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Trifluoromethyl Sulfones and Perfluoroalkanesulfonamides of the Azole Series

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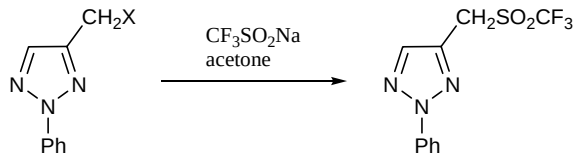
Abstract—2-Phenyl-4-trifluoromethylsulfonylmethyl-2*H*-1,2,3-triazole was synthesized from 4-bromomethyl-2-phenyl-2*H*-1,2,3-triazole and sodium trifluoromethanesulfinate CF_3SO_2Na. 1(2)-Ethyl-4-nitro-1(2)*H*-1,2,3-triazoles and 4-nitro-2-phenyl-2*H*-1,2,3-triazole were reduced to the corresponding amines. Intermediate 1,2-bis(1-ethyl-1*H*-1,2,3-triazol-4-yl)diazene 1-oxide exists as a mixture of *syn* and *anti* isomers, the former being stabilized via formation of a strong intramolecular hydrogen bond. The reduction of 2-ethyl-4-nitro-2*H*-1,2,3-triazole in the presence of HCl afforded the target 4-amino-2-ethyl-2*H*-1,2,3-triazole and also 4-amino-5-chloro-2-ethyl-2*H*-1,2,3-triazole. Treatment of alkyl-substituted 4-amino-1,2,3-triazoles with trifluoromethanesulfonyl chloride and pentafluoroethanesulfonyl chloride gave N-triazolyl-substituted trifluoromethane- and pentafluoroethanesulfonamides and -imides.

Trifluoromethanesulfinic acid salts CF_3SO_2M (M = K, Na) are known to behave as weak ambident nucleophiles. They react with alkyl halides to give products of either O- or S-alkylation, and the former readily rearrange into the latter [1, 2]. Insofar as trifluoromethanesulfinate ion $CF_3SO_2^-$ is a weak nucleophile, the formation of trifluoromethyl sulfones CF_3SO_2R is a slow process which requires elevated temperature, dipolar aprotic solvents, and the presence of activating acceptor groups and good leaving groups in the substrate [3].

In continuation of our studies on trifluoromethyl sulfones of the azole series [4], in the present work we made an attempt to introduce a trifluoromethylsulfonyl group into the side chain of some 1,2,3-triazoles. We have found that 4-halomethyl-2-phenyl-2*H*-1,2,3-triazoles are weakly reactive toward sodium trifluoromethanesulfinate in acetone. The reaction of bromomethyl derivative **Ib** with sodium trifluoromethanesulfinate was slow, and chloride **Ia** failed to react at all (Scheme 1). Triazoles having a chloromethyl group on the nitrogen atom in position *1* or *2* did not react with CF_3SO_2Na. With a view to enhance the nucleofugality of the halogen atom, 1(2)-chloromethyl-4-nitro-1(2)*H*-1,2,3-triazoles were converted into the corresponding iodides via exchange reaction with NaI in acetone. However, compounds **V** and **VI** also failed to replace the iodine atom by trifluoromethylsulfonyl group (Scheme 2).

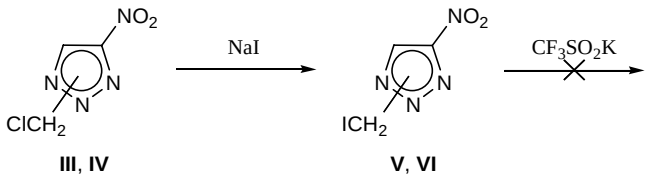
Scheme 1.



Ia, **Ib** **II**

X = Cl (**a**), Br (**b**).

Scheme 2.

