The Aza Curtius Rearrangement

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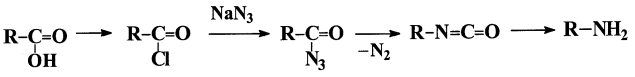
On interaction of *N*-(trifluoromethylsulfonyl)carboximidoyl chlorides (analogs of acyl chlorides in which the carbonyl oxygen atom is substituted by the more strongly electron-withdrawing $=NSO_2CF_3$ group) with sodium azide in glyme or acetonitrile at –5 to +10 °C, dinitrogen is eliminated quantitatively and carbodiimides $RN=C=NSO_2CF_3$ are formed in high yield. In other words, an aza Curtius rearrangement occurs. The carbodiimides react with water, alcohols, and secondary amines to give corresponding ureas, isoureas, and guanidine derivatives. Imidoyl chlorides with substituents other than SO_2R_F do not enter into the aza Curtius reaction.

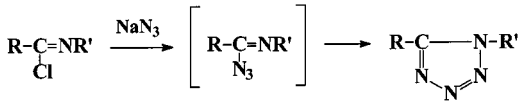
Introduction

The Curtius reaction is one of the most important methods for the transformation of carboxylic acids into isocyanates and amines (Scheme 1).



Scheme 1. Curtius reaction

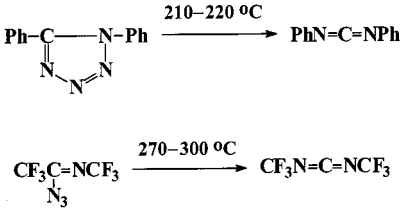
However, when the carbonyl oxygen atom in acyl chlorides is substituted by an imino group $=NR'$, cyclization into tetrazole occurs, rather than a Curtius reaction (Scheme 2).[1–3]



R = Alk, CF_3, Ar; R' = Ar, CH_2SO_2Ph

Scheme 2. Cyclization to tetrazole

A few cases are known in which imidoyl azides formally undergo Curtius rearrangements to give carbodiimides $RN=C=NR'$, but these products are formed only at extremely high temperatures (Scheme 3).[4,5]



Scheme 3. High-temperature reactions

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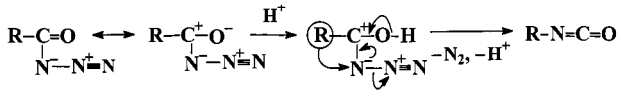
We have established previously that replacement of an sp^2-hybridized oxygen atom (bonded to various elements) with the $=NSO_2CF_3$ group enhances the electron-withdrawing capability, which makes it possible to change the properties of organic compounds radically. Hence, for example, it is possible to increase the acidity strongly,[6,7] or to activate halogen atoms in nucleophilic substitution reactions of aromatic substances.[8]

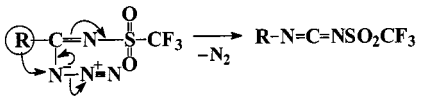
Having considered the available data on the mechanism of the Curtius reaction, we conjectured that substitution of the carbonyl oxygen atom in acyl chlorides with the much stronger electron-acceptor group $=NSO_2CF_3$ would make it possible to conduct Curtius-type rearrangements under mild conditions.

The necessary prerequisite for the Curtius rearrangement is a large cationic charge on the carbonyl carbon atom. This, in particular, is increased by the addition of a proton onto the oxygen atom during acid catalysis. This charge weakens the N^1-N^2 bond in the azido group, renders the adjacent nitrogen atom electron-deficient, and promotes the anionotropic migration of the group R to this site (Scheme 4).



Scheme 4. Curtius reaction mechanism

The $=NSO_2CF_3$ group is so much stronger as an electron acceptor that there is no need for acid catalysis, and the aryl group easily migrates to the electron-deficient nitrogen atom. At the same time, tetrazole ring closure is hampered because of the drawing off of electron density from the imine nitrogen atom by the SO_2CF_3 group (Scheme 5).



Scheme 5. Aza Curtius reaction mechanism

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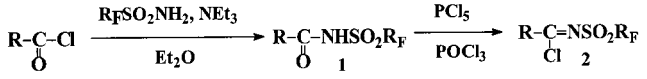
Results and Discussion

The starting compounds, *N*-perfluoroalkylsulfonylcarboximidoyl chlorides **2**, were obtained from the corresponding acyl chlorides by the sequence of transformations shown in Scheme 6 (Table 1).

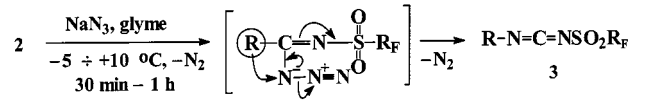


Scheme 6. Synthesis of carboximidoyl chlorides **2**

Table 1. *N*-Perfluoroalkylsulfonylbenzamides and *N*-trifluoromethylsulfonylpivalamide **1a−g**, and *N*-perfluoroalkylsulfonylcarboximidoyl chlorides **2a−g**

R	R_F	Compound	Yield [%]	Compound	Yield [%]
Ph	CF_3	**1a**	82	**2a**	94
4-MeC_6H_4	CF_3	**1b**	97	**2b**	89
4-FC_6H_4	CF_3	**1c**	83	**2c**	95
4-ClC_6H_4	CF_3	**1d**	84	**2d**	81
4-$NO_2C_6H_4$	CF_3	**1e**	83	**2e**	78
CMe_3	CF_3	**1f**	80	**2f**	83
4-FC_6H_4	C_4F_9	**1g**	75	**2g**	76

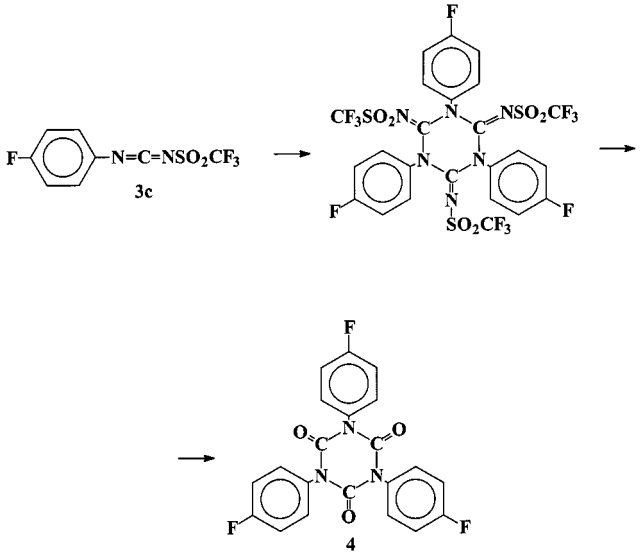
On treatment of imidoyl chlorides **2** with sodium azide in a glyme solution without any catalyst, it was found that dinitrogen was evolved quantitatively even at temperatures of −5 to + 10 °C, and carbodiimides **3** were formed in high yield (Scheme 7).



