Cycloaddition of fluorinated oxazoles

N. V. Vasil´ev,[a] V. M. Koshelev,[a] D. V. Romanov,[a]★ K. A. Lyssenko,[b] M. Yu. Antipin,[b] and G. V. Zatonskii[c]

[a]Military University of Radiation, Chemical, and Biological Defense,
13 Brigadirskii per., 107005 Moscow, Russian Federation.
[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: SRS@ineos.ac.ru
[c]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
E-mail: Zatonsk@cacr.ioc.ac.ru

Cycloaddition reactions of polyfluorinated 1,3-oxazoles with cyclic and acyclic alkenes were studied. The results of these reactions were interpreted using quantum chemical calculations. An unusual product, *viz.*, fluorine-containing acylpyrrole, was studied by X-ray diffraction.

Key words: oxazole, cycloadduct, hydroxypyridine, acylpyrrole.

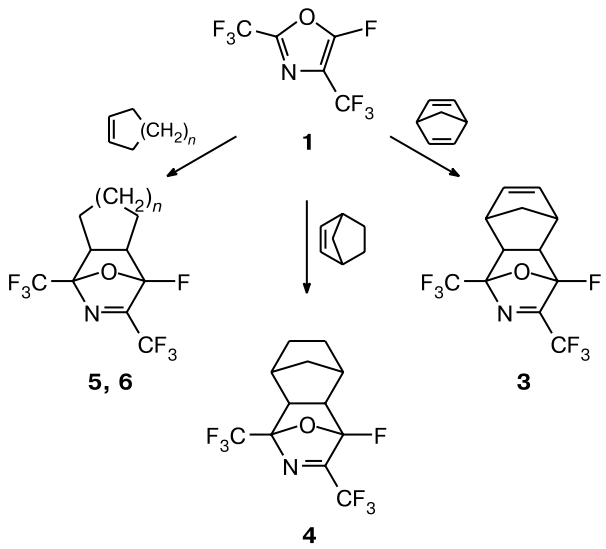
Cycloaddition reactions of oxazoles have been known for many years and were studied in-depth.[1—4] These reactions with fluorine-containing oxazoles are less well studied. Earlier, we have noted rather high activity of fluorinated oxazoles[5,6] in cycloaddition reactions. To the contrary, the reactivity of 5-ethoxy-4-trifluoromethyloxazole was reported to be low.[7] It should be noted that the reactions of this oxazole do not stop at the cycloaddition step and afford 3-hydroxypyridines. The aim of the present study was to investigate cycloaddition of 5-fluoro-2,4-bis(trifluoromethyl)oxazole (**1**) and 5-cyano-2,4-bis(trifluoromethyl)oxazole (**2**).[8,9]

The ease of the reactions of oxazole **1** with cyclic alkenes increases in the series cyclohexene < cyclopentene < norbornene < norbornadiene, *i.e.*, with increasing strain of the double bonds (E_{ster} is 2.6, 6.9, 23.6, and 31.6 kcal mol^{-1}, respectively[10]). The mildest conditions are typical of the reactions of oxazole **1** with norbornadiene, in the presence of which the reaction starts already at 80 °C. Unlike the reactions of most oxazoles[4] containing usual substituents, the reactions of fluorine-containing oxazole **1** with alkenes stop at the [2+4] cycloaddition step giving rise to rather stable polycyclic adducts **3—6** (Scheme 1).

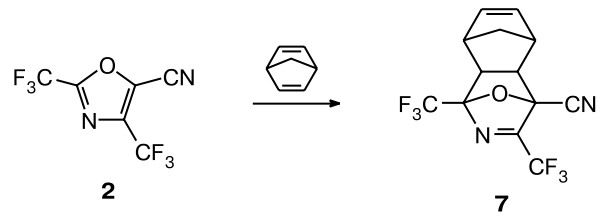
Cyanooxazole **2**, like **1**, is involved in [2+4] cycloaddition to norbornadiene giving rise to adduct **7** (Scheme 2). However, attempts to perform the reactions of **2** with other cyclic alkenes failed even at high temperatures.

