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Trifluoromethanesulfonamides and Related Compounds

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1. INTRODUCTION

Since the publication of the first review on trifluoromethane-sulfonic (hereinafter triflic) acid and its derivatives,¹ the chemistry of triflates has become an actively developing field of research due to unique physical and chemical properties of various derivatives of this most strong organic acid. It is

sufficient to mention the ubiquitous use of alkyl, aryl, vinyl, and silyl triflates as efficient electrophiles in numerous reactions,^{2,3} the rare-earth metal triflates as water-tolerant Lewis acid catalysts,⁴ ionic liquids with triflate and triflimide anions with melting points down to -70°C ,⁵ etc. A number of trifluoromethanesulfonamide derivatives are used as drugs in medicine or as pesticides, insecticides, fungicides, etc. in agriculture. Trifluoromethanesulfonamide (hereinafter “triflamine” for brevity) and its various N-substituted derivatives represent, apparently, the most numerous class of triflic compounds. However, in spite of several surveys highlighting specific aspects of the triflamine chemistry,^{6–9} so far no general review covering this class of compounds has appeared in the literature. The aim of the present review is to fill this gap by compiling the most recent accomplishments in the chemistry of triflamine $\text{CF}_3\text{SO}_2\text{NH}_2$, its higher perfluoroalkyl analogues $\text{R}_\text{F}\text{SO}_2\text{NH}_2$, and their N-substituted derivatives $\text{R}_\text{F}\text{SO}_2\text{NXY}$, where X and Y are alkyl, aryl, or hetaryl functional groups. The main focus is made on the synthetic chemistry (sections 2 and 3), but more specific sections 4–7 highlighting applications of the compounds under consideration for preparation of ionic liquids and in use as catalysts, fuel cells components, and pharmaceuticals are also included.

2. TRIFLUOROMETHANESULFONAMIDES (TRIFLAMIDES)

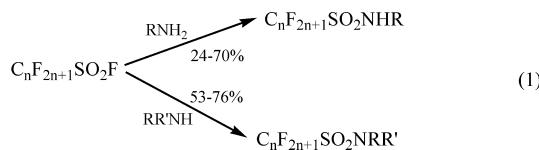
2.1. Preparation

Two principal synthetic approaches to triflamine and other perfluoroalkylsulfonamides are the reaction of the corresponding fluoroalkylsulfonyl fluorides $\text{R}_\text{F}\text{SO}_2\text{F}$ with ammonia or amines.^{10–15} Trifluoromethanesulfonyl chloride $\text{CF}_3\text{SO}_2\text{Cl}$ or triflic anhydride $(\text{CF}_3\text{SO}_2)_2\text{O}$ (normally, in the presence of triethylamine to bind the eliminated triflic acid) can also be used for amination,^{1,6,16} but $\text{CF}_3\text{SO}_2\text{F}$ is preferable because it is the first and hence the cheapest product on the way from simple organic ancestor to a large family of triflic compounds via electrochemical fluorination of methanesulfonyl chloride. Moreover, in some cases $\text{CF}_3\text{SO}_2\text{Cl}$ can act not only as a sulfonylating but also as a chlorinating agent, at least with respect to ammonia, primary amines, OH and CH-acids, being reduced to sulfonates.^{17–19} Recently, a large series of mono- and disubstituted perfluoroalkanesulfonamides $\text{C}_n\text{F}_{2n+1}\text{SO}_2\text{NHR}$ and $\text{C}_n\text{F}_{2n+1}\text{SO}_2\text{NR}_2$ ($n = 4, 8$) was synthesized in moderate to good yields by the reaction of the corresponding perfluoroalkanesulfonyl fluorides $\text{C}_n\text{F}_{2n+1}\text{SO}_2\text{F}$ with primary and secondary amines using triethylamine as a base.²⁰

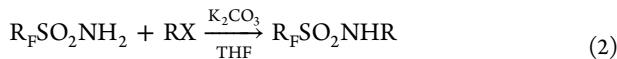
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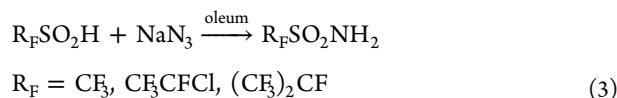




N-Substituted triflamides and their higher homologues, polyfluoroalkylsulfonamides, are prepared also by alkylation of the primary parent compounds with alkyl halogenides or tosylates in the presence of potassium carbonate in aprotic medium.¹⁴



A more specific method is the oxidative amidation of polyfluoroalkanesulfonic acids with sodium azide in oleum up to 70% yield.²¹



2.2. Structure, Acidity, Basicity, and Associates in the Gas Phase and Solution

Structurally, considering the planarity of the amino group, triflamides are intermediate between carboxamides and non-fluorinated sulfonamides (Figure 1).

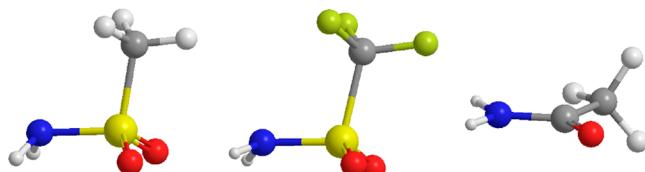


Figure 1. Planarization of the nitrogen atom on going from methanesulfonamide to triflamine and acetamide.

Thus, HF/6-31G** calculations of $\text{CF}_3\text{SO}_2\text{NH}_2$ gave the sum of the angles around the nitrogen atom Σ_N of 346.3° .²² Our B3LYP/6-311G** calculations show the nitrogen atom in $\text{CF}_3\text{SO}_2\text{NH}_2$ being even more planar, $\Sigma_N = 348.9^\circ$.²³ At the same level of theory, the nitrogen atom in the nonfluorinated analogue, MeSO_2NH_2 , is practically tetrahedral, $\Sigma_N = 330.9^\circ$.²³ With this, on going from MeSO_2NH_2 to $\text{CF}_3\text{SO}_2\text{NH}_2$, all angles (HNH and SNH) are increased similarly, from ~ 110 to $\sim 116^\circ$. Introduction of one methyl group at nitrogen has negligible overall effect in $\text{CF}_3\text{SO}_2\text{NHMe}$ ($\text{HNC } 117.1^\circ, \text{SNH } 110.4^\circ, \text{SNC } 120.6^\circ, \Sigma_N = 348.1^\circ$) but dimethylation makes the nitrogen atom in $\text{CF}_3\text{SO}_2\text{NMe}_2$ almost planar ($\text{CNC } 117.1^\circ, \text{SNC } 119.4^\circ, \Sigma_N = 356.0^\circ$).²³ A detailed analysis of the IR and Raman spectra of triflamine is given for the solid state²² and in the gas phase (Table 1).^{24,25}

Strong differences between the positions and the intensities of the bands in different aggregate states and temperature dependence of the IR spectra allowed for the assumption of the presence of equilibrium between the monomers and the H-bonded dimers of triflamine even in the gas phase up to 435 K.²⁴ In inert solvents, the structure of clusters of triflamine is determined by the polarity of the solvent. In low-polarity CCl_4 and C_2Cl_4 , the cyclic tetramer is formed with two H-bonds $\text{NH}\cdots\text{O=S}$ in each monomer link; in chloroform, as a solvent of moderate polarity, cyclic trimers exist; in highly polar

Table 1. IR Vibrational Frequencies (ν, cm^{-1}) for Triflamine $\text{CF}_3\text{SO}_2\text{NH}_2$

	experimental		calculated		assignment ²²
	gas (458 K) ²³	crystal ²¹	B3LYP/6-31G* ²⁴	HF/6-31G*** ^{a22}	
3501 w	3392 v.s	3633	3529	$\nu_{as}(\text{NH}_2)$	
3395 w	3280 v.s	3516	3408	$\nu_s(\text{NH}_2)$	
1537 w	1522 s	1613	1557	$\delta(\text{NH}_2)$	
1428 v.s	1357 v.s	1380	1374	$\nu_{as}(\text{SO}_2)$	
1238 s	1235 s	1216	1262	$\nu_s(\text{CF}_3)$	
1200 v.s	1190 v.s	1264	1284	$\nu_{as}(\text{CF}_3)$	
1150 s	1153 s	1117	1132	$\nu_s(\text{SO}_2)$	
1065 v.w	1046 v.w	1093	1060	$\rho(\text{NH}_2)$	
888 m	957 m	876	894	$\nu(\text{SN})$	
	767 v.w	758	769	$\delta_s(\text{CF}_3)$	
605 m	628 s	617	616	$\omega(\text{SO}_2)$	
	568 m	562	559	$\delta_{as}(\text{CF}_3)$	
496 w	495 s	550	495	$\delta(\text{SO}_2)$	

^aWith scaling factor of 0.9.

solvents such as C_2HCl_5 and $\text{C}_2\text{H}_4\text{Cl}_2$, linear dimers predominate.²⁶ In aprotic dipolar solvents, there is a competition between the processes of self-association of triflamine molecules and the formation of its solvate H-complexes, with the result being determined by the basicity of the medium.²⁷

A similar behavior is observed for *N*-methyltriflamine $\text{CF}_3\text{SO}_2\text{NHMe}$, for which the analysis of the IR spectrum is simplified because of the presence of only one N–H bond in the molecule.²⁸ A low-polarity cyclic dimer exists in the gas phase and in nonpolar CCl_4 , whereas a highly polar linear dimer with the energy of the H-bond $\text{N–H}\cdots\text{O=S}$ of 20.1 kJ/mol (determined by IR spectroscopy from the temperature dependence of the dimerization constant) predominates in a polar CH_2Cl_2 .²⁹ In basic solvents, the cyclic dimer can react with the rupture of one or two H-bonds and formation of solvate complexes of the linear dimer or of the monomer, respectively.³⁰ Triflamine and its *N*-monosubstituted analogues are strong NH-acids. The pK_a values for a series of *N*-substituted triflamides varying within the range of 10 orders of magnitude are listed in Table 2.

The data of Table 2 show that the acidity of triflamine and its analogues is not only determined by the electronegativity of substituent R but is also affected by the processes of their homo- and heteroassociation. For example, $(\text{CF}_3\text{SO}_2\text{NH})_2\text{CH}_2$ (no. 10) is 0.65 pK_a units less acidic than $\text{CF}_3\text{SO}_2\text{NHCH}_2\text{NHCOCH}_3$ (no. 9) in spite of a stronger electron-acceptor character of the CF_3SO_2 (σ_p 0.93) as compared to the CH_3CO group (σ_p 0.50). This was explained by different types of association of the two compounds in the solution.³²

Polyfluorinated analogues of triflamine show stronger NH-acidity, as follows from the pK_a values for compounds listed in Table 3; their acidity is close to that of the mixed imide of triflic acid and *o*-toluic acid (no. 11 in Table 2).

Triflamine and its analogues are strong hydrogen-bond donors; for example, *N*-methyltriflamine, as such, exceeds phenol and *p*-fluorophenol and is second only to *p*-nitrophenol.^{27,33}

Apart from being NH-acids, triflamine and its analogues have two centers of basicity, the nitrogen and oxygen atoms. In compliance with the aforementioned planarization of the

Table 2. Acidity of Triflamides $\text{CF}_3\text{SO}_2\text{NHR}$

no.	R	pK_a	
		in H_2O	in MeOH
1	H	6.33 ¹³ ^a	11.06 ³² (9.37 ¹⁴)
2	CH_3	7.56 ²⁹	12.70 ³²
3	Ph	4.45 ¹³	
4	<i>p</i> -ClC ₆ H ₄	3.90 ¹³	
5	<i>m</i> -MeC(O)C ₆ H ₄	3.75 ¹³	
6	<i>m</i> -CF ₃ C ₆ H ₄	3.50 ¹³	
7	<i>p</i> -MeSO ₂ C ₆ H ₄	2.84 ¹³	
8	CH ₂ SiMe ₃		12.84 ³³
9	CH ₂ NHCOCH ₃	6.25 ³²	10.11 ³²
10	CH ₂ NHSO ₂ CF ₃		10.76 ³²
11	COCH ₂ Ph		5.45 ³⁴
12	CH(CCl ₃)(2-pyrrolyl)		9.32 ³⁵
13	CH(CCl ₃)[2-(5-R-pyrrolyl)] ^b		9.68 ³⁵
14	SO ₂ CF ₃	2.8 ³² (1.7 ³¹)	2.7 ³⁶

^aEarlier, the pK_a value of 5.8 was reported in H_2O ¹⁶ and 9.7 in DMSO.³⁷ ^bR = TfNHCH(CCl₃).

Table 3. pK_a Values for Some Fluoroalkylsulfonamides $\text{R}_\text{F}\text{SO}_2\text{NH}_2$ in MeOH¹⁴

no.	R_F	pK_a
1	Cl(CF ₂) ₂	6.17
2	I(CF ₂) ₂ O(CF ₂) ₂	6.22
3	H(CF ₂) ₂ O(CF ₂) ₂	5.83
4	I(CF ₂) ₄ O(CF ₂) ₂	5.70
5	I(CF ₂) ₆ O(CF ₂) ₂	4.22
6	Cl(CF ₂) ₆ O(CF ₂) ₂	5.74
7	H ₂ NO ₂ S(CF ₂) ₂ O(CF ₂) ₂	5.67
8	H ₂ NO ₂ S(CF ₂) ₂ O(CF ₂) ₄ O(CF ₂) ₂	5.90

nitrogen atom in triflamide and, hence, a decrease of its basicity with respect to that of methanesulfonamide, the former forms only the O-H-bonded complexes with strong acids, whereas the latter is protonated at nitrogen.²³ Thus, again, in this sense triflamide occupies an intermediate position between non-fluorinated sulfonamides and carboxamides, which are normally protonated at the oxygen atom (see ref 23 and refs therein).

Of special interest is bis(trifluoromethanesulfonyl)imide ($(\text{CF}_3\text{SO}_2)_2\text{NH}$, which was synthesized as late as in 1984¹⁰ and since then attracts the attention of researchers due to its extremely high acidity and unique properties of its metal salts used in batteries^{39–42} and as water-tolerant Lewis acid catalysts.^{43–48} In the crystal, $(\text{CF}_3\text{SO}_2)_2\text{NH}$ forms chains linked by symmetrical bifurcate hydrogen bonds NH···O=S.⁴⁹ In solutions, it forms different homo- and heteroclusters

depending on the polarity and basicity of the solvent.³⁶ The chain dimer (Figure 2a) with bifurcate hydrogen bond is the monomer link of the molecular crystal of bis(trifluoromethanesulfonyl)imide. The calculated (B3LYP/6-311G**) H-bond lengths are close to those found experimentally by X-ray (2.261 Å).⁴⁹ The cyclic dimer (Figure 2b) formed by two strong H-bonds N–H···O bonds is 2.2 kcal/mol more stable.³⁶

In the gas phase, as distinct from $\text{CF}_3\text{SO}_2\text{NH}_2$ or $\text{CF}_3\text{SO}_2\text{NHMe}$ (vide supra), it exists as monomeric molecules.⁵⁰ The pK_a values for $(\text{CF}_3\text{SO}_2)_2\text{NH}$ are very similar in water, methanol, and dimethylsulfoxide (DMSO) (2.8, 2.7, and 2.1, respectively), whereas for conventional protic acids (HCl and HBr) the acidity in DMSO is much lower than in water, with the difference reaching 10 pK units.⁵¹ This is due to the fact that in the conjugate anion $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ the negative charge is strongly delocalized over the nitrogen atom, four oxygen atoms, and two trifluoromethyl groups, which drastically decreases the needs in external solvation and levels out the acidic properties in different solvents.³⁶ The large effects of water on the NMR and IR spectra of bis(perfluoroalkylsulfonyl)imides prove that in pure substrates (in the absence of water) the proton is predominantly bound to the nitrogen atom whereas in the presence of water the onium salt is formed.⁵²

2.3. Reactions of Triflamides

Hendrickson et al. reported two patterns of reactivity of the N-substituted triflamides in reactions with nucleophiles,¹⁶ that is, the rupture of the N–R bond with elimination of the triflamide anion $\text{CF}_3\text{SO}_2\text{N}(\text{R})^-$, or the rupture of the N–S bond with elimination of the triflate anion CF_3SO_2^- as a leaving group. The first type of splitting is facile only if two triflyl residues are attached to nitrogen or when R = acyl. The second type of splitting is realized, e.g., for triflamides $\text{CF}_3\text{SO}_2\text{N}(\text{Ph})\text{CH}_2\text{R}'$, having an acidic proton at the α -position to nitrogen. With nucleophiles, they are split to imines $\text{R}'\text{CH}=\text{NPh}$ and triflate anion CF_3SO_2^- , providing a new “Gabriel-type” route to the synthesis of amines (see section 2.3.2). However, sometimes even the C–S bond rupture can compete either by the intramolecular OH attack on the sulfur atom⁵³ or in the reaction with nucleophilic alkylolithium reagent provided that the $\text{CF}_3\text{SO}_2-\text{N}-\text{C}-\text{H}$ proton is not acidic enough to cause elimination of the triflate anion.⁵⁴

Very recently, the first example of the S–N bond cleavage in triflamides converting them into the parent amines by the reaction with a superelectron donor (SED), bispiridinylidene, appeared.⁵⁵

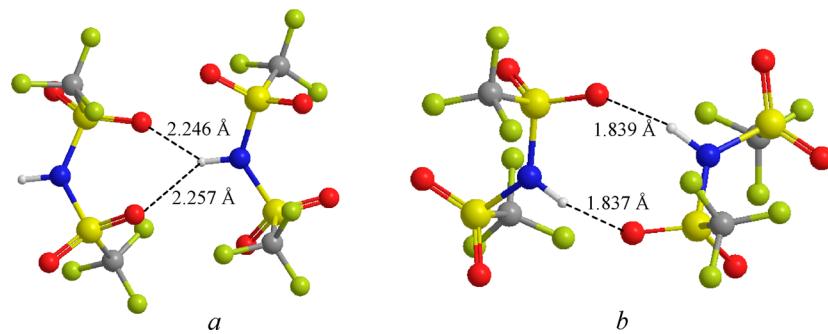
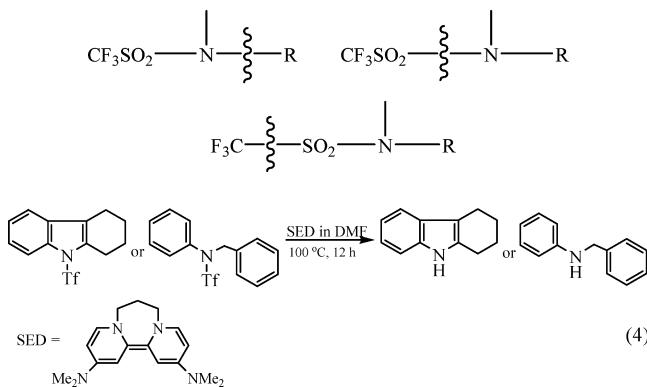
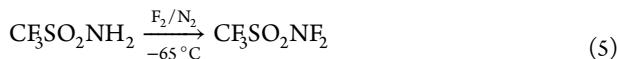


Figure 2. Chain (a) and cyclic (b) dimers of bis(trifluoromethanesulfonyl)imide.



For the NH-containing triflamides, addition to multiple bonds and the hydrogen atom displacement reactions can occur, leading to various N-substituted derivatives. The simplest reactions of the latter type are N-halogenation and N-alkylation.

2.3.1. N-Halogenation Reactions. Triflame is fluorinated with fluorine/nitrogen gas mixture in the presence of NaF/KF fusion at -65°C to give *N,N*-difluorotriflame in 33% yield.⁵⁶ The product is a pale-brown gas, explosive on impact or heating; below 10°C it is condensed into a colorless liquid.



In the same work, *N,N*-dichlorotriflame was first synthesized in 55% yield by saturation of the alkaline solution of triflame with chlorine upon cooling.⁵⁶



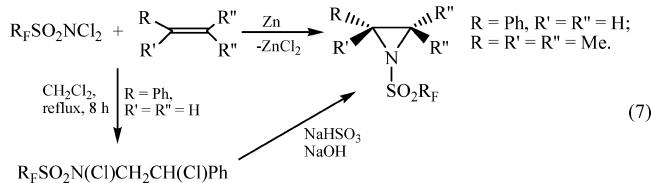
However, the authors failed to obtain the corresponding *N,N*-dibromo derivative by the reaction of triflame with hypobromous acid or by the reaction of the disodium salt of triflame with bromine.⁵⁶

N,N-Dichlorotriflame turned out to be a highly reactive species in various reactions. In a series of works, Rozentsveig et al. have shown it to react with 1,2-dichloroethylene,^{57–59} trichloroethylene,^{58,60} and vinylidene chloride⁵⁹ to give $\text{CF}_3\text{SO}_2\text{N}=\text{CHCHCl}_2$, $\text{CF}_3\text{SO}_2\text{N}=\text{CHCCl}_3$, and $\text{CF}_3\text{SO}_2\text{NHCH}_2\text{CCl}_3$, respectively. A highly electrophilic C=N bond adds various O- (water, methanol, *p*-nitrophenol), N-(PhSO_2NH_2 , triflame, acrylamide), and C-nucleophiles (phenol, thiophene, indoles, pyrazoles).^{58–63} With tribromoethylene, depending on the reaction conditions, *N,N*-dichlorotriflame gives either $\text{CF}_3\text{SO}_2\text{N}=\text{CHCBr}_2\text{Cl}$ (at $<40^{\circ}\text{C}$) or its 1:1 mixture with $\text{CF}_3\text{SO}_2\text{N}=\text{CHCBr}_3$ (when the reaction mixture is allowed to warm up to 100°C).⁶⁴

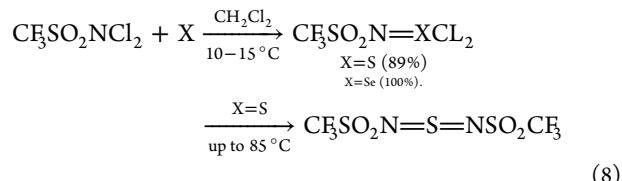
Higher *N,N*-dichloroperfluoroalkanesulfonamides $\text{R}_f\text{SO}_2\text{NCl}_2$ were prepared similarly.^{65,66} With the disodium salt of triflame $\text{CF}_3\text{SO}_2\text{NNa}_2$, *N,N*-dichlorotriflame gives “chloramine-Tf” $\text{CF}_3\text{SO}_2\text{NNaCl}$.⁵⁶ With an excess of trichloroethylene, *N,N*-dichloroperfluoroalkanesulfonamides give N-sulfonylated imines of chloral $\text{R}_f\text{SO}_2\text{N}=\text{CHCCl}_3$ and pentachloroethane⁶⁷ (cf. refs 58–60).

