ELSEVIER

Journal of Fluorine Chemistry 81 (1997) 163-168

JOURNAL OF FLUORINE CHEMISTRY

Oligomerization reactions of perfluorovinylamines catalyzed by fluoride ions

Taizo Ono *, Fumitoshi Teramoto, Haruhiko Fukaya, Naohiro Terasawa, Masakazu Nishida, Takashi Abe

Fluorine Chemistry Laboratory, Chemistry Department, National Industrial Research Institute of Nagoya, 1-1 Hirate-cho, Kita-ku, Nagoya 462, Japan

Received 21 March 1996; accepted 17 July 1996

Abstract

The fluoride ion catalyzed oligomerization of *F*-vinylamines, such as *F*-(*N,N*-dimethylvinylamine), *F*-(*N*-vinylmorpholine) and *F*-(*N*-vinylpyrrolidine), was investigated. It was found that dimers were obtained in high yields when the reaction was conducted in aprotic polar solvents, especially in DMF using cesium fluoride as a fluoride ion source. Attempts to obtain oligomers higher than dimers failed. The absence of higher oligomers is discussed in stereoelectronic and steric terms by comparison with the analogous oligomerization of hexafluoropropene. Unexpected results obtained in the reaction of *F*-(*N,N*-dimethylvinylamine) with the hexafluoropropene dimer *F*-2-methyl-2-propene are also included.

Keywords: Perfluorovinylamine; Oligomerization; Fluoride ion catalysis

1. Introduction

Oligomerization reactions of *F*-olefins such as tetrafluoroethylene and hexafluoropropene have been extensively studied [1]. To the best of our knowledge oligomerization of *F*-vinylamines has not yet been studied because of the difficulty of their synthesis [2]. We recently found a convenient high yield method for synthesizing a variety of *F*-vinylamines which seems to be easily scaled up to an industrial scale because the underlying method, so-called electrochemical fluorination, is industrially well established [3]. In contrast with other well studied *F*-olefins or *F*-vinyl ethers, much of the chemistry of *F*-vinylamines remains to be explored [4]. We, therefore, began our study of *F*-vinylamines by looking at the fluoride ion catalyzed oligomerization. The effect of the solvents and fluoride ion sources on the reaction was investigated. The results are discussed by comparison with oligomerization of hexafluoropropene.

2. Results and discussion

Before going into the oligomerization of **1a–1c**, we started to seek the best reaction conditions using compound **1a**. From the results summarized in Table 1, it is obvious that the dimerization reaction proceeds only in aprotic polar solvents (runs 1–5) in the presence of cesium fluoride. When DMF and cesium fluoride are used as a solvent and fluoride ion source respectively, the reaction proceeds smoothly at room temperature to give a mixture of dimer **2a** (E:Z = 86:14) in high yield (87%, run 1). The yield of **2a** decreased to about 70% when DMSO or NMP was used as solvent with the fluoride ion source unchanged (runs 3 and 5). HMPA and DMI decrease slightly the yield further to 65%–66% (runs 2 and 4). Acetonitrile was reported to be effective for the dimerization of hexafluoropropene [5], but was found to be unsuitable for this reaction. Thus, **2a** was obtained only in 5% yield after 40 h stirring at room temperature. THF was found not to be suitable, too. Acetonitrile and THF have lower doner numbers of 14.1 and 20.0 respectively, compared with the above effective solvents such as DMF (26.6), NMP (27.3), DMSO (29.8) and HMPA (38.8) [6]. The difference in this physicochemical parameter gives a qualitative explanation for the observed solvent effect.

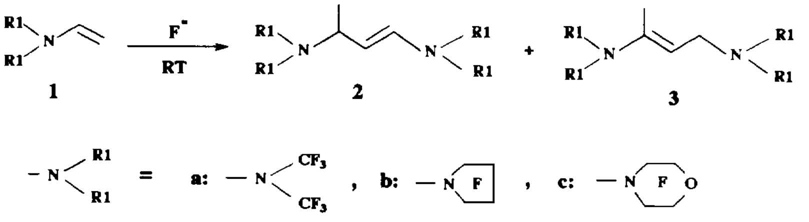
Other fluoride ion sources such as sodium fluoride and potassium fluoride were found to be ineffective, even in DMF which was selected as the best solvent for this dimerization (runs 9, 10). TBAF also had no catalytic effect in THF (run 8).