Cycloadducts **3**, **4**, and **7** were prepared as mixtures of *endo* and *exo* isomers, which is clearly evidenced by doubling of the signals in the ^{19}F NMR spectra and is, appar-

Scheme 1



Scheme 2



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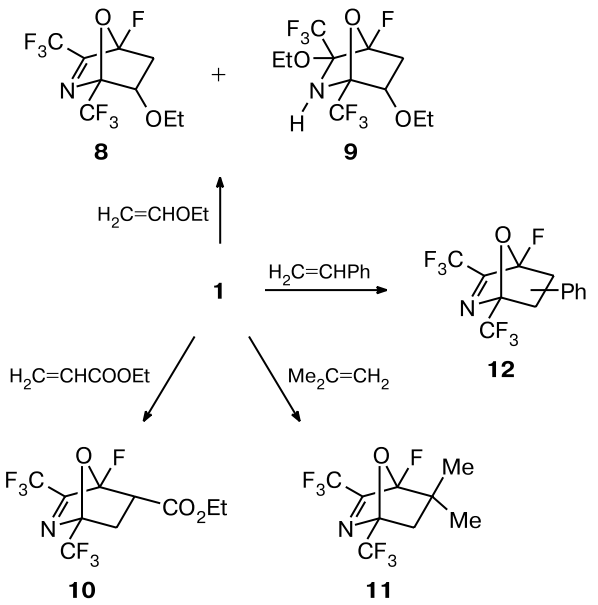
ently, associated with the presence of the norbornane fragment in these molecules. A more precise assignment of the configurations of these cycloadducts based on the NMR spectra presented difficulties. Compounds **3—7** are rather stable, but they decompose during storage at room temperature over a long period of time.

Cycloaddition of oxazole **1** to acyclic alkenes was studied for ethyl vinyl ether, ethyl acrylate, isobutylene, styrene, dimethyl fumarate, and ethylene. In contrast to the data reported in the study,[7] it appeared that cycloaddition performed under rather mild conditions (100—110 °C) stops predominantly at the first step giving rise to 7-oxa-2-azabicycloheptenes. The presence of HF impurities in the starting oxazole and the presence of moisture in the reaction mixture have an adverse effect on the reaction. For example, cycloaddition of oxazole, which was purified from HF by distillation over calcined KF, under rather mild conditions afforded bicyclic compounds **8—12** (Scheme 3).

Scheme 3



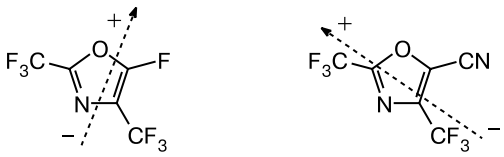
The results of these reactions depend substantially on the nature of the dienophile used. For example, cycloaddition involving styrene occurs ambiguously to form a mixture of three isomers in a ratio of ~1 : 2 : 3.

Ethyl vinyl ether reacts with oxazole **1** to give *endo*-6-ethoxy-substituted adduct **8**, as evidenced by the proton-proton coupling constants for the oxaazabicycloheptene fragment ($J_{endo,exo}$ = 2.5 Hz and $J_{exo,exo}$ = 8.5 Hz). This is consistent with the data[11] for the bicyclo[2.2.1]heptane fragment. This reaction is complicated by the formation of high-boiling compound **9**, which was identified as an addition product of ethanol and oxaazabicycloheptene **8**. The mass spectrum of compound **9** provided evidence that an ethanol molecule is eliminated. The factors responsible for the appearance of ethanol in the reaction mixture remain unclear.

By contrast to ethyl vinyl ether, the oppositely polarized ethyl acrylate forms *endo*-5-ethoxycarbonyl-substituted adduct **10**, which indicates that the reaction is charge-controlled.