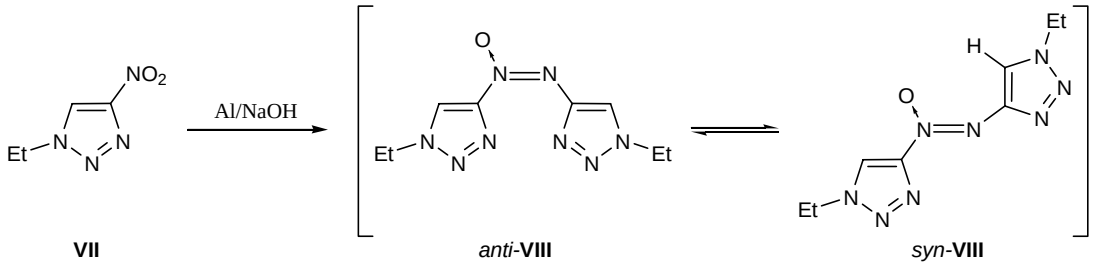


III, **IV** **V**, **VI**

III, 1-CH_2Cl; **IV**, 2-CH_2Cl; **V**, 1-CH_2I; **VI**, 2-CH_2I.

We also tried to obtain trifluorosulfonamides of the azole series via introduction of a trifluoromethylsulfonyl group into exocyclic amino group of 1,2,3-triazoles. For this purpose, we examined the reduction of some nitro azoles under different conditions with the goal of synthesizing the corresponding 1(2)-substituted 4-amino-1,2,3-triazoles. The reduction of

Scheme 3.

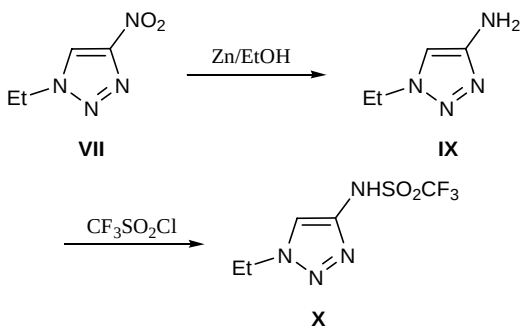


VII *anti*-**VIII** *syn*-**VIII**

1-ethyl-4-nitro-1*H*-1,2,3-triazole (**VII**) with aluminum in alkaline medium gave no desired 4-amino-1-ethyl-1*H*-1,2,3-triazole but incomplete reduction product, 1,2-bis(1-ethyl-1*H*-1,2,3-triazol-4-yl)diazene 1-oxide (**VIII**) (Scheme 3). The formation of azoxy compound **VIII** follows from the ^{1}H and ^{13}C NMR spectra which contain two sets of signals from nonequivalent ethyltriazolyl fragments, as well as from the data of elemental analysis. Compound **VIII** can exist as two isomers, *syn* and *anti*, and the former could give rise to a strong intramolecular hydrogen bond. In fact, from the reaction mixture we isolated a yellow substance. Its solution in chloroform quickly turned colorless, and colorless crystals separated therefrom upon evaporation. The crystals were dissolved in $CDCl_3$, and in the ^{1}H NMR spectrum of the solution were observed strongly different signals from the 5-H protons in the two triazole rings, δ 8.36 and 8.80 ppm. On the other hand, the positions of these signals in the spectra of both products in DMSO-d_6 were almost similar, δ 9.10 and 9.11 ppm for the colorless product and δ 9.10 and 9.12 ppm for the yellow substance. These findings led us to assign *anti* configuration to the yellow isomer and *syn* configuration to the colorless isomer. Being a weakly polar solvent, chloroform stabilizes the less polar *syn* isomer with intramolecular hydrogen bond, which is characterized by strongly different positions of the 5-H signals. Polar DMSO destroys the intramolecular hydrogen bond in the *syn* isomer, and both CH protons are involved in intermolecular hydrogen bond with the solvent; therefore, the positions of their signals differ insignificantly, and they appear in a weaker field than in the spectrum recorded from a solution in chloroform. The transformation *anti*-**VIII** ⇄ *syn*-**VIII** is reversible. This follows from the fact that the solution in DMSO-d_6 (*syn*-**VIII**) turns yellow on storage as a result of displacement of the equilibrium toward more polar *anti* isomer.

