_2F^+$ (4b)	−63.4	
$C_3ClF_2^+$ (4c)	−63.6	
$C_4H_3F_2O^+$ (3a)	−84.7	4.49
$C_5H_6FO_2^+$ (3b)	−102.9	4.30
$C_4H_3ClFO^+$ (3c)	−80.9	4.63

[a] Cation derived from corresponding cyclopropene in Table II; see references therein. [b] External reference.

Experimental Section

The ¹H and ¹⁹F NMR spectra were obtained on Varian Associates Model A56/60 or XL-100 spectrometers equipped with variable temperature accessories. The proton chemical shifts are referred to tetramethylsilane, and the fluorine chemical shifts are referred to trichlorofluoromethane. All melting and boiling points are uncorrected.

Tetrafluorocyclopropene was prepared following the procedure of Sargeant and Krespan.[4] The literature procedure[3] for the synthesis of 1,2-dichlorodifluorocyclopropene was slightly modified in order to improve the overall yield.

1,2-Dichlorodifluorocyclopropene. A mixture of 24.9 g (0.14 mol) of tetrachlorocyclopropene and 30.3 g (0.17 mol) of antimony trifluoride was placed in a single-neck flask attached to a 12-in. spinning-band column. All operations were performed in a nitrogen atmosphere. The mixture was heated to 90 °C in an oil bath and after ca. 5 min the reaction mixture vigorously boiled, although no distillate was collected. The reaction mixture was heated to 120 °C where the product began to distill, and finally to 140 °C. A total of 14.0 g (69%) of pure product was collected, bp 59 °C [lit.[3] bp 60 °C (733 mm)].

1-Methoxytrifluorocyclopropene (1a). A slurry of 27 g (0.5 mol) of sodium methoxide in 300 ml of diglyme was chilled in a dry ice/acetone bath and 56 g (0.5 mol) of tetrafluorocyclopropene was slowly introduced. The temperature was kept below −60 °C during the addition. After complete addition the reaction mixture was slowly warmed to room temperature, then stirred for 2 h. The product was flash distilled from the reaction mixture at 15–20 mm into a −78 °C trap. The trap content was fractionated to give 38.8 g (63%) of **1a:** bp 67–68 °C; ir (neat) 1907 cm⁻¹ (C=C); NMR (CCl_4) ¹H δ 3.68 (s), ¹⁹F φ −93.1 (d, 2, J = 48.2 Hz), −154.6 (t, 1, J = 48.2 Hz); mass spectrum m/e 124.0111 (P) (calcd, 124.0136).

1,2-Dimethoxydifluorocyclopropene (1b). Precondensed tetrafluorocyclopropene (22.4 g, 0.2 mol) was slowly added to a slurry of 21.6 g (0.4 mol) of sodium methoxide in 200 ml of diglyme chilled in a dry ice/acetone bath. Upon slowly warming to room temperature, the reaction mixture evolved heat and was immediately chilled in an ice bath. After stirring for ca. 30 min at 0 °C and an additional 30 min at room temperature, the product was flash distilled at 20 mm into a −78 °C trap. The trap content was redistilled, and 13.1 g (48%) of crude **1b** was collected: bp 53–55 °C (60 mm); ir (neat) 1895 cm⁻¹ (w, C=C); NMR (CCl_4) ¹H δ 3.84 (s), ¹⁹F φ −93.5 (s); redistilled, bp 74 °C (80 mm); mass spectrum (CI) 136 (P).

1-Methoxy-2-chlorodifluorocyclopropene (1c). A slurry of 16.2 g (0.3 mol) of sodium methoxide in 150 ml of diglyme was treated dropwise with 43.5 g (0.3 mol) of 1,2-dichlorodifluorocyclopropene at such a rate to keep the reaction temperature below −60 °C. After the addition was completed, the mixture was slowly warmed to room temperature and stirred for 1 h. The product was flash distilled from the reaction mixture into a −78 °C trap at ca. 10 mm and was redistilled to afford 33.1 g (79%) of **1c:** bp 61–62 °C (150 mm); ir (neat) 1832 cm⁻¹ (C=C); NMR (CCl_4) ¹H δ 3.97 (s), ¹⁹F φ −99.1 (s).