In the presence of zinc dust, under mild conditions, *N,N*-dichloroperfluoroalkanesulfonamides give rise to the corresponding nitrenes, which add to styrene or 2,3-dimethylbut-2-ene to give perfluoroalkanesulfonylaziridines.⁶⁵ In the absence of zinc dust, the reaction with styrene proceeds as a free-radical

process and affords the 1:1 adduct in 61% yield. Reduction of the latter adduct by NaHSO_3 , followed by elimination of HCl by alcoholic NaOH, gives the same *N*-fluoroalkylsulfonylaziridine.⁶⁶

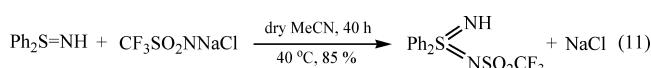
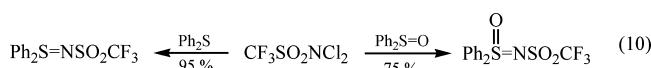
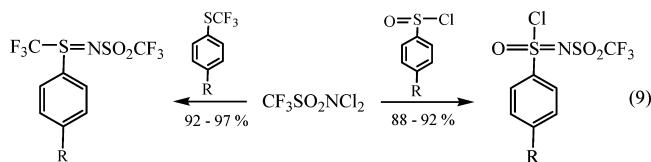


N,N-Dichlorotriflame, the sodium salt of *N*-chlorotriflame, and their higher perfluorinated analogues act as imination reagents with respect to sulfides, sulfoxides, phosphines, etc. Thus, with elemental sulfur and selenium, *N,N*-dichlorotriflame reacts to afford *N*-triflyliminosulfur chloride or selenium dichloride. Subsequent heating of the product with X = S results in the product of bisimination in quantitative yield.⁶⁸



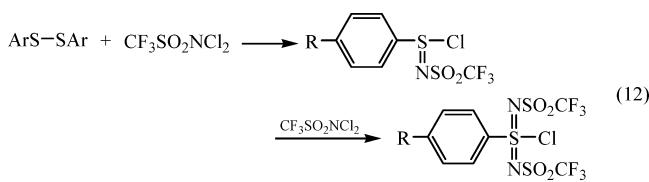
Similar products $\text{R}_f\text{SO}_2\text{N}=\text{SCl}_2$ are formed from *N,N*-dichloroperfluoroalkanesulfonamides with sulfur.⁷ Imination of trifluoromethylselenenyl chloride CF_3SeCl with *N,N*-dichlorotriflame gives *N*-triflylimino(trifluoromethyl)selenenyl chloride $\text{CF}_3\text{SO}_2\text{N}=\text{Se}(\text{Cl})\text{CF}_3$ in 75% yield.⁶⁸

Oxidative imination occurs in the reaction of *N,N*-dichlorotriflame with aryl(trifluoromethyl)sulfides⁶⁹ or arenesulfonyl chlorides.⁷⁰ Similar products, $\text{CF}_3\text{SO}_2\text{N}=\text{S}(\text{Me})\text{CF}_3$ and $\text{CF}_3\text{SO}_2\text{N}=\text{S}(\text{O})(\text{Me})\text{Cl}$, were obtained in >90% yield later by the same group from methyl(trifluoromethyl)sulfide MeSCF_3 and methylsulfinyl chloride $\text{MeS}(\text{O})\text{Cl}$, respectively.⁷¹ In the same way, *N,N*-dichlorotriflame was reacted with diphenylsulfide and diphenylsulfoxide.⁷² Diphenyl-Diphenylsulfimide was iminated using a mixture of $\text{CF}_3\text{SO}_2\text{NaCl}$ and $\text{CF}_3\text{SO}_2\text{NHNa}$.⁷²

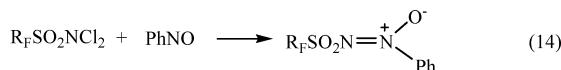
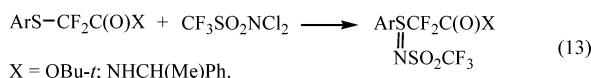


Dimethyldisulfide is split with $\text{CF}_3\text{SO}_2\text{NCl}_2$ to give quantitatively *N*-(triflyl)methylsulfimidoyl chloride, $\text{CF}_3\text{SO}_2\text{N}=\text{S}(\text{Me})\text{Cl}$.⁷¹ Diaryldisulfides are split in a stepwise manner to give first *N*-(triflyl)arylsulfimidoyl chlorides and then, upon further heating with $\text{CF}_3\text{SO}_2\text{NCl}_2$, bis(*N*-triflyl) analogues of arenesulfonyl chlorides, in which the oxygen atom is replaced with the $=\text{NSO}_2\text{CF}_3$ group in practically

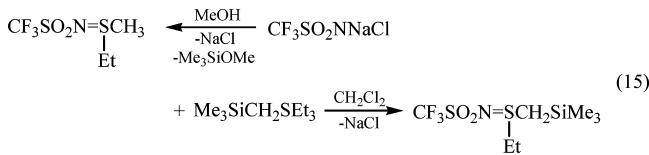
quantitative yield.⁷³ The splitting of bis(trifluoromethyl)-disulfide with $C_nF_{2n+1}SO_2NCl_2$ ($n = 1, 4$) proceeds more slowly, leading to $C_nF_{2n+1}SO_2N=S(CF_3)Cl$ after 4–6 days at 50–55 °C in 77% yield.⁷⁴



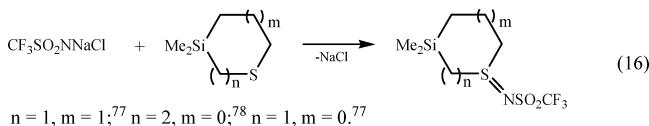
The sulfur atom in esters or amides of arylthiodifluoroacetic acid is iminated with *N,N*-dichlorotriflame in close to quantitative yield.⁷⁵ With nitrosobenzene, *N,N*-dichloro-(perfluoroalkane)sulfonamides give *N,N*-perfluoroalkanesulfonyl, *N'*-phenyldiazene *N'*-oxides.⁷⁶



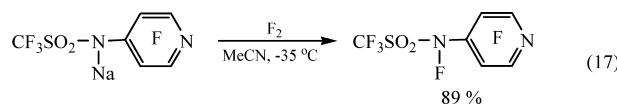
"Chloramine-Tf", $\text{CF}_3\text{SO}_2\text{NNaCl}$,⁵⁶ was used by us for oxidative imination of a series of organosilicon sulfides.^{77,78} Thus, it reacts with ethyl(trimethylsilyl)sulfide in dry methylene chloride in the presence of $\text{Et}_3\text{Bn}^+\text{Cl}^-$ to afford S-(trimethylsilylmethyl)-S-ethyl-(N-triflyl)sulfimide in 60% yield.⁷⁷ In a protic medium (methanol), the product undergoes solvolysis to give S-methyl-S-ethyl-(N-triflyl)sulfimide in 80% yield.⁷⁷



With 3,3-dimethyl-3-silathiane⁷⁷ and 4,4-dimethyl-4-silathiane,⁷⁸ it gives the corresponding cyclic S-(*N*-triflyl)imides in 80% yield. The triflyl group has a pronounced stabilizing effect on the Si,S-heterocycles, which allowed us to obtain (although, unfortunately, not to isolate) 3,3-dimethyl-1-thia-3-silacyclopentane-1-(*N*-triflyl)sulfimide ($n = 1, m = 0$), whereas its arylsulfonyl analogues could not even be detected spectroscopically.⁷⁹



No N-halogenated products were obtained by chlorination or bromination of *N*-phenyltriflamide;⁸⁰ instead, the halogenation occurred at the ortho and para positions of the aromatic ring. The reaction of *N*-phenyltriflamide with such electrophilic fluorinating reagents as fluoroxytrifluoromethane CF_3OF and bis(fluoroxy)difluoromethane $\text{CF}_2(\text{OF})_2$ proceeds similarly.⁸¹ However, direct fluorination of the sodium salt of *N*-(perfluoropyridyl)triflamide affords the stable *N*-fluoro-*N*-(perfluoropyridyl)triflamide in high yield.⁸²



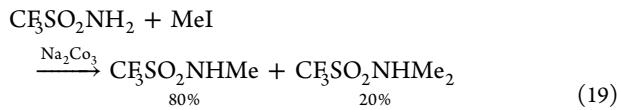
Of special interest as a source of "positive" fluorine are the halogenated derivatives of bis(trifluoromethanesulfonyl)imide (CF_3SO_2)₂NX. Thus, *N*-fluoro-bis(trifluoromethanesulfonyl)-imide (CF_3SO_2)₂NF was first synthesized by DesMarteau and co-workers,⁸³ who later on suggested an improved synthesis with the yield of the target product of 76% based on the starting $\text{CF}_3\text{SO}_2\text{F}$.⁸⁴



The above N-fluorinated triflamide derivatives are among the most powerful electrophilic NF reagents, as was summarized in the middle 1990s.⁸⁵ Since then, compounds of this type were extensively studied in the reactions with aromatics⁸⁶ and various nucleophiles.⁸⁷ Higher analogues, including nonsymmetrical *N*-fluoroimides $R_FSO_2N(F)SO_2R'_F$, have also been synthesized and studied as fluorinating reagents for enones, diketones, aromatics, etc.⁸⁸

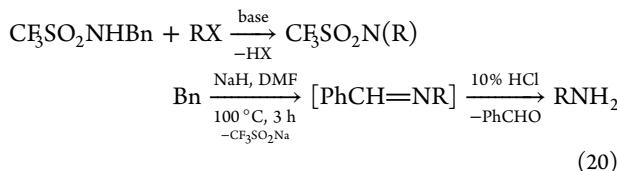
2.3.2. N-Alkylation reactions. N-Alkylation of triflamide,

LIGAND ATTACHMENT REACTIONS. IV. Annulation of triflamides, that is, the formation of new N-C bond, is an alternative route to numerous N-substituted triflamides, which, because of their high acidity and lipophilicity, imparted by the trifluoromethylsulfonyl group, is inherent to a large number of these compounds. The reaction proceeds via the intermediate triflamide anion generated by alkali metal carbonates, as exemplified in eq 19.¹

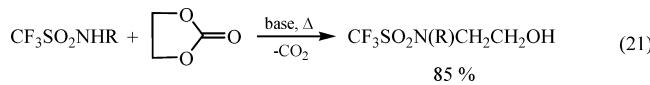


A number of monoalkylated derivatives were prepared by the K_2CO_3 -catalyzed alkylation of the primary perfluoroalkylsulfonylamides with alkyl halogenides or tosylates.¹⁴

Hendrickson and Bergeron elaborated a novel "Gabriel-type" synthesis of primary and secondary amines based on alkylation of *N*-phenyl- or *N*-benzyltriflamide with alkyl halogenides followed by deprotection by subsequent treatment with base and acid.⁸⁹ The synthesis of primary amines by the use of *N*-benzyltriflamide is represented by the following equation.

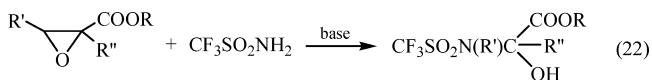


β -Hydroxyethyltriflamides are formed by the ring-opening reaction of ethylene carbonate with triflamides followed by decarboxylation.⁹⁰ The oxirane ring-opening reaction of

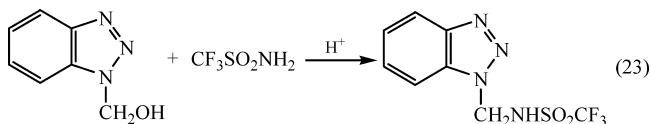


alkoxycarbonyloxiranes under heterogeneous conditions was employed to prepare α -hydroxy- β -triflamido esters in good yields and in a regio- and stereoselective fashion.⁹¹

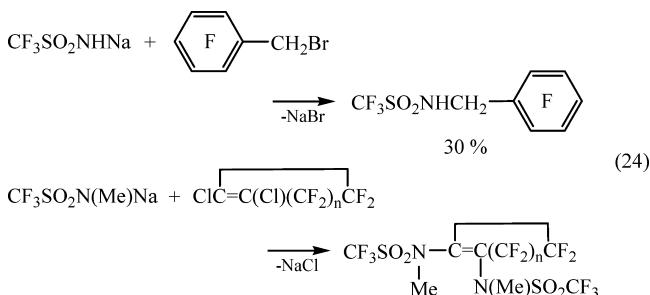
Alkylation of triflame with 1-oxymethylbenzotriazole results in the formation of *N*-(1*H*-1,2,3-benzotriazol-1-



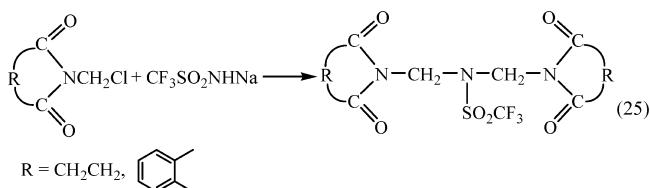
ylmethyl)triflame in ~70% yield.⁹² This product was also obtained in ~90% yield from a one-pot, three-component reaction of triflame, paraformaldehyde, and benzotriazole (see section 2.3.4).



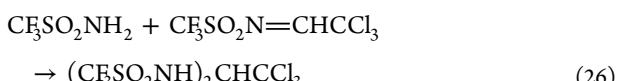
Sodium salts of triflame and *N*-methyltriflame react with 1,2-dichloroperfluorocyclobutene, 1,2-dichloroperfluorocyclopentene, benzyl bromide, and cyanuric chloride (ClCN)₃ under mild conditions to give good yields of *N*-substituted polyfluoroalkyl and polyfluoroaryl sulfonamides.⁹³ Unexpectedly, in the reaction of the sodium salt of triflame with *N*-chloromethylsuccinimide and -phthalimide, only the bis-(triflamido)-substituted derivatives were obtained, even with the equimolar ratio of the reagents, as was shown for *N*-chloromethylsuccinimide.⁹⁴ This was explained by a higher reactivity of the intermediate product of monosubstitution in the reaction with *N*-chloromethylsuccinimide.⁹⁴



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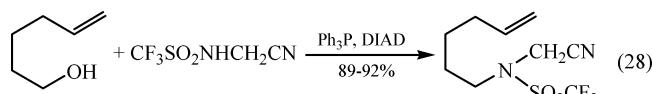
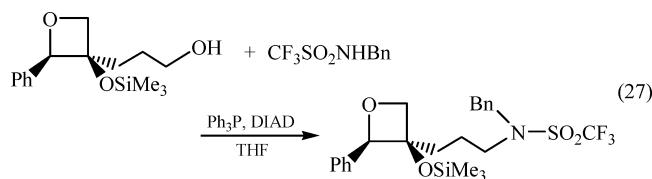


Triflame was successfully subjected to the amidoalkylation reaction with *N*-(2,2,2-trichloroethylidene)triflame.⁹⁵



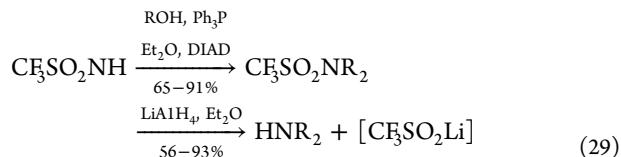
It is worth mentioning that nonfluorinated analogues of triflame, like $\text{ArSO}_2\text{N}=\text{CHCCl}_3$, do not enter this reaction.⁹⁶

Alkylation of triflamides with alcohols can be performed by the Mitsunobu reaction using diethyl (DEAD) or diisopropyl azodicarboxylate (DIAD) as exemplified by the following equation.⁹⁷ In a hope to synthesize the key precursor on the way to the quinolizidine alkaloid (-)-217A, the Mitsunobu coupling was applied to *N*-(cyanomethyl)triflame and *S*-hexenol.⁹⁸ The first step, which is the only one of interest for our review, proceeds in excellent yield. The reaction was also successfully applied to other alcohols of similar structure.⁹⁹

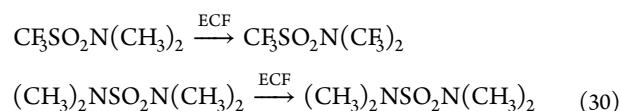


Previously, in the same group, the synthesis of the so far unknown *N*-(cyanomethyl)triflame by the reaction of aminoacetonitrile hydrochloride with triflic anhydride was elaborated.⁹⁹

The Mitsunobu reaction ($\text{Ph}_3\text{P}/\text{DIAD}/\text{ether}$) was also employed for the synthesis of tertiary triflamides with long alkyl or fluoroalkyl chain $\text{CF}_3\text{SO}_2\text{N}[(\text{CH}_2)_3\text{R}]_2$ in high yields (65–91%) by the reaction of triflame with 3-perfluoroalkyl-1-propanols of their nonfluorinated analogues. The products are easily isolated by organic or fluorous extraction, or fluorous solid–organic liquid filtration.¹⁰⁰ Deprotection of the products by reduction with lithium aluminum hydride provides secondary amines.

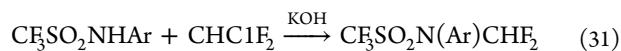


Triflamides with perfluoroalkyl groups at the nitrogen atom are prepared by the method of electrochemical fluorination (ECF). Thus, the ECF of *N,N*-dimethyltriflame and *N,N*-dimethylnonafluorbutanesulfonamide gives the corresponding perfluorinated *N,N*-bis(trifluoromethyl)perfluoroalkane-sulfonamides in good yield.¹⁰¹ Note, that the ECF of *N,N,N',N'*-tetramethylsulfondiamide $\text{SO}_2(\text{NMe}_2)_2$ proceeds similarly.¹⁰²



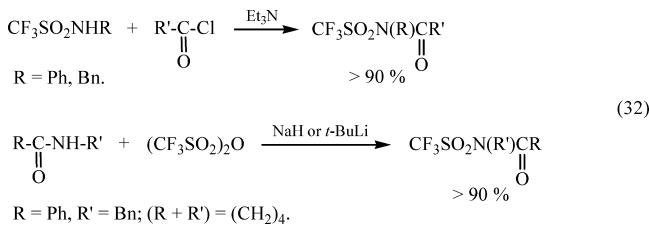
In contrast, the ECF of the nonfluorinated analogue, $\text{CH}_3\text{SO}_2\text{NMe}_2$, results in decomposition of the starting material.¹⁰¹

Triflamides with difluoromethyl group at nitrogen were obtained in moderate yield from *N*-aryltriflamides by the reaction with chlorodifluoromethane (freon-22) and solid alkali in dimethylformamide (DMF) and freon-22.¹⁰³



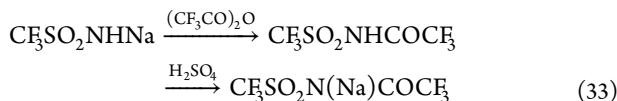
2.3.3. N-Acylation (Sulfonylation) Reactions. This section describes the reactions of triflame and its analogues with various acylating and sulfonylating agents resulting in the formation of the $\text{R}_\text{F}\text{SO}_2\text{N}-\text{C}(\text{O})\text{R}$ or $\text{R}_\text{F}\text{SO}_2\text{N}-\text{SO}_2\text{R}$ derivatives. The first study of this type, reviewed in ref 1, was by Hendrickson and Bergeron, who prepared a series of *N*-acyltriflamides and used them as acylating and triflating reagents in the reactions with methanol, phenols, and amines.¹⁰⁴ Alternatively, compounds of the same type were

prepared from amides with triflic anhydride in the presence of base.¹⁰⁴

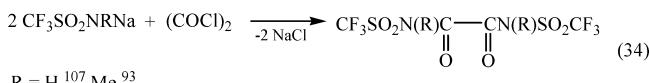


Using the same procedure, Yagupol'skii et al.¹⁰⁵ synthesized a number of *N*-aroyleperfluoroalkanesulfonamides in 75–97% yield and converted them into the corresponding imidoyl chlorides, and Flaherty et al.¹⁰⁶ prepared a series of substituted (phenylacetyl)triflamides and studied their anticonvulsant activity as a function of substituent in the benzene ring.

N-(Trifluoroacetyl)triflame was obtained by the reaction of triflame sodium salt with anhydride of trifluoroacetic acid followed by treatment with sulfuric acid.⁶⁸

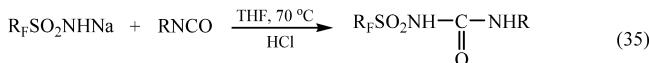


Oxalyl chloride reacts with 2 equiv of $\text{CF}_3\text{SO}_2\text{NHNa}$ to give *N,N'*-bis(triflyl)oxamide.¹⁰⁷ In the same manner, the *N,N'*-dimethyl analogue was prepared.⁹³ Another route to the

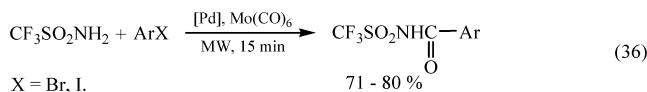


R = H,¹⁰⁷ Me.⁹³

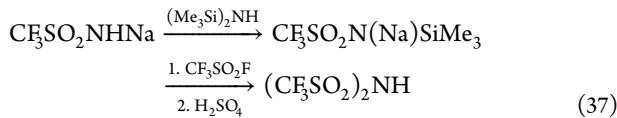
formation of the $\text{R}_\text{F}\text{SO}_2\text{N—C(O)—}$ moiety is the reaction of the corresponding sodium salts with isocyanates, which was proposed as a new synthesis of polyfluoroalkanesulfonylureas.¹⁰⁸



Microwave-assisted arylcarbonylation of triflame with aryl bromides or iodides and molybdenum hexacarbonyl proceeds in good yield and represents principally different synthetic approach to acyltriflamides and related compounds.¹⁰⁹



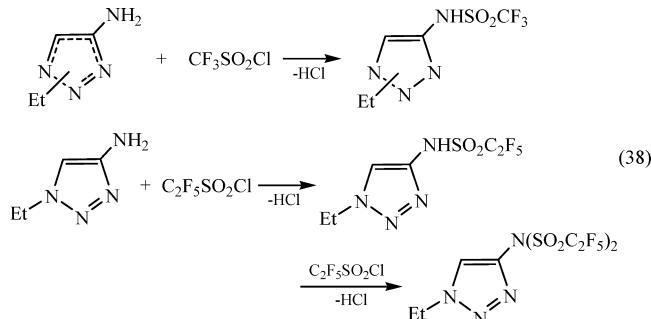
Concerning the reactions of acylation of triflame with sulfonyl halogenides, it is pertinent to note that as early as in 1984 the reaction of the sodium salt of *N*-trimethylsilyl triflame with trifluoromethanesulfonyl fluoride in autoclave was used for the synthesis of bis(triflimide), the simplest representative of bis(perfluoroalkanesulfonyl)imides.¹⁰



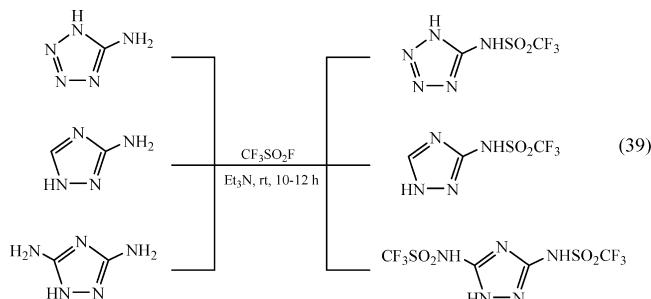
Some other compounds of this type, $(\text{R}_\text{F}\text{SO}_2)_2\text{NH}$, had been synthesized not long before.¹¹⁰

The reaction of triflame with arenesulfonyl chlorides in benzene or acetone solution at room temperature in the presence of pyridine with subsequent treatment with concentrated sulfuric acid affords mixed imides of general formula $\text{CF}_3\text{SO}_2\text{NHSO}_2\text{C}_6\text{H}_4\text{X-p}$ ($\text{X} = \text{H, Cl, NO}_2$) in 50–72% yield.⁷⁰ Using the same procedure, the triethylammonium salts of similar bisimides containing organosilicon substituents in the benzene ring were obtained as precursors of new hybrid materials.¹¹¹

Sulfonyl chlorides $\text{C}_n\text{F}_{2n+1}\text{SO}_2\text{Cl}$ react with 1(2)-ethyl-1(2)-*H*-1,2,3-triazol-4-amine to give the corresponding *N*-substituted triflamides.¹¹² Similarly, triflame derivatives of 1,2,4-triazole

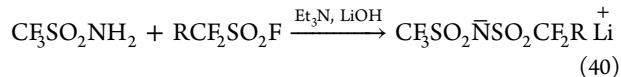


and tetrazole were recently obtained by the reaction of trifluoromethanesulfonyl fluoride with the corresponding amines. As the authors specially emphasized, in contrast to our results,¹¹² only the products of monosubstitution were formed.¹¹³

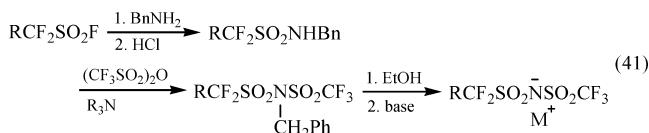


Bis(perfluorooctanesulfonyl)imide $(\text{C}_8\text{F}_{17}\text{SO}_2)_2\text{NH}$ was synthesized in 62% yield from the corresponding sulfonamide and sulfonyl fluoride in the presence of triethylamine with subsequent treatment of the formed triethylammonium salt of bisimide with the ion-exchange resin Amberlite IR-120B.¹¹⁴ Its metal salts were shown to act as effective Lewis acid catalysts for transesterification, direct esterification, Friedel–Crafts acylation, and Baeyer–Villiger oxidation reactions.¹¹⁴

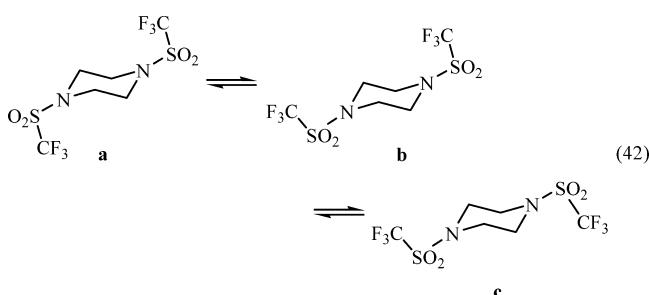
To synthesize the lithium and ammonium salts of fluorinated sulfonimides $\text{CF}_3\text{SO}_2\text{N}(\text{M})\text{SO}_2\text{CF}_2\text{R}$ ($\text{R} = \text{PhS, PhSCF}_2, \text{PhSO}_2, \text{PhSO}_2\text{CF}_2$), Langlois et al. tried the reaction of triflame with the corresponding sulfonyl fluorides in the presence of triethylamine.¹¹⁵ The yield was rather low, and the reaction was found to be very moisture-sensitive.