At the same time, the addition of isobutylene to oxazole **1** afforded 5,5-dimethyl-substituted adduct **11** corresponding to minimal steric hindrance in the transition state of the resulting molecule. This structure is evidenced by the spin-spin coupling constant $J_{Me,F}$ = 1.5 Hz observed for one of the methyl groups.

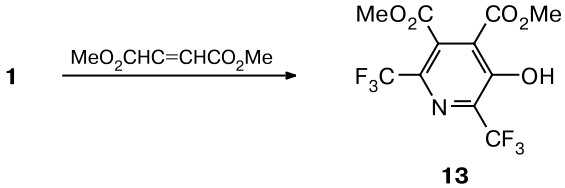
Therefore, the formation of adduct **11** is contradictory to the polarities of the reagents, *viz.*, isobutylene and oxazole **1**. The polarities of oxazoles **1** and **2** were calculated by an *ab initio* quantum chemical method with the 3-21G basis set.



Under drastic conditions (>150—160 °C), cycloaddition reactions of oxazole **1** are accompanied by further transformations of the initially formed bicycloheptenes, and we failed to reliably identify the reaction products generated under these conditions because of oligomerization of the reaction mixtures.

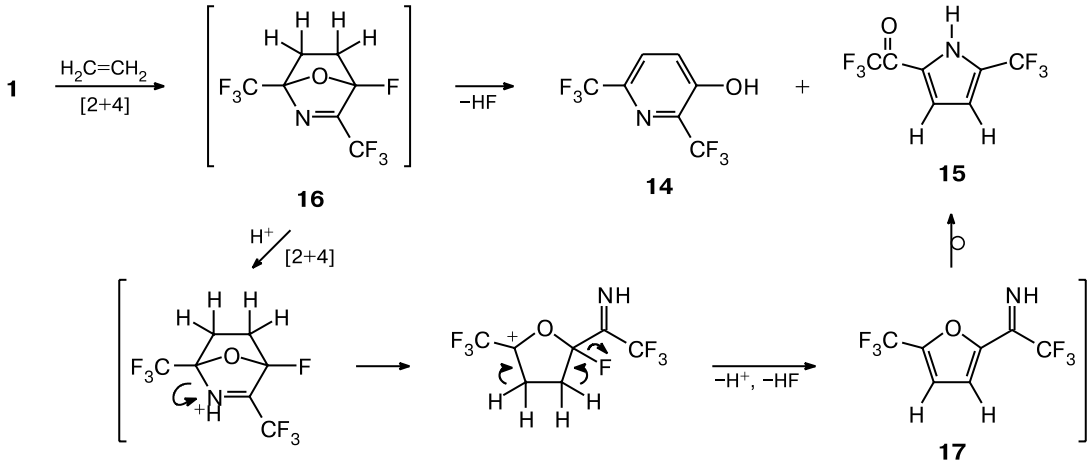
The formation of compound **13** of the 3-hydroxypyridine series was observed in the reactions of **1** with dimethyl fumarate or dimethyl maleate at high temperature (150—160 °C). Under milder conditions, the reactions do not occur (Scheme 4).

Scheme 4



On the whole, the general feature of cycloaddition involving oxazole **1** is that this compound is prone to react with electron-donor and strained dienophiles. More drastic conditions are required for the reactions with more electrophilic dienophiles to proceed. Such dienophiles as

Scheme 5



tetracyanoethylene, 1,1-bis(trifluoromethyl)dicyanoethylene, maleic anhydride, and perfluorinated alkenes are not involved in cycloaddition reactions with oxazole **1** even at 180—200 °C.