---

* Corresponding author.

PII S0022-1139(96)03519-1

Table 1
Fluoride ion catalyzed oligomerizations of *F*-vinylamines



Run	*F*-vinyl-amines	Catalyst	Solvent	Time (h)	Yield (%) [a]	
					2	3
1	1a	CsF	DMF	22	87(74) [b]	0
2	1a	CsF	HMPA	20	65	0
3	1a	CsF	DMSO	20	72	0
4	1a	CsF	DMI	20	66	0
5	1a	CsF	NMP	20	74	0
6	1a	CsF	CH_3CN	40	5	0
7	1a	CsF	THF	40	0	0
8	1a	TBAF	THF	20	0	0
9	1a	NaF	DMF	20	0	0
10	1a	KF	DMF	60	17	0
11	1b	CsF	DMF	2	0	80(62)
12	1c	CsF	DMF	20	75	0

Solvents: DMF (*N*,*N*-dimethylformamide), HMPA (hexamethylphosphoric triamide), DMSO (dimethylsulfoxide), DMI (*N*,*N*-dimethylimidazolidinone), NMP (*N*-methylpyrolidone).

[a] GC yields.

[b] Isolated yields are in parentheses.

We failed to isolate the E- and Z-isomers of **2a** since they could only be separated by capillary GC. However, ^{19}F-NMR results of the mixture are fortunately not much superimposed on each other, and the main component of the E-form is unequivocally determined by the large coupling constant (130.2 Hz) found between the two olefinic fluorine atoms, which is characteristic for the trans positions of olefinic fluorines [7]. The absence of such a large coupling constant in ^{19}F-NMR of the minor component together with other appropriate chemical shifts and additionally a very similar mass spectrum pattern support the conclusion that the minor component is a geometrical Z-isomer.

Other *F*-vinylamine derivatives, **1b** and **1c**, were subjected to the best dimerization conditions found for **1a** above. The pyrrolidino-substituted vinylamine **1b** reacted much faster than **1a** at room temperature to give **3b** in good isolated yield (62%, run 11). The compound **3b** is the sole product found in the reaction mixture and no trace of type **2** compound accompanied it. Undoubtedly, **3b** was formed through **2b** by fluoride ion catalyzed double bond migration. The morpholino-substituted **1c** is also more reactive than **1a**, but less than **1b**, giving **2c** but with no **3c** in good yield (run 12).

We have no clear explanation why cyclic *F*-vinylamines are more reactive than the non-cyclic *F*-vinylamine **1a** and why such differences in the products were found for the *F*-vinylamines examined. These are open questions and even challenging to the computational chemist. It seems worth emphasizing here that such a subtle change in the perfluorostructures from pyrrolidino to morpholino, the insertion of only one oxygen atom into a pyrrolidine ring, has an apparent effect on the reactivity, leading to the geometrically different products **3b** and **2c**.

While **2b** is susceptible to double bond migration, **2a** and **2c** are resistant under the reaction conditions. However, **2a** is also convertible to **3a** in more harsh conditions (115 °C). This rather reluctant isomerization from **2a** to **3a** is analogous to the isomerization between the hexafluoropropene dimers *F*-4-methyl-2-pentene **4** and *F*-2-methyl-2-pentene **5**.

When oligomerization of hexafluoropropene is carried out under the conditions used above, trimerization occurs [8]. By analogy, we expected the same kind of trimerization of **1a** (Fig. 1), but not even a trace amount of such trimers of **1a** was detected by GC-MS. Next, a mixture of **1a** (4.3 eq.) and **3a** (1 eq.) was stirred in an oil bath heated at 115–120 °C for 2 h, but again no trimer was obtained, only **3a**, probably for steric reasons. Then, to confirm the idea, an equivalent mixture of **1a** and **5** was stirred at room temperature for 28 h, Fig. 2. Quite differently from the expected compounds **6** and **7**, rather surprising products **8** and **9** were obtained in 32.2% and 27.7% GC yields respectively, together with 40% unchanged **5** and 4.1% **2a** (both GC yields). Routes to these unexpected products are given in the mechanisms depicted in Figs. 3 and 4.