Anal. Calcd for $C_4H_3ClF_2O$: C, 34.19; H, 2.15; F, 27.04. Found: C, 34.26; H, 2.43; F. 27.20.

Samples of **1a–c** are best stored as solids at −70 °C under argon. Materials which have been contaminated turn yellow or red and may spontaneously decompose. It is particularly difficult to store **1b**, and it is recommended that this material be used immediately when prepared.

1-Methoxy-1,2-dichloro-2,3,3-trifluorocyclopropane (2). A solution of 24.8 g (0.2 mol) of **1a** in 100 ml of methylene dichloride was protected from the light and treated slowly with 14.2 g (0.2 mol) of precondensed chlorine while keeping the reaction temperature below 0 °C. After stirring in the dark at room temperature overnight, the reaction mixture was distilled at atmospheric pressure to remove the solvent, and the residual oil was fractionated in vacuo to give 18.2 g (47%) of **2**: bp 60–63 °C (190 mm); NMR (CCl_4) ^1H δ 3.66 (s), ^{19}F ϕ −142.0, −147.2 (AB m of m, 2, $J_{AB} \simeq 166$ Hz: A, d, $J \simeq 2.8$ Hz; B, d, $J \simeq 2.2$ Hz), −152.0 (d of d, 1, $J = 2.8, 2.2$ Hz).

Anal. Calcd for $C_4H_3Cl_2F_3O$: C, 24.64; H, 1.55; F, 29.23. Found: C, 24.68; H, 1.53; F, 29.07.

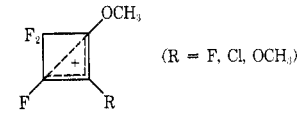
Methanolysis of 1a. A mixture of 2 ml of methanol in 10 ml of carbon tetrachloride was treated dropwise at room temperature with 1.24 g (10 mmol) of **1a**. After stirring overnight, the reaction mixture was concentrated, and the product was taken up in methylene dichloride, filtered, and concentrated to give 1.37 g (94%) of methyl *cis*-2,3-dimethoxyacrylate: bp 61–62 °C (1.2 mm); ir (neat) 1711 (C=O), 1645 cm^{-1} (C=C); NMR (CCl_4) δ 3.58 (s, 3), 3.66 (s, 3), 3.82 (s, 3), 6.90 (s, 1).

Ion Preparations. Under anhydrous conditions a solution of freshly distilled antimony pentafluoride in sulfur dioxide (ca. 2 M) was treated dropwise with 1 equiv of the respective cyclopropene (**1**) while keeping the reaction temperature below −65 °C. After the cyclopropene was added, the solutions were slowly warmed to room temperature while the sulfur dioxide was removed in a slow stream of nitrogen. The hexafluoroantimonate salts (**3**) were deposited as colorless, crystalline solids and were bottled under argon. The solutions for NMR study can be prepared by directly withdrawing samples from the reaction mixture or by redissolving the stock salts in sulfur dioxide.

Registry No.—**1a**, 59034-32-1; **1b**, 59034-33-2; **1c**, 59034-34-3; **2**, 59034-35-4; **3a**, 59015-63-3; **3b**, 59015-65-5; **3c**, 59015-67-7; cyclopropene, 2781-85-3; tetrafluorocyclopropene, 19721-29-0; 1,2-dichlorodifluorocyclopropene, 6262-45-9; methyl *cis*-2,3-dimethoxyacrylate, 59034-36-5.