Therefore, the experimental observations provide evidence for the favorable interaction between LUMO of oxazole **1** and HOMO of dienophiles in these processes, which is confirmed by the low calculated values of LUMO and HOMO of this oxazole (2.084 and −11.976 eV, respectively; *ab initio* 3-21G). Factors responsible for the low reactivity of oxazole **2**, which is not involved in cycloaddition to acyclic and cyclic dienophiles, except for norbornadiene, remain unclear. The frontier orbitals of oxazole **2** have lower values of LUMO (0.636 eV) and HOMO (−12.0 eV) compared to those of oxazole **1**. There are no radical differences in the amplitudes of the frontier orbitals. The dipole moment of oxazole **1** (1.592 D) differs substantially from that of **2** (0.9 D) (*ab initio* 3-21G), these moments being oppositely directed. The cycloaddition of the oxazoles under study is, apparently, both orbital- and charge-controlled, because oxazole **1** reacts with polar and nonpolar alkenes (in some cases, nonregioselectively), whereas oxazole **2** reacts only with nonpolar norbornadiene.

Noteworthy are the characteristic features of the reaction of oxazole **1** with ethylene (Scheme 5), where the initial formation of the cycloadduct was not detected even under mild conditions. The reaction produced two isomers isolated by crystallization. Compound **14** was identified as 3-hydroxypyridine based on NMR spectroscopic data and the character of fragmentation in the mass spectrum. The structure of another compound, whose NMR spectra show analogous groups of signals, was established by X-ray diffraction analysis. The latter compound was proved to be fluorinated acylpyrrole **15**.

The formation of acylpyrrole **15** in this reaction was unexpected because such transformations in the reactions of oxazoles have been previously unknown.[3,4] The mechanism of formation of **15** can be represented as electrophilic cleavage of the initially formed cycloadduct **16** followed by the formation of iminofuran **17** and its isomerization giving rise to acylpyrrole **15**. Apparently, the formation of the latter in this reaction can be attributed to a high concentration of HF that is eliminated in the reaction. Unlike this process, which was performed in a steel test tube, the other reactions considered above were carried out in tubes made of glass, which adsorbs hydrogen fluoride. The foregoing is partially confirmed by the fact that the percentage of acylpyrrole **15** increases in the presence of trifluoromethanesulfonic acid in the reaction mixture.

It should be noted that the geometric parameters of the molecule of acylpyrrole **15** are close to the expected values (Fig. 1, Table 1). The pyrrole ring and the carbonyl group lie in a single plane (planar within 0.032 Å). The trifluoromethyl groups are eclipsed with respect to the pyrrole ring and the carbonyl group. The F(62)—C(6)—C(5)—O(2) and F(72)—C(7)—C(4)—N(1) torsion angles are 178.1(1)° and 170.1(1)°, respectively. It should be noted that the C(6)—F(62) bond involving the F(62) atom, which lies in a plane with the carbonyl group, is

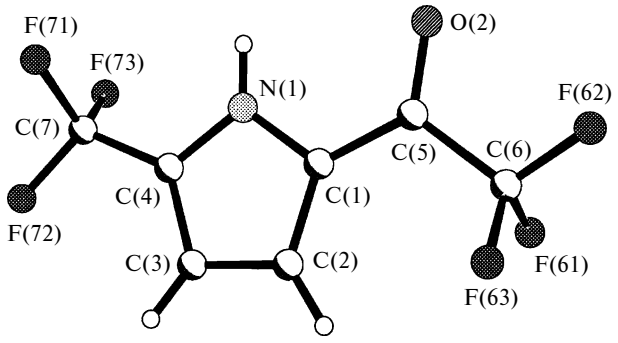


Fig. 1. Molecular structure of acylpyrrole **15**.

