ELSEVIER

Journal of Fluorine Chemistry 69 (1994) 231–236

JOURNAL OF FLUORINE CHEMISTRY

Reactions of cycloalkanecarboxylic acids with SF_4. II. Fluorination of *gem*-dichlorocyclopropanecarboxylic acids with SF_4★

Yu.M. Pustovit, P.I. Ogojko, V.P. Nazaretian*, A.B. Rozhenko

The Ukrainian Academy of Sciences, Institute of Organic Chemistry, Kiev 252094, Ukraine

Received 14 May 1993; accepted 19 September 1993

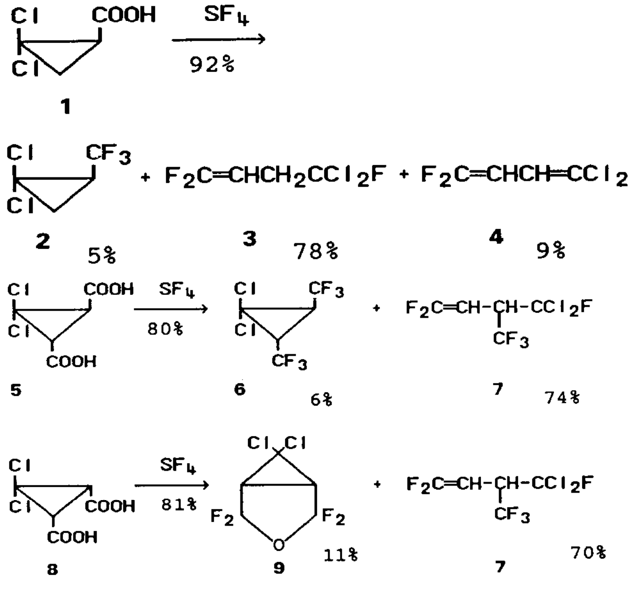
Abstract

Treatment of *gem*-dichlorocyclopropanecarboxylic acids with SF_4 yields many rearranged products, i.e. 1,1-difluoro-substituted olefins. The mechanism of the rearrangement is discussed.

Keywords: Cycloalkanecarboxylic acids; Sulphur tetrafluoride; Rearrangement mechanism; Stereochemistry; NMR spectroscopy; IR spectroscopy

1. Introduction

In contrast to cyclopropane-monocarboxylic acid [1], cyclopropanecarboxylic acids having more than one carboxylic group when treated with SF_4 readily undergo fluorination to yield the corresponding polytrifluoromethylcyclopropanes and bicyclic ethers [2]. Hence, it may be assumed that the introduction of other electronegative substituents, e.g. chlorine atoms, should also favour fluorination of the respective cyclopropanecarboxylic acids. We have found that treatment of *gem*-dichloro-substituted cyclopropanecarboxylic acids with SF_4 yields the corresponding trifluoromethylcyclopropanes as the minor products, with olefins being the major products (see Scheme 1).



Scheme 1.

2. Experimental

^1H and ^{19}F NMR spectra were measured with a Bruker WP-200 NMR spectrometer using TMS and $CFCl_3$ as internal standards, and $CDCl_3$ as the solvent (acetone-d_6 for compounds **5** and **8**). The ^{19}F upfield chemical shift values are negative. ^{13}C NMR spectra were measured with a Varian 300 NMR spectrometer using TMS as internal standard, and $CDCl_3$ as the solvent (acetone-d_6 for compounds **5** and **8**). Gas–liquid chromatography was carried out with a Chrom 5 chromatograph fitted with FID using helium as the carrier gas, and employing a stainless-steel column (2500 × 3 mm) filled with 10% polyphenylmethylsiloxane on Chromatone AW (0.20–0.25 mm). Preparative GLC was carried out with a PACHV 07 chromatograph fitted with a thermal conductivity detector using a stainless-steel column (2600 × 12 mm) filled with 10% polyphenylmethylsiloxane on Chromatone N-AW-HMDS (0.32–0.40 mm) and employing helium as the carrier

---

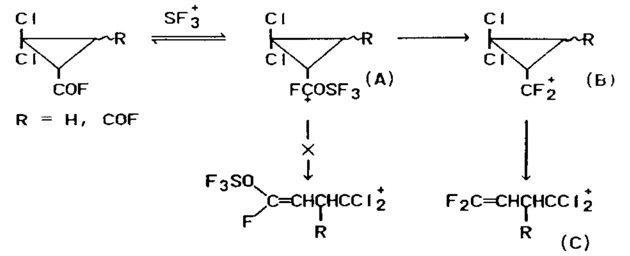
★Dedicated to Professor L.M. Yagupolskii on the occasion of his 70th birthday.