Scheme 7. Synthesis of carbodiimides **3**

Carbodiimides **3** are viscous, undistillable liquids. They are very reactive and unstable. Elemental analysis data and ^{19}F and ^{1}H NMR parameters for the compounds **3a** and **3f**, obtained as crude products after separation of inorganic salts and solvent evaporation, confirmed their purities and the completeness of conversion. Accordingly, the yields of transformation products based on compounds **3** have been calculated on the assumption of complete conversion of compounds **2**. All reactions with carbodiimides **3** were carried out at 0 to +20 °C immediately after their preparation. On long storage at room temperature or on heating in glyme solutions, compounds **3** converted into high-melting dimers or trimers. In the course of recrystallization and column chromatography on silica gel, the trimer of **3c** was hydrolyzed by atmospheric moisture into triazinetrione **4**, which was identified by X-ray diffraction analysis (Scheme 8, Figure 1).

On heating at reflux with 85% orthophosphoric acid, carbodiimide **3a** gave aniline, which was characterized as the *N*-acetyl derivative (Scheme 9). Trifluoromethylsulfonamide liberated in this reaction could be regenerated and reused.



Scheme 8. Formation of triazinetrione **4**

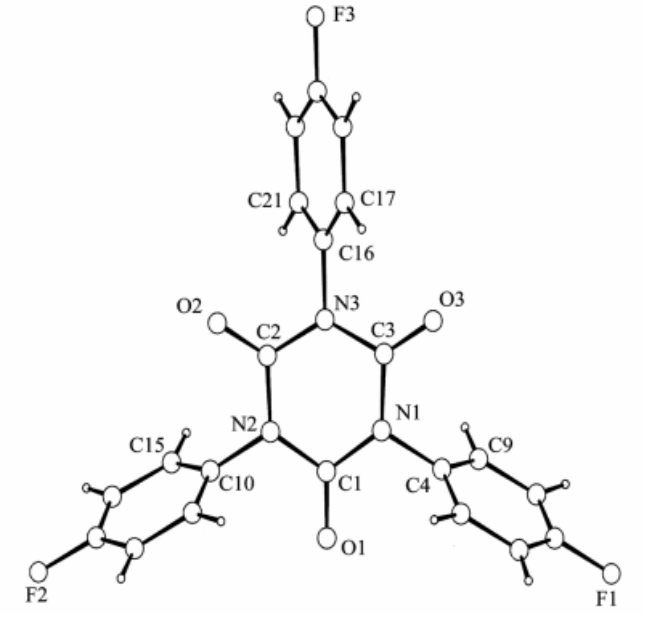
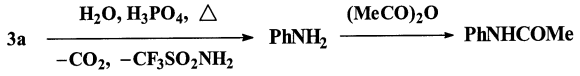
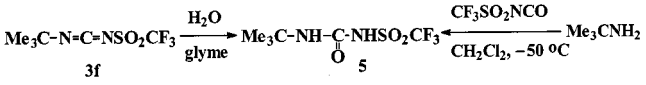


Figure 1. A perspective view and labelling scheme for molecule **4**; selected bond lengths [Å] and angles [°]: N(1)−C(1) 1.379(3), N(1)−C(3) 1.398(3), N(1)−C(4) 1.454(3), N(2)−C(1) 1.384(3), N(2)−C(2) 1.386(3), N(2)−C(10) 1.452(3), N(3)−C(2) 1.382(3), N(3)−C(3) 1.391(3), N(3)−C(16) 1.454(3), O(1)−C(1) 1.212(3), O(2)−C(2) 1.204(3), O(3)−C(3) 1.197(3), C(1)−N(1)−C(3) 124.8(2), C(1)−N(2)−C(2) 124.3(2), C(2)−N(3)−C(3) 124.8(2), N(1)−C(1)−N(2) 115.6(2), N(2)−C(2)−N(3) 115.7(2), N(1)−C(3)−N(3) 114.5(2); the central 6-membered ring of compound **4** N(1)−N(2)−N(3)−C(1)−C(1)−C(3) is planar, deviations from the least-squares plane do not exceed 0.027 Å; the C(4)−C(9), C(10)−C(15), and C(16)−C(17) benzene rings are twisted out of this plane by 66.5, 66.7, and 65.3°; the main bond lengths and angles in **4** are virtually the same as in the previously studied[9] $C_3N_3O_3(C_6H_5)_3$



Scheme 9. Hydrolysis of carbodiimide **3a**

Treatment of **3f** with water in a glyme solution resulted in the corresponding urea **5**. Compound **5** was also obtained by treatment of *tert*-butylamine with trifluoromethylsulfonyl isocyanate[10] (Scheme 10). It was identified by elemental analysis, spectral characteristics, and X-ray diffraction analysis (Figure 2).



Scheme 10. Synthesis of urea **5**

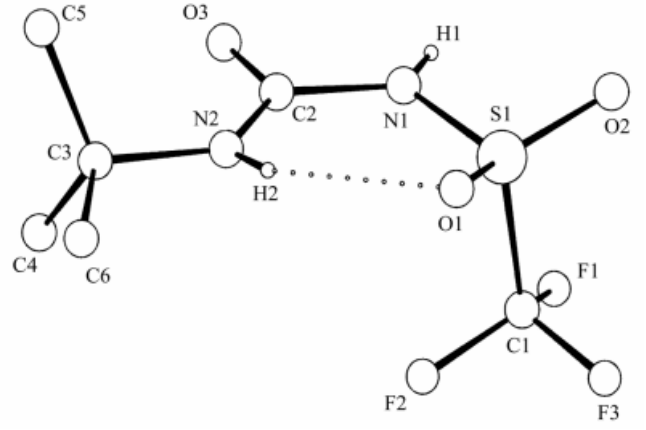
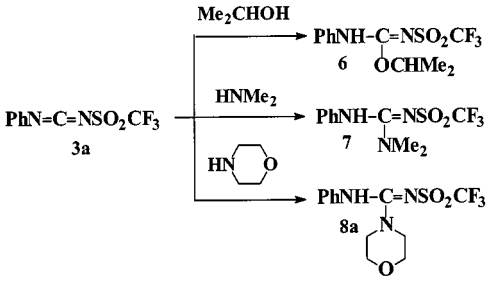


Figure 2. A perspective view and labelling scheme for molecule **5**; selected bond lengths [Å] and angles [°]: S(1)−O(1) 1.413(2), S(1)−O(2) 1.409(2), S(1)−N(1) 1.596(2), S(1)−C(1) 1.809(3), O(3)−C(2) 1.225(2), N(1)−C(2) 1.421(3), N(2)−C(2) 1.310(3), N(2)−C(3) 1.485(2), O(1)···N(2) 2.837(3); O(1)−H(2)−N(2) 142(3), S(1)−N(1)−C(2)−O(3) −168.2, N(1)−C(2)−N(2)−C(3) 178.3, O(3)−C(2)−N(2)−C(3) −1.7

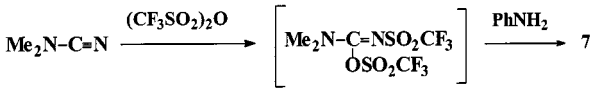
The S(1)−N(1) bond [1.596(2) Å] in **5** is noticeably shorter than in Me_2NSO_2Me [1.645(10) Å][11] and $(Me_2N)_2SO_2$ [1.651(3) Å],[12] reflecting the electron-withdrawing influence of the CF_3 group. Because of $n_N-\pi_{C=O}$ conjugation, the N(2)−C(2) bond [1.310(3) Å] is significantly shorter than the standard $N(sp^2)-C(sp^2)$ single bond value of 1.45 Å.[13] The geometric parameters of the intramolecular hydrogen bond O(1)···N(2) in **5** are unexceptional.[14,15]

Carbodiimide **3a** reacts with alcohols and secondary amines to give the corresponding isoureas and guanidine derivatives (Scheme 11).