Table 1. Bond lengths (d) and bond angles (ω) in the structure of **15**

Bond	d/Å	Angle	ω/deg
O(1)—C(5)	1.218(1)	N(1)—C(1)—C(2)	108.12(8)
C(1)—N(1)	1.374(1)	N(1)—C(1)—C(5)	119.74(7)
C(1)—C(2)	1.394(1)	C(2)—C(1)—C(5)	132.13(8)
C(1)—C(5)	1.440(1)	C(1)—C(2)—C(3)	107.21(8)
C(2)—C(3)	1.404(1)	C(4)—C(3)—C(2)	106.58(8)
C(3)—C(4)	1.386(1)	N(1)—C(4)—C(3)	109.59(8)
C(4)—N(1)	1.351(4)	N(1)—C(4)—C(7)	121.14(8)
C(4)—C(7)	1.487(1)	C(3)—C(4)—C(7)	129.27(9)
C(5)—C(6)	1.546(1)	O(1)—C(5)—C(1)	124.57(8)
C(6)—F(61)	1.331(1)	O(1)—C(5)—C(6)	117.83(8)
C(6)—F(62)	1.322(1)	C(1)—C(5)—C(6)	117.57(7)
C(6)—F(63)	1.333(1)		
C(7)—F(71)	1.332(1)		
C(7)—F(72)	1.329(1)		
C(7)—F(73)	1.338(1)		

substantially shortened (to 1.322(1) Å) compared to two other C—F bonds (1.330(1) and 1.333(1) Å). Analysis of the molecular geometry of related pyrrole derivatives using the data from the Cambridge Structural Database[12] showed that the trifluoromethyl groups, apparently, have no essential effect on the bond length redistribution in the pyrrole ring. For example, the bond lengths in the aromatic ring in compound **15** are equal to those in 2-benzopyrrole[13] within experimental error. It should be noted that the carbonyl group in 2-benzopyrrole, like that in **15**, is coplanar with the pyrrole ring, whereas the phenyl ring is twisted by 50°. Therefore, the bond length redistribution in the aromatic ring in **15** and 2-benzopyrrole depends primarily on the conjugation between the π system of the ring and the carbonyl group. It should be noted that the C(1)—C(5) bond length in compound **15** is equal to that in 2-benzopyrrole (1.445(4) Å) within experimental error.

Analysis of the data published in the literature demonstrated that the bond length distribution in the trifluoroacetyl group depends only slightly on the nature of the heterocycle. In 1,2-dimethyl-5-trifluoroacetyl-1,2-dihydrocyclopenta[*d*]pyridazine,[14] the bond lengths in the trifluoroacetyl group are identical to the analogous bonds in acylpyrrole **15**. Analysis of the crystal packing showed that the molecules form centrosymmetric H-bonded dimers through the N(1)—H(1)...O(1) hydrogen bond ($-x$, $1-y$, $1-z$) with the following geometric parameters: N(1)...O(1), 2.862(1) Å; H(1)...O(1), 2.02(1) Å; N(1)—H(1), 0.85(1) Å; and N(1)—H(1)...O(1), 165(1)°.

To summarize, 7-oxa-2-azabicycloheptene and 3-hydroxypyridine derivatives were synthesized by cycloaddition of fluorinated oxazoles, the formation of acylpyrrole unusual for these processes was observed, and the structure of the latter product was established.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 300 MHz. The ^{19}F NMR spectra were measured on a Bruker WP-200 SY spectrometer operating at 188.31 MHz and a Bruker DRX-500 spectrometer operating at 500.1 and 470.6 MHz. The chemical shifts (δ) are given relative to Me_4Si (^{1}H) and CF_3COOH (^{19}F) as the external standards. The mass spectra were obtained on a GLC-mass spectrometer based on an HP 5890 II Series gas chromatograph equipped with an HP 5972A MSD mass-selective detector. The IR spectra were recorded on a UR-20 spectrometer in a thin layer. The physicochemical characteristics of the compounds and the ^{1}H and ^{19}F NMR and IR spectroscopic data are given in Table 2. The yields, reaction conditions, and elemental analysis data are presented in Table 3. Commercial reagents and solvents used in the study were prepared according to known recommendations.[11]

X-ray diffraction study of compound **15** ($C_7H_3ONF_6$) was carried out at −124 °C on an automated four-circle Siemens P3/PC diffractometer (Mo-Kα, graphite monochromator, θ/2θ scanning technique, $2\theta < 65°$). At −124 °C, the crystals are monoclinic: $a = 4.9994(1)$ Å, $b = 17.019(4)$ Å, $c = 9.753(3)$ Å, $\beta = 97.72(1)°$, $V = 821.4(4)$ Å^3, space group $P2_1/c$, $Z = 4$, $M = 231.10$, $d_{calc} = 1.869$ g cm^{-3}, $\mu = 0.216$ mm^{-1}, $F(000) = 456$. Of a total of 3444 measured reflections, 3143 independent reflections were used in the calculations and refinement.