Compound **5** is first attacked by the anion **10** derived from **1a** to give the intermediate **11**, which is further attacked by a fluoride ion to force out the bis(trifluoromethyl)amino anion

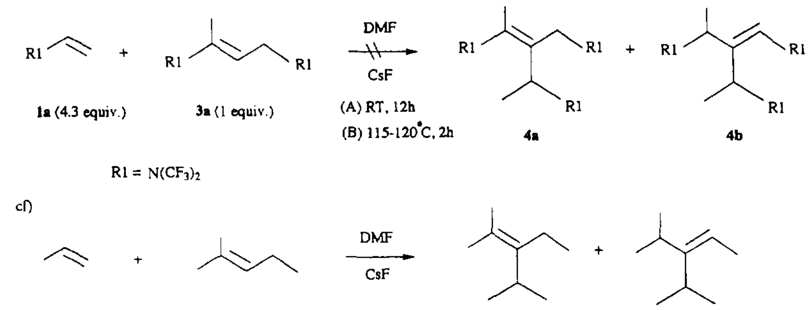


Fig. 1. Trial for preparing trimers of **1a** by analogy with the formation of hexafluoropropene trimers.

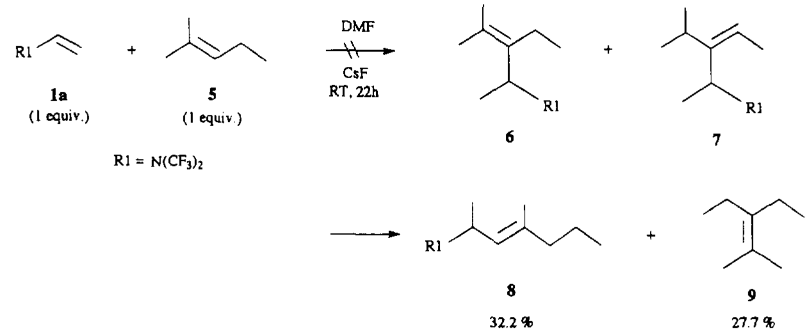


Fig. 2. Reaction of **1a** with **5**, *F*-(2-methyl-2-pentene), in the presence of cesium fluoride.

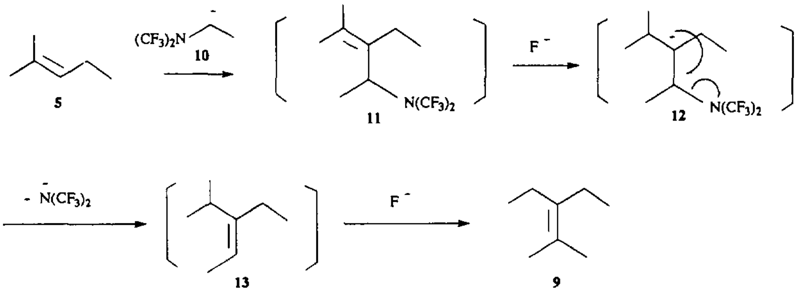


Fig. 3. Reaction mechanism for the formation of **9** obtained by the reaction of **1a** with **5**, *F*-(2-methyl-2-pentene), in the presence of cesium fluoride.

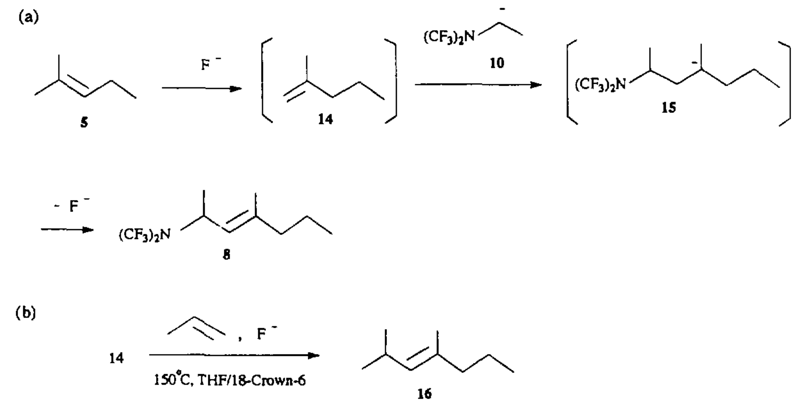


Fig. 4. (a) Reaction mechanism for the formation of **8** obtained by the reaction of **1a** with **5**, *F*-(2-methyl-2-pentene), in the presence of cesium fluoride. (b) Reaction mechanism for the formation of the hexafluoropropene trimer **16**.

from the allylic position through the intermediate anion **12**, leading to the next intermediate **13**, which is in a final step converted to the thermodynamically more stable tetra-substituted product **9** (Fig. 3).