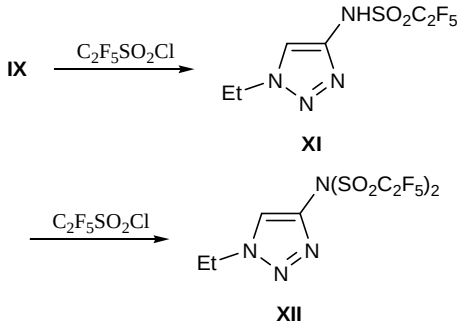
We succeeded in reducing 1-ethyl-4-nitro-1*H*-1,2,3-triazole (**VII**) to 4-amino-1-ethyl-1*H*-1,2,3-triazole (**IX**) using zinc dust in ethanol. Aminotriazole **IX** reacted with trifluoromethanesulfonyl chloride to give *N*-(1-ethyl-1*H*-1,2,3-triazol-4-yl)trifluoromethanesulfonamide (**X**) (Scheme 4). The reaction of aminotriazole **IX** with pentafluoroethanesulfonyl chloride occurred in a similar way, but in this case both mono- and disubstituted products **XI** and **XII** were formed (Scheme 5).

Scheme 4.



VII **IX** **X**

Scheme 5.



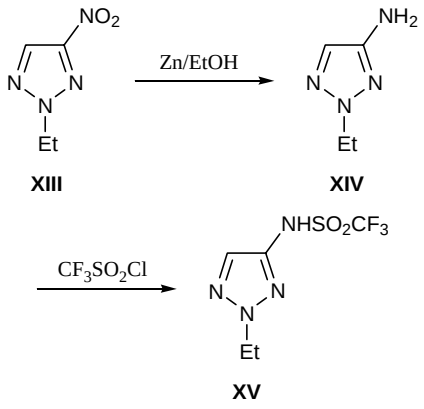
XI **XII**

Unfortunately, we failed to isolate analytically pure samples of compounds **XI** and **XII**; nevertheless, the obtained elemental compositions, C:N:F:S = 6.1:4:4.7:0.8 and C:N:F:S = 8:4:10.6:2.1 for amide **XI** and imide **XII**, respectively, are fairly consistent with the assumed structures. The structure of **XI** and **XII** was also confirmed by the NMR spectra. The ^{1}H NMR spectrum of imide **XII** lacks NH signal, while

signals from the other protons are displaced downfield relative to the corresponding signals of amide **XI**; the downfield shift is the stronger the closer the proton is located to the electron-acceptor $N(SO_2C_2F_5)_2$ group. In the ^{13}C NMR spectrum of imide **XII**, the C^4 signal appears strongly downfield relative to the corresponding signal of amide **XI** ($\Delta\delta_C$ = 16 ppm); as a result, the C^4 signal in the spectrum of **XI** is located in a stronger field than those of the C_2F_5 group, and in the spectrum of **XII**, in a weaker field.

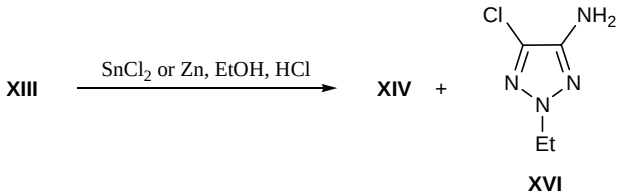
2-Ethyl-4-nitro-2*H*-1,2,3-triazole (**XIII**) was reduced with zinc dust in boiling ethanol in the presence of $CaCl_2$ according to the procedure described in [5]. The resulting 4-amino-2-ethyl-2*H*-1,2,3-triazole (**XIV**) was treated with trifluoromethanesulfonyl chloride to obtain *N*-(1-ethyl-1*H*-1,2,3-triazol-4-yl)trifluoromethanesulfonamide (**XV**) (Scheme 6).

Scheme 6.



When triazole **XIII** was reduced with tin(II) chloride or zinc dust in ethanol in the presence of hydrochloric acid, apart from compound **XIV** we isolated 4-amino-5-chloro-2-ethyl-2*H*-1,2,3-triazole (**XVI**) (Scheme 7). The structure of product **XVI** is confirmed by the presence in the ^1H NMR spectrum of a singlet from protons of the amino group and the absence of 5-H signal. The ^{13}C NMR spectrum (*J*-modulated) of **XVI** contained two signals from quaternary carbon atoms of the triazole ring at δ_C 135 (C^4) and 149 ppm (C^5). Analysis of the reaction