Scheme 11. Reactions between carbodiimide **3a** and alcohols and secondary amines

Compound **7** had previously been obtained by an alternative route, by treatment of the reaction product of dimethylcyanamide and trifluoromethylsulfonic anhydride with aniline[16] (Scheme 12). The spectral characteristics of **7** prepared by the two methods were identical.



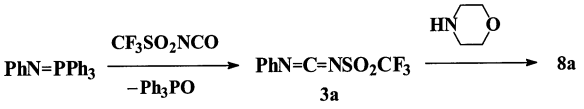
Scheme 12. Alternative pathway to **7** (see also ref.[16])

All the compounds **3** obtained by the aza Curtius reaction added morpholine to form easily recrystallizable products of type **8**, which were used for identification of the carbodiimides (Table 2).

Table 2. 4-[*N*-Aryl(alkyl)-*N'*-perfluoroalkylsulfonylamidino]morpholines **8a−g**

R	R_F	Compound	Yield [%]
Ph	CF_3	**8a**	54
4-MeC_6H_4	CF_3	**8b**	50
4-FC_6H_4	CF_3	**8c**	58
4-ClC_6H_4	CF_3	**8d**	44
4-$O_2NC_6H_4$	CF_3	**8e**	47
CMe_3	CF_3	**8f**	48
4-FC_6H_4	C_4F_9	**8g**	44

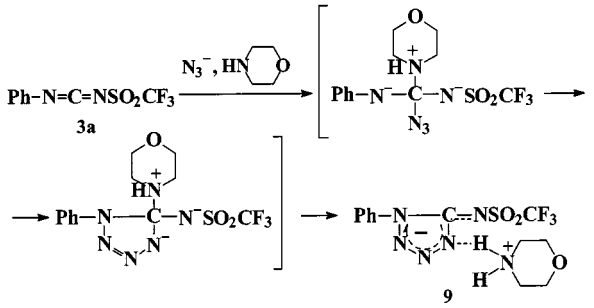
The morpholine derivative **8a** was also prepared from the carbodiimide **3a**, synthesized by Wittig reaction (Scheme 13). The samples of **8a** obtained by both methods showed no mixed melting point depression and had identical spectral characteristics (IR, ^1H and ^{19}F NMR), which fully confirmed the structure of carbodiimide **3a**.



Scheme 13. Alternative pathway to **8a**

On treatment with morpholine in the presence of an excess of sodium azide, carbodiimide **3a** also gave, in addition

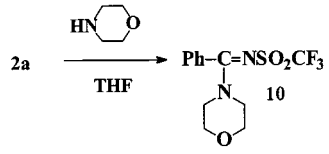
to the major product **8a**, the by-product **9**, containing a tetrazole ring. Its formation can be explained by the addition of a morpholine molecule to the intermediate azide, increasing the electron density on the aniline nitrogen atom and thus assisting the tetrazole ring closure. The morpholinium salt **9** was isolated by column chromatography on silica gel and identified by X-ray diffraction analysis (Scheme 14, Figure 3).



Scheme 14. Formation of morpholinium salt **9**

It was found that, in the solid state, compound **9** incorporates a sulfonyltetrazolimidate anion and a morpholinium cation (Figure 3), connected by a strong[15] NH···N hydrogen bond [N(4)···N(6) 2.822(4) Å, N(4)−H−N(6) 168(3)°]. The N(1)−N(2)−N(3)−N(4)−C(7) heterocycle is planar within 0.005 Å; the C(1)−C(6) benzene ring is twisted out of this plane by 41.4°. The N(5), S(1), and O(1) atoms lie almost in the plane of the tetrazole heterocycle, deviating from this plane only by 0.07, −0.12, and 0.12 Å respectively, the torsion angle S(1)−N(5)−C(7)−N(1) being −170.7(2)°. The S(1)=O(1), S(1)=O(2), and S(1)−C(8) bond lengths in **9** are similar to those in **5**, whereas the S(1)−N(5) bond [of 1.531(3) Å] is significantly shorter than the corresponding bond in **5** [1.596(2) Å] and is among the shortest $S^{IV}-N(sp^2)$ bonds.[17,18] In turn, the N(5)−C(7) bond [1.351(4) Å] is noticeably elongated in comparison with the standard N=C double bond (1.27 Å),[14] but shorter than the standard $N(sp^2)-C(sp^2)$ single bond (1.45 Å).[12] In this regard, one may suppose significant delocalization of the negative charge over the whole tetrazolimidate-sulfonyl system.

It should be noted that the solvent plays a very important role in the aza Curtius reaction. Thus, on treating imidoyl chloride **2a** with sodium azide in diethyl ether, tetrahydrofuran, or dioxane for a few hours under the same conditions as in glyme (at −5 to + 20 °C), no evolution of dinitrogen occurred. Inorganic salts isolated from the reaction mixture by filtration did not contain chloride ions. After the addition of morpholine to any one of the above solutions, only the substitution product of chlorine in **2a** with morpholine − that is, compound **10** − was isolated (Scheme 15). It is likely that glyme activates the substitution of the azido group for a chlorine atom in **2** by complexation with sodium azide. In acetonitrile, the aza Curtius reaction proceeded readily at even lower temperatures than in glyme, owing to the higher solubility of sodium azide in this solvent.



Scheme 15. Synthesis of substitution product **10**

Particular attention should be paid to the exclusion of moisture in the solvents, as the hydrolysis rate of imidoyl chlorides **2** in polar media is extremely high.

It was of interest to clear up the course of the reaction of sodium azide with imidoyl chlorides possessing the SO_2Ph substituent − a close structural analog of the SO_2CF_3 group but possessing lesser electron-withdrawing power (its σ_p value is 0.68 as against 1.04 for SO_2CF_3) − at the nitrogen atom.