The structure of **15** was solved by direct methods and refined anisotropically by the full-matrix least-squares method. The hydrogen atoms were located from difference electron density syntheses and included in the final refinement with isotropic displacement parameters.

The final R factors were as follows: $R = 0.039$ for 2985 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1005$, GOOF = 1.02 based on all measured reflections. All calculations were carried out using the SHELXL program package (version 5).

Reactions of oxazoles 1 and 2 with dienophiles; synthesis of compounds 3—13 (general procedure). A mixture of oxazole **1** (or **2**) (13.5 mmol) and a dienophile (16.2 mmol) stabilized with hydroquinone was heated in a glass tube during half of the time given in Table 3. Then an additional amount of the dienophile (16.2 mmol) was added, and the reaction mixture was heated and fractionated *in vacuo* (pyridine **13** was additionally purified by recrystallization from a 3 : 1 heptane—chloroform mixture).

MS **9** (EI, 70 eV), m/z: (I_{rel})): 341 $[M]^+$ (21), 295 $[M - HOEt]^+$ (28), 246 $[M - HOEt - CF_2]^+$ (34), 200 $[M - HOEt - CF_3CN]^+$ (100), 172 (40), 150 $[200 - CF_2]^+$ (22), 103 $[172 - CF_3]^+$ (17), 75 (31), 69 $[CF_3]^+$ (28), 57, 41.

Reaction of oxazole 1 with ethylene. Synthesis of 3-hydroxy-2,6-bis(trifluoromethyl)pyridine (14) and 2-trifluoroacetyl-5-trifluoromethylpyrrole (15). A mixture of oxazole **1** (5.0 g, 22.4 mmol) and condensed ethylene (6.3 g, 224 mmol) was heated in a 100 mL steel autoclave at 110 °C for 10 h. Excess ethylene was distilled off, and the reaction mixture was evacuated at 50 Torr. The residue was washed with hot chloroform (5×10 mL), concentrated to dryness, and sublimed at 50 Torr. The crystals were recrystallized from *n*-heptane. 3-Hydroxypyridine **14** was obtained in a yield of 0.95 g (18.3%).

MS **14** (EI, 70 eV), m/z: (I_{rel} (%)): 231 $[M]^+$ (100), 212 $[M - F]^+$ (17), 192 $[M - F - HF]^+$ (10), 183 $[M - HF - CO]^+$

Table 2. Physicochemical characteristics and ^1H and ^{19}F NMR and IR spectroscopic data for compounds **3—15**