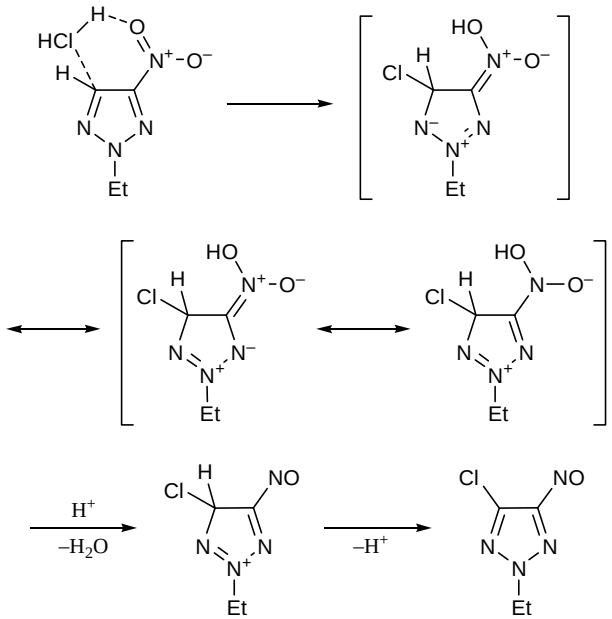
Scheme 7.



mixture by gas chromatography–mass spectrometry showed the presence of two compounds in approximately equal amounts. Compound **XVI** gave the molecular ion peak with *m/z* 146, whose isotope composition corresponded to the presence of one chlorine atom in the molecule.

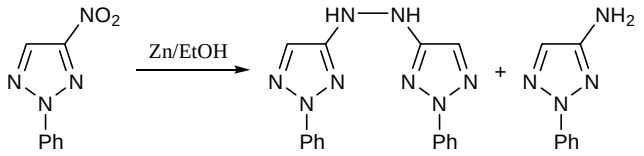
Scheme 8 shows a probable reaction sequence which rationalizes the formation of compound **XVI** using the reaction of nitrotriazole **XIII** with HCl as an example. Obviously, an analogous scheme may be proposed for the reaction of HCl with partially reduced intermediates, e.g., those containing a nitroso or hydroxylamino group. This scheme explains the formation of just 2-ethyl-5-chloro-1,2,3-triazole, but it is hardly applicable to 1-ethyl- and 2-phenyl-substituted analogs (see below). 1-Ethyl derivative could not give rise to a resonance-stabilized structure, while the formation of such structure from 2-phenyl derivative requires rupture of conjugation between the benzene and triazole rings. According to Scheme 8, product **XVI** cannot be obtained via chlorination of completely reduced compound **XIV**. In fact, no product **XVI** was detected in the reaction mixture (by TLC) obtained in a special experiment with pure aminotriazole **XIV**.

Scheme 8.



The reduction of 4-nitro-2-phenyl-2*H*-1,2,3-triazole **XVII** with zinc dust in ethanol gave a mixture of 1,2-bis(2-phenyl-2*H*-1,2,3-triazol-4-yl)-hydrazine (**XVIII**) (partial reduction product) and the desired 4-amino-2-phenyl-2*H*-1,2,3-triazole (**XIX**) (Scheme 9).

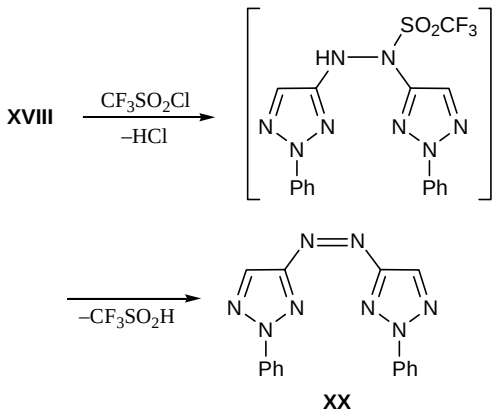
Scheme 9.



Compounds **XVIII** and **XIX** were separated by column chromatography; they are characterized by very similar elemental compositions and positions of signals in the ^{1}H and ^{13}C NMR spectra (except for the NH signal). However, the melting point of substituted hydrazine **XVIII** is much higher than that of amine **XIX**, the NH signal of the former in the ^{1}H NMR spectrum ($CDCl_3$) appears 2.1 ppm downfield relative to the corresponding signal of **XIX,** and its relative intensity is twice as low.