The formation of another product **8** can be explained by a mechanism analogous to the formation of the counterpart of the hexafluoropropene trimer **16**, *F*-2,4-dimethyl-3-heptene (Fig. 4) [9]. Thus, **5** was first isomerized to the terminal olefin **14** in the presence of fluoride ions [10], which was then attacked by the anion **10** to give a geometrical mixture of **8** (32.2% GC yield) by the addition-elimination mechanism. Both geometrical isomers of **8** were isolated by GC and the structures were confirmed by ^{19}F-NMR IR, MS, and elemental analysis except the E- and Z-forms. Two peaks corresponding to **8** eluted with peak area ratios of 1 to 9 (called peak-1 and peak-2 hereafter). Both peaks have very similar MS patterns, which lack molecular ions (*m*/*z* 533) but have M-F (*m*/*z* 514) and M-CF_3 (*m*/*z* 464) ions in very low intensities, 0.1, 3.8 and 0.05, 2.3 respectively. These MS results imply that the compounds are adducts of **1a** and **5** with very similar structures and at first, based on their MS results, these were considered to be the expected products **6** and **7**. However, after isolation by GC, the ^{19}F-NMR spectra were measured and found to be inconsistent with the structures of **6** and **7**. For example, four types of CF_3 with the intensities 2:1:1:1 were found at −52.10, −58.84, −78.12, −81.75 ppm for peak-1 and at −52.40, −56.70, −78.27, −81.69 ppm for peak-2 respectively. These results are contradictory to **6** which demands five types of CF_3 with intensities 2:1:1:1:1, and also to **7** which demands four types of CF_3 with intensities 2:2:1:1. Consistency was attained with the structure of **8** from both the numbers of types of CF_3 and their intensity ratios. The position of the double bond of **8** was determined by considering the above four chemical shift values. The most critical for the determination were −52.10 and −52.40 ppm found in the lower magnetic field. These are characteristic of the $(CF_3)_2N$-moiety which is not bonded directly to a double bond [1]. If this moiety is bonded directly to a double bond, the corresponding signals should be found at around −57 ppm which were observed in the compounds **2a** and **3a**. The two chemical shifts observed at about −78 and −81 ppm are too high (in a negative sense) for the chemical shifts for the CF_3 groups bonded to the double bond, which are usually in the range −60 to −68 ppm in the perfluorosystem having no heteroatoms in the vicinity of the concerned part of the structure. The last chemical shifts observed at about −57 ppm are somewhat low for CF_3 bonded to the double bond, but the corresponding CF_3 of **16** were reported as −56.5 (bd) for the E-isomer and as −60.8 (dtt) for the Z-isomer by Ishikawa and Maruta [11]. Aside from the reason for such a lower shift, the signals at −58.84 and −56.70 ppm found in **8** look reasonable for the assigned structure.

Assignment of the E- and Z-forms of **8** is very difficult. Ishikawa's data suggest that peak-1 with −58.84 ppm has a Z-form and peak-2 with −56.70 ppm has an E-form. However, some inconsistency was observed on the CF_2 groups bonded to the double bond of **8**. An AB quartet was found at −105.7 and −113.7 ppm in peak-2 and a doublet of multiplet ($J=31.0$ Hz) was found at −105.0 ppm in peak-1. Without doubt these values belong to the CF_2 groups bonded to the double bond. Ishikawa's data on **16** reported −105.0 ppm (broad doublet) and −110.2 ppm (d,q,q,t) for the corresponding CF_2 groups of Z- and E-forms respectively. These data support the above-mentioned tentative assignment of E- and Z-forms for **8** again, but why an AB quartet for the E-form and no AB quartet for the Z-form is uncertain. There is one asymmetric carbon at C2 in **8**. The CF_2 group concerned is facing the asymmetric center in the cis-configuration in the case of the Z-form, but in the case of the E-form these groups are far away from each other in the trans-configuration, which gives a ground for assigning the Z-form to the AB quartet peak-2 and the E-form to the non-AB-quartet peak-1. Therefore, the E- and Z-forms of **8** remain to be determined.