We found that treatment of imidoyl chloride **11**, bearing the SO_2Ph group at the nitrogen terminus, with sodium azide in glyme was accompanied by evolution of dinitrogen, which started at 48−50 °C and was completed within a few

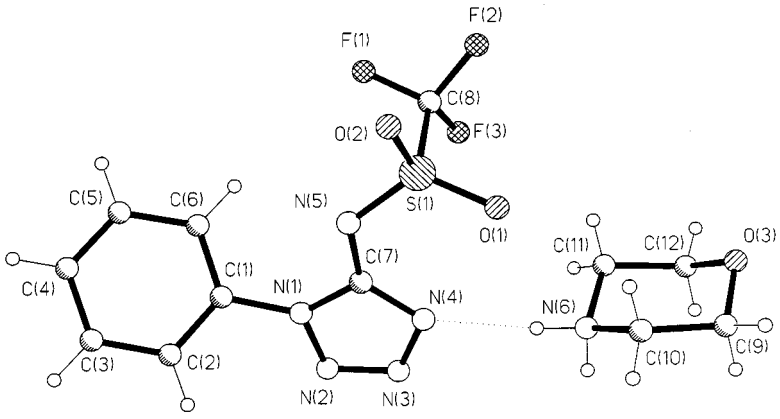
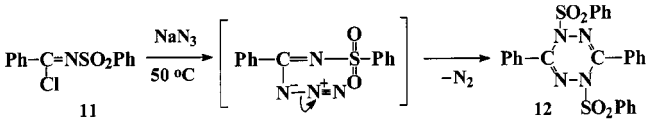


Figure 3. A perspective view and labelling scheme for molecule **9**; selected bond lengths [Å] and angles [°]: S(1)−O(1) 1.419(2), S(1)−O(2) 1.431(2), S(1)−N(5) 1.531(3), S(1)−C(8) 1.806(4), N(1)−C(7) 1.355(4), N(1)−N(2) 1.356(4), N(1)−C(1) 1.427(4), N(2)−N(3) 1.284(4), N(3)−N(4) 1.351(4), N(4)−C(7) 1.330(4), N(5)−C(7) 1.351(4); N(2)−N(1)−C(7) 108.5(2), N(1)−N(2)−N(3) 105.9(3), N(2)−N(3)−N(4) 112.1(2), N(3)−N(4)−C(7) 105.9(3), N(1)−C(7)−N(4) 107.5(3), S(1)−N(5)−C(7) 123.5(2)

hours. No Curtius-like rearrangement occurred, however, and the intermediate product was transformed into dihydrotetrazine **12** (Scheme 16). Therefore, the electron-acceptor ability of the $=NSO_2Ph$ group is sufficient to weaken the N−N bond in the azido group and to promote the ejection of dinitrogen, but insufficient to assist the migration of the phenyl group from the carbon atom to the electron-deficient nitrogen atom. The structure of the dihydrotetrazine **12** was established by X-ray diffraction analysis (Figure 4).



Scheme 16. Formation of the dihydrotetrazine **12**

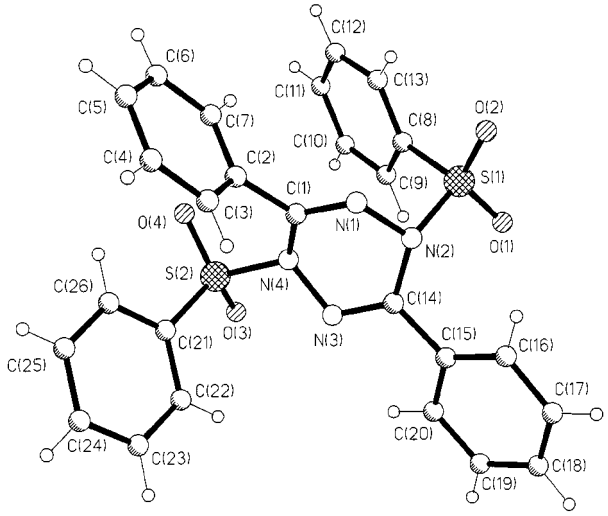


Figure 4. A perspective view and labelling scheme for molecule **12**; selected bond lengths [Å] and angles [°]: S(1)−N(2) 1.667(5), S(1)−C(8) 1.763(7), S(2)−N(4) 1.708(5), S(2)−C(21) 1.749(7), N(1)−C(1) 1.269(7), N(1)−N(2) 1.458(6), N(2)−C(14) 1.416(7), N(3)−C(14) 1.271(7), N(3)−N(4) 1.411(6), N(4)−C(1) 1.409(7); N(2)−N(1)−C(1) 113.8(5), N(1)−N(2)−C(14) 115.4(4), N(4)−N(3)−C(14) 114.4(4), N(3)−N(4)−C(1) 116.5(4), N(1)−C(1)−N(4) 121.0(5), N(2)−C(14)−N(3) 120.9(5)

The central N(1)−N(2)−N(3)−N(4)−C(1)−C(2) heterocycle of molecule **12** is significantly nonplanar and has a boat conformation, the C(1)−N(1)−C(14)−N(3) "bottom" is planar within 0.035 Å, the "edges" C(1)−N(3)−N(4) and N(1)−N(2)−C(14) form dihedral angles of 30.0 and 28.2° with this plane. The C(2)−C(7) and C(15)−C(20) benzene rings are twisted out of the C(1)−N(1)−C(14)−N(3) plane by 86.6 and 21.8°. Geometrical parameters of the 6-membered heterocycle in **12** are similar to the corresponding Tablevalues in 1,4-dihydro-1,2,4,5-tetrazine.[19]

Conclusion

In summary, the substitution of the $=NSO_2CF_3$ group for the carbonyl oxygen atom in acyl azides makes a Curtius-type rearrangement of the compounds possible. This reaction offers considerable scope for preparation of various compounds containing the trifluoromethylsulfonylimino group.

Experimental Section

General: Moisture-sensitive reactions were carried out under dry argon, using flame-dried glassware. All chemicals were of reagent grade or were purified by standard methods before use. Solvents were distilled from the appropriate drying agents immediately prior to use. − All reactions were monitored by thin layer chromatography (TLC) on precoated Kieselgel 60 F/UV_{254} silica gel plates (Merck); spots were viewed with UV light. Purification of most products was performed by column chromatography (CC) on 70−230 mesh 60A silica gel (Aldrich). − ^1H, ^{19}F, and ^{13}C NMR spectra were recorded at 299.5 MHz, 282.2 MHz, and 75.3 MHz, respectively, with a Varian VXR-300 spectrometer, and chemical shifts are given in ppm relative to Me_4Si and CCl_3F, respectively, as internal standards. Coupling constants are given in Hz. − IR spectra were recorded with a VR-20 instrument (KBr). − Melting points were determined in open capillaries and are uncorrected. − Elemental analysis was performed in the Analytical Laboratory of the Institute of Organic Chemistry, NAS of Ukraine, Kiev.

General Procedure for the Synthesis of *N*-Perfluoroalkylsulfonylbenzamides and *N*-Trifluoromethylsulfonylpivalamide 1a−g: A solution of acyl chloride (0.03 mol) in anhydrous diethyl ether (30 mL) was added dropwise over 20 min to a stirred mixture of perfluoroalkanesulfonamide (0.03 mol) and triethylamine (6.1 g, 0.08 mol) in anhydrous diethyl ether (100 mL) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was refluxed for 2 h. After cooling, the precipitate was filtered off and washed twice with diethyl ether (20 mL). The filtrate was cocnentrated in vacuo and the resulting oil was treated with 50% H_2SO_4 at 0 °C. Filtration, air-drying, and recrystallization (from benzene) of the resultant precipitate gave analytically pure **1**.

***N*-Trifluoromethylsulfonylbenzamide (1a):** M.p. 110−112 °C; ref.[20] 112.5−114.5 °C.− ^1H NMR ([D$_6$]DMSO): δ = 7.39−7.93 (m, 5 H, ArH), 9.73 (s, 1 H, NH).− ^{19}F NMR ([D$_6$]DMSO): δ = −76.97 (s, 3 F, SO_2CF_3).