Much better results were obtained using the following sequence of reactions finalized by simple deprotection of the nitrogen atom by treatment with alcohol.¹¹⁵



Triflic derivatives such as 1-triflyl-1*H*-imidazole¹¹⁶ and *N*-phenyltriflimide (CF_3SO_2)₂NPh¹⁰⁴ can be used as acylating (trifluoromethanesulfonating) agents in addition to trifluoromethanesulfonyl fluoride and triflic anhydride. *N*-Phenyltriflimide, for example, readily and in high yield reacts with primary amines and piperidine, but the secondary aromatic amines do not enter this reaction. In spite of the apparent simplicity of the method, sometimes errors cannot be avoided; thus, the compound obtained from piperidine and *N*-phenyltriflimide, which was described as *N*-triflyl piperidine,¹⁰⁴ was later shown to be the salt, piperidine triflate.¹¹⁷ *N*-Triflyl piperidine and *N*-triflated derivatives of morpholine, piperazine, and thiomorpholine have been synthesized from the corresponding *N*-heterocycles and triflic anhydride,¹¹⁷ and their dynamic behavior was studied by low-temperature NMR spectroscopy.¹¹⁸ For all compounds, the equilibrium between the conformers with the triflyl group "inward" and "outward" was shown, as depicted in the scheme in eq 42 for 1,4-



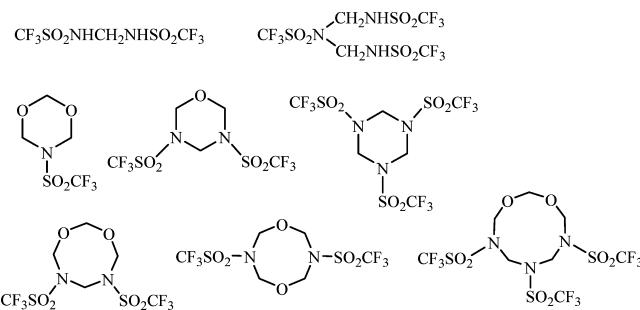
bis(trifluoromethylsulfonyl)piperazine, for which the ratio of the conformers **a**/**b**/**c** at 183 K was measured to be 3:28:69, in good correlation with their relative energies calculated at the B3LYP/6-311+G(d,p) level of theory.¹¹⁸

2.3.4. Condensation Reactions of Triflameide. A new type of reaction of triflameide was discovered when studying transformations occurring in the system triflameide–parafomaldehyde under strongly acidic conditions. Strange as it may seem, in spite of the well-known ability of sulfonamides to enter condensation reactions with carbonyl compounds,¹¹⁹ no such reactions were observed until recently. A possible reason is that the basicity of nitrogen in triflameide is lower than in other sulfonamides (*vide supra*), and it does not react even with highly electrophilic chloral molecule, which gives adducts with sulfonamides without special activation.¹²⁰

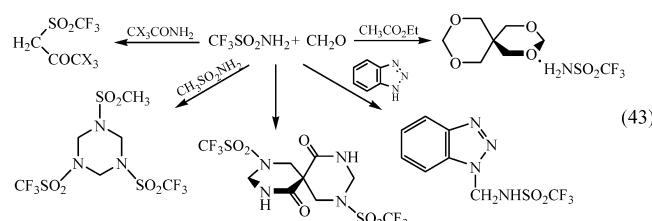
We have first found that triflame reacts with paraformaldehyde in or in the presence of concentrated sulfuric acid to give a number of the open-chain and cyclic condensation products, whose ratio is strongly dependent on the reaction conditions.^{121,122}

The formation of all condensation products is launched by addition of triflame to the molecule of formaldehyde activated by protonation to oxymethyl cation $^+\text{CH}_2\text{OH}$ and formation of the methylol derivative $\text{CF}_3\text{SO}_2\text{NHCH}_2\text{OH}$. Subsequent stepwise condensation with triflame and formaldehyde results in a variety of products.

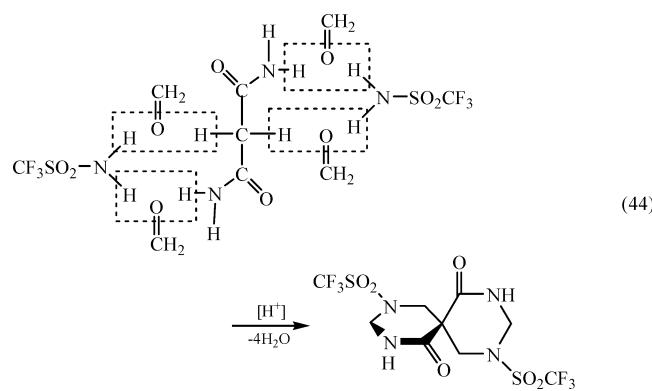
Triflamide also enters one-pot, three-component condensations with a third amide or sulfonamide molecule to give



various mixed compounds.^{92,121,123-125} For the formed six-membered *N*-triflyl-substituted heterocycles, conformational analysis was performed by low-temperature NMR spectroscopy and quantum chemical calculations.¹²⁶⁻¹²⁹ Because the results of some of these studies have been reviewed recently,⁸ here we briefly discuss the most important results.

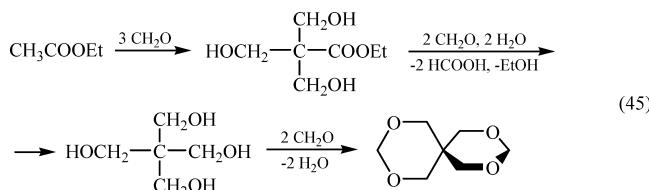


An unexpected result was obtained in the three-component condensation reaction of malonamide and triflamide with paraformaldehyde. X-ray analysis showed the product to be 4,10-bis(trifluoromethylsulfonyl)-2,4,8,10-tetraazaspiro[5.5]-undecane-1,7-dione, which is apparently formed by three-component heterocyclization with participation of both the amide groups of malonamide and its active methylene group.¹²³

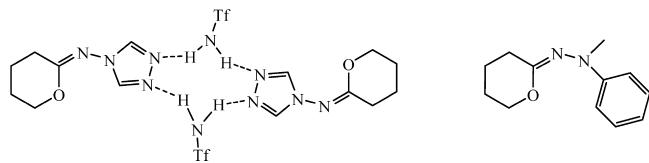


One of the most remarkable manifestations of the strong influence of the reaction conditions is the reaction of triflamine with paraformaldehyde in ethyl acetate in the presence of H_2SO_4 . At room temperature, 5-triflyl-1,3-dioxazinane was the major product. Upon heating to 80 °C, a 1:1 complex of triflamine with 2,4,8,10-tetraoxospiro[5,5]undecane, whose structure was proved by X-ray analysis, was isolated. Its formation is absolutely unexpected because no reagent contained a quaternary carbon atom. Apparently, the product is formed by cyclization of pentaerythritol with formaldehyde. Pentaerythritol, in turn, is formed (by analogy with the industrial method of its manufacturing by the reaction of formaldehyde with acetaldehyde) as a result of triple aldol condensation of formaldehyde to the activated methyl group of ethyl acetate followed by reduction of the ester group in the

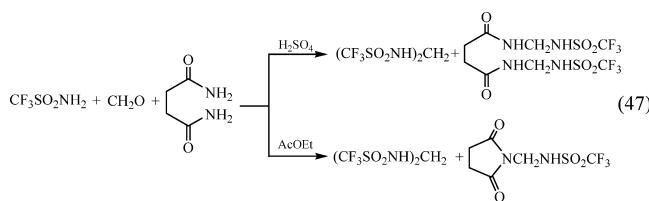
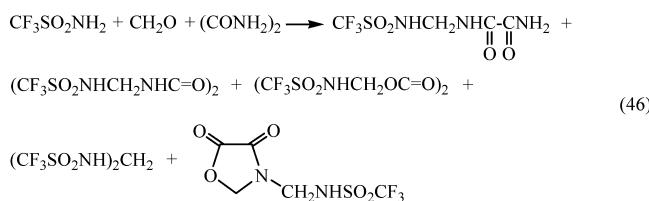
intermediate ethyl ester of 3-hydroxy-2,2-bis(hydroxymethyl)-propionic acid and oxidation of formaldehyde. The reaction scheme can be represented as follows.¹²² To the best of our knowledge, this reaction is the first example of reduction of ester group COOR to alcohol group CH₂OH under the action of formaldehyde.



We have found only one example of the formation of the H-complex of triflamide with a heterocyclic base, namely, with tetrahydro-*N*-(4*H*-1,2,4-triazol-4-yl)-2*H*-pyrane-2-imine, as shown below.¹²⁷ Interestingly, with less basic *N*-methyl-*N*-phenylhydrazone of tetrahydro-2*H*-pyran-2-one (below, right), triflamide does not form an adduct.¹³⁰

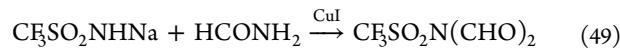
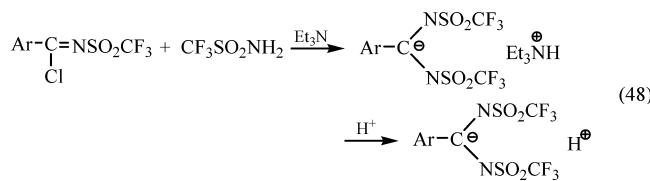


From the three-component system triflamide–paraformaldehyde–oxamide, the following products were obtained, isolated as individuals and their structure proved by NMR spectroscopy. The distribution of the products is dependent on the reaction conditions.¹²⁵ With succinimide as a third component,⁹⁴ the reaction proceeds differently in sulfuric acid and in ethyl acetate.

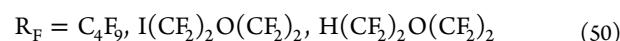
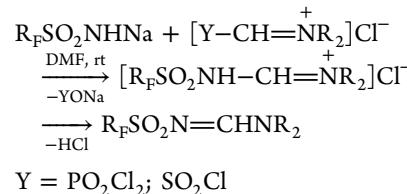


2.3.5. Miscellaneous Reactions of Triflamides. N -(Triflyl)carboxyimidoyl chlorides $\text{Ar}-\text{C}(\text{Cl})=\text{NSO}_2\text{CF}_3$, iso-electronic to aryl chlorides, react with triflame in the presence of triethylamine to give salts, which, after acidification give N,N -bis(triflyl)benzamidines.¹³¹ Because of the super-strong electron-withdrawing ability of the triflame residue $\text{CF}_3\text{SO}_2\text{N}=$ (vide infra), the product has the ionic structure as depicted below.

The first *N*-formyl triflamide was prepared by us recently by the CuI-catalyzed reaction of the sodium salt of triflamide with formamide.¹³²

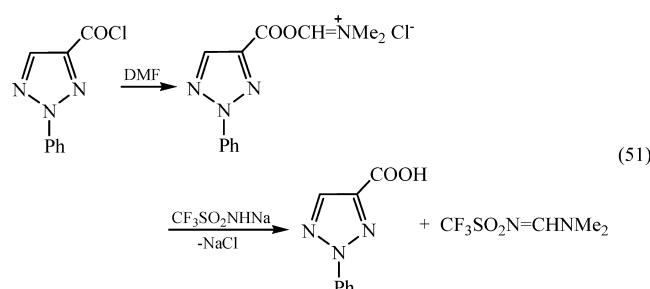


N,N-Dialkyl-*N'*-perfluoroalkanesulfonylformamidines, $R_2SO_2N=CHNR_2$, were synthesized from the sodium salts of perfluoroalkanesulfonamides and Vilsmeier reagents in 75–83% yield.¹³³

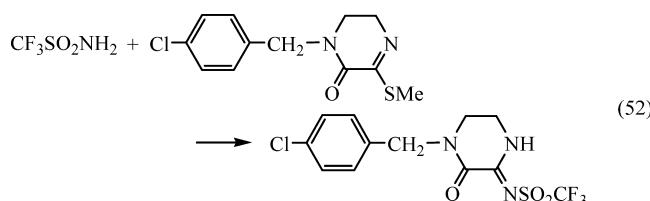


The same compounds were synthesized by the CF-catalyzed reaction of N-trimethylsilylated nonafluorobutanesulfonamide $C_4F_9SO_2NHSiMe_3$ with dimethylformamide,¹³⁴ or by the reaction of perfluoroalkanesulfonylazides with ketones and secondary amines.¹³⁵

The simplest representative, N -[(dimethylamino)methylidene]triflamide $\text{CF}_3\text{SO}_2\text{N}=\text{CHNMe}_2$, was obtained in 94% yield by the reaction of 2-phenyl-2*H*-1,2,3-triazol-4-ylcarbonyl chloride with the sodium salt of triflamide in DMF.¹³⁶ The mechanism apparently includes the formation of the "Vilsmeier-type" adduct of acyl chloride with DMF, which further reacts with the triflamide salt with regeneration of 2-phenyl-2*H*-1,2,3-triazol-4-yl carboxylic acid.¹³⁶



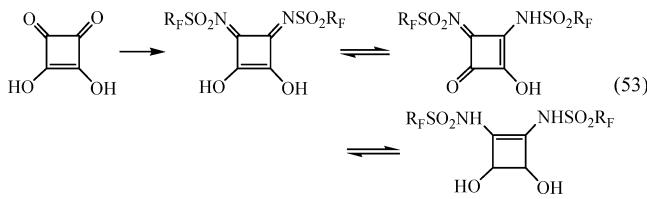
An unusual reaction of substitution of the thiomethyl group in 1-[(6-chloropyridin-3-yl)methyl]-3-(methylthio)-5,6-dihdropyrazin-2(1*H*)-one by triflame.¹³⁷



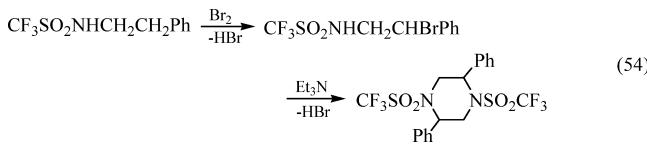
The product is formed in a low yield and only when using THF as a solvent; in ethanol, the thiomethyl group is replaced by the ethoxy group. This was explained by the very low nucleophilicity of triflamide, and, indeed, with other nucleo-

philes RNH_2 (cyanamide, hydroxylamide, etc.) the reaction proceeds in ethanol in good yield.¹³⁷

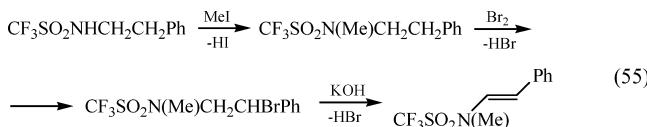
Interesting derivatives of triflame were prepared by replacement of the carbonyl groups in squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) by triflame residues.¹³⁸



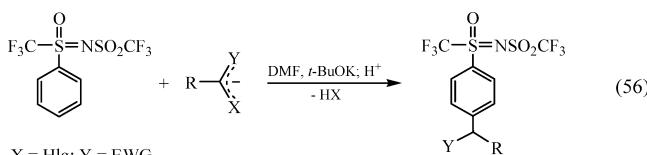
The latter tautomeric form contains the $\text{R}_\text{F}\text{SO}_2\text{NH}-\text{C}=\text{C}<$ fragment, which is of great interest from the viewpoint of existence and properties of unsaturated perfluoroalkanesulfonamides. Until recently, no compounds of the general formula $\text{CF}_3\text{SO}_2\text{N}(\text{R})\text{CH}=\text{CH}-\text{R}'$ were described in the literature. In a hope to obtain *N*-(2-phenylethenyl)triflame $\text{CF}_3\text{SO}_2\text{NHC}\text{H}=\text{CHPh}$, we have synthesized $\text{CF}_3\text{SO}_2\text{NHC}\text{H}=\text{CH}_2\text{CH}_2\text{Ph}$, brominated it to $\text{CF}_3\text{SO}_2\text{NHCH}_2\text{CHBrPh}$, and debrominated it with triethylamine.¹³⁹ Unexpectedly, 2,5-diphenyl-1,4-bis(trifluoromethylsulfonyl)piperazine was obtained identical to that prepared from styrene and triflame under oxidative conditions (vide infra).¹³⁹



Apparently, heterocyclization is possible only in the presence of the NH proton in the N-substituted triflame; therefore, to rule out such a possibility, we first protected the NH group with methyl iodide. Then, after the same sequence of transformations, the first representative of *N*-alkenyl triflamides, *N*-methyl-*N*-(*E*)-2-phenylethenyltriflame, was obtained.¹⁴⁰

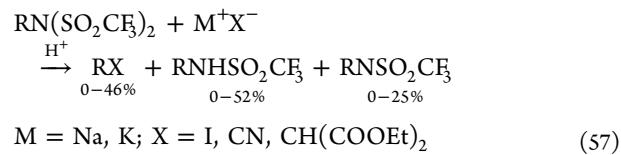


Using the procedure elaborated by Yagupol'skii and co-workers,¹⁴¹ *N*-[oxido(phenyl)(trifluoromethyl)- λ^4 -sulfanylidene]triflame was synthesized and the vicarious nucleophilic substitution in it was studied.¹⁴² The substitution occurs exclusively in the para position. This is the first example of the vicarious substitution at a benzene ring activated by an electron-withdrawing group other than a nitro group.



$\text{X} = \text{Hlg}; \text{Y} = \text{EWG}$.

In an early work, *N*-alkylbistriflimides were shown to undergo splitting with nucleophiles in hexamethylphosphorus triamide (HMPT) as a solvent according to the following scheme.¹⁴³

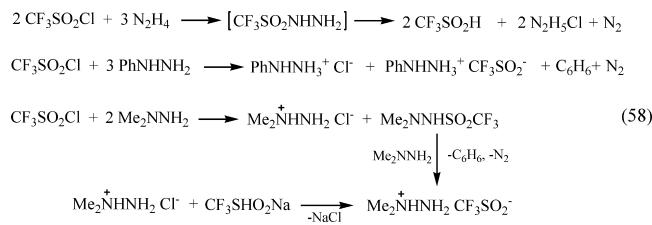


3. N-FUNCTIONAL DERIVATIVES OF TRIFLAMIDES AND RELATED COMPOUNDS

3.1. *N*-Trifluoromethanesulfonylhydrazines

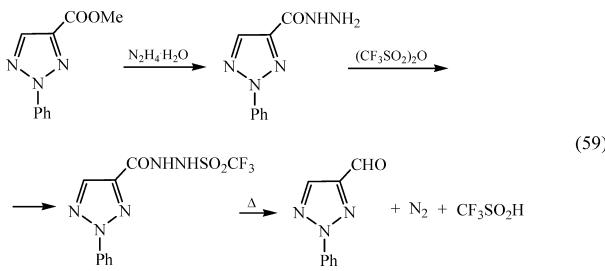
The literature data on the hydrazides of trifluoromethanesulfonic acid (trifluoromethanesulfonyl hydrazides) and their perfluoroalkanesulfonyl analogues are very scarce.¹ Although methanesulfonyl hydrazide ($\text{MeSO}_2\text{NHNH}_2$, CAS no. 10393-86-9, melting point (mp) 46–48 °C) is a commercial product, its fluorinated analogue $\text{CF}_3\text{SO}_2\text{NHNH}_2$ has never been obtained. Trifluoromethanesulfonyl fluoride was shown to be reduced by hydrazine to the derivatives of trifluoromethanesulfonic acid,^{1,6,144,145} but in neither of these studies was the intermediate hydrazide $\text{CF}_3\text{SO}_2\text{NHNH}_2$ isolated as an individual compound or at least characterized. From the *N*-substituted hydrazides $\text{R}_\text{F}\text{SO}_2\text{NHNH}_2$, only the functionally substituted hydrazides of triflic acid $\text{CF}_3\text{SO}_2\text{NHNH}_2$ are known ($\text{X} = \text{PhCO, } t\text{-BuOCO}$), which are used for oxidation of alkyl halogenides to the corresponding hydrazone of aldehydes or ketones, being themselves reduced to triflates.¹⁴⁶ As late as in 2004 we first systematically studied the reactions of triflic chloride and triflic anhydride with hydrazine, phenylhydrazine, and 1,1-dimethylhydrazine.¹⁴⁷

The reaction of $\text{CF}_3\text{SO}_2\text{Cl}$ with excess hydrazine in dry tetrahydrofuran (THF) at -50°C proceeds without evolution of nitrogen. In the ^{13}C NMR spectrum taken at -30°C , a quartet of the CF_3 at 122 ppm with coupling constant $^{1}\text{J}_{\text{CF}}$ 322.8 Hz is observed that belongs to hydrazide $\text{CF}_3\text{SO}_2\text{NHNH}_2$. When warmed to room temperature, vigorous evolution of nitrogen occurs, and a new signal appears in the ^{13}C NMR spectrum at 125–126 ppm with coupling constant of 350–360 Hz (depending on the solvent). The ^{19}F NMR signal is shifted from -78 to -86 ppm. The new signals belong to the CF_3 group in trifluoromethanesulfonic acid $\text{CF}_3\text{SO}_2\text{H}$ and its salts. Because the position of the signals in the ^{13}C (119–122 ppm) and ^{19}F NMR spectra (-74 to -79 ppm) and the value of constant $^{1}\text{J}_{\text{CF}}$ (319–321 Hz) are characteristic for all triflates $\text{CF}_3\text{SO}_2\text{X}$ ($\text{X} = \text{OH, OSO}_2\text{CF}_3, \text{Cl, NH}_2, \text{NR}_2, \text{NHSO}_2\text{CF}_3, \text{N}_3$) irrespective of X , the above differences provide useful spectroscopic criteria for discrimination between the derivatives of trifluoromethanesulfonic and trifluoromethanesulfonic acids. Using these criteria, the reactions of trifluoromethanesulfonamide with hydrazines were shown to proceed according to the following equations.¹⁴⁷



We expected 2-phenyl-2*H*-1,2,3-triazole-4-carbohydrazide prepared by the reaction of methyl ester of 2-phenyl-2*H*-1,2,3-triazole-4-carboxylic acid with hydrazine hydrate to react

with triflic anhydride or trifluoromethanesulfonyl chloride similar to the functionalized hydrazides $X\text{NHNH}_2$ ($X = \text{PhCO}$, $t\text{-BuOCO}$)¹⁴⁶ with the formation of trifluoro-N'-(2-phenyl-2*H*-1,2,3-triazol-4-ylcarbonyl)methanesulfonylhydrazide. Indeed, the latter turned out to be more stable than its analogues containing no electron-withdrawing groups. However, in an attempt to purify the compound by sublimation, it was thermally decomposed with evolution of nitrogen and formation of 2-phenyl-2*H*-1,2,3-triazole-4-carbaldehyde and trifluoromethanesulfonic acid.¹⁴⁷

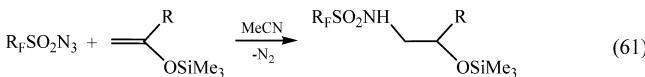


3.2. Perfluoroalkanesulfonylazides, -Nitrenes, and Their Precursors

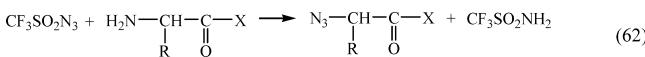
Trifluoromethanesulfonyl azide $\text{CF}_3\text{SO}_2\text{N}_3$ was first prepared from triflic anhydride and sodium azide by Ruff in 1965¹⁴⁸ and not by Cavender and Shiner in 1972¹⁴⁹ as stated in ref 1. The synthesis was then improved by Nazaretyan and Yagupol'skii, who also found that with excess of sodium azide trifluoromethanesulfonyl azide eliminates nitrogen and gives sodium triflate.¹⁵⁰



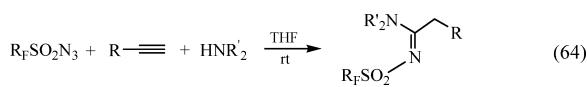
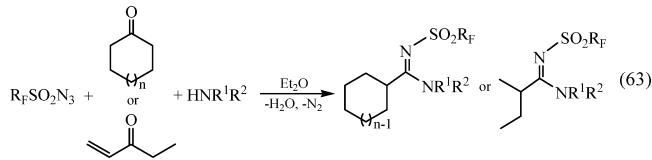
The compound is explosive and must be handled accordingly. Perfluoroalkanesulfonylazides were synthesized by Zhu and used as precursors of the corresponding nitrenes.^{66,151} Zhu and co-workers made the principal contribution in the chemistry of perfluoroalkanesulfonylazides by studying numerous reactions of these compounds with a variety of organic substrates. Trifluoromethanesulfonyl azide and its polyfluorinated analogues react with different substrates either with evolution of nitrogen, as a source of the corresponding nitrenes acting as amidating reagents,^{66,151–153} as exemplified by the scheme in eq 61, or more seldom as



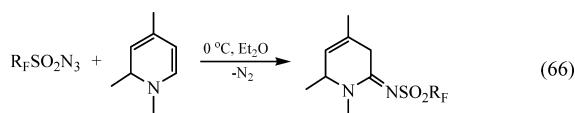
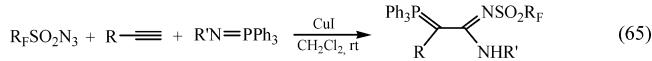
diazotizing reagents with respect to the amino group; in the latter case they can be considered as carriers of the azido group (scheme in eq 62).^{149,154,155} Three-component reaction of



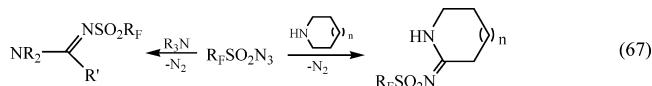
perfluoroalkanesulfonylazides with ketones and secondary amines was proposed as a one-pot synthesis of fluorinated amidines.^{135,156} Amidines of the same structure but with other substituents at the central carbon atom were obtained by the copper(I)-catalyzed one-pot, three-component reaction of perfluoroalkanesulfonylazides with 1-alkynes and secondary amines.¹⁵⁷ A similar reaction with iminophosphoranes instead of secondary amines gives rise to *N*-fluoroalkanesulfonylphos-



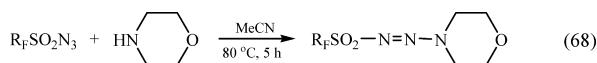
phorous amidines.¹⁵⁸ Perfluoroalkanesulfonylamidines are also formed in the reaction of perfluoroalkanesulfonylazides with



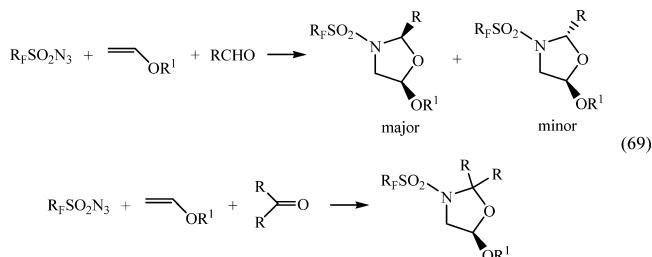
cyclic enamines.¹⁵⁹ Secondary and tertiary amines react with perfluoroalkanesulfonylazides to give amidines; the authors suggest a single electron transfer mechanism from the molecule of amine to the azide.¹⁶⁰ Unexpectedly, the reaction with



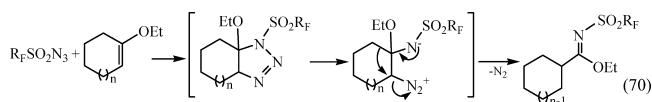
morpholine proceeds in a different manner, giving stable diazenes.¹⁶¹ Another three-component, "one-pot" reaction of



perfluoroalkanesulfonylazides with vinyl ethers and aldehydes¹⁶² or ketones¹⁶³ diastereoselectively gives oxazolidines.