Unexpectedly, our attempt to introduce one or two trifluoromethylsulfonyl groups to one or both nitrogen atoms in 1,2-disubstituted hydrazine **XVIII** via reaction with trifluoromethanesulfonyl chloride resulted in isolation of the oxidation product, (*Z*)-1,2-(2-phenyl-1,2,3-triazol-4-yl)diazene (**XX**) (Scheme 10). Probably, the first reaction stage is replacement of one NH proton by trifluoromethylsulfonyl group; the intermediate thus formed can be regarded as an *N*,*N*′-disubstituted trifluoromethanesulfonic acid hydrazide. Published data on perfluoro-alkanesulfonic acid hydrazides are very limited [6–8]; moreover, these compounds were neither isolated nor characterized. It is known that they are relatively stable only at reduced temperature (below –30°C) and that at room temperature they decompose with liberation of nitrogen and formation of perfluoroalkanesulfinic acids R_FSO_2H. As applied to our case, elimination of potassium trifluoromethanesulfinate under conditions of phase-transfer catalysis in the presence of potassium carbonate was proved by thin-layer chromatography using an authentic sample.

Scheme 10.



EXPERIMENTAL

The NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400 (^{1}H), 100 (^{13}C), and 376 MHz (^{19}F) using HMDS as internal reference for ^{1}H and ^{13}C; the ^{19}F chemical shifts were measured relative to CCl_3F. Gas chromatographic–mass spectrometric analysis was performed on a Hewlett-Packard HP 5890 gas chromatograph coupled with an HP 5971A mass-selective detector (70 eV); Ultra-2 column (5% of phenylmethylsilicone); injector temperature 250°C; oven temperature programming from 70 to 280°C at 20 deg/min.

2-Phenyl-4-trifluoromethylsulfonylmethyl-2*H*-1,2,3-triazole (II). To a solution of 2 g (8.4 mmol) of bromomethyltriazole **Ib** in 20 ml of acetone we added in portions 2.62 g (16.8 mmol) of sodium trifluoromethanesulfinate. The mixture was stirred for 50 h on heating under reflux, poured into cold water, and treated with diethyl ether. The extract was dried over $MgSO_4$ and evaporated, and the residue was purified by passing through a column charged with Al_2O_3 (eluent diethyl ether–hexane, 1:2). The crystalline product was washed with hexane and dried. Yield 0.5 g (20%), mp 78–80°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 5.35 s (2H, CH_2), 7.45 m (1H, *p*-H), 7.58 m (2H, *m*-H), 8.08 m (2H, *o*-H), 8.18 s (1H, 5-H). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 47.86 (CH_2), 119.27 (C^o), 120.27 q ($^1J_{CF}$ = 327.3 Hz), 128.83 (C^p), 130.13 (C^m), 135.83 (C^i), 137.97 (CH=N), 139.96 (C=N). ^{19}F NMR spectrum (acetone-d_6): δ_F –75.09 ppm. Found, %: C 41.11; H 2.87; F 19.50; N 14.75; S 10.88. $C_{10}H_8F_3N_3O_2S$. Calculated, %: C 41.24; H 2.77; F 19.57; N 14.43; S 11.01.

1-Iodomethyl-4-nitro-1*H*-1,2,3-triazole (V). A mixture of 2.5 g (0.015 mol) of 1-chloromethyl-4-nitro-1*H*-1,2,3-triazole (**III**), 3.14 g (0.017 mol) of NaI·$2H_2O$, and 20 ml of acetone was stirred at 50°C until NaCl no longer precipitated. The salt was filtered off, the filtrate was evaporated, and the residue was recrystallized from alcohol with addition of hexane. Yield 2.54 g (65%), mp 112°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 6.54 s (2H, CH_2), 9.28 s (1H, CH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 9.94 (CH_2), 124.86 (C^5), 154.43 (C^4). Found, %: C 14.74;

H 0.63; I 50.21; N 21.51. $C_3H_3IN_4O_2$. Calculated, %: C 14.19; H 1.19; I 49.96; N 22.06.

2-Iodomethyl-4-nitro-2*H*-1,2,3-triazole (VI) was synthesized in a similar way. Yield 81%, mp 92–93°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 6.54 s (2H, CH_2), 8.57 s (1H, CH). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 16.29 (CH_2), 133.13 (C^5), 154.67 (C^4). Found, %: C 14.70; H 0.48; I 51.37; N 22.31. $C_3H_3IN_4O_2$. Calculated, %: C 14.19; H 1.19; I 49.96; N 22.06.