*Corresponding author.

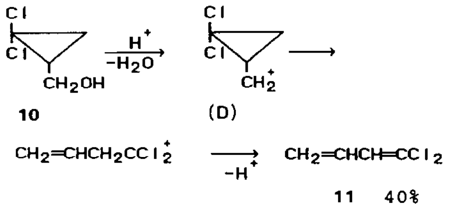
0022-1139/94/$07.00
SSDI 0022-1139(93)02995-Q

Table 1
Reactions of carboxylic acids with SF_4

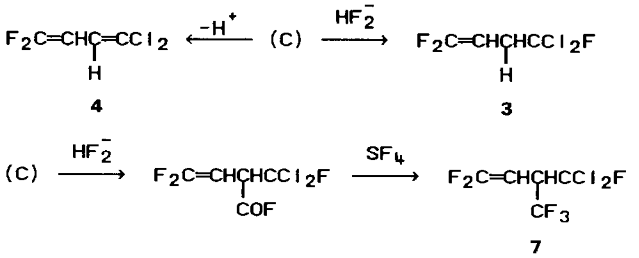
Acid		SF_4 (mmol)	Reaction conditions		Reaction product(s), yield (%)
No.	mmol		Temp. (°C)	Time (h)	
1	20	110	140	4	**2**, 5; **3**, 78; **4**, 9
5	20	120	140	4	**6**, 6; **7**, 74
8	50	300	140	6	**9**, 11; **7**, 70



Scheme 2.



Scheme 3.

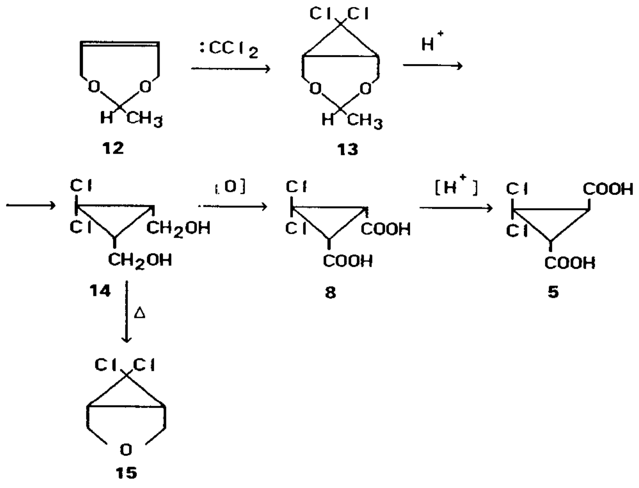


Scheme 4.

gas. All boiling and melting points are reported uncorrected. Vapour-phase infrared spectra were measured with a UR-20 (Zeiss) spectrometer.

2,2-Dichlorocyclopropanecarboxylic acid (1)

$KMnO_4$ (33 g, 210 mmol) was added to a stirred solution of 2,2-dichlorocyclopropylmethanol [3] (14.1 g, 100 mmol) and 6.7 g (27 mmol) of $MgSO_4 \cdot 7H_2O$ in 100 ml of water at such a rate that the temperature was maintained at 75 °C. After addition was complete, the mixture was stirred for an additional 0.5 h. Excess permanganate was destroyed by the addition of methanol. The reaction mixture was filtered to remove MnO_2, acidified with dilute HCl to pH = 2, and evaporated to dryness. The residue was extracted with hot acetone.



Scheme 5.

The solvent was removed under reduced pressure to yield crude **1** (13.0 g, 84%). Recrystallization from hexane afforded 1 as colourless crystals, m.p. 75 °C (lit. value [4]: m.p. 76 °C).

cis-3,3-Dichlorocyclopropan-1,2-dicarboxylic acid (8)

$KMnO_4$ (39 g, 247 mmol) was added to a stirred solution of *cis*-1,2-bis(oxymethyl)-3,3-dichlorocyclopropane **14** (10.26 g, 60 mmol) and 8 g (32 mmol) of $MgSO_4 \cdot 7H_2O$ in 100 ml of water at such a rate that the temperature was maintained at 75–80 °C. After addition was complete, the mixture was stirred for an additional 0.5 h. Excess permanganate was destroyed by the addition of methanol. The reaction mixture was filtered to remove MnO_2, acidified with dilute HCl to pH = 2, and evaporated to dryness. The residue was extracted with hot acetone. The solvent was removed under reduced pressure to yield crude **8** (8.5 g, 71%). Recrystallization from CH_3COOH afforded **8** as colourless crystals.