Compound	b.p./°C (*p*/Torr) [m.p./°C]	n_D^{20}	NMR ($CDCl_3$, δ, *J*/Hz)		IR, ν/cm^{-1}
			^1H	^{19}F	
3 (*endo* : *exo* 1 : 1)[a]	74 (1)	1.3996	1.4—1.7 (m, 2 H, CH_2); 2.2—2.5 (m, 2 H, CH); 2.9 (br.s, 1 H, CH); 3.1 (m, 1 H, CH); 6.3 (m, 2 H, =CH)	−8.2, −7.0 (both d, 3 F each, CF_3, J = 5.0); −1.9, −1.7 (both s, 3 F each, CF_3); 76.2, 85.2 (both m, 1 F each, CF)	2950 (CH); 1650 (C=N)
4 (*endo* : *exo* 1 : 2)[a]	88 (2)	1.3980	1.2—1.7 (m, 6 H, CH_2); 2.3 (d, 1 H, CH, J = 6.0); 2.7 (br.s, 1 H, CH); 3.2 (m, 2 H, CH)	−10.2, −9.3 (both d, 3 F each, CF_3, J = 5.0); −2.6, 0.4 (both s, 3 F each, CF_3); 78.8, 83.6 (both m, 1 F each, CF)	2900 (CH); 1640 (C=N)
5	55 (1)	1.3775	1.5—1.7 (m, 6 H, CH_2); 3.1, 3.5 (both m, 1 H each, CH)	−9.0 (d, 3 F, CF_3, J = 5.0); 1.4 (s, 3 F, CF_3); 77.0 (m, 1 F, CF)	2900 (CH); 1670 (C=N)
6	62 (1)	1.3975	1.4—1.7 (m, 8 H, CH_2); 3.2 (m, 1 H, CH_2); 3.4 (m, 1 H, CH)	−9.8 (d, 3 F, CF_3, J = 5.0); 0.7 (s, 3 F, CF_3); 78.9 (m, 1 F, CF)	2950 (CH); 1650 (C=N)
7	63 (1)	1.4205	1.6 (m, 2 H, CH_2); 2.4, 3.2 (both m, 2 H each, CH); 6.3 (br.s, 2 H, =CH)	−9.3, −8.1, −2.2, 1.0 (all s, 3 F each, CF_3)	2950 (CH); 2220 (C≡N); 1650 (C=N)
endo-**8**	60 (15)	1.3552	0.9 (t, 3 H, CH_3, J = 7.0); 1.42 (ddd, 1 H, CH_2, J = 12.5, J = 2.5, J = 1.2); 2.03 (ddd, 1 H, CH_2, J = 12.5, J = 8.5, J = 10.0); 3.13 (m, 2 H, CH_2CH_3); 4.25 (dd, 1 H, CH, J = 8.5, J = 2.5)	−8.7 (d, 3 F, CF_3, J = 4.0); −0.8 (s, 3 F, CF_3); 72.2 (br.dq, 1 F, CF, J = 4.0, J = 10.0)	2950 (CH); 1650 (C=N)
9	102 (17)	1.3790	1.08, 1.06 (both q, 3 H each, CH_3, J = 7.0); 2.11 (dm, 2 H, CH_2, J_{AB} = 13.3); 3.43 (q, 2 H, CH_2); 3.71 (br.s, 1 H, NH); 3.63—3.80 (m, 2 H, CH_2); 4.27 (dd, 1 H, CH, J = 2.6, J = 9.3)	1.0 (m, 3 F, CF_3); 6.8 (s, 3 F, CF_3); 70.1 (m, 1 F, CF)	3300 (NH); 2990 (CH)
endo-**10**	50—52 (1)	1.3681	1.3 (q, 3 H, CH_3, J = 7.0); 2.28 (dd, 1 H, CH_2, J = 12.8, J = 5.0); 2.84 (dd, 1 H, CH_2, J = 12.8, J = 10.0); 3.48 (ddd, 1 H, CH, J = 5.0, J = 10.0, J = 7.5); 4.25 (q, 2 H, CH_2CH_3, J = 7.0)	−9.4 (d, 3 F, CF_3, J = 5.0); 1.7 (s, 3 F, CF_3); 76.5 (m, 1 F, CF)	2980 (CH); 1740 (C=O); 1690 (C=N)
11	40 (13)	1.3520	1.2 (br.s, 3 H, CH_3); 1.4 (br.d, 3 H, CH_3, J = 1.5); 1.85, 2.30 (both d, 1 H each, CH_2, J_{AB} = 12.0)	−11.0 (d, 3 F, CF_3, J = 5.0); 1.2 (s, 3 F, CF_3); 90.0 (m, 1 F, CF)	2900 (CH); 1650 (C=N)
12 (1 : 2 : 3)[b]	76 (1)	1.4305	1.7—2.3 (m, 2 H, CH_2); 2.9—3.2 (m, 1 H, CH); 7.2 (m, 5 H, Ph)	−9.5, −9.0, −8.7 (all d, 3 F each, CF_3, J = 4.0); −0.1, 1.7, 1.9 (all s, 3 F each, CF_3); 75.4, 79.4, 81.7 (all m, 1 F each, CF)	2900 (C—H); 1670 (C=N)
13	124 (1) [91—92]	—	4.0, 4.1 (both s, 3 H each, CH_3); 11.0 (s, 1 H, OH)	−13.1, −9.5 (both s, 3 F each, CF_3)	3300 (OH); 2980 (CH); 1740 (C=O); 1690 (arom)
14	[132]	—	7.72, 7.92 (both d, 1 H each, CH, J_{AB} = 8.7); 10.7 (br.s, 1 H, OH)	−10.06, 10.07 (both s, 3 F each, CF_3)	3350 (OH); 2950 (CH); 1690 (arom)
15	[68—71]	—	6.7, 7.2 (both br.s, 1 H each, CH); 10.1 (br.s, 1 H, NH)	−2.5, −14.9 (both s, 3 F each, CF_3)	3320 (NH); 3000 (CH); 1700 (C=O)