***N*-Trifluoromethylsulfonyl-*p*-toluamide (1b):** M.p. 130−132 °C. − $C_9H_8F_3NO_3S$ (267.2): calcd. C 40.45, H 3.02; found C 40.39, H 3.00.

4-Fluoro-*N*-(trifluoromethylsulfonyl)benzamide (1c): M.p. 152−153 °C; ref.[20] 148−150 °C. − ^1H NMR ($CDCl_3$): δ = 7.22−7.91 (m, 4 H, ArH), 8.77 (s, 1 H, NH). − ^{19}F NMR ($CDCl_3$): δ = −75.37 (s, 3 F, SO_2CF_3), −102.35 (s, 1 F, ArF).

4-Chloro-*N*-(trifluoromethylsulfonyl)benzamide (1d): M.p. 156−158 °C; ref.[20] 156.5−158 °C.

4-Nitro-*N*-(trifluoromethylsulfonyl)benzamide (1e): Obtained according to the general procedure, but in acetone solution and treatment with 96% H_2SO_4. − M.p. 144−145 °C; ref.[20] 140−145 °C. − IR (KBr): $\tilde{\nu}$ = 1730 (C=O), 3250 cm^{-1} (NH).

***N*-Trifluoromethylsulfonylpivalamide (1f):** M.p. 74−75 °C. − ^1H NMR ([D$_6$]DMSO): δ = 1.10 (s, 9 H, Me_3C), 7.80 (s, 1 H, NH). − ^{19}F NMR ([D$_6$]DMSO): δ = −75.74 (s, 3 F, SO_2CF_3). − IR (KBr): $\tilde{\nu}$ = 1730 (C=O), 3250 cm^{-1} (NH). − $C_6H_{10}F_3NO_3S$

(233.2): calcd. C 30.90, H 4.32, N 6.01; found C 30.89, H 4.44, N 6.13.

4-Fluoro-*N*-(nonafluorobutylsulfonyl)benzamide (1g): M.p. 180−182 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 7.13−7.97 (m, 4 H, ArH), 9.64 (s, 1 H, NH). − ^{19}F NMR ([D$_6$]DMSO): δ = −80.30 (m, 3 F, CF_3), −110.16 (s, 1 F, ArF), −113.62 (m, 2 F, CF_2), −120.93 (s, 2 F, CF_2), −125.59 (s, 2 F, CF_2). − IR (KBr): $\tilde{\nu}$ = 1705 (C=O), 3370 cm^{-1} (NH). − $C_{11}H_5F_{10}NO_3S$ (421.2): calcd. C 31.35, H 1.19, N 3.33; found C 31.60, H 1.42, N 3.38.

General Procedure for the Synthesis of *N*-Perfluoroalkylsulfonylcarboximidoyl Chlorides 2a−g: A mixture of carboxamide **1** (0.03 mol), PCl_5 (6.56 g, 0.0315 mol), and $POCl_3$ (15 mL) was stirred and heated to reflux until evolution of HCl ceased (ca. 2 h). Once the reaction was complete, $POCl_3$ was distilled off in vacuo (20 Torr) at 50 °C and the residue was purified by vacuum distillation (except for **2e**, which was recrystallized).

***N*-Trifluoromethylsulfonylbenzimidoyl Chloride (2a):** M.p. 83−85 °C. − B.p. 111−113 °C (0.06 Torr). − ^{19}F NMR ($CDCl_3$): δ = −79.84 (s, 3 F, SO_2CF_3). − $C_8H_5ClF_3NO_2S$ (271.7): calcd. Cl 13.05; found Cl 13.10.

***N*-Trifluoromethylsulfonyl-*p*-toluimidoyl Chloride (2b):** M.p. 67−68 °C. − B.p. 120−121 °C (0.05 Torr). − ^{19}F NMR ($CDCl_3$): δ = −79.26 (s, 3 F, SO_2CF_3). − $C_9H_7ClF_3NO_2S$ (285.7): calcd. Cl 12.40; found Cl 11.98.

4-Fluoro-*N*-(trifluoromethylsulfonyl)benzimidoyl Chloride (2c): M.p. 87− 88 °C. − B.p. 93−94 °C (0.03 Torr). − ^{19}F NMR ($CDCl_3$): δ = −79.11 (s, 3 F, SO_2CF_3), −98.38 (s, 1 F, ArF). − $C_8H_4ClF_4NO_2S$ (289.6): calcd. Cl 12.24, N 4.84; found Cl 12.22, N 5.12.

4-Chloro-*N*-(trifluoromethylsulfonyl)benzimidoyl Chloride (2d): M.p. 55−56 °C. − B.p. 125−127 °C (0.03 Torr). − ^{19}F NMR ($CDCl_3$): δ = −78.92 (s, 3 F, SO_2CF_3). − $C_8H_4Cl_2F_3NO_2S$ (306.1): calcd. Cl 23.16; found Cl 22.96.

4-Nitro-*N*-(trifluoromethylsulfonyl)benzimidoyl Chloride (2e): M.p. 124−126 °C (hexane). − ^{19}F NMR ($CDCl_3$): δ = −78.80 (s, 3 F, SO_2CF_3). − $C_8H_4ClF_3N_2O_4S$ (316.6): calcd. Cl 11.19, N 8.84; found Cl 10.88, N 8.78.

***N*-Trifluoromethylsulfonylpivalimidoyl Chloride (2f):** B.p. 90−91 °C (0.5 Torr). − ^{1}H NMR ($CDCl_3$): δ = 1.10 (s, 9 H, Me_3C). − ^{19}F NMR ($CDCl_3$): δ = −79.45 (s, 3 F, SO_2CF_3). − $C_6H_9ClF_3NO_2S$ (251.7): calcd. C 28.63, H 3.60, Cl 14.08; found C 28.60, H 3.61, Cl 14.14.

4-Fluoro-*N*-(nonafluorobutylsulfonyl)benzimidoyl Chloride (2g): B.p. 128−129 °C (0.06 Torr). − ^{19}F NMR ($CDCl_3$): δ = −81.19 (m, 3 F, CF_3), −98.28 (s, 1 F, ArF), −113.53 (m, 2 F, CF_2), −121.22 (s, 2 F, CF_2), −126.40 (m, 2 F, CF_2). − $C_{11}H_4ClF_{10}NO_2S$ (439.7): calcd. C 30.05, H 0.92, Cl 8.06; found C 29.79, H 1.17, Cl 8.14.

General Procedure for the Synthesis of *N*-Aryl(Alkyl)-*N*′-perfluoroalkylsulfonylcarbodiimides 3a−g: Finely powdered sodium azide (0.36 g, 0.0055 mol) was added to a vigorously stirred solution of imidoyl chloride **2** (0.005 mol) in anhydrous glyme (15 mL) at −5 °C. The reaction mixture was stirred at −5 to +10 °C until nitrogen evolution (110−115 mL) ceased (ca. 0.5−1 h). The precipitate of inorganic salts was filtered off under dry argon and washed with anhydrous glyme (5 mL). The filtrate was a solution of **3**, pure enough for the next step. After concentration in vacuo (0.05 Torr) at 15 °C, it afforded pure, undistillable oil **3**, which gave high-melting oligomerization products on long storage at room temperature or on heating.