trans-3-3,3-Dichlorocyclopropan-1,2-dicarboxylic acid (5)

cis-3,3-Dichlorocyclopropan-1,2-dicarboxylic acid (**8**) (7 g, 35 mmol) and 5 cm^3 of concentrated HCl were

Table 2
Physical properties of compounds prepared

Compound No.	B.p./mmHg [m.p.] (°C)	d_4^{22} (g cm^{-3})	n_D^{22}	Elemental analyses		
				Found (%)	Molecular formula	Calc.%
3^a	86/760	1.393	1.384	C 26.8	$C_4H_3Cl_2F_3$	26.8
				H 1.6		1.7
				Cl 39.5		39.6
				F 31.8		31.8
5	[218]	–	–	C 30.2	$C_5H_4Cl_2O_4$	30.2
				H 2.0		2.0
				Cl 35.6		35.6
7^b	93/760	1.534	1.355	C 24.4	$C_5H_2Cl_2F_6$	24.3
				H 0.8		0.8
				Cl 28.7		28.7
				F 46.0		46.2
8	[195]	–	–	C 30.2	$C_5H_4Cl_2O_4$	30.2
				H 2.0		2.0
				Cl 35.6		35.6
9	135/760	1.641	1.395	C 26.6	$C_5H_2Cl_2F_4O$	26.7
				H 0.8		0.9
				Cl 31.5		31.5
				F 33.7		33.8
13	107/10 [52]	–	–	C 42.5	$C_7H_{10}Cl_2O_2$	42.7
				H 5.1		5.1
				Cl 36.0		36.0
14	121/0.3 [71]	–	–	C 35.1	$C_5H_8Cl_2O_2$	35.1
				H 4.6		4.7
				Cl 41.4		41.5
15^c	78/20	1.374	1.498	C 39.2	$C_5H_6Cl_2O$	39.2
				H 3.9		4.0
				Cl 46.3		46.3

[a] IR(cm^{-1}): 1790 (C=C).
[b] IR(cm^{-1}): 1763 (C=C).
[c] Lit. value [6]: b.p. 80 °C/15 mmHg; n_D^{22} = 1.4982.

heated at 200 °C (1 h) in a sealed tube and then cooled to room temperature. The colourless precipitate was collected by filtration and dried *in vacuo* at 100 °C. Yield, 6.8 g (97%).

2.1. Treatment of carboxylic acids with SF_4. General procedure

An acid and SF_4 were reacted in a stainless-steel cylinder using the appropriate amounts of reactant, reaction time and temperature as indicated in Table 1. The gaseous products were released and the liquid residue poured into ice/water, the organic layer separated, dried over P_2O_5 and purified by distillation or preparative GLC, as necessary. The physical properties and analyses of the products are listed in Table 2 and the NMR spectral data is recorded in Table 3.

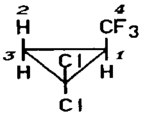
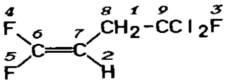
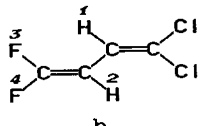
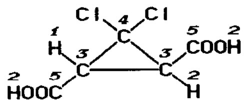
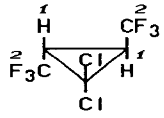
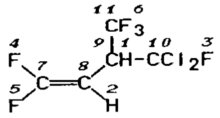
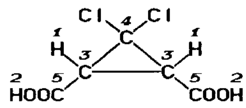
1,1-Dichlorobuta-1,3-diene (11)

2,2-Dichlorocyclopropylmethanol (**10**) (4.2 g, 30 mmol) was added dropwise to P_2O_5 (4.30 g, 30 mmol). The reaction mixture was warmed for some time with a flame and the low boiling products were then distilled off. The product with b.p. 103 °C (decomp.) was collected (1.9 g, 51%) and identified as 1,1-dichlorobuta-1,3-diene (**11**) [5].