References and Notes

(1) R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, **4**, 50 (1965).
(2) J. D. Park, R. J. McMurtry, and J. H. Adams, *Fluorine Chem. Rev.*, **2**, 55 (1968).
(3) D. C. F. Law, S. W. Tobey, and R. West, *J. Org. Chem.*, **38**, 768 (1973).
(4) P. B. Sargeant and C. G. Krespan, *J. Am. Chem. Soc.*, **91**, 415 (1969).
(5) J. T. Barr et al., *J. Am. Chem. Soc.*, **72**, 4480 (1950).
(6) J. D. Park, C. M. Snow, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 2342 (1951).
(7) J. D. Park, S. M. Sharrah, and J. R. Lacher, *J. Am. Chem. Soc.*, **71**, 2337 (1949).
(8) J. D. Park, S. Cohen, and J. R. Lacher, *J. Am. Chem. Soc.*, **84**, 2919 (1962).
(9) B. E. Smart and G. S. Reddy *J. Am. Chem. Soc.*, submitted for publication.
(10) J. G. Astin in "Determination of Organic Structures by Physical Methods", Vol. I, E. A. Brande and F. C. Nachod, Ed., Academic Press, New York, N.Y., 1955, p 525.
(11) Barriers to rotation about the carbonyl-carbon oxygen bond in methylated or protonated ketones and aldehydes are not experimentally known; calculated barriers for the protonated carbonyl species range from a minimum of 17 kcal/mol [D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **86**, 879 (1967)] to 25–30 kcal/mol [P. Roos, *J. Chem. Phys.*, **49**, 4902 (1968)].
(12) This assumes that the chemical shift difference of the protons or fluorines between **5a** and **5b** is sufficiently large that line shape effects will be observed in the temperature range studied. (The exchange rate at coalescence for a two-site exchange process is approximately proportional to the differences of the individual site resonance frequencies.) This is the case in the homologous series of cyclobutenyl cations **6** which have observed activation barriers to methoxy rotation of ca. 15–17 kcal/mol (ref 9).



6

(13) E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, **13**, 209 (1974).
(14) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1266 (1961).

Stabilization of Cyclopropenium Ion and Cyclopropenone by Guaiazulene[1]

Israel Agranat* and Eliezer Aharon-Shalom

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Received November 19, 1975

$C_3Cl_3^+AlCl_4^-$ (from tetrachlorocyclopropene and aluminum chloride) reacts with 2 molar equiv of guaiazulene (**8**) in dichloromethane solution to give, after aqueous workup, di-3-guaiazulenylcyclopropenone (**7**). An analogous reaction of $C_3Cl_3^+AlCl_4^-$ with 3 molar equiv of **8** followed by treatment of perchloric acid (70%) afforded tri-3-guaiazulenylcyclopropenium perchlorate (**6**). The dipole moment of **7**, 5.13 D, is analyzed in terms of the dipole moment orientations of the azulenyl groups relative to the cyclopropenone moiety. The ^1H NMR spectra of **6** and **7** are analyzed in comparison with the corresponding spectra of **8** and various of its 3-acyl derivatives. The interactions of the guaiazulenyl groups with the cyclopropenone (in **7**) and the cyclopropenium ion (in **6**) are discussed. The high pK_{R^+} of **6**, >10, indicates the remarkable effect of the three guaiazulenyl groups in delocalizing the positive charge of the three-membered ring.

Azulene (**1**)[2,3] and cyclopropenium ion (**2**)[3-7] are considered two independent milestones in the chemistry of nonbenzenoid aromatics. The interest in azulene, the "aromatic" nonalternant polycyclic prototype, had somewhat declined during the past decade. The origin of this decline may be traced to the dominant role played by the Hückel $4n + 2$ rule and its experimental "verifications" for $n \neq 1$.[8] Recent cyclopropenium ion (**2**) and cyclopropenone (**3**)[9,10] studies have focused on the stabilization of the "aromatic" but highly strained $2\pi 3C$ ring system by appropriate electron-donating substituents, particularly heteroatoms.[11-14] In a search for alternative substituents which are capable of delocalizing the positive charge of the three-membered ring, we have considered the azulenyl group. The rationale underlying this approach is based on the extra "aromatic" stabilization of 1-azulenylcarbenium ion (**4**), a variation of the tropylium ion theme.[9,15] 1-Azulenylcyclopropenium ion (**5**) may formally be considered as a triapentafulvalene system condensed to tropylium ion (**5a**). We report straightforward syntheses and various properties of cyclopropenium ion and cyclopropenone *totally* substituted by guaiazulenyl groups: tri-3-guaiazulenylcyclopropenium perchlorate (**6**) and di-3-guaiazulenylcyclopropenone (**7**). Few examples of azulenyl- (and pseudoazulenyl-) *diphenyl*cyclopropenium salts have previously been described.[16-18] Azulene derivatives of cyclopropenone are unknown.[10]

The synthetic route of choice was the electrophilic substitution of aromatic substrates by trichlorocyclopropenium-salts via a Friedel–Crafts pathway (method of West and Tobey),[10,19-22] applied in dichloromethane. In principle, this