***N*-Phenyl-*N*′-(trifluoromethylsulfonyl)carbodiimide (3a):** Oil. − ^{1}H NMR (CD_3CN): δ = 7.59−7.62 (m, 5 H, ArH). − ^{19}F NMR (CD_3CN): δ = −78.48 (s, 3 F, SO_2CF_3). − $C_8H_5F_3N_2O_2S$ (250.2): calcd. C 38.40., H 1.99, N 11.19; found C 38.21., H 2.28, N 11.25.

***N*-*tert*-Butyl-*N*′-(trifluoromethylsulfonyl)carbodiimide (3f):** Oil. − ^{1}H NMR (CD_3CN): δ = 1.54 (s, 9 H, Me_3C). − ^{19}F NMR (CD_3CN): δ = −78.16 (s, 3 F, SO_2CF_3). − $C_6H_9F_3N_2O_2S$ (230.2): calcd. C 31.30., H 3.94, N 12.17; found C 31.15., H 3.76, N 11.82.

Hydrolysis of Carbodiimide 3a: Carbodiimide **3a** (0.005 mol), obtained after concentration of the glyme solution in vacuo, was treated with 85% orthophosphoric acid (10 mL) at 0 °C. After stirring at 150 °C for 1 h, the reaction mixture was poured onto crushed ice and extracted with diethyl ether (3× 10 mL). The organic phase was dried with magnesium sulfate and concentrated to dryness, to give $CF_3SO_2NH_2$ (0.34 g, 45%). − M.p. 118−120 °C. − The aqueous phase was treated with 30% NaOH until pH = 10 was reached, and extracted with diethyl ether (3 × 10 mL). The mixture was concentrated at atmospheric pressure to 3 mL volume and treated with a mixture of acetic anhydride (1 mL), sodium acetate (0.25 g), and water (10 mL). After stirring at 25 °C for 1 h, the precipitate formed was filtered off. The crude product was recrystallized from ethanol to give acetanilide (0.25 g, 36%); m.p. 110−112 °C.

1,3,5-Tris(4-fluorophenyl)-2,4,6-trioxoperhydro-*s*-1,3,5-triazine (4): A glyme solution of carbodiimide **3c** was stirred and heated at reflux for 5 h and then concentrated to dryness. Purification of the crude product by recrystallization failed. Column chromatography (eluent: benzene/ethyl acetate, 2:1) afforded **4** (0.39 g, 57%). − M.p. 265−267 °C.

***N*-(*tert*-Butyl)-*N*′-trifluoromethylsulfonylurea (5). − Method A:** Water (5 mL) was added dropwise over 20 min to a stirred glyme solution of carbodiimide **3f** at 0 °C. After stirring for 2 h at room temperature, the reaction mixture was extracted with diethyl ether (3 × 10 mL). The organic phase was dried with magnesium sulfate and concentrated to dryness. The crude product was recrystallized from benzene to afford **5** (0.53 g, 43%). − **Method B:** A solution of trifluoromethylsulfonyl isocyanate[10] (0.87 g, 0.005 mol) in anhydrous dichloromethane (10 mL) was added dropwise over 20 min to a stirred solution of *tert*-butylamine (0.36 g, 0.005 mol) in anhydrous dichloromethane (10 mL) at −50 °C. After stirring for 1 h at −50 °C and for 2 h at room temperature, the precipitate formed was filtered off. The crude product was recrystallized from benzene to give the desired product (0.62 g, 50%). − M.p. 110−111 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.35 (s, 9 H, Me_3C), 6.46 (s, 1 H, NH). − ^{19}F NMR ($CDCl_3$): δ = −76.11 (s, 3 F, SO_2CF_3). − ^{13}C NMR ([D$_6$]DMSO): δ = 28.3 (s, CH_3), 50.6 (s, CMe_3), 119.6 (d, J = 322 Hz, CF_3), 150.7 (s, C=O). − IR (KBr): $\tilde{\nu}$ = 1720 (C=O), 3415 cm^{-1} (NH). − $C_6H_{11}F_3N_2O_3S$ (248.2): calcd. C 29.03, H 4.47, N 11.29; found C 28.98, H 4.44, N 11.20.

2-Isopropyl-1-phenyl-3-(trifluoromethylsulfonyl)isourea (6): A solution of 2-propanol (0.60 g, 0.01 mol) in anhydrous glyme (3 mL) was added dropwise over 20 min to a stirred glyme solution of carbodiimide **3a** at 0 °C. After stirring for 1 h at room temperature and for 4 h at 70 °C, the solvent was evaporated in vacuo. Column chromatography (eluent: benzene) of the residue and recrystallization from hexane gave **6** (0.93 g, 60%). − M.p. 60−61 °C. − ^{1}H NMR (CD_3CN): δ = 1.33 (d, J = 6 Hz, 6 H, 2 CH_3), 5.28 (sept, 1 H, CH), 7.30−7.41 (m, 5 H, ArH), 9.04 (s, 1 H, NH). − ^{19}F

NMR (CD_3CN): δ = −78.91 (s, 3 F, SO_2CF_3). − IR (KBr): ṽ = 1595 (C=N), 3290 cm^{-1} (NH). − $C_{11}H_{13}F_3N_2O_3S$ (310.3): calcd. C 42.58, H 4.22, N 9.03; found C 42.29, H 4.08, N 9.21.

1,1-Dimethyl-3-phenyl-2-(trifluoromethylsulfonyl)guanidine (7): A solution of dimethylamine (0.23 g, 0.005 mol) in anhydrous glyme (5 mL) was added dropwise over 20 min to a stirred glyme solution of carbodiimide **3a** at 0 °C. After stirring for 8 h at room temperature, the solvent was evaporated in vacuo. Column chromatography (eluent: benzene/ethyl acetate, 20:1) of the residue afforded **7** (0.78 g, 53%). − M.p. 133−135 °C. − ^1H NMR ($CDCl_3$): δ = 2.91 (br.s, 6 H, CH_3), 6.99 (m, 2 H, ArH), 7.21 (m, 1 H, ArH), 7.37 (m, 2 H, ArH), 8.44 (s, 1 H, NH) [ref. [16] ^1H NMR ($CDCl_3$): δ = 2.91 (br.s, 6 H, CH_3), 7.00 (m, 2 H, ArH), 7.21 (m, 1 H, ArH), 7.37 (m, 2 H, ArH), 8.41 (s, 1 H, NH)]. − ^{19}F NMR ($CDCl_3$): δ = −79.31 (s, 3 F, SO_2CF_3). − $C_{10}H_{12}F_3N_3O_2S$ (295.3): calcd. C 40.67, H 4.10, N 14.23; found C 40.24, H 3.87, N 13.99.

General Procedure for the Synthesis of 4-[*N*-Aryl(Alkyl)-*N*′-perfluoroalkylsulfonylamidino]morpholines 8a−g: A solution of morpholine (0.44 g, 0.005 mol) in anhydrous glyme (5 mL) was added dropwise over 20 min to a stirred solution of carbodiimide **3**, obtained according to the general procedure, at 0 °C. After stirring for 5 h at room temperature (TLC monitoring; eluent: benzene/ethyl acetate, 20:1), the solvent was evaporated in vacuo and the crude product was purified by column chromatography (eluent: benzene/ethyl acetate, 20:1).