1,2-Bis(1-ethyl-1*H*-1,2,3-triazol-4-yl)diazene 1-oxide (VIII). To a mixture of 5 g (0.0352 mol) of compound **VII**, 2.85 g (0.106 mol) of aluminum powder, and 50 ml of ethanol we added dropwise under vigorous stirring 52 ml of a 20% solution of sodium hydroxide. The mixture warmed up to 50°C and gradually divided into layers, and crystals separated from the organic phase. The mixture was stirred until the initial nitrotriazole disappeared (TLC), the organic phase was separated, washed with a saturated solution of sodium chloride, and partially evaporated, and the yellow crystals were filtered off, dried in air, and recrystallized from ethanol. Yield 3.1 g (75%), mp 216–218°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.63 t (3H, CH_3), 1.46 t (3H, CH_3), 4.51 q (2H, CH_2), 4.53 q (2H, CH_2), 8.36 s (1H, =CH), 8.80 s (1H, =CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.14 (CH_3), 15.26 (CH_3), 45.88 (CH_2), 46.53 (CH_2), 113.86 (C), 118.82 (CH), 119.44 (CH), 148.45 (C). Found, %: C 40.16; H 5.10; N 47.37. $C_8H_{12}N_8O$. Calculated, %: C 40.67; H 5.12; N 47.43.

4-Amino-1-ethyl-1*H*-1,2,3-triazole (IX). A mixture of 10 g (0.07 mol) of compound **VII**, 75 g of zinc dust, and 5 g of calcium chloride in 200 ml of 78% ethanol was stirred for 2–3 h on heating under reflux (the progress of the reaction was monitored by TLC). The mixture was filtered while hot, and the precipitate of zinc dust was washed with hot alcohol. The solvent was distilled off, and the residue was distilled under reduced pressure. A fraction with bp 108–110°C (2 mm) crystallized on cooling to give a colorless solid with mp 56–58°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.34 t (3H, CH_3, J = 7.3 Hz), 4.18 q (2H, CH_2), 4.71 s (2H, NH_2), 7.12 s (1H, =CH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 15.32 (CH_3), 44.53 (CH_2), 106.83 (=CH), 152.19 (C). Found, %: C 42.74; H 7.51; N 49.79. $C_4H_8N_4$. Calculated, %: C 42.85; H 7.19; N 49.96.

***N*-(1-Ethyl-1*H*-1,2,3-triazol-4-yl)trifluoromethanesulfonamide (X).** A solution of 2.26 g (13.4 mmol) of trifluoromethanesulfonyl chloride in 5 ml of anhydrous methanol was added dropwise over a period of 30 min to a solution of 1 g (8.9 mmol) of compound **IX** in 20 ml of anhydrous methanol. The mixture was stirred for 2 h at 40°C and for 30 min at 60°C until the initial amine disappeared (TLC). The most part of the solvent was distilled off, the residue was poured into ice water, and the precipitate was filtered off, washed with a small amount of ice water, and dried in air. Yield 0.51 g (24%). The product was recrystallized from alcohol with addition of hexane. mp 133–135°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.43 t (3H, CH_3), 4.40 q (2H, CH_2), 8.01 s/br.s (2H, CH, NH); the CH and NH signals are resolved in chloroform [δ, ppm: 1.58 (CH_3), 4.42 (CH_2), 7.61 (CH), 10.07 (NH)]. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.78 (CH_3), 46.53 (CH_2), 117.42 (CH), 120.23 q (CF_3, $^1J_{CF}$ = 324.3 Hz), 142.17 (C^4). ^{19}F NMR spectrum (DMSO-d_6): δ_F –74.25 ppm. Found, %: C 25.20; H 2.85; N 22.56; S 13.27. $C_5H_7F_3N_4O_2S$. Calculated, %: C 24.59; H 2.89; N 22.94; S 13.13.

The reaction of 4-amino-1-ethyl-1*H*-1,2,3-triazole (**IX**) with pentafluoroethanesulfonyl chloride was carried out in a similar way. However, the reaction did not come to completion even on prolonged heating under reflux. After removal of methanol and unreacted pentafluoroethanesulfonyl chloride, the residue containing the initial amine and products **XI** and **XII** was separated by column chromatography on silica gel using diethyl ether–hexane (3:1) as eluent. We failed to isolate pure compounds; therefore, the products were identified by the NMR spectra of fractions enriched in compound **XI** (liquid) and **XII** (crystalline).