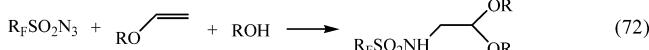
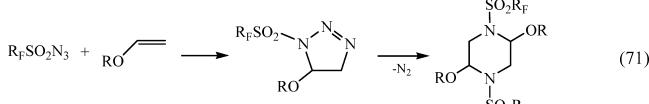


It is worth mentioning that, unlike arylazides, perfluoroalkanesulfonylazides do not give products of 1,3-cycloaddition with cyclic vinyl ethers but rather form perfluoroalkanesulfonylamidines with the ring contraction.^{164,165}

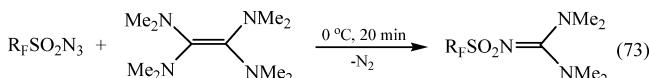


With simple vinyl ethers, perfluoroalkanesulfonylazides give substituted 1,2,3-triazolines, which undergo slow dimerization with elimination of nitrogen into the symmetrically substituted piperazines (eq 71).¹⁶⁶ Reaction 71 is solvent-free; in a one-pot,

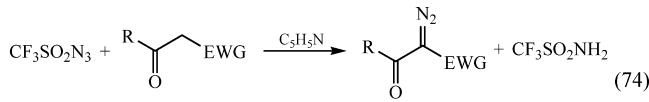
three-component reaction with alcohol, N-protected α -amino aldehyde acetals were synthesized (eq 72).¹⁶⁶



More electron-rich tetrakis(dimethylamino)ethylene reacts with perfluoroalkanesulfonylazides even more readily, with splitting of the C=C bond, to give 1,1,3,3-tetramethyl-2-(perfluoroalkanesulfonyl)guanidines ($(Me_2N)_2C=NSO_2R_F$).¹⁶⁷

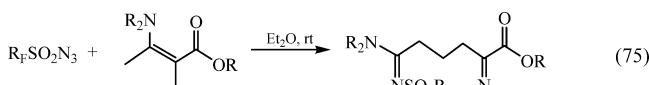


Trifluoromethanesulfonylazide acts as a diazotizing agent with respect to compounds with activated methylene group to give the corresponding α -cyano- α -diazocarbonyl compounds under mild conditions and in high yield.^{168,169} The diazo group is

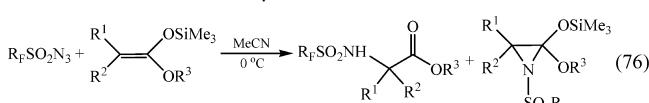


EWG = CN; SO₂Ph; COOR.

transferred from perfluoroalkanesulfonylazides to β -ketoester enamines under mild conditions to give the products containing both the diazo and the amidine group.¹⁷⁰

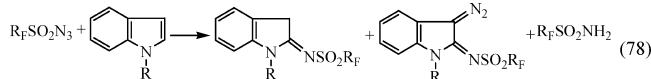
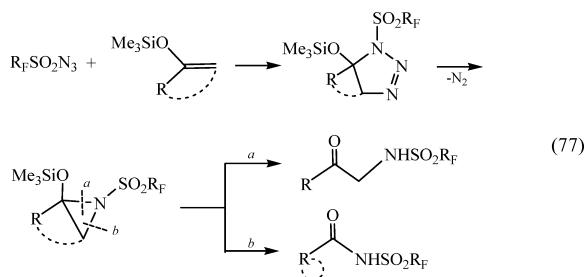


The reaction of perfluoroalkanesulfonylazides with disilylated ketene acetals $R^1R^2C=C(OSiR'_3)_2$ proceeds in good yield and represents a novel method for preparation of α -aminoacids protected at the nitrogen atom by the sulfonyl group.¹⁷¹ Similarly occurs the reaction with monosilylated ketene acetals, but in this case *N*-sulfonylaziridines are formed as well.¹⁷²

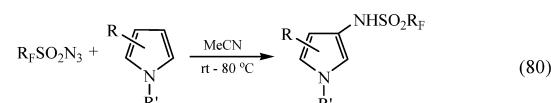
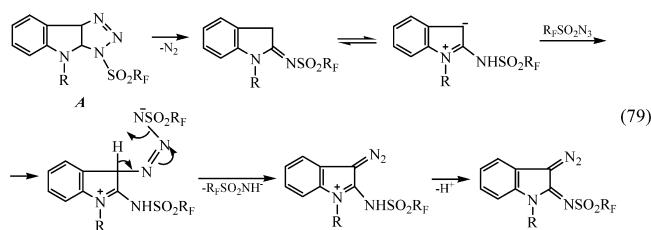


With cyclic silyl ethers, however, mixed imides of perfluoroalkanesulfonic and carbocyclic carboxylic acids $RC(O)NHSO_2R_F$ are formed.¹⁷³ The mechanism suggested to explain the observed different behavior includes the formation of the [3 + 2] adduct (triazoline), which eliminates nitrogen to give the intermediate aziridine, which, in turn, is opened via two routes, *a* and *b*.¹⁷³

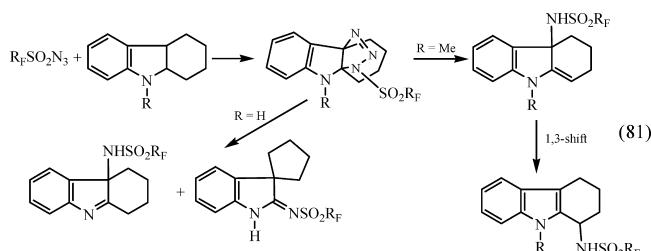
With indoles, perfluoroalkanesulfonylazides react with the formation of the products of imidation and diazotation (eq 78). The ratio of the products is solvent-dependent: in ether or 1,4-dioxane, the former compounds, 2-(*N*-substituted-indolinylidene)fluoroalkane sulfonylimines, are the major products, whereas in ethanol, unexpectedly, 2-fluoroalkanesulfonylimino-3-diazo-indolines are formed in good yield.^{174,175}



The mechanism of reaction 78 via the intermediate triazolines *A*, which decompose with elimination of N_2 and 1,2-H shift to form amidines, which, in turn, further react with the next molecule of the azide, was suggested, as shown in the scheme in eq 79.^{174,175} Pyrroles give the products of perfluoroalkanesulfonylamidation exclusively in the 3-position, which is not typical for electrophilic reactions with pyrroles.¹⁷⁶

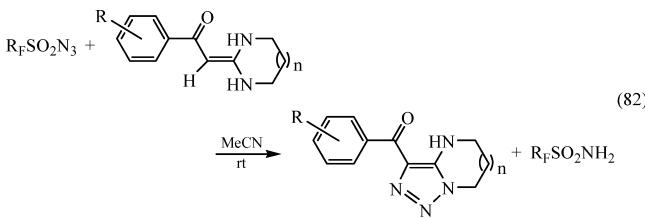


In a rather complicated manner the reaction of perfluoroalkanesulfonylazides with NH- and NMe-1,2,3,4-tetrahydrocarbazoles proceeds.¹⁷⁷ As with silylated vinyl ethers, it starts with [3 + 2]-cycloaddition, but with the NH-carbazole perfluoroalkanesulfonylamidines with ring contraction and the 4a-substituted derivatives are formed, whereas with the NMe-carbazole the 1-perfluoroalkanesulfonylamidation occurs.¹⁷⁷

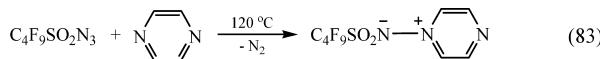


The reaction of perfluoroalkanesulfonyl azides, acting as a diazo transfer reagent, with heterocyclic ketene amines proceeds as a 1,3-dipolar cycloaddition and, after spontaneous elimination of perfluoroalkanesulfonyl amide, results in 1,3-diazaheterocycle-fused 1,2,3-triazoles in good to quantitative yield.¹⁷⁸

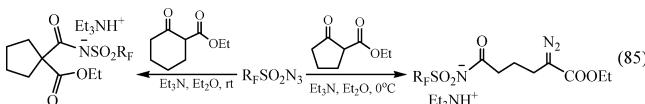
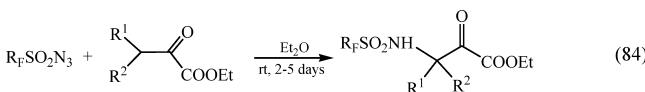
Thermal decomposition of nonafluorobutanesulfonyl azide mixed with the equimolar amount of pyrazine proceeds as the oxidation of the electron-rich pyrazine by the electron-deficient nitrene formed from the azide, similar to oxidation of N-



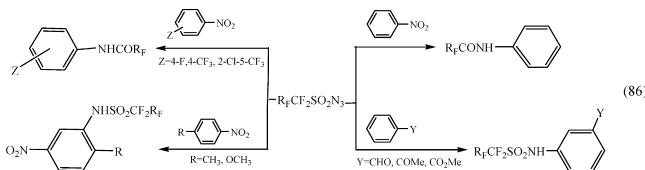
heterocycles to N-oxides.¹⁷⁹ The presence of a positively charged nitrogen atom in the *N*-ylide product prevents the formation of the disubstituted ylide even upon further heating with excess of the azide.



Perfluoroalkanesulfonylazides react with α - and β -ketoesters in a different manner. The reaction takes place in the presence of secondary amines and with α -ketoesters leads to N-sulfonylated β -amino- α -ketoesters in good yield, which allowed the authors to propose this reaction as a new method for the synthesis of N-protected β -amino- α -ketoesters.¹⁸⁰ With cyclic β -ketoesters, the reaction with perfluoroalkanesulfonylazides proceeds according to the following scheme.¹⁸¹

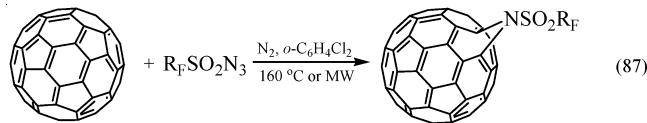


A variety of products was obtained upon the thermolysis of perfluoroalkanesulfonylazides in the presence of aromatic compounds.^{65,182,183} With electron-rich benzenes, usual electrophilic substitution occurs, giving rise to amides $\text{R}_\text{F}\text{SO}_2\text{NH}_2$ and $\text{R}_\text{F}\text{SO}_2\text{NAr}$.^{65,182} In accordance with the orientation rules, electron-deficient arenes, such as benzaldehyde, methyl benzoate, or acetophenone react similarly.¹⁸³ In contrast, with substituted nitrobenzenes, apart from "normal" products of electrophilic substitution and amides $\text{R}_\text{F}\text{SO}_2\text{NH}_2$, the products containing the $\text{R}_\text{F}\text{CONH}$ instead of the $\text{R}_\text{F}\text{SO}_2\text{NH}$ moiety were obtained.¹⁸³ The reaction can be represented by the following scheme (eq 86). The mechanism of the reaction is not clear; the only assumption made by the authors is that the carbonyl group comes from the difluoromethylene group $-\text{CF}_2\text{SO}_2-$ of the reagents.¹⁸³

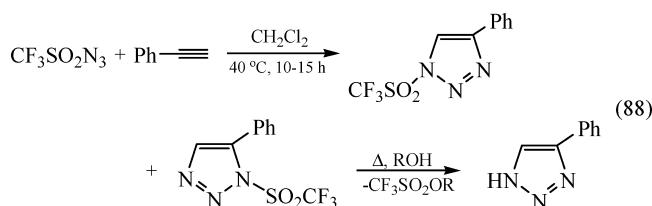


The reactions of [60]fullerene with excess perfluoroalkanesulfonyl azides under thermal or microwave (MW)-induced generation of the corresponding nitrenes results in mono-adducts, [5,6]-bridged azafulleroids.¹⁸⁴

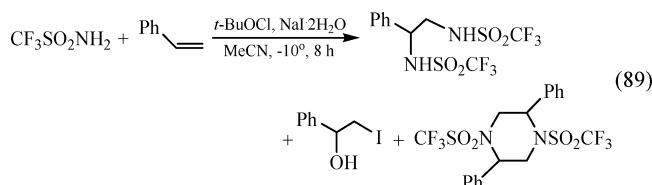
Trifluoromethanesulfonylazide reacts with phenylacetylene under mild conditions to give two regioisomers, 1-triflyl-4-



phenyl-1*H*-1,2,3-triazole and 1-triflyl-5-phenyl-1*H*-1,2,3-triazole, in the 4:1 ratio.¹⁸⁵ This is in contrast with tosylazide, which gives the corresponding adduct after 6 days reflux.¹⁸⁶ When carrying out the reaction in ethanol, the main product was 4-phenyl-1*H*-1,2,3-triazole formed by solvolysis. Because the similar adduct with tosylazide is hydrolyzed only in 90% H_2SO_4 , the reaction with trifluoromethanesulfonylazide may be a convenient route to unsubstituted triazoles.¹⁸⁵



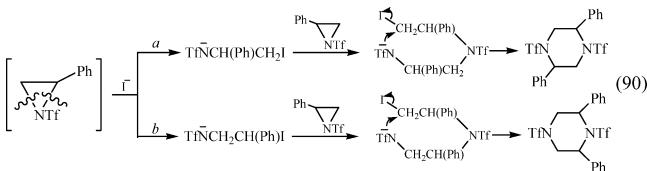
As follows from the aforesaid, under appropriate (rather severe) conditions trifluoromethanesulfonylazide and its analogues generate the corresponding nitrenes, which, being trapped by alkenes, can form *N*-perfluoroalkanesulfonylaziridines.^{66,151,172,173} Other potential precursors of trifluoromethanesulfonylnitrene are *N*-halogenated triflamides $\text{CF}_3\text{SO}_2\text{NH}\text{Hlg}$. To examine their potential applicability for the synthesis of *N*-triflylaziridines, we have used the oxidative system (*t*-BuOCl + NaI) in MeCN, which has been suggested and successfully used for aziridination of various alkenes with different sulfonamides.¹⁸⁷ However, no aziridine was obtained. Instead, the main product was the product of oxidative triflamidation, and 2,5-diphenyl-1,4-bis(trifluoromethylsulfonyl)piperazine, whose structure was proved by X-ray, was isolated in 14% yield.¹⁸⁸



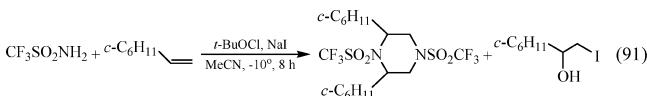
It is not clear whether the obtained piperazine is formed by dimerization of the intermediate aziridine or by another mechanism, although such a dimerization induced by iodide ion is known in the literature.¹⁸⁹ It is noteworthy that simple NMR and elemental analysis is insufficient to prove the formation of aziridines. To distinguish them from their dimers, piperazines, X-ray analysis, or, at least, measuring of ${}^1\text{J}_{\text{CH}}$ constants (which in aziridines are much higher than in unstrained compounds, 170–180 versus 140–150 Hz)¹⁹⁰ is required.

A puzzling result was obtained when carrying out the reaction with dry NaI instead of its dihydrate. In addition to the above linear products, the isomeric 2,6-diphenyl-1,4-bis(trifluoromethylsulfonyl)piperazine was isolated.¹⁹¹ The reasons of such a dramatic sensitivity of the course of the reaction to subtle variation of the conditions are not clear; a tentative mechanism assumes the rupture of the less crowded N–C³ bond in the intermediate aziridine by the action of solvated

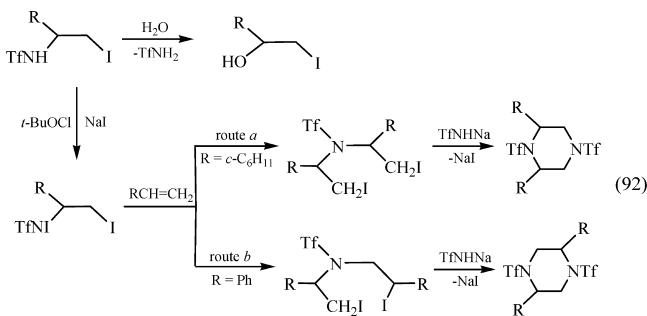
iodide ion (route *a*) and the rupture of more crowded N—C² bond (by more favorable attack of the benzylic carbon atom) by less bulky unsolvated iodide ion (route *b*).¹⁹¹



Later, to explain the results of the reaction of triflamine with vinylcyclohexane (eq 91) and taking into account that no

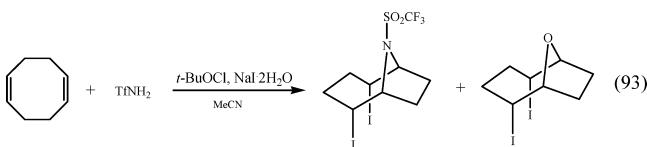


aziridines could be detected and that perfluoroalkanesulfonylazides are formed (at least, from the corresponding azides) only at high temperatures,¹⁷² an alternative mechanism was suggested.¹⁹² It includes iodotriflamidation of the alkene by the intermediate *N*-iodotriflamine and further transformations of the adduct, as shown in the scheme in eq 92).

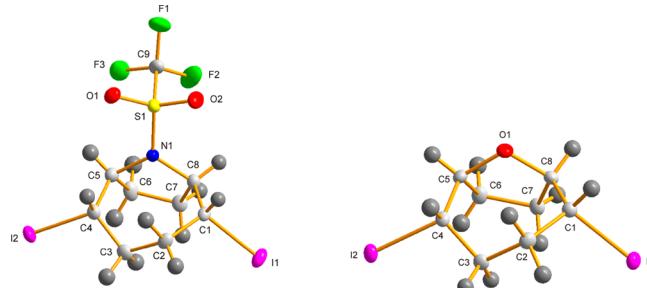


Different regioselectivity in routes *a* and *b* in eq 92 is due to the fact that in vinylcyclohexane the highest occupied molecular orbital (HOMO) is mostly localized on the terminal carbon, whereas in styrene – on the internal olefinic carbon atom.¹⁹² No linear product of bistriflamidation of vinylcyclohexane TfNHCHRCH₂NHTf was detected. Its absence can be due to the extremely low nucleophilicity of triflamine unable to substitute the iodine atom in the adduct RCH(NHTf)CH₂I. In the reaction with styrene, the anchimeric assistance of the phenyl group facilitates the substitution and results in the formation of the diadduct.

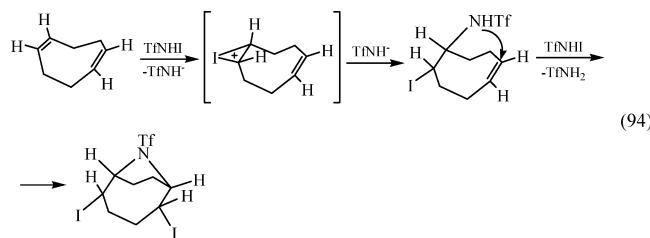
The products of oxidative triflamidation were obtained also with some other alkenes.¹⁹³ The reaction with 1,5-cyclooctadiene represents the first example of direct assembling of 9-heterobicyclo[4.2.1]nonanes. The structure of both products was proved by X-ray.¹⁹³



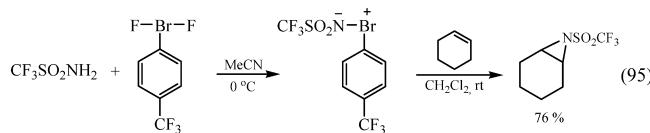
The endo-arrangement of the two iodine atoms allows one to suggest the mechanism. Apparently, the trans-addition of the intermediate *N*-iodotriflamine CF₃SO₂NHI to 1,5-COD leads to bicyclo[4.2.1]nonane rather than the isomeric bicyclo[3.3.1]-



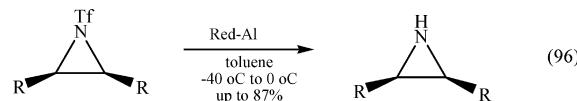
nonane due to more easy attack of the nitrogen atom at the closer olefinic carbon atom in the intermediate adduct.¹⁹³



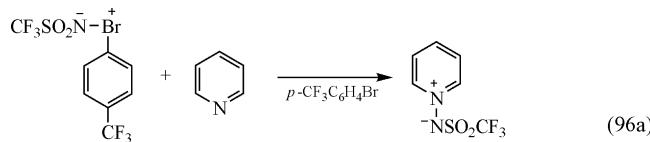
Recently, Ochiai et al. synthesized triflylimino-λ³-bromane as a new precursor of trifluoromethanesulfonylnitrene by the reaction of *p*-trifluoromethylphenyl(difluoro)-λ³-bromane with triflamine and used it for mild noncatalytic aziridination of alkenes.¹⁹⁴



For comparison, the use of a well-known aziridinating agent, Ph—I=NTs, requires 5-fold excess of the substrate and copper perchlorate as a catalyst and gives the same product in a lower yield.¹⁹⁵ Aziridination proceeds in a stereospecific manner with retention of configuration, that is, the cis-olefins R¹—CH=CH—R² give cis-*N*-triflylaziridines and the trans-olefins give the trans-isomers.¹⁹⁵ A modification of this procedure is preparation of the diacetoxymethyl derivative from the above difluoro-λ³-bromane, which is an analogue of the well-known diacetoxymethyl-λ³-iodane, PhI(OAc)₂, and its further reaction with alkenes and triflamine.¹⁹⁶ The *N*-triflylaziridines can be further deprotected by reductive detrifylation with sodium bis(2-methoxyethoxy)-aluminum dihydride (Red-Al).¹⁹⁷



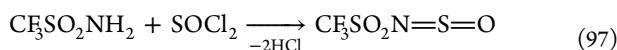
As a triflamidating agent, triflylimino-λ³-bromane reacts also with pyridines and related N-heterocycles to give *N*-iminoammonium ylides.¹⁹⁸ Noteworthy is that only triflamine



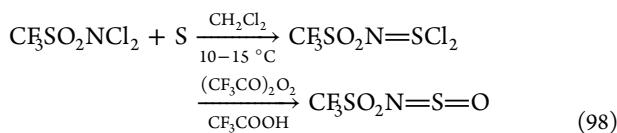
gives the above sulfonylimino- λ^3 -bromane; arenesulfonamides react with the same difluoro- λ^3 -bromane in a different manner, giving rise to the Hofmann rearrangement products $\text{ArNH-SO}_2\text{F}$.¹⁹⁹

3.3. Use of *N*-Sulfinyltriflamide and its Analogues in Organic Synthesis

N-Sulfinyltriflamide $\text{CF}_3\text{SO}_2\text{NH}=\text{S}=\text{O}$ is an alternative for triflamine, which reacts more actively than its progenitor in different reactions. First it was synthesized by Roesky in <40% yield by prolonged reflux of triflamine in excess of thionyl chloride.²⁰⁰

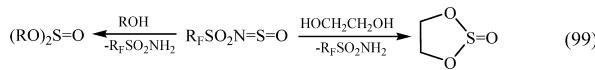


Yagupol'skii et al. suggested another method for preparation of *N*-sulfinyltriflamide by the reaction of *N,N*-dichlorotriflamine with sulfur followed by heating of the formed product with trifluoroacetic anhydride in up to 90% yield.⁷⁰

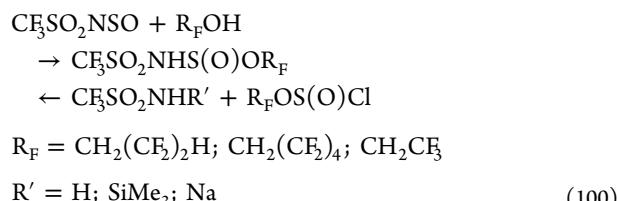


Higher *N*-sulfinylperfluoroalkanesulfonamides $\text{R}_\text{F}\text{SO}_2\text{N}=\text{S}=\text{O}$ were prepared by Zhu et al. in moderate yield by reflux of the parent sulfonamides with excess of thionyl chloride.²⁰¹ These heterocumulenes are versatile reagents for introduction of the $\text{R}_\text{F}\text{SO}_2\text{N}$ moiety in different organic molecules.