It is worth noting the low yield of **2a**, which indicates that the cross reaction between **1a** and **5** is much faster than the self-reaction of **1a**. Therefore, **3a** was proved to be much less reactive than **5** against attack by the anion **10** derived from **1a**. Compound **3a** has the structure analogous to **5**. Substitution of two trifluoromethyl groups with *F*-dimethylamino groups at both ends of the *F*-pentene skeleton of **5** leads to **3a**. The bulkiness of the *F*-dimethylamino group might be one of the reasons for the lower reactivity of **3a**, but also the electron donating nature of nitrogen, which was once proved by the reactivity at the juxtaposition of nitrogen of perfluorotertiary amines [12], raises the LUMO level of the double bond, decreasing the reactivity of the double bond towards nucleophiles. As a result, **3a** is sterically and electronically less reactive than **5**, allowing **1a** only for dimerization but not for trimerization.

3. Experimental details

F-Vinyl amines were prepared according to the reported method [3]. All solvents used were distilled over calcium hydride except THF which was distilled over sodium diphenylketyl. Cesium fluoride was dried at 300 °C in vacuo overnight. Spray dried potassium fluoride was a gift from Morita Chemical Industries Co. Ltd. Sodium fluoride was used as purchased. The liquid phase used for GC analysis, Fomblin (YH/VAC 40/11), was a gift from AUSIMONT K.K. *F*-2-methyl-2-pentene was prepared by a literature method [5].

IR spectra were measured on a JASCO IR-810 spectrometer. Mass spectra (EI, 70 eV) were run on a Shimadzu QP-5000 quadrupole mass spectrometer using a capillary column (60 m × 0.25 i.d., 1.5 ;*gm*m NEUTRA BOND-1, GL Sciences Inc.). ^{19}F-NMR spectra were measured with a Hitachi R-90F spectrometer operating at 84.68 MHz. Chemical shifts of ^{19}F-NMR are reported on the δ scale, with $CFCl_3$ as an internal standard and negative for upfield shifts. Elemental analyses were performed by Beller Microanalytisches Laboratorium, Göttingen, Germany.

3.1. F-(1,3-bis(N,N-dimethylamino)-1-butene) (2a) (nc)

Into a 25 ml Schlenk tube equipped with a gas-tight Teflon seal were placed a magnetic stirrer bar, 2 ml of dry DMF, and dried cesium fluoride (608 mg, 4 mmol). The tube was connected to the vacuum line and **1a** (6.99 g, 30 mmol) was transferred into the tube. The reaction was conducted at room

---

[1] The chemical shifts of the $(CF_3)_2N$-moieties are −53.3 ppm for $(CF_3)_2NCF_2CF_2H$, −52.7 ppm for $(CF_3)_2NCF_2CF_2I$, −52.8 ppm for $(CF_3)_2NCF_2CF_2Br$, −53.1 ppm for $(CF_3)_2NCF_2CF_2COF$ and −58.3 ppm for $(CF_3)_2NCF{=}CF_2$ (unpublished data).

temperature for 22 h and the reaction mixture obtained was poured onto 10 ml water. The lower layer was separated, dried over anhydrous magnesium sulfate, filtered, and distilled at atmospheric pressure to give a fraction boiling at 100–106 °C (5.14 g, 74% yield). This fraction was found to consist of 86% of the E-form and 14% of the Z-form by GC-MS analysis.

^{19}F-NMR (CDCl$_3$) δ: (E-form) −52.5 (m, 6F), −57.4 (bs, 6F), −78.4 (d, septet, J = 13.0, 6.5 Hz, 3F), −110.1 (ddm, J = 130.2, 20.8 Hz, 1F), −143.2 (m, 1F), −146.2 (dm, 130.2 Hz, 1F); (Z-form) −52.3 (m, 6F), −57.38 (bs, 6F), −77.5 (m, 3F), −93.3 (m, 1F), −131.0 (m, 1F), −143.9 (m, 1F). MS (EI, 70 eV, m/z): (E-form) 466 (M, 4.2), 447 (M-F, 15.9), 397 (40.3), 359 (5.2), 314 (21.7), 309 (20.1), 226 (48.4), 221 (24.2), 176 (8.4), 114 (25.5), 69 (100); (Z-form) 446 (M, 0.6), 397 (9.1), 309 (5.1), 226 (11.3), 221 (7.1), 114 (9.3), 69 (100). IR (KBr, neat) λ_{max} (cm^{-1}): 1745 (w, $\nu_{c=c}$), 1200–1400 (br), 995 (s), 895 (m), 740 (m).