4-(*N*-Phenyl-*N*′-trifluoromethylsulfonylamidino)morpholine (8a). − Method A: According to general procedure. − **Method B:** Triphenyl(phenylimino)phosphorane (0.35 g, 0.001 mol) in anhydrous dichloromethane (5 mL) was added to a stirred solution of trifluoromethylsulfonyl isocyanate (0.18 g, 0.001 mol) in anhydrous dichloromethane (5 mL) at 0 °C. After stirring at 0 °C for 4 h, the reaction mixture was treated with morpholine (0.17 g, 0.002 mol) in anhydrous dichloromethane (3 mL). After stirring at room temperature for 8 h, the solvent was evaporated in vacuo and the crude product was dissolved in benzene (10 mL) and Ph_3PO removed by filtration through Al_2O_3. Column chromatography (eluent: benzene/ethyl acetate, 20:1) afforded **8a** (0.24 g, 71%). − M.p. 112−114 °C. − ^1H NMR (CD_3CN): δ = 3.51 (m, 4 H, $2CH_2$), 3.67 (m, 4 H, $2CH_2$), 7.18−7.42 (m, 5 H, ArH), 8.21 (s, 1 H, NH). − ^{19}F NMR (CD_3CN): δ = −78.94 (s, 3 F, SO_2CF_3). − IR (KBr): ṽ = 1590 (C=N), 3360 cm^{-1} (NH). − $C_{12}H_{14}F_3N_3O_3S$ (337.3): calcd. C 42.72, H 4.18, N 12.45; found C 42.60, H 4.26, N 12.18.

4-(*N*-Tolyl-*N*′-trifluoromethylsulfonylamidino)morpholine (8b): M.p. 117−118 °C. − ^1H NMR (CD_3CN): δ = 2.34 (s, 3 H, CH_3), 3.51 (m, 4 H, $2CH_2$), 3.63 (m, 4 H, $2CH_2$), 7.07−7.20 (dd, 4 H, ArH), 8.16 (s, 1 H, NH). − ^{19}F NMR (CD_3CN): δ = −78.93 (s, 3 F, SO_2CF_3). − IR (KBr): ṽ = 1585 (C=N), 3375 cm^{-1} (NH). − $C_{13}H_{16}F_3N_3O_3S$ (351.4): calcd. C 44.43, H 4.59, N 11.96; found C 44.52, H 4.67, N 11.89.

4-[*N*-(4-Fluorophenyl)-*N*′-trifluoromethylsulfonylamidino]-morpholine (8c): M.p. 142−144 °C. − ^1H NMR (CD_3CN): δ = 3.51 (m, 4 H, $2CH_2$), 3.66 (m, 4 H, $2CH_2$), 7.09−7.29 (m, 4 H, ArH), 8.14 (s, 1 H, NH). − ^{19}F NMR (CD_3CN): δ = −79.06 (s, 3 F, SO_2CF_3), −116.8 (s, 1 F, ArF). − IR (KBr): ṽ = 1585 (C=N), 3310 cm^{-1} (NH). − $C_{12}H_{13}F_4N_3O_3S$ (355.3): calcd. C 40.56, H 3.68, N 11.83; found C 40.26, H 3.55, N 11.52.

4-[*N*-(4-Chlorophenyl)-*N*′-trifluoromethylsulfonylamidino]-morpholine (8d): M.p. 148−150 °C. − ^1H NMR (CD_3CN): δ = 3.53 (m, 4 H, $2CH_2$), 3.68 (m, 4 H, 2 CH_2), 7.10−7.42 (dd, 4 H, ArH), 8.16 (s, 1 H, NH). − ^{19}F NMR (CD_3CN): δ = −79.04 (s, 3 F, SO_2CF_3). − IR (KBr): ṽ = 1580 (C=N), 3300 cm^{-1} (NH). − $C_{12}H_{13}ClF_3N_3O_3S$ (371.8): calcd. C 38.77, H 3.52, N 11.30; found C 38.59, H 3.42, N 11.19.

4-[*N*-(4-Nitrophenyl)-*N*′-trifluoromethylsulfonylamidino]morpholine (8e): M.p. 217−219 °C. − ^1H NMR (CD_3CN): δ = 3.61 (m, 4 H, $2CH_2$), 3.73 (m, 4 H, $2CH_2$), 7.32−8.22 (dd, 4 H, ArH), 8.17 (s, 1 H, NH). − ^{19}F NMR (CD_3CN): δ = −79.15 (s, 3 F, SO_2CF_3). − IR (KBr): ṽ = 1590 (C=N), 3285 cm^{-1} (NH). − $C_{12}H_{13}F_3N_4O_5S$ (382.3): calcd. C 37.69, H 3.42, N 14.65; found C 37.61, H 3.50, N 14.64.

4-(*N*-*tert*-Butyl-*N*′-trifluoromethylsulfonylamidino)morpholine (8f): M.p. 132−133 °C. − ^1H NMR (CD_3CN): δ = 1.38 (s, 9 H, Me_3C), 3.50 (m, 4 H, $2CH_2$), 3.72 (m, 4 H, $2CH_2$), 5.61 (s, 1 H, NH). − ^{19}F NMR (CD_3CN): δ = −78.24 (s, 3 F, SO_2CF_3). − IR (KBr): ṽ = 1590 (C=N), 3360 cm^{-1} (NH). − $C_{10}H_{18}F_3N_3O_3S$ (317.3): calcd. C 37.85, H 5.71, N 13.24; found C 37.92, H 5.80, N 13.06.

4-[*N*-(4-Fluorophenyl)-*N*′-nonafluorobutylsulfonylamidino]-morpholine (8g): M.p. 127−129 °C. − ^1H NMR (CD_3CN): δ = 3.43 (m, 4 H, $2CH_2$), 3.66 (m, 4 H, $2CH_2$), 6.99−7.45 (m, 4 H, ArH), 8.95 (s, 1 H, NH). − ^{19}F NMR (CD_3CN): δ = −80.28 (m, 3 F, CF_3), −113.20 (m, 2 F, CF_2), −117.44 (s, 1 F, ArF), −120.67 (s, 2 F, CF_2), −125.61 (m, 2 F, CF_2). − IR (KBr): ṽ = 1590 (C=N), 3290 cm^{-1} (NH). − $C_{15}H_{13}F_{10}N_3O_3S$ (505.3): calcd. C 35.65, H 2.59, N 8.32; found C 35.46, H 2.45, N 8.16.