***N*-(1-Ethyl-1*H*-1,2,3-triazol-4-yl)-1,1,2,2,2-pentafluoro-1-ethanesulfonamide (XI).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.46 t (3H, CH_3), 4.30 q (2H, CH_2), 7.48 s (1H, CH), 8.82 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.15 (CH_3), 48.09 (CH_2), 110.52 (CH), 114.61 t.q (CF_2, $^1J_{CF}$ = 303.94, $^2J_{CF}$ = 35.78 Hz), 119.16 q.t (CF_3, $^1J_{CF}$ = 286.9, $^2J_{CF}$ = 33.0 Hz), 146.38 (C^4). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –77.87 (3F, CF_3), –116.45 (2F, CF_2).

1-Ethyl-4-bis(perfluoroethylsulfonyl)amino-1*H*-1,2,3-triazole (XII). mp 140°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.56 t (3H, CH_3), 4.57 q (2H, CH_2), 8.09 s (1H, CH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.58 (CH_3), 50.28 (CH_2), 111.83 t.q (CF_2, $^1J_{CF}$ = 287.5, $^2J_{CF}$ = 36.6 Hz), 119.00 q.t (CF_3, $^1J_{CF}$ = 286.6, $^2J_{CF}$ = 33.8 Hz), 126.84 (CH), 140.27 (C^4). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –77.18 (3F, CF_3), –116.17 (2F, CF_2).

4-Amino-2-ethyl-2*H*-1,2,3-triazole (XIV) was synthesized by the procedure described in [5]. Yield 32%, bp 86-87°C (5 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.22 t (3H, CH_3, J = 7.3 Hz), 3.90 br.s (2H, NH_2), 4.01 q (2H, CH_2), 6.69 s (1H, CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.05 (CH_3), 48.69 (CH_2), 120.16 (=CH), 150.88 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 112 (70) $[M]^+$, 97 (100) $[M - CH_3]^+$, 70 (38) $[M - CH_3 - HCN]^+$, 42 (42) $[NH_2CN]^+$. Found, %: C 41.83; H 7.65; N 50.26. $C_4H_8N_4$. Calculated, %: C 42.85; H 7.19; N 49.96.

***N*-(2-Ethyl-2*H*-1,2,3-triazol-4-yl)trifluoromethanesulfonamide (XV)** was synthesized as described above for compound **X**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.52 t (3H, CH_3), 4.46 q (2H, CH_2), 7.63 s (1H, CH), 10.26 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.57 (CH_3), 50.67 (CH_2), 119.57 q (CF_3, $^1J_{CF}$ = 320.3 Hz), 125.56 (CH), 140.90 (C^4). ^{19}F NMR spectrum ($CDCl_3$): δ_F –76.20 ppm. Found, %: C 25.31; H 2.87; N 23.13; S 13.55. $C_5H_7F_3N_4O_2S$. Calculated, %: C 24.59; H 2.89; N 22.94; S 13.13.

4-Amino-5-chloro-2-ethyl-2*H*-1,2,3-triazole (XVI). Concentrated hydrochloric acid, 18.5 ml, was added dropwise to a mixture of 5 g (0.035 mol) of compound **XIII**, 36 g of $SnCl_2 \cdot 2H_2O$, 50 ml of water, and 10 ml of ethanol, heated to 40°C. The mixture was heated for 2 h at the boiling point, cooled, poured into excess 10% aqueous NaOH, and extracted with diethyl ether. The extract was dried over $MgSO_4$ and evaporated, and the residue (2.3 g) was distilled under reduced pressure; bp 88-90°C (5 mm). We thus isolated 1.36 g of a mixture of approximately equal amounts of 4-amino-2-ethyl-2*H*-1,2,3-triazole (**XIV**) and 4-amino-5-chloro-2-ethyl-2*H*-1,2,3-triazole (**XVI**). The reduction of **XIII** with zinc dust in methanol in the presence of HCl occurred in a similar way. Products **XIV** and **XVI** were separated by column chromatography on Al_2O_3 using diethyl ether–hexane (2:1) as eluent. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 t (3H, CH_3), 3.76 br.s (2H, NH_2), 4.20 q (2H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.49 (CH_3), 50.11 (CH_2), 121.13 (C^4), 146.81 (C^5). Mass spectrum, *m*/*z* (I_{rel}, %): 146 (54) $[M]^+$, 131 (100) $[M - CH_3]^+$, 118 (5) $[M - C_2H_4]^+$, 42 (30) $[NH_2CN]^+$.