3.2. F-(1,3-bis(N,N-dimethylamino)-2-butene) (3a) (nc)

Into a 25 ml Schlenk tube with a magnetic stirrer bar were added dried cesium fluoride (608 mg, 4 mmol), dried DMF (4 ml), and **2a** (3.73 g, 8 mmol). The tube was immersed in an oil bath heated at 110–115 °C and stirred vigorously for 3 h. The reaction mixture was poured onto 10 ml water and the lower layer was collected (2.76 g). This clear liquid is almost pure **3a** (74%), dried over anhydrous magnesium sulfate, distilled at atmospheric pressure. The fraction boiling at 96–98 °C was collected (2.16 g, 58%). GC analysis using a column (3 mm i.d. × 5 m) packed with 12.1% Fomblin (YH/VAC 40/11) on Chromosorb P (AW-DMCS, 100–120 mesh) shows that this fraction consists of 86% of the E-form and 14% of the Z-form.

^{19}F-NMR (CDCl$_3$) δ: (E-form) −54.43 (m, 6F), −56.63 (bs, 6F), −65.21 (d, J = 18.6 Hz, 3F), −82.59 (bs, 2F), −100.1 (m, 1F); (Z-form) −52.44 (m, 6F), −57.36 (bs, 6F), −61.99 (m, 3F), −81.74 (m, 2F), −96.06 (m, 1F). MS (EI, 70eV) m/z: (E-form) 466 (M, 0.8), 447 (M-F, 0.5), 359 (2.7), 333 (1.1), 314 (6.0), 309 (1.2), 271 (1.0), 264 (4.1), 226 (7.2), 176 (5.6), 114 (8.0), 93 (1.2), 69 (100); (Z-form) 466 (M, 0.8), 447 (M-F, 1.5), 359 (2.9), 314 (5.6), 309 (1.6), 271 (1.6), 264 (4.5), 226 (7.2), 202 (1.2), 195 (1.3), 176 (4.8), 114 (7.7), 93 (1.4), 69 (100).

3.3. F-(1,3-dipyrrolidino-2-butene) (3b) (nc)

Into a 25 ml Schlenk tube equipped with a gas-tight Teflon seal were placed a magnetic stirrer bar, 4 ml of dry DMF, and dried cesium fluoride (608 mg, 4 mmol) and **1b** (5.90 g, 20 mmol). The reaction was conducted at room temperature for 2 h. The lower layer was separated, dried over anhydrous magnesium sulfate, and filtered to give a clear liquid (4.7 g). The distillation at atmospheric pressure gave a fraction boiling at 140–147 °C (3.7 g, 62% yield). This fraction was found to be a 3:1 mixture of E- and Z-forms of **3b** by GC-MS analysis. The following ^{19}F-NMR and IR data were taken using this geometrical isomer mixture.

^{19}F-NMR (CDCl$_3$) δ: (E-form) −64.48 (m, 3F), −83.32 (bs, 2F), −91.84 (s, 4F × 2), −96.36 (m, 1F), −132.95 (s, 4F × 2); (Z-form) −60.76 (m, 3F), −81.74 (bs, 2F), −92.20 (s, 4F × 2), −94.45 (bs, 1F), −132.45 (s, 4F × 2). MS (EI, 70 eV, m/z): (E-form) 590 (M, 3.7), 571 (M-F, 5.2), 521 (M-CF$_3$, 14.3), 376 (41.5), 326 (22.8), 264 (15.1), 231 (8.6), 176 (8.2), 169 (26.4), 150 (9.8), 131 (15.1), 119 (9.4), 114 (9.8), 100 (41.2), 93 (7.3), 69 (100); (Z-form) 590 (M, 3.5), 571 (M-F, 7.3), 521 (M-CF$_3$, 12.8), 376 (33.1), 326 (19.6), 264 (12.2), 231 (7.3), 176 (7.8), 169 (25.9), 150 (8.9), 145 (5.3), 145 (5.3), 131 (14.1), 119 (8.5), 114 (10.6), 100 (40.2), 93 (7.3), 69 (100). IR (KBr, neat) λ_{max} (cm^{-1}): 1700 (shoulder), 1685 (w, $\nu_{c=c}$), 1120–1380 (s, br), 1030 (s), 970 (s), 880 (m), 760 (s), 695 (m).