N-Sulfinyltriflamide is easily hydrolyzed in air moisture (within several minutes) to give pure triflamine. With simple alcohols, ethylene glycol or phenol, *N*-sulfinyltriflamide and higher *N*-sulfinylperfluoroalkanesulfonamides react with the formation of the parent sulfonamides and dialkyl(aryl)-sulfites.²⁰²



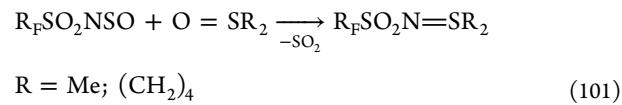
The authors have made a discouraging conclusion that all trials to isolate the intermediate amidosulfites $\text{R}_\text{F}\text{SO}_2\text{NHS(O)-OR}$ failed.²⁰² However, amidosulfites of this type were obtained by us by the reaction of *N*-sulfinyltriflamide with fluorinated alcohols $\text{R}_\text{F}\text{OH}$ and proved by independent synthesis from chlorosulfites $\text{R}_\text{F}\text{OS(O)Cl}$ and triflamine, or its sodium salt, or trimethylsilyl derivative.²⁰³



The obtained products, which are easily hydrolyzed to triflamine, alcohols $\text{R}_\text{F}\text{OH}$, and SO_2 , are the first NH-containing amidosulfites. So far, the only stable compounds of this type were cyclic amidosulfites, which were first synthesized in 1966²⁰⁴ (contrary to the assertion of the authors of the later work²⁰⁵ of their priority).

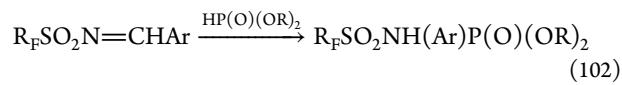
The above reaction represents a rather rare case of addition of OH acids to the N=S bond of *N*-sulfinyltriflamide. Earlier, the adducts of general formula $\text{R}_\text{F}\text{SO}_2\text{NHS(O)X}$ were obtained

by Zhu and co-workers by the reaction of *N*-sulfinylperfluoroalkanesulfonamides with PH- and CH-acids [X = P(O)(OMe)₂, CH(CHCOOEt)₂].²⁰² *N*-Sulfinyltriflamide and higher *N*-sulfinylperfluoroalkanesulfonamides enter various condensation reactions with evolution of SO_2 . Thus, with sulfoxides (DMSO or tetramethylene sulfoxide) they give the corresponding *N*-(dialkyl- λ^4 -sulfanylidene)perfluoroalkanesulfonamides.^{206,207}

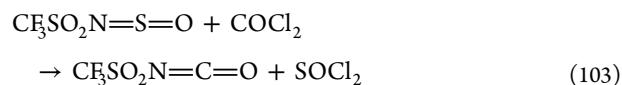


Note that compounds of the same type, $\text{CF}_3\text{SO}_2\text{N}=\text{SR}'\text{R}^2$, were obtained by oxidative amidation of sulfides with *N,N*-dichlorotriflamine,⁷² or with triflamine in the presence of lead tetraacetate in pyridine,²⁰⁸ or with the Ochiai reagent, triflylimino- λ^3 -bromane.²⁰⁹ The above-mentioned oxidative imination of sulfoxides with *N,N*-dichlorotriflamine,⁷² or with triflamine in the presence of $\text{Pb}(\text{OAc})_4$, affords sulfoximides $\text{CF}_3\text{SO}_2\text{N}=\text{S(O)R}_2$.²⁰⁸

The reaction with various carbonyl-containing compounds $\text{RR}'\text{C=O}$ (aromatic and heteroaromatic aldehydes,^{207,210–212} cyclopentanone,²⁰⁷ and DMF²¹²) also proceeds with evolution of SO_2 and formation of the products of condensation $\text{R}_\text{F}\text{SO}_2\text{N}=\text{CRR}'$. The products of condensation with benzaldehydes $\text{R}_\text{F}\text{SO}_2\text{N}=\text{CHAr}$ are easily hydrolyzed to the amide $\text{R}_\text{F}\text{SO}_2\text{NH}_2$ and aldehyde ArCHO .²⁰¹ They also react with dialkylphosphites to afford the adducts.^{207,211}



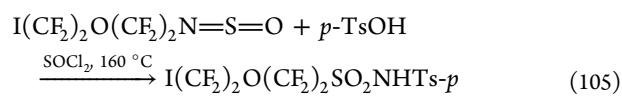
However, in the reaction of *N*-sulfinyltriflamide with phosgene, thionyl chloride rather than sulfur dioxide is evolved and the reaction proceeds as the exchange of the sulfinyl group by the carbonyl group.²⁰⁶



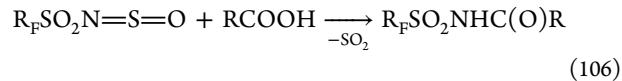
N-Sulfinyltriflamide is also capable of self-condensation; thus, upon UV radiation for 48 h, it dimerizes with evolution of SO_2 and formation of *N,N'*- λ^4 -sulfanediylidenebis(triflame) in 32% yield.²⁰⁶



Under severe conditions, *N*-sulfinylperfluoroalkanesulfonamides react with *p*-TsOH to afford the mixed imides of perfluoroalkanesulfonic and *p*-tolylsulfonic acid in up to 70% yield.²¹³ Interestingly, triflic acid itself does not enter this reaction.²¹³

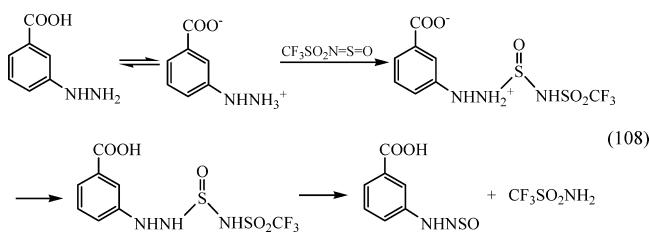
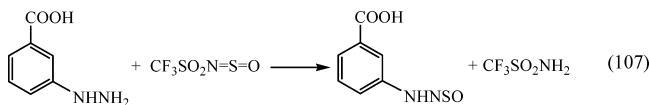


N-Sulfinyltriflamide and its homologues react with carboxylic acids to give mixed imides of perfluoroalkanesulfonic and carboxylic acids $\text{R}_\text{F}\text{SO}_2\text{NHC(O)R}'$.^{213,214}

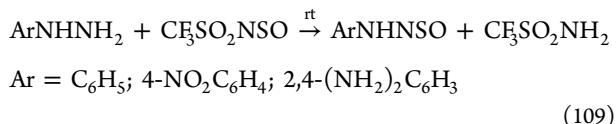


The reaction is catalyzed by SOCl_2 and, for the substrates with long perfluorinated chain R_F , requires high temperatures, up to 150–160 °C,²¹¹ whereas with *N*-sulfinyltriflame we performed the reaction at room temperature in close to quantitative yields.²¹⁴ The stronger the acid, the lower is the yield and the more severe conditions are required; thus, no products could be isolated from the reaction of $\text{CF}_3\text{SO}_2\text{NSO}$ with trichloroacetic, pentafluoropropionic, or perfluoronanoic acid.²¹⁴ This is consistent with the inertness of triflic acid with respect to $R_F\text{SO}_2\text{NSO}$.²¹³

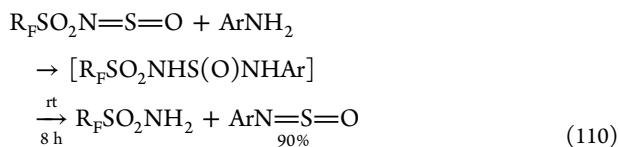
Unexpectedly, in the reaction of *N*-sulfinyltriflame with *m*-hydrazinobenzoic acid the carboxylic group is retained and the reaction proceeds as the exchange of the sulfinyl moiety between *N*-sulfinyltriflame and the hydrazino residue.²¹⁴ To explain the different behavior of *m*-hydrazinobenzoic and other aromatic acids, the following mechanism was proposed.²¹⁴



Taking into account the absence of data on the reactions of *N*-sulfinylsulfonamides RSO_2NSO with hydrazines and to verify the generality of the above result, the reaction of *N*-sulfinyltriflame with a series of arylhydrazines was studied and the formation of 1-aryl-2-sulfinylhydrazines in good yield in all cases was proved.²¹⁵ This is the first example of the transfer of the sulfinyl group from *N*-sulfinylsulfonamides to hydrazines.



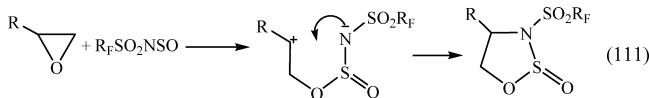
It is noteworthy that the transfer of the sulfinyl group from *N*-sulfinylperfluoroalkanesulfonamides to anilines is described; the reaction, presumably, proceeds via the intermediate unstable adduct.²⁰²



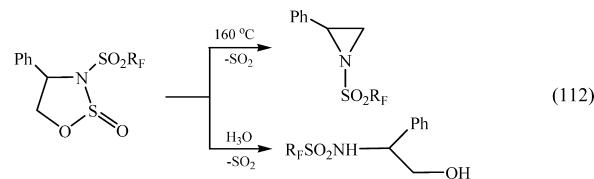
In contrast to *N*-sulfinyltriflame, which is hydrolyzed by air moisture within several minutes, 1-aryl-2-sulfinylhydrazines are very stable and can be crystallized from boiling aqueous ethanol.²¹⁵ The MP2/6-311+G* theoretical analysis of the molecules of *N*-sulfinyltriflame and 1-phenyl-2-sulfinylhydrazine containing the NSO group attached to the strong electron acceptor (CF_3SO_2) or π -donor (NH) showed the heterocumulene moiety $\text{N}=\text{S}=\text{O}$ to be sharply different. In the former molecule, the positive charge on the electrophilic center, the sulfur atom, is much larger; its lowest unoccupied molecular orbital (LUMO) lies substantially lower and is localized mainly

(>40%) at the sulfur atom, whereas in the latter molecule the LUMO is mainly localized at the phenyl group and only <4% at sulfur. Therefore, 1-aryl-2-sulfinylhydrazines are much poorer electrophiles than *N*-sulfinyltriflame in both the charge- and orbital-controlled reactions, in full accordance with the experiment.²¹⁵

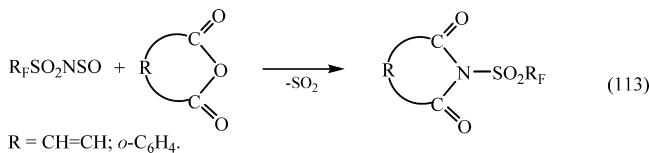
N-Sulfinyltriflame reacts with oxiranes via a ring-opening/ring-closure sequence of reactions to afford 2-oxa-3-fluoroalkanesulfonfonyl-1,2,3-oxathiazolidines.²¹⁶ Above 160 °C, the product



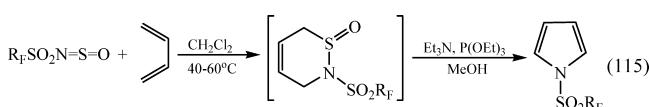
with $\text{R} = \text{Ph}$ decomposes with elimination of SO_2 and formation of azidine, whereas the acidic hydrolysis results in *N*-(1-phenyl-2-hydroxyethyl)perfluoroalkanesulfonamide.²¹⁶



Phthalic and maleic anhydrides react with *N*-sulfinylperfluoroalkanesulfonamides to give the corresponding *N*-triflylimides in good yield. Acetic anhydride does not enter this reaction.⁷ In an early work, Roesky and Holtschneider reported the formation of a linear 1:1 adduct of *N*-sulfinyltriflame to 2,3-dimethylbutadiene in low yield.²⁰⁶

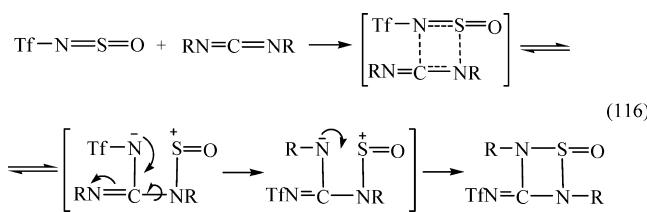


The alternative isomeric structure of the Diels–Alder cycloadduct was excluded on the basis of IR and NMR spectroscopy data.²⁰⁶ Nevertheless, this result seems dubious in view of the later work of Zhu et al.,²¹⁷ who obtained inseparable mixtures of products in the reaction of *N*-perfluoroalkanesulfonamides with 2,4-dimethyl-1,3-butadiene or 2-methyl-1,3-butadiene. With unsubstituted 1,3-butadiene, however, the reaction proceeds with the formation of *N*-perfluoroalkanesulfonyl pyrroles in 60–65% yield and provides a simple and efficient method for the synthesis of these interesting compounds.



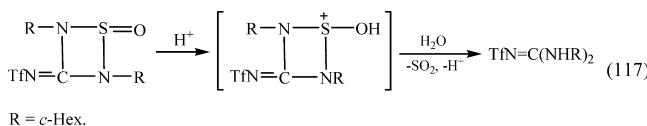
The aforementioned rare cases of cycloaddition reactions of *N*-sulfinyltriflame or its analogues were recently complemented by the reaction with carbodiimides.²¹⁸ The ¹H, ¹³C, and ¹⁵N NMR spectroscopic studies showed that the product has two identical alkylamino groups NR_2 ; therefore, the mechanism was suggested including rearrangement of the first

formed intermediate $[2\pi + 2\pi]$ cycloadduct via the ring-opening–ring-closure sequence of reactions.²¹⁸

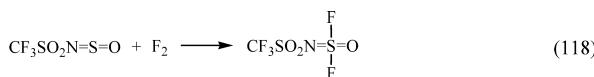


Note that for the reaction of MeSO_2NSO or TsNSO with carbodiimides the structure of asymmetric $[2\pi + 2\pi]$ cycloadducts was reported,²¹⁹ although the proton spectra in ref 219 contain only one NCH ($\text{R} = i\text{-Pr}$) or NCH_2 ($\text{R} = n\text{-Bu}$) signal and, thus, evidence *against* the suggested structure (the ^{13}C NMR spectra were not recorded).

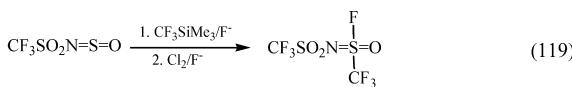
The acidic hydrolysis of the above cycloadduct gives 1,3-dicyclohexyl-2-(trifluoromethylsulfonyl)guanidine, which is identical to the authentic sample obtained quantitatively by the reaction of triflamine with dicyclohexylcarbodiimide,²²⁰ providing an independent support for the symmetrical structure. The sulfur atom in *N*-sulfinyltriflame is oxidized



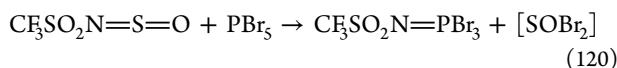
by elemental fluorine upon UV radiation to give (trifluoromethylsulfonyl)imidatosulfuryl difluoride in low yield.²⁰⁶ Strongly electron-deficient *N*-



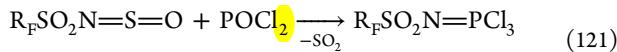
(trifluoromethylsulfonyl)trifluoromethanesulfonimidoyl fluoride is formed from *N*-sulfinyltriflame in the fluorinating system $\text{CF}_3\text{SiMe}_3/\text{F}^-$.²²¹ *N*-Sulfinyltriflame reacts exothermi-



cally with phosphorus pentabromide to give the corresponding phosphorimide in good yield.²²²

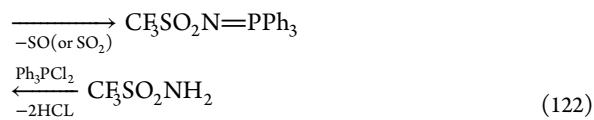
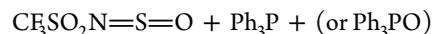


Phosphorus oxychloride POCl_3 reacts with *N*-sulfinylperfluor-alkanesulfonamides²⁰⁷ to give the corresponding phosphorimides $\text{R}_\text{F}\text{SO}_2\text{N}=\text{PCl}_3$ in good yield.

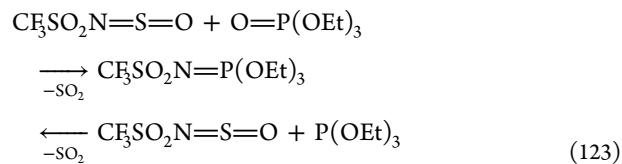


The simplest representative $\text{CF}_3\text{SO}_2\text{N}=\text{PCl}_3$ was prepared earlier from triflame and phosphorus pentachloride.²⁰⁰

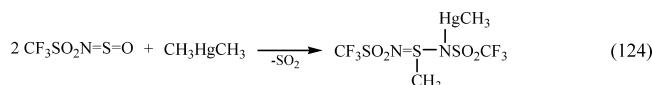
N-Sulfinyltriflame reacts with triphenylphosphine and its oxide to give the corresponding phosphazenes.²²³ With this, the reaction with triphenylphosphine proceeds in benzene at room temperature in a close to quantitative yield, whereas with triphenylphosphine oxide the conversion after 2 h at 80 °C was as low as 7%.



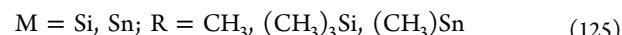
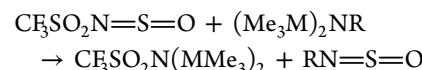
The much lower activity of triphenylphosphine oxide as compared to triphenylphosphine, in our opinion, is explained by different mechanisms of the reaction. With Ph_3P , the reaction proceeds as a nucleophilic attack of the lone pair of the phosphorus atom to the electron-deficient nitrogen atom in $\text{TfN}^+-\text{S}=\text{O}$. On the contrary, the reaction with triphenylphosphine oxide is the nucleophilic attack of the lone pair of the nitrogen atom of *N*-sulfinyltriflame to the electrophilic phosphorus atom of $\text{Ph}_3\text{P}=\text{O}$, and a very low basicity of nitrogen in $\text{CF}_3\text{SO}_2\text{NSO}$ is responsible for the observed low reactivity.²²³ $\text{CF}_3\text{SO}_2\text{N}=\text{PPPh}_3$ was independently synthesized by the reaction of triflame with dichloro(triphenyl)-phosphorane prepared *in situ* by chlorination of PPh_3 with PCl_5 .²²³ The reaction of *N*-sulfinyltriflame with triethylphosphate and triethylphosphite as well as the reaction of triflame with dichloro(triethoxy)phosphorane $\text{Cl}_2\text{P}(\text{OEt})_3$ proceed similarly.²²⁴



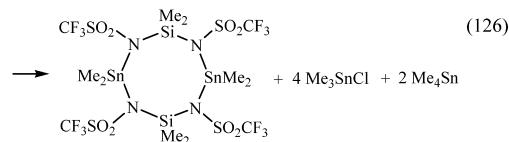
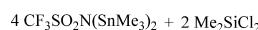
In a series of works,^{225–227} Roesky and co-workers have studied the reactions of *N*-sulfinyltriflame with organometallic compounds. Thus, *N*-sulfinyltriflame cleaves dimethyl mer-



cury (eq 124) and undergoes the exchange reaction with trimethylsilyl- and trimethylstannylamines (eq 125).²²⁵

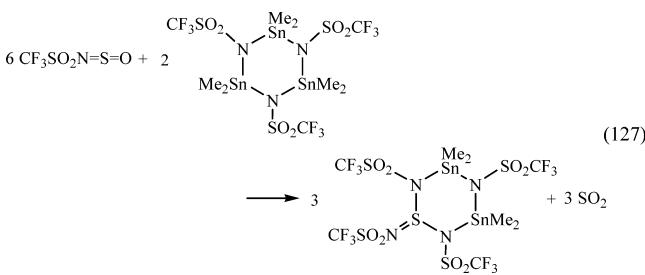


The organometallic triflamides formed may enter the reaction with dimethylidichlorosilane to give unusual azametallocycles.²²⁶ Another interesting example of the formation of *N*-triflamo-containing metallacycles is the reaction of *N*-sulfinyltriflame with *syn*-triazatristannacyclohexane.²²⁷

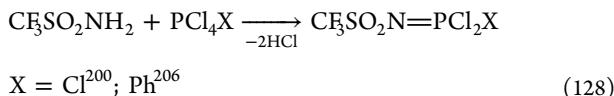


3.4. *N*-Triflyl Iminopnictoranes and Their Analogues

N-Triflyl- and *N*-perfluoroalkanesulfonyliminopnictoranes, that is, compounds of the general formula $\text{R}_\text{F}\text{SO}_2\text{N}=\text{MX}_3$, where $\text{M} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$, are very interesting both from the structural

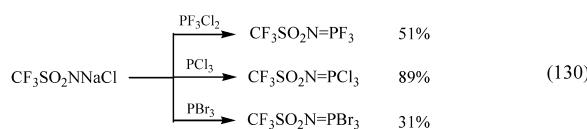
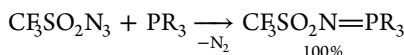
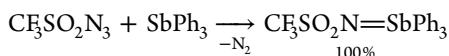
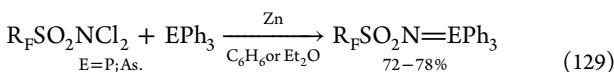


point of view and as reactive intermediates. The first phosphorus derivatives of triflame, $\text{CF}_3\text{SO}_2\text{N}=\text{PCl}_2\text{X}$, were obtained in low to moderate yields in 1970 by the reaction of triflame with the corresponding derivatives of pentavalent phosphorus.^{200,206}



Note that the similar nonfluorinated analogues were studied as long ago as in the 1950s of the last century by Kirsanov²²⁸ or in the 1960s by Kresze and Wucherpfennig²²⁹ and Senning.²³⁰

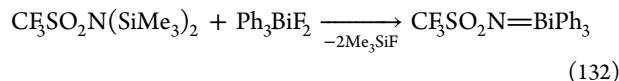
Later on, other approaches to these compounds were elaborated, and also different perfluoroalkanesulfonylimine derivatives of phosphorus and its analogues of the general formula $\text{R}_f\text{SO}_2\text{N}=\text{MX}_3$ ($\text{M} = \text{P}^{207}, \text{As}^{231}, \text{Sb}^{232}, \text{Bi}^{233}$) have been synthesized by the groups of Zhu and Yagupol'skii. For the oxidative imination the authors have used dichlorides $\text{R}_f\text{SO}_2\text{NCl}_2$ ²³¹ (eq 129), the sodium salt of *N*-chlorotriflame $\text{CF}_3\text{SO}_2\text{NNaCl}$ ²³² (eq 130) or trifluoromethanesulfonylazide $\text{CF}_3\text{SO}_2\text{N}_3$ (eq 131).