Cisoid-4-methyl-8,8-dichloro-3,5-dioxabicyclo[5.1.0]-octane (13)

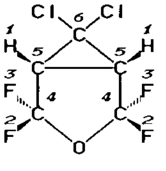
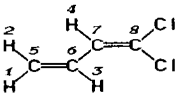
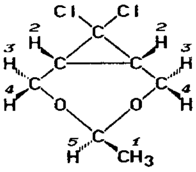
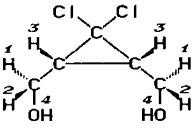
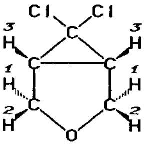
A solution consisting of 1120 g (20 mol) KOH in 1 dm^3 of water was added to a vigorously stirred solution of freshly distilled *cis*-2-butene-1,4-diol acetal (**12**) (114 g, 1 mol) in 810 cm^3 of $CHCl_3$. During this procedure, the reaction temperature was maintained below 30 °C by means of a cold water bath. Subsequently, the reaction mixture was left at room temperature for 8 h. The resulting precipitate was filtered off and washed with $CHCl_3$ (3×100 cm^3). The organic layer was separated, washed with water (3×300 cm^3), dried over sodium sulfate and concentrated *in vacuo*. The residue was distilled under reduced pressure. Yield, 60 g (30.5%).

Table 3
NMR data of compounds prepared

Formula	Nucleus No.	Signal struct.	Chemical shift (ppm)	Coupling constants (Hz)
 **2**	1	m	2.59	
	2, 3	m	1.88–2.20	
	4	d	−64.5[a]	$^{3}J_{4,1}=7$
 **3**	1	m	3.17	$^{3}J_{1,2}=7.6$; $^{3}J_{1,3}=13$; $^{4}J_{1,4(5)}=1.4$
	2	m	4.40	$^{3}J_{2,1}=7.6$; $^{3}J_{2,4}=23$; $^{3}J_{2,5}=1.4$
	3	t	−54.0	$^{3}J_{3,1}=13$
	4	d d	−87.5	$^{2}J_{4,5}=31.5$; $^{3}J_{4,2}=23$
	5	d d	−84.7	$^{2}J_{5,4}=31.5$; $^{3}J_{5,2}=1.4$
	6 {H}	d d	158.3	$^{1}J_{6,4(5)}=289$; $^{1}J_{6,5(4)}=292$
	7 {H}	m	71.7	$^{2}J_{7,4(5)}=19$; $^{2}J_{7,5(4)}=29.5$; $^{3}J_{7,3}=4.4$
	8 {H}	d d	42.9	$^{2}J_{8,3}=25.3$; $^{3}J_{8,4}=5.9$; $^{3}J_{8,5}=5.9$
	9 {H}	m	119.8	$^{1}J_{9,3}=298$; $^{4}J_{9,4(5)}=3.7$; $^{4}J_{9,5(4)}=5.1$
 **4**[b]	1	d	6.35	$^{3}J_{1,2}=11$
	2	d d	5.19	$^{3}J_{2,1}=11$; $^{3}J_{2,3}=24$
	3	d d	−82.3	$^{2}J_{3,4}=15$; $^{3}J_{3,2}=24$
	4	d	−84.4	$^{2}J_{4,3}=15$
 **5**	1	s	3.00	
	2	b s	10.0	
	3	s	38.0	
	4	s	58.9	
	5	s	165.9	
 **6**	1	m	2.76	
	2	d	−64.5[c]	$^{3}J_{2,1}=4$
 **7**	1	m	3.97	$^{3}J_{1,3}=7$; $^{3}J_{1,6}=7$; $^{3}J_{1,2}=10$
	2	m	4.55	$^{3}J_{2,1}=10$; $^{3}J_{2,4}=22$
	3	m	−54.5	$^{3}J_{3,1}=7$; $^{4}J_{3,6}=14$
	4	t	−81.6	$^{2}J_{4,5}=22$; $^{3}J_{4,2}=22$
	5	d	−80.3	$^{2}J_{5,4}=22$
	6	m	−65.5	$^{3}J_{6,1}=7$; $^{4}J_{6,3}=14$
	7 {H}	d d	159.7	$^{1}J_{7,4(5)}=289$; $^{1}J_{7,5(4)}=294$
	8 {H}	d d	71.2	$^{2}J_{7,4(5)}=18$; $^{2}J_{7,5(4)}=37$
	9 {H}	m	54.8	$^{2}J_{9,3}=29.8$; $^{2}J_{9,6}=29$; $^{3}J_{9,4}=6.8$; $^{3}J_{9,5}=6.8$
	10 {H}	d	117.4	$^{1}J_{10,3}=300$
	11 {H}	q	122.9	$^{1}J_{11,6}=282$
 **8**	1	s	3.09	
	2	b s	9.9	
	3	s	36.7	
	4	s	59.2	
	5	s	156.6	

(*continued*)

Table 3 (*continued*)