3.4. F-(1,3-dimorpholino-2-butene) (2c) (nc)

Into a 25 ml Schlenk tube equipped with a gas-tight Teflon seal were placed a magnetic stirrer bar, 2 ml of dry DMF, and dried cesium fluoride (304 mg, 2 mmol) and **1c** (3.11 g, 10 mmol). The reaction was conducted at room temperature for 20 h. The lower layer separated was clear and almost pure **2c** (2.3 g, 75% yield). GC-MS analysis shows it consists of 82% of the E-form and 18% of the Z-form. Since the following ^{19}F-NMR and IR data were taken using this geometrical isomer mixture, data for the Z-isomer of **2c** were unavailable.

^{19}F-NMR (CDCl$_3$) δ: (E-form) −79.4 (s, 3F), −86.7–−94.8 (s, 2F × 8), −107.8 (dd, J = 131.5, 24.8 Hz, 1F), −145.4 (d, J = 24.8 Hz, 1F), −147.1 (d, J = 131.5 Hz, 1F). MS (EI, 70 eV, m/z): (E-form) 622 (M, 0.8), 603 (M-F, 1.8), 553 (M-CF$_3$, 12.6), 415 (1.9), 392 (8.4), 387 (3.8), 342 (2.8), 276 (1.3), 271 (1.3), 254 (1.6), 226 (8.4), 221 (2.0), 204 (1.3), 183 (1.5), 181 (3.3), 176 (5.6), 164 (2.9), 138 (3.1), 131 (2.3), 120 (2.0), 119 (100), 114 (6.5), 112 (1.4), 100 (18.5), 97 (6.4), 95 (1.1), 93 (2.0), 76 (1.2), 69 (43.8), 50 (3.3), 47 (1.5); (Z-form) 533 (M-CF$_3$, 10.6), 415 (1.8), 392 (9.3), 387 (2.3), 342 (3.1), 276 (2.0), 271 (1.3), 254 (1.9), 226 (10.8), 221 (2.1), 204 (1.1), 183 (1.6), 181 (3.7), 176 (5.8), 164 (3.0), 138 (2.7), 131 (2.0), 120 (1.8), 119 (100), 114 (6.8), 112 (1.9), 100 (19.0), 97 (5.4), 95 (1.5), 93 (2.5), 76 (1.9), 69 (43.3), 57 (1.2), 55 (1.5), 50 (4.3), 47 (1.4). IR (KBr, neat) λ_{max} (cm^{-1}): 1740 (w, $\nu_{c=c}$), 1080–1360 (s, br), 1040 (s), 918 (s), 802 (m), 745 (m).

3.5. F-2-dimethylamino-4-methyl-3-heptene, (8) (nc) and F-3-ethyl-2-methyl-2-pentene, (9)

Into a 25 ml Schlenk tube equipped with a gas-tight Teflon seal were placed a magnetic stirrer bar, 2 ml of dry DMF, dried cesium fluoride (152 mg, 1 mmol) and **5** (1.5 g, 5 mmol). The gaseous reagent **1a** (1.17 g, 5 mmol) was transferred into the vessel using a vacuum line. After 28 h stirring at room temperature, the lower layer of the reaction mixture was analyzed by GC: **2a** (4.1% GC yield), **8** (32.2% GC yield, isomer ratio 1:9) and **9** (27.7% GC yield). Spectral data were as follows. The compound **9** is not new [13], but its spectral data are included here, because no such data are available in the literature.