Similarly, perfluoroalkanesulfonyl azides $\text{R}_f\text{SO}_2\text{N}_3$ ($\text{R}_f = \text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2, \text{H}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2, \text{C}_4\text{F}_9$) react with triphenylphosphine with quantitative evolution of nitrogen to afford $\text{R}_f\text{SO}_2\text{N}=\text{PX}_3$ ($\text{X} = \text{Bu, Ph}$).²³¹

Note that trifluoromethanesulfonylazide does not react with phosphorus trihalogenides but replacement of one chlorine by the phenyl group allows to carry out the oxidative imidation quantitatively. Diethylaminodichlorophosphine Et_2NPCl_2 reacts with trifluoromethanesulfonylazide very slowly.²³²

The corresponding bismuth derivative of triflame was prepared from bisilylated triflame and triphenylbismuthdifluoride.²³³



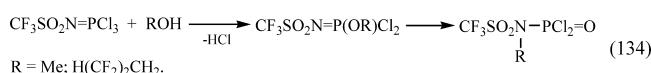
An analogue of the latter compound, $\text{CF}_3\text{SO}_2\text{N}=\text{BiAr}_3$, was prepared by an alternative method, from Ar_3BiCl_2 and triflame.²³⁴ Its X-ray structural analysis revealed that the bismuth center possesses a distorted trigonal-bipyramidal geometry and the Bi–N bond length falls in the range of known Bi–N single bonds, suggesting a polarized $\text{Bi}^+–\text{N}^-$ bond rather than a Bi=N double bond.²³⁴

Perfluoroalkanesulfonylated phosphazenes are easily hydrolyzed at the N=P bond to give the corresponding perfluoroalkanesulfonylamides and triphenylphosphine oxide.^{151,231}



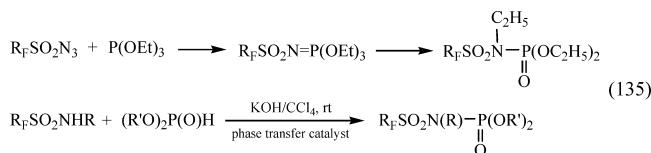
The experimental (Fourier transform infrared (FT-IR), Raman spectroscopy) and theoretical (HF, MP2, density functional theory (DFT) calculations) analysis of *N*-(triflyl)-trichlorophosphazene $\text{CF}_3\text{SO}_2\text{N}=\text{PCl}_3$ was recently performed.²³⁵

The chlorine atoms in *N*-(triflyl)trichlorophosphazene $\text{CF}_3\text{SO}_2\text{N}=\text{PCl}_3$ can be substituted by the alkoxy groups, as was shown on the example of formation of the product of complete substitution $\text{CF}_3\text{SO}_2\text{N}=\text{P}(\text{OR})_3$ in the reaction with sodium hexanolate in benzene.²³² However, our monitoring of the reaction of $\text{CF}_3\text{SO}_2\text{N}=\text{PCl}_3$ with methanol and trifluoroopropanol has shown that the reaction is not as simple as that. First, *N*-(triflyl)(alkoxydichloro)phosphazenes are formed, which rearrange upon standing into dichlorides of *N*-alkyl-*N*-(triflyl)amidophosphoric acids.²³⁶



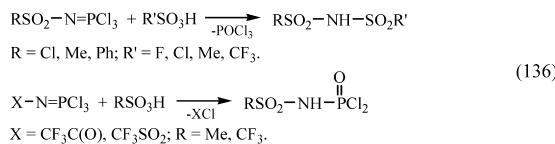
The ease of isomerization is a function of electronegativity of substituent R: for $\text{R} = \text{CH}_3$ the rearrangement proceeds much easier than for $\text{R} = \text{CH}_2\text{C}_2\text{F}_4\text{H}$, as should be expected for migration of an electropositive group to the nitrogen atom. The comparison with the literature data allowed the authors to conclude that the migration of the methyl group from oxygen to nitrogen is easier the higher the electronegativity of substituent X in XSO_2 is; for $\text{X} = \text{Ar}$ the rearrangement occurs only at 200°C ,²³⁷ for $\text{X} = \text{CF}_3$ it takes several days at room temperature,²³⁶ and for the most electronegative $\text{X} = \text{F, Cl}$, it is completed in 20 min at $35–40^\circ\text{C}$.²³⁸

The phosphorus atom in triethylphosphite $\text{P}(\text{OEt})_3$ is oxidized by perfluoroalkanesulfonylnitrenes generated from perfluoroalkanesulfonylazides to form triethyl *N*-triflylphosphorimidate, which is readily rearranged into diethyl ethyl(*N*-triflyl)phosphoramidate.⁶⁶ The same phosphoramidates were prepared by countersynthesis from perfluoroalkanesulfonylamides and various dialkylphosphites.^{66,239}



Phosphazenes of the general formula $\text{EWG}-\text{N}=\text{PCl}_3$ (EWG = electron-withdrawing group) undergo interesting transformations when treated with acids.²⁴⁰ Variation of the strength

of the acid and the nucleofugality of the EWG drastically alters the course of the reaction, as is evident from the following equation.



It is worth mentioning that the action of strong acids is principally different from that of weak OH acids, like alcohols or phenols, which give the products of partial or complete chlorine substitution (see, e.g., refs 232 and 236). In other words, with strong acids, “N-protonation” takes place, whereas with weak acids, due to weak basicity of the nitrogen atom in phosphazenes, the “P-oxygenation” predominates. In the former case, the fate of the protonated intermediate depends on the relative nucleofugality of the P–Cl chlorine atom and the N–EWG electron-withdrawing group. With good nucleophiles, like $\text{CF}_3\text{C}(\text{O})$ or CF_3SO_2 , the process of the N–EWG bond rupture becomes preferable and mixed sulfonylphosphonylimides are formed.²⁴⁰

3.5. Compounds Having the $\text{CF}_3\text{SO}_2\text{N}=$ Moiety: The New Principle of the Design of Superelectron-Acceptor Substituents

Several examples of compounds having the $\text{CF}_3\text{SO}_2\text{N}=$ moiety have been already given above. Nevertheless, it seems reasonable to make here a short review of these compounds in connection with the concept of the design of superelectron-acceptor substituents originally proposed and realized by Yagupol'skii and co-workers. In the first papers,^{141,210,241} the authors synthesized $\text{ArCH}=\text{NSO}_2\text{CF}_3$ (by the reaction of ArCHO with $\text{CF}_3\text{SO}_2\text{NSO}$), $\text{ArP}(\text{R}_\text{F})_2=\text{NSO}_2\text{CF}_3$ [by the reaction of $\text{ArP}(\text{R}_\text{F})_2$ with $\text{CF}_3\text{SO}_2\text{NCl}_2$], $\text{ArI}=\text{NSO}_2\text{CF}_3$ [by the reaction of ArIF_2 with $\text{CF}_3\text{SO}_2\text{N}(\text{SiMe}_3)_2$], $\text{ArS}(\text{CF}_3)=\text{NSO}_2\text{CF}_3$ [by the reaction of ArS(O)CF_3 with triflamine in triflic anhydride], and $\text{ArS(O)(CF}_3)=\text{NSO}_2\text{CF}_3$ [by the reaction of $\text{ArS(O)(CF}_3)\text{NNa}$ with triflic anhydride] and determined the σ -constants of the $\text{CH}=\text{NSO}_2\text{CF}_3$, $\text{P}=\text{NSO}_2\text{CF}_3$, $\text{I}=\text{NSO}_2\text{CF}_3$, $\text{S}=\text{NSO}_2\text{CF}_3$, and $\text{S(O)}=\text{NSO}_2\text{CF}_3$ groups using the ^{19}F NMR spectroscopy method. Comparison of the obtained values with those of the $\text{CH}=\text{O}$, $\text{P}=\text{O}$, $\text{S}=\text{O}$, SO_2 , and $\text{I}=\text{O}$ groups has shown that the substituents containing the $\text{CF}_3\text{SO}_2\text{N}=$ group are much stronger electron acceptors than those with the isoelectronic $\text{C}=\text{O}$, $\text{P}=\text{O}$, $\text{S}=\text{O}$, or $\text{I}=\text{O}$ groups.^{141,210,241} Later on, this concept was successfully developed in numerous papers,^{31,68,131,242–247} and the up-to-date available σ -constants are summarized in Table 4.

It follows from Table 4 that both the σ_m - and σ_p -constants of the substituents with the $=\text{NSO}_2\text{CF}_3$ moiety are much larger (by up to 0.73 units) than those of their oxygen analogues and are the largest among all neutral substituents. The largest difference $\Delta\sigma = \sigma_{\text{E}=\text{O}} - \sigma_{\text{E}=\text{NTf}}$ of >0.7 units is observed for the iodine derivatives ($\text{E} = \text{I}$). Note also that the values of $\Delta\sigma_m$ and $\Delta\sigma_p$ are very close for all substituents except for $\text{E} = \text{C}$, for which the value of $\Delta\sigma_p$ (0.41) is notably larger than that of $\Delta\sigma_m$ (0.32); this is indicative of negligible contribution or the absence of conjugation effect for all substituents except for the carbonyl and *N*-triflylimino groups.

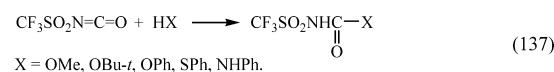
As their carbonyl analogues, acyl chlorides $\text{RC}(\text{Cl})=\text{O}$, imidoyl chlorides $\text{RC}(\text{Cl})=\text{NSO}_2\text{R}_\text{F}$ undergo the aza-Curtius

Table 4. σ -Constants of Substituents R in the *m*- and *p*-Substituted Fluorobenzenes

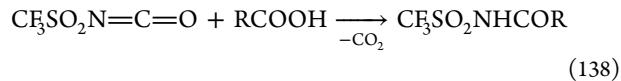
R	σ_I	σ_R	σ_m	σ_p	ref
$\text{CH}=\text{O}$	0.30	0.29	0.44	0.59	196
$\text{CH}=\text{NSO}_2\text{CF}_3$	0.53	0.47	0.76	1.00	196
$(\text{C}_3\text{F}_7)_2\text{P}=\text{O}$	0.79	0.31	0.95	1.10	196
$(\text{C}_3\text{F}_7)_2\text{P}=\text{NSO}_2\text{CF}_3$	1.11	0.26	1.24	1.37	196
$\text{I}=\text{O}$	0.56	0.06	0.58	0.62	196
$\text{I}=\text{NSO}_2\text{CF}_3$	1.24	0.11	1.30	1.35	196
$\text{CF}_3\text{S}=\text{O}$	0.66	0.12	0.72	0.78	228
$\text{CF}_3\text{S}=\text{NSO}_2\text{CF}_3$	1.08	0.20	1.18	1.28	228
CF_3SO_2	0.76	0.29	0.91	1.05	229
$\text{CF}_3\text{S(O)}=\text{NSO}_2\text{CF}_3$	1.06	0.34	1.23	1.40	228
FSO_2	0.75	0.26		1.01	231
$\text{FS(O)}=\text{NSO}_2\text{CF}_3$	1.11	0.37		1.48	231
$\text{FS}(\text{S})=\text{NSO}_2\text{CF}_3$	1.34	0.42		1.76	231

rearrangement in the reaction with sodium azide via the intermediate azides $\text{RC}(\text{N}_3)=\text{NSO}_2\text{R}_\text{F}$ to give unstable carbodiimides $\text{RN}=\text{C}=\text{NSO}_2\text{R}_\text{F}$, which on long storage or heating are converted into high-melting dimers or trimers.¹⁰⁵ The similar carbodiimides $\text{ArN}=\text{C}=\text{NSO}_2\text{R}_\text{F}$ are formed by the aza-Lossen rearrangement of the corresponding *N*-triflylimides of arenehydroxamic acids $\text{ArC}(\text{NOH})=\text{NSO}_2\text{R}_\text{F}$ ²⁴⁸ or by the aza-Hofmann rearrangement of amidines $\text{ArC}(\text{NH}_2)=\text{NSO}_2\text{R}_\text{F}$.²⁴⁹

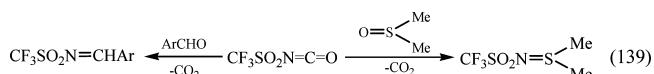
The above-mentioned carbodiimides $\text{CF}_3\text{SO}_2\text{N}=\text{C}=\text{NR}$ are heterocumulene derivatives of triflame. More typical representatives of this class of compounds having the $\text{CF}_3\text{SO}_2\text{N}=$ residue are triflyl isocyanate $\text{CF}_3\text{SO}_2\text{N}=\text{C}=\text{O}$ and triflyl isothiocyanate $\text{CF}_3\text{SO}_2\text{N}=\text{C}=\text{S}$. The former compound was first synthesized by Roesky and Holtschneider from $\text{CF}_3\text{SO}_2\text{NSO}$ and phosgene²⁰⁶ (see above) and some years later by Behrend and Haas, who used the exchange reaction of triflame with chlorosulfonyl isocyanate and performed a detailed study of the reactivity of the product.²⁵⁰ Its sulfur analogue, triflyl isothiocyanate, is formed by the reaction with phosphorus pentasulfide. Both these heterocumulenes are easily hydrolyzed to CO_2 and triflame. The reactivity of triflyl isocyanate, in general, is similar to that of *N*-sulfinyltriflame except for a higher stability of the primarily formed adducts, which do not eliminate CO_2 and often are the final products, whereas *N*-sulfinyltriflame with the same reagents forms triflame with elimination of SO_2 (see section 3.3). For example, with weak acids like alcohols, phenol, thiophenol, and aniline, the esters, thioester, and anilide of *N*-triflycarbamic acid were obtained.²⁵⁰ With stronger carboxylic



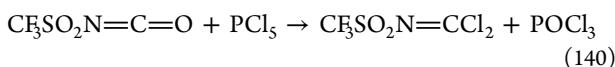
acids, the reaction proceeds with elimination of CO_2 and formation of mixed imides of triflic and the carboxylic acid. With formic acid, however, the reaction goes further and carbon monooxide is evolved to give triflame.²⁵⁰



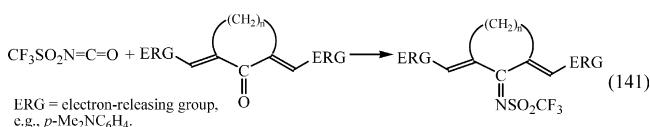
Evolution of CO_2 occurs also in the reaction with aldehydes or DMSO ,²⁵⁰ giving rise to the same products as those obtained from *N*-sulfinyltriflame.^{212,206} The reaction with phosphorus



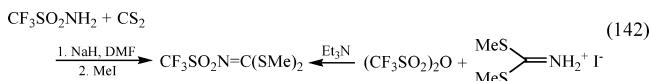
pentachloride converts the carbonyl group into the isoelectronic dichloromethylene group.²⁵⁰



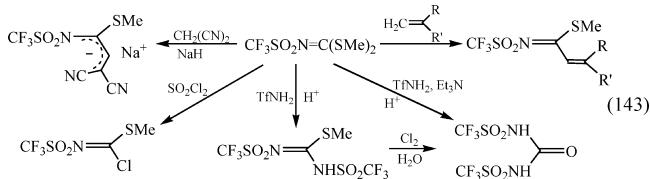
Triflyl isocyanate reacts with carbonyl compounds $\text{RR}'\text{C}=\text{O}$ containing electron-donating substituents R and R' to give the corresponding *N*-triflylimines in which the push–pull effect is strongly pronounced as follows from the UV spectroscopic studies.²⁵¹ Dithioacetal of triflyl isocyanate, $\text{CF}_3\text{SO}_2\text{N}=\text{C}(=\text{O})\text{SMe}_2$



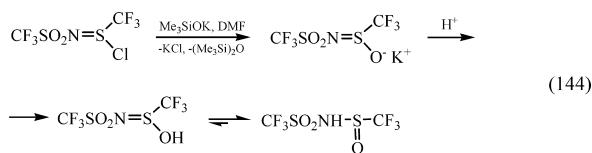
$\text{C}(\text{SMe})_2$ was synthesized from triflamide and carbon disulfide or from triflic anhydride and *S,S*-dimethyliminodithiocarbonate hydroiodide.²⁵²



It was shown to be an efficient building block for the preparation of carbonic and thiocarbonic acids derivatives containing *N*-triflylimino group $\text{CF}_3\text{SO}_2\text{N}=\text{C}$.²⁵² Thus, with ammonia and amines, it gives the products of mono $\text{CF}_3\text{SO}_2\text{N}=\text{C}(\text{SMe})\text{NR}_2$ or disubstitution $\text{CF}_3\text{SO}_2\text{N}=\text{C}(\text{NR}_2)_2$ (*N*-triflylguanidines). Some other examples demonstrating the reactivity of $\text{CF}_3\text{SO}_2\text{N}=\text{C}(\text{SMe})_2$ are given below.²⁵²

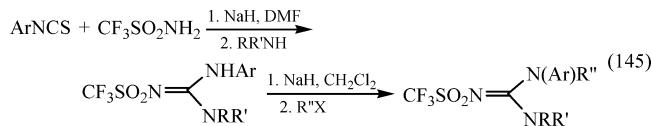


As mentioned above, the splitting of bis(trifluoromethyl)-disulfide with $\text{CF}_3\text{SO}_2\text{NCl}_2$ results in sulfinimidoyl chloride $\text{CF}_3\text{SO}_2\text{N}=\text{S}(\text{CF}_3)\text{Cl}$.⁷⁴ When treated with potassium trimethylsilanolate, it affords potassium *N*-(triflyl)-trifluorosulfinimidate from which the free *N*-(triflyl)-trifluorosulfinimidic acid was recovered by acidification with concentrated sulfuric acid or by passing through H⁺-cationite.²⁵³ From the data of ¹H NMR and IR spectroscopy, the acid exists predominantly in the NH- rather than OH-form.²⁵³

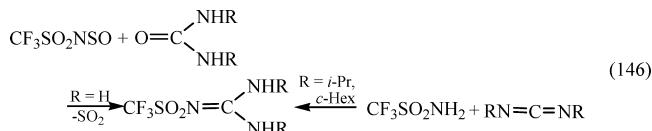


N-Triflylguanidines and their perfluoroalkanesulfonyl analogues $(\text{R}_2\text{N})_2\text{C}=\text{NSO}_2\text{R}_F$ are interesting from the synthetical point of view because they are efficient reagents for the

guanidinylation of amines and from the structural point of view as push–pull imines. First *N*-triflylguanidines with protecting groups at the amine nitrogen atoms were synthesized from the properly diprotected guanidines and triflic anhydride.^{254–256} Different *N*-triflylguanidines were synthesized by Yagupolskii and co-workers using substrates that already contained the $\text{CF}_3\text{SO}_2\text{N}=$ moiety.^{105,248,249,252} A one-pot method for preparation of trisubstituted *N*-triflylguanidines was suggested by the reaction of aryl isothiocyanates with triflamide followed by treatment with secondary amines.²⁵⁷ The tetrasubstituted derivatives were obtained by alkylation of the remaining NH group. Most recently, we have proposed two new approaches to



the synthesis of *N*-triflylguanidines in practically quantitative yield from the reaction of *N*-sulfinyltriflamide ureas and by addition of triflamide to carbodiimides.^{220,258}



For the compound with R = cyclohexyl, an X-ray structure was obtained (Figure 3)²²⁰ that proved the presence of the H-

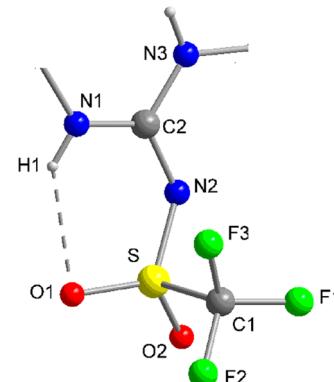


Figure 3. Molecular structure of 1,3-dicyclohexyl-2-(triflyl)guanidine.²²⁰ The O1···H1 distance is 2.14 Å.

bond with one of the amino groups in accordance with the results of NMR and IR spectroscopy.²⁵⁸ The ¹H NMR spectrum contains two NH signals in 1:1 ratio: a narrow peak at 6.77 ppm and a broad singlet at 8.82 ppm belonging to the free and the intramolecularly H-bonded amino groups, respectively. Comparison of the IR spectra in the solid state and solutions of different concentrations in different solvents also supports the presence of the intramolecular hydrogen bond (for details, see ref 258).

The geometry of the guanidine fragment of the molecule in Figure 3 is very similar to that of (2'-*i*-propoxycarbonyl-1'-difluoromethyl)sulfonylbis(dimethylamino)imine.¹⁶⁶

We have compiled all available structural data for *N*-triflylguanidines and related compounds (Table 5). Analysis of the data in Table 5 reveals the most interesting feature of *N*-triflylguanidines and related compounds. This is a longer C–N

Table 5. C–N Bond Lengths (Å) in the Molecules Containing the $\text{NH}-\text{C}=\text{NTf}$ Moiety (NH¹ Refers to the NH Group Forming the N–H \cdots O=S Hydrogen Bond, Where Possible)

Entry	Molecule	C–NTf	C–N ¹	C–N ²	Ref.
1		1.358(2)	1.329(2)	1.325(2)	220
2		1.347	1.336	1.335	166
3		1.341	1.302		249
4		1.315	1.307		248
5		1.351	1.335	1.330	105
6		1.341	1.337	1.342	259
7		1.334 1.344	1.347 1.335	1.334 1.340	259
8		1.310	1.374	1.344	255

^aMorpholinium cation as a counterion.

distance for the formally double C2–N2 bond relative to the formally single C2–N1 and C2–N3 bonds (entries 1–5). This clearly points to a very strong conjugation of the N1 and N3 lone pairs with the C=NSO₂ moiety.

For entries 6 and 7, the “imine” and “amine” bonds are practically equal or very close in length. Therefore, there is only one clear-cut instance of a “normally” shorter C=NTf bond as compared to the C–N bonds (entry 8), which is realized in the molecule, in which the conjugation of the lone pairs of the N1 and N2 atoms with the *t*-Boc group diminishes their conjugation with the azomethine C=NTf group.

Another indication of specific interactions in *N*-triflylguanidines comes from the analysis of the crystal packing of phenylhydroxamic acid triflimide TfN=C(Ph)NHOH.²⁴⁸ In spite of a low basicity of the sulfonamide oxygen atoms, the molecules in the crystal are bound by N–H \cdots O=S and O–H \cdots O=S intermolecular hydrogen bonds, with the azomethine nitrogen atom not being involved in the hydrogen bond formation. This is indicative not only of a strong conjugation of the amino group with the C=N bond but also of a significant shift of the electron density from the N–C=N fragment to the triflyl group.

Quantitative estimation of the effect of the triflyl group for compound number 1 in Table 5 at the MP2/6-311G(d,p) level of theory gave the energy of the (n_{N1} + n_{N3}) \rightarrow π^* _{C=N2} interaction of 219.4 and 28.6 kcal/mol for compound number 1 in Table 5 and for 1,3-dicyclohexylguanidine, respectively. Even if to add the value for the (n_{N1} + n_{N3}) \rightarrow σ^* _{C=N2} interaction (which is absent in triflyl guanidine), the corresponding values are 219.4 and 70.7 kcal/mol, that is, the effect of the triflyl group amounts to \sim 150 kcal/mol.²²⁰

4. SALTS AND IONIC LIQUIDS WITH TRIFLAMIDE AND TRIFLIMIDE ANIONS

Consideration of triflimide ionic liquids (ILs) as such is beyond the scope of the present review. Nevertheless, because it is the ILs with the triflimide anion that have been recognized as being low viscous, being highly conductive, and having the lowest melting points, that is, possessing the main advantages of ILs, it seems reasonable to give here a brief survey of the methods of synthesis and properties of these compounds. There are a number of reviews on the synthesis, characterization, and applications of ILs with fluorinated anions, in particular, with the triflimide and related anion,^{5,260–270} so we refer the reader to these reviews for more details and references and will focus here on specific questions raised in recent studies concerning the ILs with triflimide and related anions.

It is worth mentioning that different molecular-simulation approaches allowing for the prediction of different properties of the triflimide-containing ILs were recently suggested.^{271,272} The triflimide anion in ILs can adopt either cis or trans conformation²⁷³ (Figure 4); in the liquid the predominant form is trans,^{273,274} although in the crystal it is cis²⁷⁵ (apparently due to packing effects).

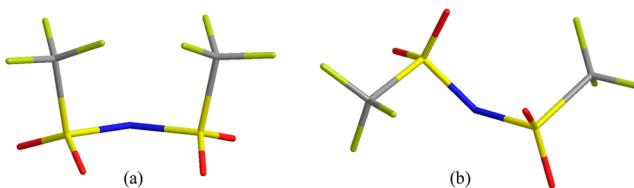


Figure 4. Cis (a) and trans (b) conformations of the triflimide anion.