Morpholinium 1-Phenyl-5-(trifluoromethylsulfonylimino)tetrazolide (9): Morpholine (0.2 g, 0.0022 mol) was added dropwise to the reaction mixture obtained as described for **3a**, but without filtration of inorganic salts, from **1a** (0.54 g, 0.002 mol), sodium azide (0.26 g 0.004 mol), and glyme (3 mL). After stirring at room temperature for 48 h, the precipitated inorganic salts were filtered off and washed with glyme (3 mL). The filtrate was concentrated in vacuo. Column chromatography (eluent: benzene/ethyl acetate, 20:5) yielded **8a** (0.18 g, 26%) and the desired salt (0.32 g, 42%); m.p. 171−172 °C. − ^1H NMR (CD_3CN): δ = 3.29 (m, 4 H, 2 CH_2), 3.93 (m, 4 H, 2 CH_2), 7.48−7.79 (m, 5 H, ArH), 8.10 (br. s, 2 H, H_2N^+). − ^{19}F NMR (CD_3CN): δ = −77.50 (s, 3 F, SO_2CF_3). − $C_{12}H_{15}F_3N_6O_3S$ (380.4): calcd. C 37.89, H 3.97, N 22.09; found C 38.15, H 3.83, N 21.90.

***N*-Trifluoromethylsulfonylbenzimidoyl Morpholide (10):** Finely powdered sodium azide (0.14 g, 0.0022 mol) was added to a vigorously stirred solution of imidoyl chloride **2a** (0.54 g, 0.002 mol) in anhydrous THF (10 mL) at 0 °C. The reaction mixture was stirred for 2 h at room temperature and for 1 h at 40 °C, but no evolution of nitrogen occurred. After cooling, the precipitate of inorganic salts was filtered off under dry argon and washed with anhydrous THF (3 mL). The filtrate was treated with morpholine (0.4 g, 0.0045 mol) at 0 °C. After stirring at room temperature for 2 h, precipitated morpholine hydrochloride was filtered off, the filtrate was concentrated to dryness, and the residue was recrystallized from benzene/hexane (1:1) to give the desired product (0.48 g, 75%). − M.p. 136−138 °C. − ^1H NMR (CD_3CN): δ = 3.31 (m, 2 H, CH_2), 3.62 (m, 2 H, CH_2), 3.81 (m, 2 H, CH_2), 3.93 (m, 2 H, CH_2), 7.46−7.56 (m, 5 H, ArH). − ^{19}F NMR (CD_3CN): δ = −78.64 (s, 3 F, SO_2CF_3). − IR (KBr): ṽ = 1565 cm^{-1} (C=N). − $C_{12}H_{13}F_3N_2O_3S$ (322.3): calcd. C 44.72, H 4.06, N 8.69; found C 44.58, H 3.98, N 8.74.

1,4-Dihydro-3,6-diphenyl-1,4-bis(phenylsulfonyl)-1,2,4,5-tetrazine (12): Finely powdered sodium azide (0.14 g, 0.0022 mol) was added to a vigorously stirred solution of imidoyl chloride **11**[21] (0.55 g, 0.002 mol) in anhydrous glyme (10 mL) at 0 °C. After stirring at

Table 3. Crystal data and structure refinement parameters for compounds **4**, **5**, **9**, and **12**

	4	**5**	**9**	**12**
Empirical formula	$C_{21}H_{12}F_3N_3O_3$	$C_6H_{11}F_3N_2O_3S$	$C_{12}H_{15}F_3N_6O_3S$	$C_{26}H_{20}N_4O_4S_2$
Cell parameters:				
a [Å]	11.687(3)	6.291(1)	10.550(2)	10.422(2)
b [Å]	7.504(2)	9.039(1)	19.996(4)	14.892(3)
c [Å]	21.278(4)	9.764(1)	8.128(2)	16.203(3)
α [°]	90	93.50(1)	90	90
β [°]	92.05(2)	94.12(1)	105.85(3)	90
γ [°]	90	92.60(1)	90	90
V [Å^3]	1865.0	552.03	1649.5	516.6
Z	4	2	4	4
$D_{calcd.}$ [gcm^{-3}]	1.47	1.49	1.53	1.36
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
μ [cm^{-1}]	10.00	29.56	23.04	2.52
Radiation	Cu-K_α	Cu-K_α	Cu-K_α	Mo-K_α
F(000)	843	812	784	1072
Crystal size [mm]	0.15×0.25×0.44	0.22×0.28×0.38	0.06×0.16×0.41	0.25×0.31×0.50
Index ranges	$0 < h < 11$	$0 < h < 7$	$-3 < h < 11$	$0 < h < 12$
	$0 < k < 8$	$-10 < k < 10$	$-13 < k < 22$	$0 < k < 17$
	$-24 < l < 24$	$11 < l < 11$	$-9 < l < 8$	$0 < l < 19$
θ_{max} [°]	65	65	60	25
No of reflections:				
collected	3338	2221	2582	2516
independent	2920	1883	2439	2516
in refinement	1960 [$I > 3\sigma(I)$]	3069 [$I > 3\sigma(I)$]	1820 [$I > 2\sigma(I)$]	1625 [$I > 2\sigma(I)$]
R(int)	0.023	0.018	0.061	0
No. of refined parameters	319	144	281	325
Final R indices:				
$R_1(F)$	0.042	0.042	0.046	0.052
$R_w(F)$	0.044	0.049		
R_w (F^2)			0.115	0.102
GOF	1.150	1.114	0.950	1.018
Weighting coefficients:	1.19, 0.30, 0.93, 0.02, 0.29	2.82, 2.71, 2.66,0.93, 0.69	0.076, 0.759	0.055
Largest peak/hole [ecm^{-3}]	0.16/−0.21	0.28/−0.28	0.22/−0.26	0.19/−0.23

48−50 °C for 2 h, the calculated amount of nitrogen (45 mL) had been evolved. The precipitate of inorganic salts was filtered off and the filtrate was concentrated to dryness. Recrystallization of the residue from benzene/hexane (1:1) afforded the desired product (0.31 g, 61%). − M.p. 168−170 °C (dec). − $C_{26}H_{10}N_4O_4S_2$ (516.6): calcd. C 60.44, H 3.91, S 12.41; found C 60.00, H 3.87, S 12.35.

X-ray Crystallography: Crystal data, data collection, and processing parameters are given in Table 3. All crystallographic measurements were performed at 20 °C with a CAD-4-Enraf−Nonius diffractometer, using the ω-2θ scan mode (ratio of the scanning rates ω/2θ = 1.2). All data were corrected for Lorentz and polarization effects, but not for absorption. All structures were solved by direct methods. Non-hydrogen atoms were refined by full-matrix, least-squares technique in the anisotropic approximation. All hydrogen atoms in **4**, **5**, and **9** were located in difference Fourier maps, in **12** they were placed in calculated positions. In **4** and **9**, all hydrogen atoms were refined isotropically, in **5** only the atoms H(1) and H(2) were refined, in **12** all hydrogen atoms were included in the final refinement riding their supporting carbon atoms. The weighting scheme $w^{-1} = \sigma^2(F_o^2) + (AP)^2 + BP$ with $P = (F_o^2 + 2F_c^2)/3$ was used for **9** and **12**. The Chebushev weighting scheme[22] was used for **4** and **5**. For **4** and **5**, all structural calculations were carried out using the CRYSTALS program package,[23] for **9** and **12** using SHELXS-86[24] and SHELXS-93.[25] Crystallographic data for the structures reported (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-141592 (**4**), -146591 (**5**), -144594 (**9**), and -146593 (**12**), and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1 EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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