8. ^{19}F-NMR ($CDCl_3$) δ: (peak-1) −52.10 (m, 6F), −58.84 (septet, J = 11.2 Hz, 3F), −78.12 (m, 3F), −81.75 (td, J = 9.9, 3.7 Hz, 3F), −81.2– −82.3 (m, 1F), −105.0 (2F, dm, J = 31.0 Hz, 2F), −123.1 (m, 2F), −131.7 (m, F); (peak-2) −52.40 (m, 6F), −56.70 (m, 3F), −78.27 (m, 3F), −81.69 (t, J = 9.9 Hz, 3F), −85.01 (m, F), −105.7, −113.7 (ABq, J_{AB} = 293 Hz, d septet, J = 44.7, 9.3 Hz for 1F, m for 1F), −125.1 (dm, J = 23.6, 2F), −137.4 (m, 1F). MS (EI, 70 eV, m/z): (E-form) 514 (M-F, 0.1), 464 ($M-CF_3$, 3.8), 426 (1.2), 381 (5.3), 376 (1.2), 338 (1.1), 326 (1.7), 288 (1.1), 281 (1.8), 243 (1.7), 238 (2.0), 181 (1.3), 119 (4.1), 114 (1.3), 100 (1.0), 93 (1.1), 69 (100); (Z-form) 514 (M-F, 0.05), 464 ($M-CF_3$, 2.3), 426 (1.8), 381 (4.6), 376 (2.3), 281 (1.9), 243 (1.4), 238 (2.3), 181 (2.6), 119 (3.7), 114 (1.2), 100 (1.1), 69 (100). IR (capillary, KBr) ν_{max} (cm^{-1}): 1678 ($\nu_{C=C}$, w), 1357 (s), 1318 (s), 1287 (m), 1248 (s), 1210 (s), 1182 (s), 1137 (m), 1120 (m), 1021 (m), 981 (m), 902 (m), 878 (m), 759 (w), 743 (m), 720 (w), 682 (m). Analysis found: C, 22.63; F, 74.6; N, 2.69. Calculated for $C_{10}F_{21}N$: C, 22.53; F, 74.8; N, 2.63.

9. ^{19}F-NMR($CDCl_3$) δ: −59.0 (s, 6F), −74.1 (s, 6F), −98.5 (s, 4F). MS (EI, 70 eV, m/z): 381 (M-F, 2.7), 331 ($M-CF_3$, 5.6), 293 (6.0), 243 (17.5), 193 (2.9), 181 (1.4), 155 (1.2), 143 (2.8), 131 (1.5), 124 (2.3), 119 (13.6), 100 (1.1), 93 (2.9), 69 (100), 50 (1.3). IR (a gas cell with 5 cm light path equipped with KBr window) λ_{max} (cm^{-1}): 1322 (w), 1300 (w), 1256 (s), 1238 (s), 1210 (m), 1137 (w), 1100 (m), 733 (w). Analysis found: C, 24.15; F, 76.1. Calculated for C_8F_{16}: C, 24.02; F, 75.98.

References

[1] R.D. Chambers, *Fluorine in Organic Chemistry*, Wiley, New York, 1973.

[2] R.N. Haszeldine and A.E. Tipping, *J. Chem. Soc. C*, (1968) 399. R.E. Banks, K. Mullen and G.E. Williamson, *J. Chem. Soc. C*, (1968) 2608. R.E. Banks, A.J. Parker, M.J. Sharp and G.F. Smith, *J. Chem. Soc., Perkin, Trans. 1*, (1973) 5.

[3] T. Abe and E. Hayashi, *Chem. Lett.*, (1988) 1887. T. Abe, E. Hayashi and T. Shimizu, *Chem. Lett.*, (1989) 905.

[4] A. Vij, R.L. Kirchmeier, J.R. Shreeve, T. Abe, H. Fukaya, E. Hayashi, Y. Hayakawa and T. Ono, *Inorg. Chem., 32* (1993) 5011.A. Vij, R.L. Kirchmeier, J.R. Shreeve, T. Abe, H. Fukaya, E. Hayashi, Y. Hayakawa and T. Ono, *Inorg. Chem., 33* (1994) 628.

[5] N. Ishikawa and M. Maruta, *Yuki Gousei Kagaku Kyokai Shi, 39* (1981) 51.

[6] V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978.

[7] J.W. Emsley, J. Feeney and L.H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon, Oxford, 1966.

[8] N. Ishikawa and A. Sekiya, *Nippon Kagaku Kaishi*, (1972) 2214.

[9] W. Dmowski, W.T. Flowers and R.N. Haszeldine, *J. Fluorine Chem., 9* (1977) 94

[10] G. Tsukamoto and N. Ishikawa, *Chem. Lett.*, (1972) 577. T. Ono, K. Yamanouchi and K.V. Scherer, *J. Fluorine Chem., 73* (1995) 267.

[11] N. Ishikawa and M. Maruta, *Nippon Kagaku Kaishi*, (1977) 1411.

[12] Y. Inoue, Y. Arakawa, Y. Naito, T. Ono, C. Fukara, K. Yamanouci, and K. Yokoyama, *J. Fluorine Chem., 38* (1988) 303.

[13] R. Fields, R.N. Haszeldine and I. Kumadaki, *J. Chem. Soc., Perkin Trans. 1*, (1982) 2211.