The calculated potential energy maps for the perfluoroalkyl groups rotation relative to each other about the S–C bonds in the isolated anion Tf₂N[–] [as well as in (C₂F₅SO₂)₂N[–] and Tf₂SO₂CF₃[–]] show only small energy barriers for the rotation.²⁷⁶

1-Ethyl-2-methyl-3-benzyl-imidazolium triflimide was the first triflimide salt whose structure was determined by single-crystal X-ray diffraction, and the absence of strong hydrogen bonds between the cation and anion was shown.²⁷⁷ Later on, a single-crystal X-ray structure was reported for two low-melting (down to -10.8 °C) triflimide ILs; the triflimide anion may adopt either the cis or trans conformation.²⁷⁸

Most of the known ILs containing the triflimide or related anions are alkylimidazolium-based,^{266,279–281} although the triflimide salts of other types of cations such as pyrrolidinium,²⁸² imidazolinium (including chiral ILs),²⁸³ triazolium, oxazolidinium, pyridinium, morpholinium, phosphonium, etc. are also known.^{264,284} Specific properties of the triflimide anion, which are responsible for low melting points of the triflimide ILs, are its nonspherical shape, high degree of fluorination, and a highly diffuse negative charge.⁵ For example, the latter effect (the size of the anion and delocalization of the charge over 11 electronegative atoms: nitrogen, four oxygens, and six fluorines) results in the hydrogen-bonding affinity decreasing from chloride to hexafluorophosphate and triflimide salts of 1,3-dimethylimidazolium.²⁷³ At the same time, the association of the anion with the π -system of the ring was found to increase with the size of the anion and the decrease in the charge density, that is, in the order Cl[–] < [PF₆][–] < [NTf₂][–].²⁷³ In some cases, the use of asymmetric 2,2,2-trifluoro-*N*-triflylace-

tamide anion $[\text{TfNC(O)CF}_3]^-$ strongly reduces the melting points of the salts even with small aliphatic quaternary ammonium cations making them liquid at room or even lower temperatures (RTILs).²⁸⁵

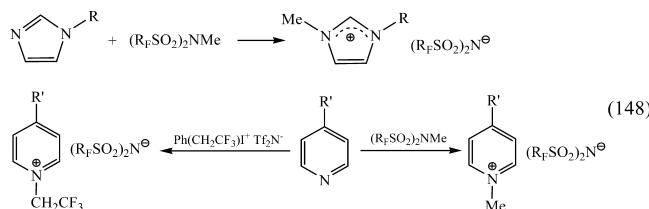
Another advantage is high conductivity and prevention of hydrolysis of the lithium anode in lithium–air batteries. For example, the cell using IL consisting of 1-ethyl-3-methyl imidazolium cation and triflimide anion showed the best electrolyte performance; it worked for 56 days in air, and the cathode carbon materials showed high discharge capacity of 5360 mAh g⁻¹.²⁸⁶

A large series of RTILs on the basis of imidazolium cations and symmetric and asymmetric bis(perfluoroalkanesulfon)amides $\text{R}_\text{F}\text{SO}_2\text{NHSO}_2\text{R}'_\text{F}$ was synthesized in good yield. They showed high densities and a wide temperature range for the liquid state.²⁸⁷

Normally, the triflimide anion is introduced in ILs by the metathesis reaction of the corresponding halogenide (or, sometimes, triflate) ILs with lithium salt of triflimide, $(\text{CF}_3\text{SO}_2)_2\text{NLi}$.^{260,264,284,288–296} In spite of the fact that this route is multistep and requires the removal of metal halogenides, it is still preferable in most cases.

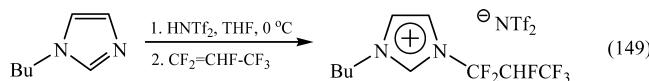


An alternative approach is the direct alkylation of free organic bases (*N*-alkylimidazoles and pyridines) with separately prepared *N*-methyl-bis(perfluoroalkanesulfonyl)imides $(\text{R}_\text{F}\text{SO}_2)_2\text{NMe}$ ($\text{R}_\text{F} = \text{CF}_3, \text{C}_4\text{F}_9$) or phenyl(trifluoroethyl)-iodonium triflimide $[\text{Ph}(\text{CF}_3\text{CH}_2)\text{I}]^\text{+}(\text{CF}_3\text{SO}_2)_2\text{N}^-$.²⁹⁷ Recently,



N-benzyltriflimide and *N*-allyltriflimide were also shown to be good alkylating reagents, either via the oxonium intermediate (after treatment with ethanol) or by direct neutralization with organic basis.^{115,298}

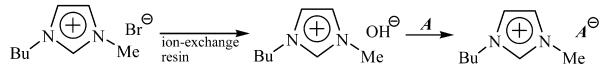
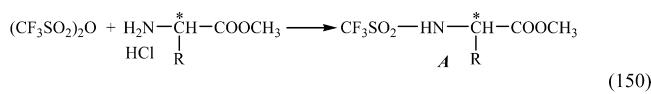
Another route employed for the one-pot synthesis of 1-alkyl-3-polyfluoroalkyl imidazolium ILs is the reaction of 1-alkylimidazole with fluoroalkenes in the presence of triflimide.²⁹⁹ On the example of various metal salts of triflimide,



an interesting and unusual (from the classical point of view) effect was discovered. The triflimide salts of Ag, Al, Co, Ni, and Y were shown to be readily soluble in triflimide imidazolium ILs.²⁹⁶ This is in sharp contrast with the known problem of very limited solubility of metal salts in a number of ILs. Moreover, because this is the case for salts and ILs having different anions, the presence of a common anion, by analogy with aqueous solvents, must further decrease the solubility according to the so-called “common ion” effect. The observed behavior allowed the authors to conclude that (i) care must be taken when applying concepts typical of molecular liquids to

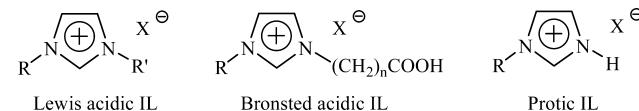
explain phenomena occurring in ILs and (ii) the solution of a metal salt in an IL having the same anion gives a sort of liquid organic–inorganic mixed salt that can be considered as a new ionic system (ionic liquid).³⁰⁰

The chirality to an IL can be imparted by the presence of a chiral center not only in the cation^{301,302} but also in the anion. For the triflimide-based ILs, such an approach was realized by Fukumoto and Ohno, who synthesized *N*-triflyl derivatives of optically active amino acids and used them for the synthesis of chiral ILs.³⁰³



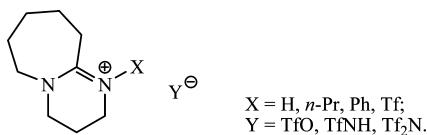
Because the key characteristic of the anion in IL, responsible for its low-melting point, is delocalization of the negative charge decreasing the interionic interactions, asymmetric anions of the type $[\text{CF}_3\text{SO}_2\text{NCOCF}_3]^-$ should also provide the same effect as triflimide anion. Indeed, ILs with this and various unsymmetrical bis(perfluoroalkanesulfonyl)imides were synthesized and shown to have lowered both the melting points and viscosities.^{115,263,266,303–306}

Mostly, ILs are aprotic and cannot dissociate to the conjugate base of the cation and free acid; in terms of a recent review,³⁰⁷ they are “Lewis acidic ILs”, as distinct from “Brønsted acidic ILs”, which can act as proton donors. The Brønsted acidic ILs, in turn, can be subdivided into those having an acidic function (like COOH or SO₃H) in the side-chain of the cation and the so-called protic ILs (PILs) having the protonated organic cation.



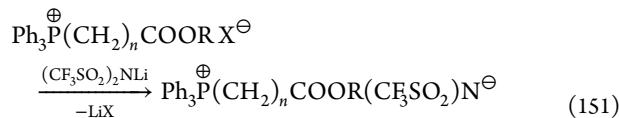
PILs are formed through the transfer of a proton from a Brønsted acid to a Brønsted base.²⁶⁹ The cations most commonly used in PILs are ammonium ions, imidazolium ions, caprolactam, and guanidinium ions. Among a variety of anions coupled with these cations are triflimide anion and its higher analogue, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$.²⁶⁹ It is clear that PILs can be considered as real ILs only if the degree of proton transfer is close to 100%, or, as was questioned by MacFarlane and Seddon, “how high does the degree of proton transfer have to be, in order for the substance to be properly termed an ionic liquid?”³⁰⁸ Taking into account very good charge delocalization in triflimide and related ions, they are the best candidates for this purpose. A very recent example is triethylammonium triflimide PIL, which showed good thermal and transport properties and was found to exhibit good performances as promising electrolyte for supercapacitor applications.³⁰⁹ Triflamide, triflimide, and triflate salts and ionic liquids based on DBN (1,5-diazabicyclo[4.3.0]non-5-ene) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) have been synthesized by us either by direct protonation of the corresponding bases DBN and DBU or by the metathesis reaction of the corresponding chloride ILs with lithium triflimide.³¹⁰

Investigation of their solubility in water and organic solvents confirmed hydrophobic character of the triflimide salts, which are insoluble in water but readily soluble in ethanol, acetone,



acetonitrile, chloroform, and methylene chloride.³¹⁰ We have tried preparation of the DBN- and DBU-based ILs by the direct reaction of the corresponding bases with *N*-phenyltriflimide. Unlike the readily occurring $S_{\text{N}}2$ reactions of organic N-bases with *N*-methyl-,²⁹⁷ *N*-benzyl-, or *N*-allyltriflimide,²⁹⁸ the reaction of DBN and DBU with *N*-phenyltriflimide should be strongly hampered. To our surprise, the reaction successfully gave the *N*-phenylated triflimide salts of DBN and DBU.³¹⁰ Because in the previous studies Tf_2NPh with N-bases gave only the products of the triflyl group transfer,⁶ the structure of the products with DBN and DBU was the principal question. The comparison of the ^1H and ^{13}C NMR spectra of the products with those of the starting Tf_2NPh showed strong differences. Thus, in Tf_2NPh the H_p atom resonates in the lowest field (7.6 ppm), whereas in the products it gives the highest field signal (6.9 ppm). The H_o and H_m signals are shifted from 7.4 and 7.5, respectively, to 7.1 ppm. In the ^{13}C NMR spectra a large (>10 ppm) upfield shift of the C_p signal and even larger (>13 ppm) downfield shift of the C_i signal is observed C_n .³¹⁰ The observed changes are consistent with the change of the substituent in the phenyl ring from Tf_2N to the DBN or DBU residue and cannot be explained for the *N*-triflyl salts with the $[\text{TfNPh}]^-$ as the counterion. Considering a possible mechanism of the Ph group transfer from Tf_2NPh , we believe that it cannot proceed via the benzyne mechanism, which is realized only for extremely strong bases (like NH_2^-). As to $S_{\text{N}}1\text{Ar}$ mechanism, the only well-documented example is decomposition of arenediazonium salts. It was suggested³¹¹ also for aryltriflates but was disproved in the latter work.³¹² Therefore, the reaction probably follows the $S_{\text{N}}2\text{Ar}$, which, although disfavored by the absence of acceptor substituents in the ring, is strongly favored by high basicity of DBN or DBU and extremely high nucleofugality of the triflimide residue. However, synthetically, although the ILs obtained were spectroscopically pure, they were dark colored, so this method cannot be recommended for preparative purposes.³¹⁰

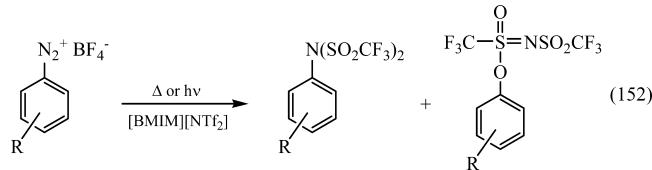
There are only a few recent studies on phosphonium ILs having the triflimide anion.^{293,313,314} For example, triphenylphosphonium triflimide biodegradable ILs were prepared by the metathesis reaction of the corresponding bromides or iodides with lithium triflimide.³¹³



Recently, we have studied the reaction of triflimide with a series of P-nucleophiles and obtained practically quantitative yields of the triflimide salts of triphenylphosphine Ph_3PH^+ Tf_2N^- , triphenylphosphine oxide Ph_3POH^+ Tf_2N^- , triethylphosphite $(\text{EtO})_3\text{PH}^+$ Tf_2N^- , triethylphosphate $(\text{EtO})_3\text{POH}^+$ Tf_2N^- , and dimethyl phosphite $(\text{MeO})_2(\text{HO})\text{PH}^+$ Tf_2N^- .³¹⁵ However, we failed to obtain the products of direct arylation of the studied phosphorus compounds by the reaction with *N*-phenyltriflimide.

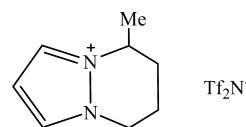
Although the triflimide ILs are generally stable, there is an interesting pattern of reactivity that cannot be omitted from consideration, namely, the decomposition of arenediazonium

tetrafluoroborates in $[\text{BMIM}][\text{Tf}_2\text{N}]$ IL.³¹⁶ Unlike the decomposition of phenyldiazonium tetrafluoroborate in $[\text{BMIM}][\text{Br}]$ IL, which results in bromobenzene as a sole product,³¹⁷ the reaction in $[\text{BMIM}][\text{Tf}_2\text{N}]$ IL gives the products of trapping of the presumed “innocent” Tf_2N^- anion.³¹⁷



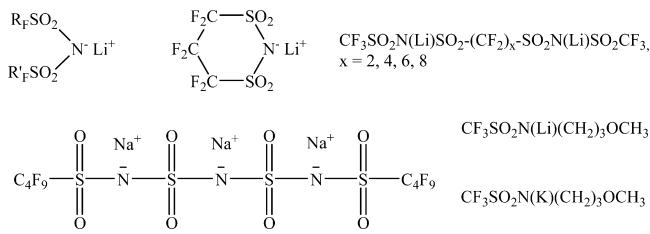
No metathesis reaction resulting in the triflimide diazonium salts (earlier prepared at reduced temperatures from arenediazonium chlorides with triflimide or its sodium salt^{318,319}) was observed. The triflimide anion behaves as an ambident nucleophile, its O-activity being ca. 12 times higher than the N-activity,³¹⁶ which is fully consistent with our estimations of the relative O- versus N-basicity of triflimide.²³

Triflimide ILs are of practical interest as components of lithium batteries, fuel cells, solar cells, solvents for electrodeposition, etc.^{320,321} A comparative critical analysis of the key characteristics of ILs containing Tf_2N^- , $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $[\text{TfNC(O)CF}_3]^-$, and other fluorinated anions, such as mp, density, viscosity, conductivity, transport numbers, diffusion coefficients, etc., was performed to estimate their possible application in aluminum electroplating, lithium batteries, and electrochemical capacitors.³²² In a search for energy-saving technologies, triflimide ILs were examined as solvents for electrodeposition of aluminum metal from solutions of AlCl_3 onto different substrates (glassy carbon, gold, platinum, and iron) at temperatures below 100 °C (as compared to the classical process in molten cryolite bath at 960 °C). The electrodeposition successfully occurs even for moderate concentrations by elevating the temperature to 80 °C.³²³ Similarly, in view of the application for refractory metal electrodeposition, the electrochemical behavior of NbF_6^- , WF_7^- , and VOF_4^- anions was studied in *N*-butyl-*N*-methylpyrrolidinium triflimide IL.³²⁴ The triflimide salt of 5-methyl-5,6,7,8-tetrahydropyrazolo[1,2-*a*]pyridazin-4-iium cation having a disklike shape was the first single-phase, ion-conducting organic plastic crystal. Its conductivity is increased when doped with lithium triflimide.³²⁵

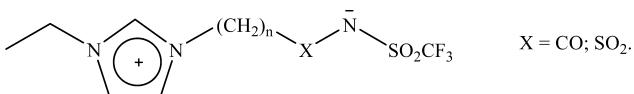


Lithium triflimide salt was extensively studied as a dopant in various electrolytes. As compared to other lithium fluorinated salts (LiBF_4 , LiPF_6 , LiAsF_6 , and LiTf) it has excellent solubility, chemical and thermal stability, and high conductivity, but, at the high oxidation potentials, it corrodes the aluminum electrode collector.^{115,326} Other polyfluorinated lithium and other alkali metal imide salts were also synthesized and examined as new electrolytes.^{327–330}

A number of works were devoted to the investigation of electrolytes prepared by dissolving lithium triflimide in polymers, in particular in poly(ethylene oxide) (PEO).^{331–337} Note that addition of the pyrrolidinium³³⁶ or piperidinium³³⁷ triflimide ILs strongly increases the conductivity of the



electrolytes. New electrolytes were prepared and their solvate structures were studied for the mixtures of Tf_2NLi with urea (RTIL was formed from two solids),³³⁸ monoglyme and diglyme,³³⁹ and succinonitrile.³⁴⁰ In the latter case, only two of a series of the studied lithium salts do not form crystalline adducts at low concentration, namely, Tf_2NLi and LiBF_4 . Triflimide salts of lithium and *N*-methylpyrrolidinium cations upon mixing can form, depending on the ratio of the components, either RTILs or plastic crystalline phases.³⁴¹ 1-Butyl-3-methylimidazolium triflimide-based poly(methyl methacrylate)poly(vinyl chloride) (PMMA–PVC) gel polymer electrolytes were prepared by solution-casting technique and showed the highest ionic conductivity of $8.08 \times 10^{-4} \text{ S cm}^{-1}$ at 80°C for the content of the triflimide salt of 60 wt %.³⁴² From the same polymer, PMMA–PVC conducting thin films, plastisized by lithium triflimide, ethylene carbonate, and propylene carbonate, were prepared and the conductivities were studied as a function of temperature and PVC content.^{343,344} The synthesis, polymerization, and conducting properties of a new IL composed from methacrylate as a polymerizable group, tri(ethylene oxide) as a spacer, and imidazolium triflimide as an ionogen was described. The new IL has shown a good thermal stability and a high ionic conductivity of $2.1 \times 10^{-3} \text{ S cm}^{-1}$ at 20°C ; only a slight decrease of conductivity ($6.5 \times 10^{-4} \text{ S cm}^{-1}$ at 20°C) was observed for the corresponding homopolymer.³⁴⁵ Zwitterions of the type shown below were synthesized, and the properties of their equimolar mixtures with Tf_2NLi were studied to elucidate the effect of the cation, the spacer, and the anion.³⁴⁶

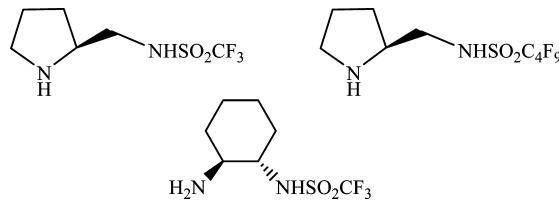


The mixture of high-melting zwitterion and lithium triflimide turned liquid at room temperature and showed an ionic conductivity of $\sim 10^{-5} \text{ S cm}^{-1}$ at 50°C . The modification of the cation site has only a little effect, but the melting point can be lowered by increasing the spacer length; the optimum was found for $n = 5–7$, when the mixtures had high thermal stability and high ionic conductivity.³⁴⁶

5. CATALYSTS WITH TRIFLAMIDE MOIETY

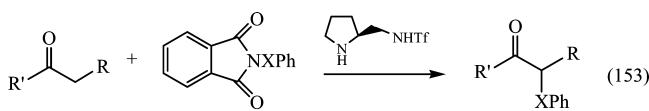
Catalysts containing the triflamide or triflimide moiety are widely used in many reactions, including the Michael addition, Mannich reaction, Friedel–Crafts reaction, Diels–Alder reaction, different coupling reactions, etc. However, to the best of our knowledge, there is no review summarizing the flurry of research on this topic. The present section does not intend to be a comprehensive review of the subject but rather intends to provide illustrative examples and to give appropriate references to facilitate the reader to search for proper information.

Wang et al. used chiral triflamide and nonafluorobutane-sulfonamide derivatives of pyrrolidine and 1,2-diaminocyclohexane



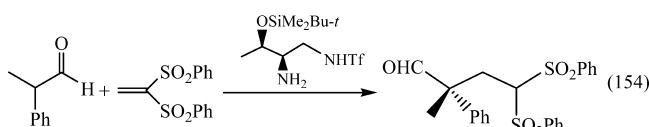
as catalysts for highly enantioselective Michael-type addition reactions,^{347–357} like addition of aldehydes and ketones to nitrosobenzene (α -aminoxylation reaction),³⁴⁷ nitroolefins^{348–351} and benzaldehydes,^{352,353} silyl enol ethers to α,β -unsaturated aldehydes,³⁵⁴ ketones to chalcones,³⁵⁵ cyclohexanones to maleimides,³⁵⁶ or tandem Michael–aldol reaction of 2-mercaptopbenzaldehyde to 3-phenylpropenal to directly form chiral thiochromenes.³⁵⁷ Generally, the developed catalysts are superior to L-proline, typically used for these reactions, in their catalytic activity and stereoselectivity. The analysis of the effect of NH-acidity and H-bonding ability for various amine organocatalysts in the conjugate addition reactions has shown that the most NH-acidic catalyst (the above derivative of 1,2-diaminocyclohexane) is most effective in the catalytic activity and enantioselectivity.³⁵⁸

The above *N*-(pyrrolidin-2-ylmethyl)triflamide also catalyzes α -sulfonylation³⁵⁹ and α -selenenylation³⁶⁰ of a wide series of aldehydes and ketones, being especially efficient (in comparison with L-proline) for the reaction of ketones. As a source of phenylsulfonyl and phenylselenenyl substituents, *N*-(phenylthio)- and *N*-(phenylseleno)phthalimide, respectively, were used.

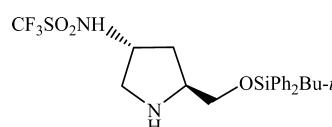


X = S, Se.

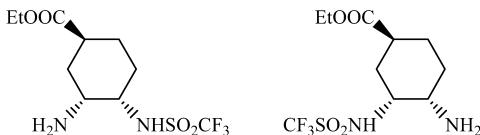
About a dozen novel L-threonine-derived bifunctional organocatalysts containing primary amine and sulfonamide groups were examined in the reaction of asymmetric conjugate addition of α,α -disubstituted aldehydes to 1,1-bis(benzenesulfonyl)ethylene, and the triflamide derivative showed the highest enantioselectivity.³⁶¹ Excellent catalytic



activity and enantioselectivity was shown for the *N*-(3*R*,5*S*)-5-[(*tert*-butyl)(diphenyl)silyloxymethyl]pyrrolidin-3-yl triflamide in the asymmetric Michael addition of cyclohexanone to nitrostyrene.³⁶²

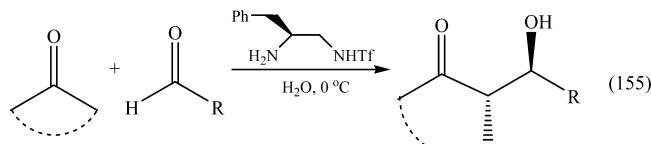


The use of two different chiral triflamide organocatalysts based on *cis*-diaminocyclohexane

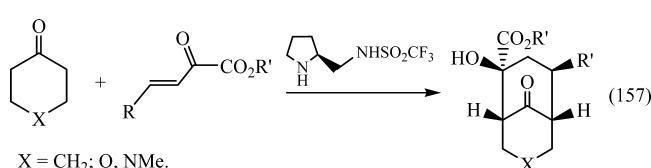
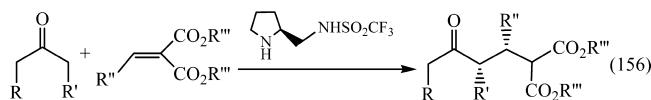


was shown to result in a complete switch of stereoselectivity in asymmetric direct aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde.³⁶³

A similar linear triflamide catalyst, (*S*)-*N*-(2-amino-3-phenylpropyl)triflamide, promoted the direct asymmetric aldol reactions of aldehydes with ketones to afford the anti-aldol products in moderate to excellent yields with up to 97% ee.³⁶⁴

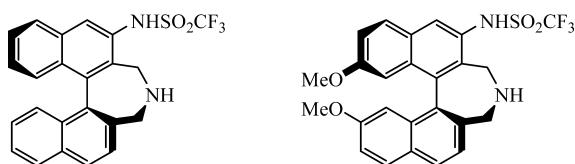


Wang's catalyst, *N*-(pyrrolidin-2-ylmethyl)triflamide, was successfully used in the Michael addition of ketones to alkylidene malonates³⁶⁵ and for one-step construction of bicyclic skeletons with four chiral centers.³⁶⁶ Another chiral triflamide, 2-

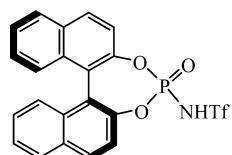


X = CH₂; O, NMe.

triflamido-4,5-dihydro-3*H*-naphtho[2,1,19,18-*cde*]azepine³⁶⁷ and its 10,13-dimethoxylated analogue,³⁶⁸ were shown to be efficient catalysts for the asymmetric Mannich reaction³⁶⁷ and aldol condensation.³⁶⁸



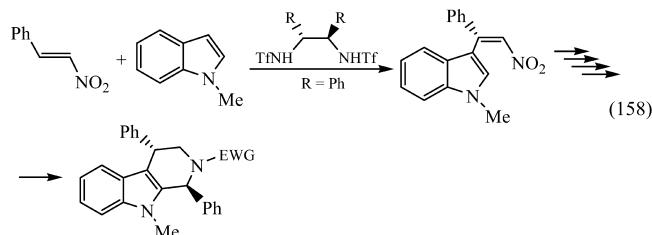
That the catalytic and stereoselective activity of triflamide catalysts is as a result of their strong NH-acidity was proved in a number of works.^{369–371} Yamamoto and co-workers have synthesized a novel chiral Brønsted acid catalyst,³⁶⁹ which exerted good catalytic activity and enantioselectivity in the asymmetric Diels–Alder reaction³⁶⁹ or enantioselective 1,3-dipolar cycloaddition of nitrones to ethyl vinyl ether.³⁷⁰



Later it was shown that, while the BINOL-derived phosphoric acid diesters are not effective in the reaction of Brønsted acid-catalyzed nucleophilic substitution of γ -hydrox-

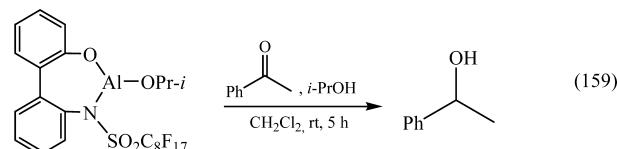
ylactams with indole, more acidic *N*-triflyl-substituted analogues afford the desired products in good yield.³⁷¹

Chiral 1,2-bis(triflamido)-1,2-diphenylethane was developed by Jørgensen and co-workers as the most effective catalyst for enantioselective Friedel–Crafts-type addition of indoles to nitro-olefins for the synthesis, finally, of optically active tetrahydro- β -carbolines.³⁷² The same group showed the above



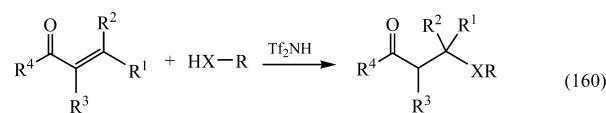
catalyst and its analogues with R = *t*-Bu and *cyclo*-Hex to be good catalysts for the Mukaiyama-aldol, hetero-Diels–Alder, and Friedel–Crafts reactions of carbonyl compounds.³⁷³

The Meerwein–Ponndorf–Verley reduction of ketones with hydrogen transfer from *i*-PrOH on aluminum alkoxide catalysts containing the triflamide or perfluoroalkanesulfonamide moiety was shown to be much more effective on nonfluorinated analogues with the yield up to 99%.³⁷⁴



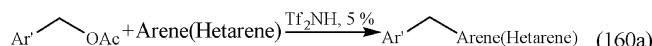
Bis[chloro(methyl)aluminum]triflamide TfN[Al(Me)Cl]₂, which is a catalyst of the same type, was efficient in catalysis of intramolecular Diels–Alder reaction.^{375–377} In the latter cases,^{374–377} the perfluorosulfonylamido-containing catalysts have no NH group and act not as Brønsted acids but rather as strong Lewis acids due to the increased electron deficiency of the metal center under the action of the electron-acceptor perfluorosulfonylamido group.