Formula	Nucleus No.	Signal struct.	Chemical shift (ppm)	Coupling constants (Hz)
 **9**	1	m	3.92	$^3J_{1,2}=14$
	2	AB	−57.0	$^2J_{2,3}=154$
	3	AB	−82.6	$^2J_{3,2}=154$
	4	m	125.9	$^1J_{4,2}=262$; $^1J_{4,3}=262$; $^3J_{4,2(3)}=2.3$; $^3J_{4,3(2)}=6.5$
	5	d d	37.7	$^2J_{5,2(3)}=29$; $^2J_{5,3(2)}=42$
	6	t	56.5	$^3J_{6,2(3)}=7.6$
 **11**	1,2	m	5.20–5.44	
	3,4	m	6.33–6.57	
	5 {H}	s	120.5	
	6(7) {H}	s	129.3	
	7(6) {H}	s	131.0	
	8 {H}	s	122.2	
 **13**	1	d	1.30	$^3J_{1,5}=5.1$
	2	m	2.22	
	3	m	3.61–3.74	
	4	m	4.46–4.58	
	5	q	4.58	$^3J_{5,1}=5.1$
 **14**	1(2)	d d	3.55	$^2J_{1,2}=12$; $^3J_{1(2),\,3}=8$
	2(1)	d d	3.93	$^2J_{2,1}=12$; $^3J_{2(1),\,3}=6$
	3	m	1.95	
	4	b s	3.89	
 **15**	1,2	m	3.94–4.03	
	3	m	2.43	

[a] Lit. value [7]: −64.15 ppm.

[b] IR (cm^{-1}): 1630 ($C{=}CCl_2$); 1758 ($C{=}CF_2$).

[c] Lit. value [7]: −64.95 ppm.

cis-1,2-Bis(oxymethyl)-3,3-dichlorocyclopropane (14)

A mixture consisting of **13** (55 g, 279 mmol) and 50 cm^3 of 1% HCl was heated at 80 °C (3 h) while the acetaldehyde formed in the reaction was distilled off. Excess water was evaporated off and the residue distilled *in vacuo* (b.p. 121 °C/0.3 mmHg) or crystallized from benzene. Yield, 45.5 g (95%).

Attempted distillation of *cis*-1,2-bis(oxymethyl)-3,3-dichlorocyclopropane (**14**) at 160–165 °C/20 mmHg resulted in the formation of 6,6-dichloro-3-oxabicyclo[3.1.0]hexane (**15**) [6]. Yield, 55%.

3. Results and discussion

The formation of olefins may proceed via the carbocations A or B, as shown in Scheme 2. The opening of the cyclopropane ring more probably proceeds after formation of the difluorocarbocation B, but not at the earlier stage of formation of a mesomeric trifluorosulfuroxyfluorocarbocation A, which is less electrophilic than the difluorocarbocation B [8].

This conclusion has been confirmed indirectly from an experiment where carbocation D which is more electrophilic than difluorocarbocation B was generated (Scheme 3).

Opening of the cyclopropane ring in difluorocarbocation B proceeds at the most substituted bond, as shown in other reactions of cyclopropanes [9]. Subsequent transformation of the intermediate olefins C into final olefins proceeds (in the case R = H) with proton elimination or by neutralization with HF_2^- to give **4** or **3**. When R = COF, neutralization of the intermediate olefin C with HF_2^- is followed by fluorination of the fluoroformyl group. The previous unknown *gem*-dichlorocyclopropanecarboxylic acids **5** and **8** were prepared as shown in Scheme 5.

References

[1] W. Dmowski and R.A. Kolinski, *Pol. J. Chem., 52* (1978) 547.

[2] Yu.M. Pustovit, P.I. Ogojko, V.P. Nazaretian and L.B. Faryat'eva, *J. Fluorine Chem., 69* (1994) 225.

[3] A. Kh. Khusid, G.V. Kryshtal, V.F. Kucherov and L.A. Yanovskaya, *Synthesis,* (1977) 428.

[4] R.C. Woodworth and P.S. Skell, *J. Am. Chem. Soc., 79* (1957) 2542.

[5] F. Guibe, Yang Ting Xian and G. Balavoine, *J. Organomet. Chem., 306* (1986) 267.

[6] J.C. Anderson and C.B. Reese, *Chem. Ind. (London),* (1963) 575.

[7] R. Fields, R.N. Haszeldine and D. Peter, *J. Chem. Soc.,* (1969) 165.

[8] Yu.M. Pustovit and V.P. Nazaretian, *J. Fluorine Chem., 55* (1991) 29.

[9] L.A. Yanovskaya, V.A. Dombrovskij and A. Kh. Khusid, *Cyklopropany s funkcyonalnymi gruppami,* Nauka, Moscow, 1980, pp. 107, 151.