4-Amino-2-phenyl-2*H*-1,2,3-triazole (XVII) was synthesized by the procedure reported in [9]. Yield 86% (cf. no more than 73% in [9]), mp 70°C; published data [9]: mp 68–69°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.02 s (2H, NH_2), 7.13 s (1H, =CH), 7.18 t (1H, *p*-H), 7.36 t (2H, *m*-H), 7.88 d (2H, *o*-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 117.46 (C^o), 123.41 (C^5), 125.98 (C^p), 128.97 (C^m), 139.64 (C^i), 152.25 (C^4). Found, %: C 60.07; H 5.17; N 34.42. $C_8H_8N_4$. Calculated, %: C 59.99; H 5.03; N 34.98.

1,2-Bis(2-phenyl-2*H*-1,2,3-triazol-4-yl)-hydrazine (XVIII). Compound **XVII**, 3 g (0.016 mol), was added over a period of 1 h under vigorous stirring to a cooled mixture of 10.5 g of zinc dust and 1.2 g of $CaCl_2$ in 50 ml of 78% ethanol. The mixture was stirred for 30 min at room temperature, carefully heated to 50°C (self-heating), and heated for 4 h under reflux (the progress of the reaction was monitored by TLC). The mixture was filtered while hot, and the precipitate was washed with hot ethanol. The filtrate was cooled, and the yellow crystals were filtered off. Yield 0.86 g (34%), mp 185–187°C. ^{1}H NMR spectrum, δ, ppm: DMSO-d_6: 7.26 t (1H, *p*-H), 7.47 t (2H, *m*-H), 7.53 s (1H, =CH), 7.87 d (2H, *o*-H), 8.43 s (1H, NH); $CDCl_3$: 6.14 s (1H, NH), 7.25 t (1H, *p*-H), 7.41 m (3H, =CH, *m*-H), 7.93 d (2H, *o*-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 117.05 (C^o), 123.17 (C^5), 126.16 (C^p), 129.48 (C^m), 139.42 (C^i), 156.97 (C^4). Found, %: C 60.29; H 4.41; N 35.01. $C_{16}H_{14}N_8$. Calculated, %: C 60.37; H 4.43; N 35.20.

The mother liquor was evaporated, and the residue was subjected to column chromatography to isolate 0.88 g (35%) of amine **XIX**.

(*Z*)-1,2-Bis(2-phenyl-2*H*-1,2,3-triazol-4-yl)diazene (XX). A solution of 0.57 g (3.4 mmol) of trifluoromethanesulfonyl chloride in 3 ml of methanol was added dropwise to a suspension of 0.43 g (1.4 mmol) of compound **XIX** in 10 ml of methanol. After stirring for 1 h at room temperature, the mixture contained only initial hydrazine **XVIII** (TLC). Phase-transfer catalysts, dicyclohexyl-18-crown-6 (0.03 g, 0.07 mmol), $KF \cdot 2H_2O$ (7 mg, 0.07 mmol), and K_2CO_3 (0.1 g, 0.7 mmol), were added, and the mixture was heated for 3 days under reflux, new portions of trifluoromethanesulfonyl chloride being added as the mixture boiled away. The dark yellow precipitate was filtered off and washed with cold methanol. Yield 0.34 g (80%), mp 230°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.42 t (1H, *p*-H), 7.53 t (2H, *m*-H), 8.20 d (2H, *o*-H), 8.24 s (1H, =CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 119.22 (C^o), 126.28 (C^5), 128.50 (C^p), 129.49 (C^m), 139.66 (C^i), 160.86 (C^4); the C^5 and C^p signals were assigned using two-dimensional {^{1}H–^{13}C} NMR technique. Found, %: C 60.32; H 3.71; N 35.43. $C_{16}H_{12}N_8$. Calculated, %: C 60.75; H 3.82; N 35.42.

The mother liquor was evaporated, and the residue was recrystallized from ethanol–hexane to obtain white crystals which were identified as potassium trifluoromethanesulfinate (by TLC using an authentic sample).

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