[a] The isomer ratio.
[b] A mixture of regioisomers and stereoisomers.

(80), 164 $[183 - F]^+$ (42), 133 $[M - HF - CF_2 - CO]^+$ (36), 114 $[133 - F]^+$ (13), 107, 88, 69 $[CF_3]^+$ (100), 64, 57, 38, 28 (12).

After partial evaporation of the filtrate at room temperature, acylpyrrole **15** was isolated by filtration in a yield of 0.3 g (6.0%).

Table 3. Yields, reaction conditions, and elemental analysis data for compounds **3—15**

Compound	Yield (%)	τ/h	*T*/°C	Found / Calculated (%)			Molecular formula
				C	H	N	
3	62.0	4	100—110	45.35	2.11	4.50	$C_{12}H_8F_7NO$
				45.73	2.56	4.44	
4	59.5	6	100—120	45.32	2.95	4.57	$C_{12}H_{10}F_7NO$
				45.44	3.18	4.42	
5	53.0	8	110	41.56	2.47	4.90	$C_{10}H_8F_7NO$
				41.25	2.77	4.81	
6	45.2	18	130—140	43.58	3.15	4.16	$C_{11}H_{10}F_7NO$
				43.29	3.30	4.59	
7	67.0	20	120—130	48.77	2.34	9.07	$C_{13}H_8F_6N_2O$
				48.46	2.50	8.69	
8	30.2	4	100	36.86	2.31	4.26	$C_9H_8F_7NO_2$
				36.62	2.73	4.75	
9	21.0	4	100	38.39	3.75	4.05	$C_{11}H_{14}F_7NO_3$
				38.72	4.14	4.10	
10	16.7	16	110	37.41	2.43	4.18	$C_{10}H_8F_7NO_3$
				37.17	2.50	4.33	
11	17.0	8	110	39.11	2.52	4.93	$C_9H_8F_7NO$
				38.72	2.89	5.02	
12	53.0	8	100	47.55	2.81	3.90	$C_{13}H_8F_7NO$
				47.72	2.46	4.28	
13	61.2[a]	20	140—160	38.35	1.82	4.15	$C_{11}H_7F_6NO_5$
	55.1[b]	20	140—160	38.06	2.03	4.03	
14	18.3	10	110	36.67	1.45	5.74	$C_7H_3F_6NO$
				36.38	1.31	6.06	
15	6.0	10	110	36.10	1.07	5.93	$C_7H_3F_6NO$
				36.38	1.31	6.06	

[a] From dimethyl fumarate.
[b] From dimethyl maleate.

MS (**15**) (EI, 70 eV *m/z*: (I_{rel})): 231 $[M]^+$ (81), 212 $[M - F]^+$ (13), 162 $[M - CF_3]^+$ (100), 142 $[M - CF_3 - HF]^+$ (89), 114 $[142 - CO]^+$ (42), 107, 88, 69 $[CF_3]^+$ (100), 64, 57, 38.

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