Triflimide Tf₂NH and its derivatives also display catalytical activity in different reactions. Thus, it catalyzes the hetero-Michael addition of alcohols, thiols, and carbamates to α,β -unsaturated ketones, alkylidene malonates, and acrylimides. The scope, reaction rates, and yields were shown to be superior to a number of mineral, carboxylic, and sulfonic acids, including triflic acid.³⁷⁸ Triflimide was found to efficiently catalyze the



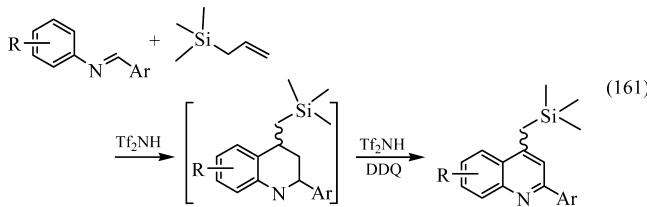
X = O, S, NH.

formation of a wide diversity of diaryl- and aryl(hetaryl)-methanes from benzylic acetates and arenes or heteroarenes.³⁷⁹

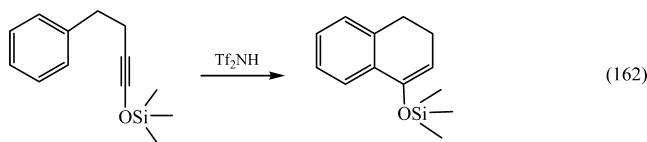


The reaction is catalyzed equally effectively by triflic acid, except for some hetaryl esters, like 2-thienylacetate, for which, with triflimide as a catalyst, the yield was 98%, whereas with triflic acid no reaction occurred.³⁷⁹

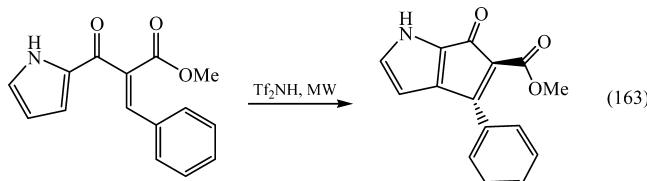
[2 + 2]-Cycloaddition of methyl acrylate to silyl enol ethers of cyclohexanone is catalyzed by triflimide to afford the correspondingly substituted [4.2.0]octanes in almost quantitative yield.³⁸⁰ Similarly, triflimide catalyzes the [2 + 2]-cycloaddition of allylsilanes to electron-deficient olefin to afford cyclobutane derivatives,³⁸¹ their [3 + 2]-cycloaddition of aldimines to give pyrrolidines,³⁸² and the formation of quinolines via the one-pot sequence of hetero-Diels–Alder reaction and oxidative aromatization promoted by DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone).³⁸³



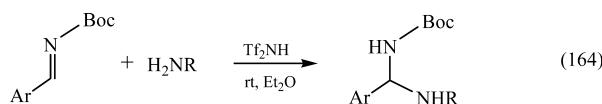
Kozmin and co-workers in a series of works summarized in ref 384 have developed a general approach to the formation of the C–C bond based on Brønsted acid-mediated activation of siloxy alkynes, followed by interception of the formed ketenium ion by arenes, alkenes, or alkynes. They found Tf₂NH to be a superior promoter of these reactions compared to a range of other Brønsted acids due to its high NH-acidity and low nucleophilicity of the conjugate anion, as exemplified in eq 162.



The triflimide-catalyzed new C–C bond formation occurs also in the MW-assisted Nazarov reaction of pyrrole derivatives to give cyclopenta[*b*]pyrrole derivatives in excellent yields with high trans selectivity.³⁸⁵ New C–N bond formation by the

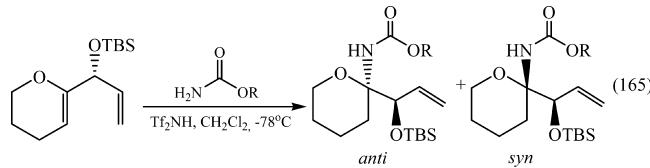


reaction of N-protected aldimines with various amides, sulfonamides, and carbamates catalyzed by triflimide proceeds under mild conditions in up to quantitative yields.³⁸⁶



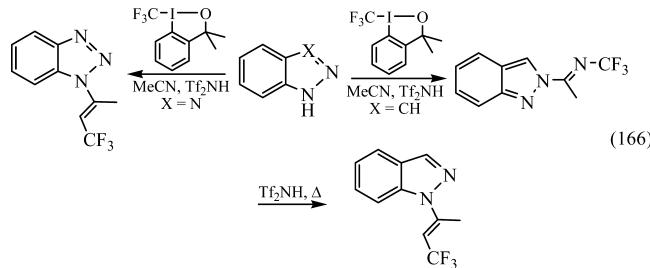
Anomeric substitution of the dihydropyran derivative with O-alkylcarbamates catalyzed by Tf₂NH proceeds stereoselectively with the diastereoselectivity increasing with the concentration of the catalyst up to anti/syn of 50:1.³⁸⁷

Other Brønsted acids were either ineffective or (at higher temperatures) gave a low yield of the product.³⁸⁷ Triflimide showed very specific catalytic activity in the reaction of ring-opening polymerization of cyclic siloxane [Me₂SiO]₄; no

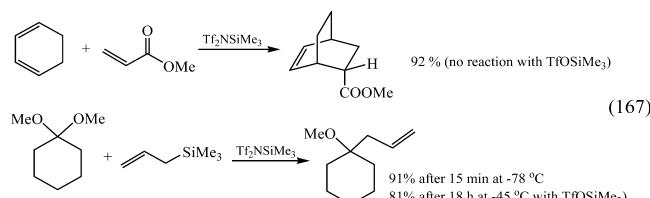


reaction occurred in the presence of Tf₂O, TfOSiMe₃, Tf₂NLi, or Tf₂NSiMe₃.³⁸⁸

Benzotriazole and indazole undergo the triflimide-catalyzed Ritter-type reaction with acetonitrile. In the latter case, the originally formed 2-substituted product is smoothly converted to its regiosomer, also catalyzed by triflimide.³⁸⁹ Triflimide has been reported to effectively catalyze other C–C bond-forming reactions such as Friedel–Crafts, Mukaiyama, 1,2- and 1,4-addition, and C-glycosidation reactions.³⁹⁰



N-Trimethylsilyltriflimide is a triflimide-based catalyst acting as a Lewis acid similar to a well-known catalyst TMS-triflate. In some cases Tf₂NSiMe₃ is superior to TfOSiMe₃ as a carbonyl-activating reagent, as in the Diels–Alder reaction of 1,3-cyclohexadiene and methyl acrylate³⁹¹ or in allylation of dimethylacetal of cyclohexanone with allyltrimethylsilane.³⁹²



N-Trimethylsilyltriflimide was also used as a strong Lewis acid catalyst for the Mukaiyama–aldol and Sakurai–Hosomi allylation reactions^{393,394} and, formed in situ, for conjugate allylation of α,β -unsaturated carbonyl compounds with allyltrimethylsilane.³⁹⁵

Metal salts of triflimide represent a special and extensively developing class of Lewis acid catalysts. They often surpass their metal halide or triflate analogues in the catalytic activity due to the fact that the negative charge on the oxygen atom in triflates is delocalized to one triflyl group whereas the negative charge on the nitrogen atom in triflimides is delocalized to two triflyl group (by the same reason, the gas-phase acidity of triflimide is higher than that of triflic acid, although in solution it is reversed due to solvation effects). The literature on metal triflimides is vast and cannot be reviewed here; luckily, recently, an excellent review on this subject has been published.³⁹⁶ Therefore, in addition to the works already cited,^{43–48} only several later publications and some works not covered in this review³⁹⁶ will be considered below.

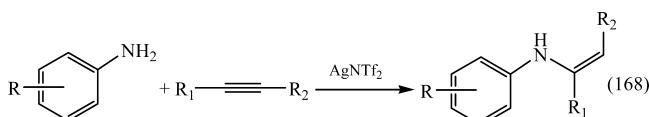
Although metal salts M(NTf₂)_n are usually water-tolerant; some reactions catalyzed by them are water-sensitive, so often anhydrous salts are required. The procedures described in the

review in ref 396 or published by the same group independently³⁹⁷ include (i) the reaction of an organometallic compound R_nM or Ph_nM with $HNTf_2$ with evolution of alkanes or benzene, (ii) electrochemical dissolution of the desired metal in the presence of triflimide with evolution of dihydrogen, or (iii) oxidative dissolution of metal powders in the presence of triflimide affording anhydrous salts as solvates with DMSO molecules.

In addition to various cyclization, rearrangement, alkylation, and acylation reactions of formation of C–C and C–heteroatom bonds,³⁹⁶ some other applications of the triflimide metal salts should be mentioned. Thus, $Yb(NTf_2)_3$ and triflimide itself^{398,399} as well as *N*-trimethylsilyltriflimide⁴⁰⁰ were shown to be good catalysts for glycosidation reactions.

In a series of works, Nishikido and co-workers developed new catalysts, like $Sn(NTf_2)_4$, $Sc(NTf_2)_3$, $Yb(NTf_2)_3$, $Hf(NTf_2)_4$, and its higher fluorinated analogue $Hf[N-(SO_2C_8F_{17})_2]_4$,⁴⁰¹ working in recyclable fluorous media for Baeyer–Villiger oxidation, Diels–Alder reaction, esterification and transesterification reactions, and Friedel–Crafts acylation;⁴⁰² these studies were summarized in two reviews.^{403,404}

$Hf[N(SO_2C_8F_{17})_2]_4$ salt was shown to be the best catalyst (as compared to other metal salts) for the Hantzsch synthesis of polyhydroquinoline derivatives.⁴⁰⁵ The construction of benzofuran,⁴⁰⁶ 4-hydroxycoumarin,⁴⁰⁷ and 1,5-benzodiazepine⁴⁰⁸ frameworks with the use of $AuNTf_2$ or $AgNTf_2$ catalysts was described. The use of $AgNTf_2$ was recently shown to result in highly regioselective intermolecular hydroamination of a large series of internal alkynes with anilines.⁴⁰⁹



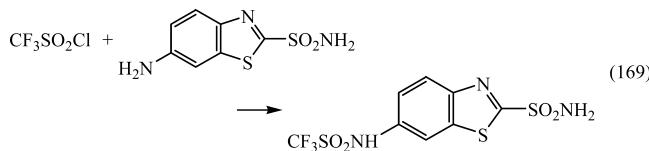
6. BIOLOGICAL ACTIVITY OF TRIFLAMIDE DERIVATIVES

The increase of biological activity on going from nonfluorinated to fluorinated sulfonamides was discovered about 40 years ago; these works are partly referred to in the earlier review.¹ The biological activity of triflimide derivatives to a great extent is due to their lipophilicity imparted by the presence of the CF_3SO_2NH moiety, and their high acidity, although the latter often has the opposite effect and leads to inactivation of the triflimide derivatives relative to their less acidic analogues. It is a topic of a separate review to cover all aspects of biological activity of tremendously numerous triflimide derivatives. Therefore, it is not a goal of this section to present a complete overview of all biologically active triflamides; rather, we will concentrate on selected examples of specific and/or especially high activity, referring mainly to the last two decades. The papers in which the triflimide and its derivatives were used only as intermediates for the synthesis of the target compounds (like *N*-phenyltriflimide as a widely used triflating agent) are not discussed here, either.

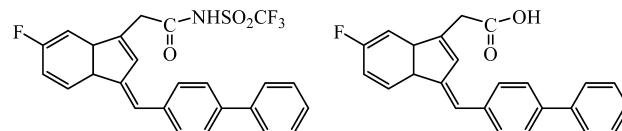
Lipophilicity of triflamides makes them good uncouplers, that is, compounds that facilitate the transfer of protons from the mitochondrial inner-membrane space into the mitochondrial matrix. For a series of *N*-aryl triflamides $CF_3SO_2NHC_6H_4X-p$, the uncoupling activity was tested in rat liver mitochondria. RCI_{50} concentrations (respiratory control index) varied from 0.67 to $>1000 \mu M$; the triflamides with $X =$

Cl and CH_2CF_2O substituents showed the best results.⁴¹⁰ Triflimide itself and its metal (alkali, alkaline-earth) and organic (amine) salts were patented as antiglaucoma drugs.⁴¹¹

A series of the zinc and copper complexes of the *N*-substituted triflamides with the sulfonamide moiety in the chain was synthesized and showed good inhibitory activity against isozymes of carbonic anhydrase.⁴¹² Later on, the same group of Supuran synthesized and tested a large library of triflimide, perfluoroalkanesulfonamide, and pentafluorobenzenesulfonamide derivatives of aromatics and heteroaromatics with the sulfonamide moiety in the chain, as exemplified for the triflimide derivative of 6-aminobenzo[*d*]thiazole-2-sulfonamide in the scheme in eq 169. A number of them has demonstrated good inhibitory properties against isozymes I, II, and IV of carbonic anhydrase⁴¹³ and of murine mitochondrial isozyme carbonic anhydrase.⁴¹⁴

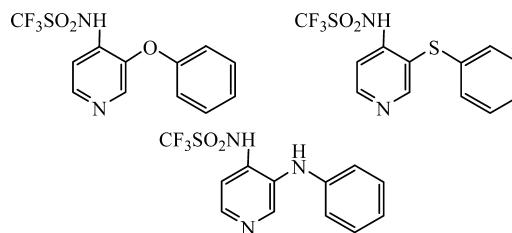


The triflimide derivative below (mixed imide of triflic and carboxylic acids) as well as its precursor, the free carboxylic acid itself, are representatives of nonsteroidal anti-inflammatory drugs (NSAIDs).



The former compound was recently shown to be most active in inhibition of cyclooxygenase COX-1 ($IC_{50} = 470 \text{ nM}$), which is of prime importance in the background for the gastric ulcerogenic response to NSAIDs.⁴¹⁵

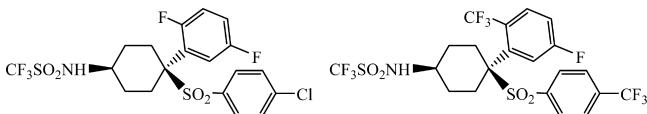
Earlier, *N*-(3-phenoxy-4-pyridinyl)trifluoromethanesulfonamide³⁷⁵ and its analogues with $-S-$ and $-NH-$ linkers^{416–419}



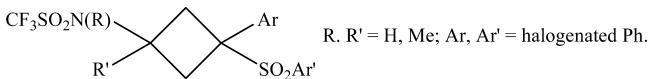
were synthesized in five steps starting from 3-bromopyridine and showed in vitro (whole-blood assay) a strong inhibitory activity on the cyclooxygenase enzymes COX-1 and COX-2 ($IC_{50} = 2.2$ and $0.4 \mu M$, respectively⁴¹⁶).

N-[*cis*-4-[(4-Chlorophenyl)sulfonyl]-4-(2,5-difluorophenyl)cyclohexyl]triflimide (MRK-560)^{420,421} and *N*-[*cis*-4-[(4-trifluoromethylphenyl)sulfonyl]-4-(2-trifluoromethyl-5-difluorophenyl)cyclohexyl]triflimide⁴²² were shown to be highly potent compounds that strongly lower the level of Alzheimer's amyloid- β peptides in brains and cerebrospinal fluid by inhibiting the activity of γ -secretase responsible for generating the $A\beta$ protein.

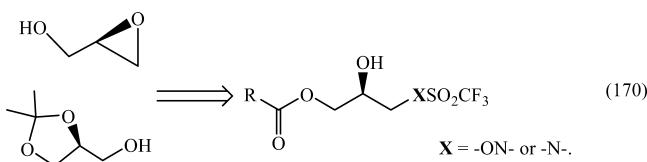
Recently, a new class of the cyclobutane triflimide derivatives inhibiting the processing of the amyloid proteins by the



putative γ -secretase and, thus, useful in the treatment or prevention of Alzheimer's disease was patented.⁴²³



New triflamido or oxytriflamido-containing therapeutically potent phosphomimetics of lysophosphatidic acid (LPA) and phosphatidic acid (PA) were synthesized starting from *R*-glycidol and *S*-solketal.⁴²⁴



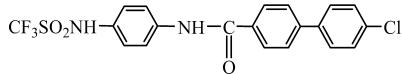
The angiotensin II antagonists of the general type of *N*-[(quinolin-2-yl)phenyl]sulfonamides were patented as compounds with great potential as a remedy for hypertension.⁴²⁵ Among the 3*H*-imidazo[4,5-*b*]pyridine derivatives of the similar quinoline-based compounds patented as preventives or remedies for muscle tissue degenerations, the triflamide derivative was proved to be the most preferable in terms of prophylaxis and treatment effect.⁴²⁶



Various biphenyl triflamide derivatives have been also tested as angiotensin II antagonists.^{427,428}

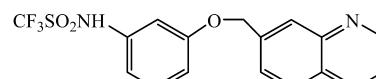
Compounds possessing inhibitory properties with respect to carbonic anhydrase (enzyme that catalyzes the rapid interconversion of CO₂ + H₂O to H⁺ + HCO₃⁻) are widely used in the treatment or prevention of many diseases associated with acid-base disequilibria. Although triflamide itself was found to be one of the most potent inhibitors of carbonic anhydrase isozyme,⁴²⁹ its toxicity has denied its clinical development,⁴³⁰ so further studies in this field are supposed to be based on low-toxic triflamide derivatives.

Peroxisome proliferator-activated receptor (PPAR) α agonists are lipid-lowering agents in humans, which prevent the development of diabetes and help to reduce cardiovascular risk. As potent PPAR α agonists, a new family of N-substituted triflamides was synthesized and the in vitro and in vivo studies showed the compound below to be the most potent one.⁴³¹

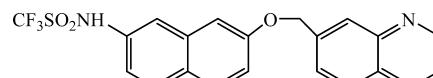


N-[3-(2-Quinolinylmethoxy)phenyl]triflamide and its naphthyl analogue have been shown to be hundreds of times more potent as LTD₄ antagonist (overproduction of leucotriene D₄ is responsible for inflammation in asthma and allergic rhinitis by

causing contraction of bronchial muscles) as compared with the standard (LY-171,883).^{432,433}

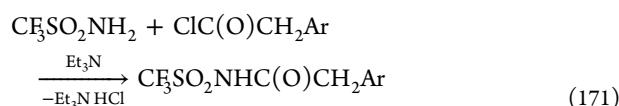


Ritolukast (Wy-48,252)



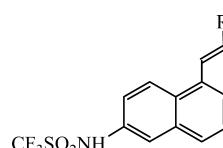
Wy-48,090

N-(Arylacetyl)triflamides, prepared by acylation of triflamide with arylacetylchlorides, exhibited high anticonvulsant activity against maximal electroshock seizures or subcutaneous pentylentetrazol seizures.¹⁰⁶

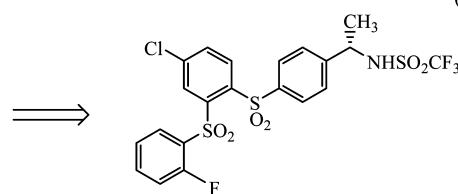
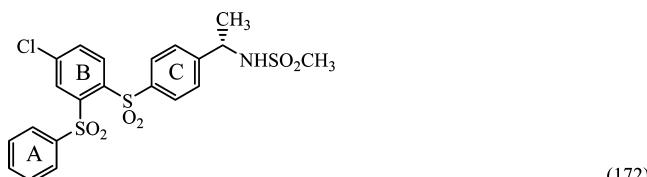


The substituents in the benzene ring did not enhance efficacy, so the unsubstituted compound was chosen as the most attractive drug candidate based on favorable protective index determined as the ratio of the median effective dose to the median toxic dose (PI = ED₅₀/TD₅₀).¹⁰⁶

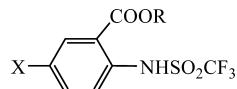
A number of 1,6-substituted naphthalenes was synthesized and examined as selective human cytomegalovirus (HCMV) protease inhibitors (note that HCMV infects ~60% of the population in the developed and >90% in the developing countries).⁴³⁴ For one of the most active inhibitors (R = 6-chloro-2-quinolyl in the structure below), the replacement of the triflamide residue with carboxyl, or amino group, or even methylsulfonamido group, as well as its N-methylation, led to loss of potency.⁴³⁴ Therefore, the presence of strongly acidic NH is an imperative.



In a search for new cannabinoid-2 receptor ligands based on the triaryl bis-sulfone compounds, the A, B, and C ring systems of the previously found (by the same group of researchers) CB2-selective compound were modified and the triflamide derivative was found to be the most promising candidate.⁴³⁵



2-Alkoxy carbonyl trifluorosulfonylanilides of the general formula



were synthesized from the corresponding anilines and triflic anhydride and their miticidal activity was tested.⁴³⁶ The compound with R = Me, X = Cl ("amidoflumet") has been developed as a new miticide for house dust mites, which are known to be the major household allergens to children and the elderly to cause asthma and atopic dermatitis.⁴³⁶

7. CONCLUSIONS

The above analysis of the chemical properties of triflamides and related compounds has shown that the presence of the trifluoromethyl or perfluoroalkyl group may strongly affect the reactivity as compared to the alkyl- or arylsulfonamides. This is clearly exemplified not only by the structural differences, like the planarity of the nitrogen atom in the N-substituted triflamides versus tetrahedral configuration of MeSO_2NH_2 (section 2.2), or by the inversion of the sites of protonation from nitrogen in alkyl- or arylsulfonamides to oxygen in triflamide,²³ but also by the reactions of condensation (section 2.3.4), the inertness of triflamide to strong electrophiles that easily react with other sulfonamides,¹²⁰ the different courses of the reactions with alkenes in the same oxidative system (*t*-BuOCl + NaI),^{187,188} and other specific patterns of reactivity demonstrated by triflamide and its analogues. The reason for such a different behavior is not straightforward. On the one hand, it is clear that this specificity is due to the strong electron-withdrawing effect of the CF_3 group, but on the other hand, the CF_3 group here acts only as a "modifier" of the electronic properties of the RSO_2 group, which itself is a strong electron acceptor. For example, the ^{19}F NMR inductive constants σ_{F} of MeSO_2 , PhSO_2 , and CF_3SO_2 groups are 0.59, 0.63, and 0.84, respectively,⁴³⁷ that is, the "modifying" effect of the CF_3 group is close to that of chlorine as a substituent with respect to hydrogen. So, one may conclude that a strong acceptor effect of the sulfonyl group brings the sulfonamides to such a threshold of reactivity after which even a moderate modifying effect of the CF_3 group may (and does) give rise to the transition from quantity to quality and makes triflamides and related compounds interesting objects for further theoretical and experimental studies.

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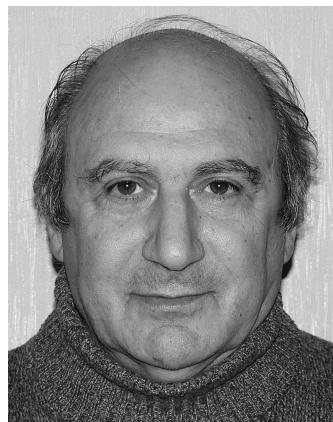
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Notes

The authors declare no competing financial interest.

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