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4-ARYL(BENZYL)SULFONYL-2-CHLORO-5-POLYFLUOROALKYL-1,2,3-TRIAZOLES. THE FIRST MONOCYCLIC N-CHLORO-1,2,3-TRIAZOLES

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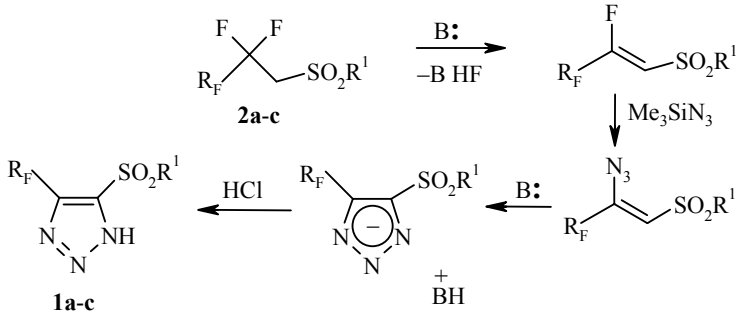
Treatment of 4-aryl(benzyl)sulfonyl-5-polyfluoroalkyl-v-triazoles with NaOCl gave the 4-aryl(benzyl)-sulfonyl-2-chloro-5-polyfluoroalkyl-v-triazole derivatives which contain a chlorine atom only on the $N_{(2)}$ atom of the heterocycle. The structure of 2-chloro-5-(1,1,2,2,3,3-hexafluoropropyl)-4-(p-tolyl-sulfonyl)-2H-[1,2,3]triazole has been established by X-ray structural investigation. The presence of a highly polarized N–Cl bond with a positive halogen atom causes the N-chlorotriazoles to react with KCN and KF as strong acids to form the potassium salts of the triazoles and to form 4-arylsulfonyl-2-(2-chloro-1-ethoxyethyl)-5-polyfluoroalkyl-2H-[1,2,3]triazoles with vinyl ethyl ether. It was found that chlorination of 4-arylsulfonyl-5-polyfluoroalkyl-v-triazoles in the presence of KF gives 4-chloro-5-polyfluoroalkyl-2H-[1,2,3]triazoles.

Keywords: 1,1-dihydropolyfluoroalkyl sulfone, v-triazole, N-chlorotriazole, X-ray structural analysis.

1,2,3-Triazoles have been extensively studied as compounds having varied biological activity [1]. Amongst the many 1,2,3-triazoles the most studied are the N-substituted derivatives [1, 2]. Vicinal fluorinated 1,2,3-triazoles [3] are somewhat less studied but fluorinated heterocycles of other types are widely used in medicine and in agriculture [4].

We recently suggested a method for the synthesis of 5-polyfluoroalkyl-4-*p*-tolyl(benzyl)sulfonyl-v-triazoles **1a-c** from 1,1-dihydropolyfluoroalkyl sulfones **2a-c** [5] as a novel type of fluorine containing vicinal 1,2,3-triazoles. The method was based on the reaction of sulfones **2a-c** with trimethylsilyl azide in the presence of base to give the 1,2,3-triazoles **1a-c** [5].



1, 2 a $R_F = H(CF_2)_3$, R^1 = *p*-Tol, **b** $R_F = CF_3$, R^1 = *p*-Tol, **c** $R_F = CF_3$, R^1 = Bn

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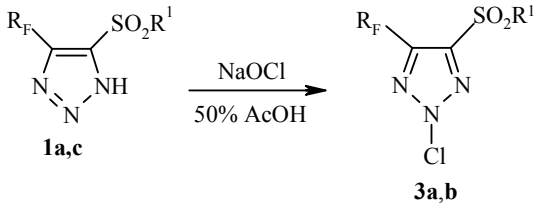
An extremely important problem arising in the chemical modification of v-triazoles is the regioselectivity of the exchange reaction of the hydrogen atom on the nitrogen for another substituent. In most cases studied a mixture of 1- and 3-substituted 1,2,3-triazole derivatives is obtained [6] as a result of such reactions.

In this work we have studied the effect of electron-acceptor substituents on the regioselectivity of the chlorination reaction of 5-polyfluoroalkyl-4-*p*-tolyl(benzyl)sulfonyl-v-triazoles **1** and the properties of the N-chloro compounds obtained.

Compounds **1a,c** react with sodium hypochlorite at room temperature to form only one of the three possible regioisomers with the chlorine atom at position 2, i.e. the 2-chloro-5-polyfluoroalkyl-4-*p*-tolyl-(benzyl)sulfonyl-1,2,3-triazoles **3a,b**.



3 a $R_F = H(CF_2)_3$, R^1 = *p*-Tol, **b** $R_F = CF_3$, R^1 = Bn

The ^1H and ^{19}F NMR spectra of compounds **3a,b** show only one set of signals for the protons and fluorine atoms and we are able to deduce that they form a single regioisomer. The structure of the regioisomer **3a** was confirmed by X-ray analysis (Fig. 1).

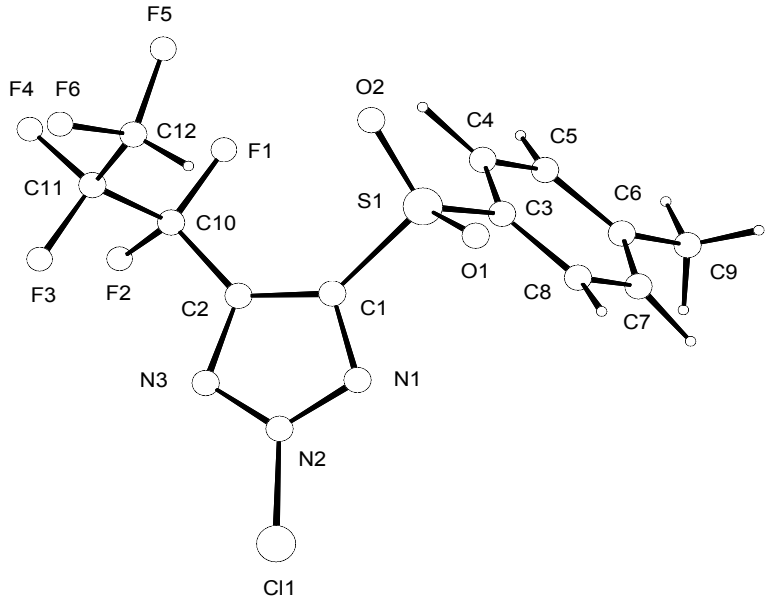


Fig. 1. General view of the **3a** molecule.

Basic bond lengths and valence angles: $Cl_{(1)}–N_{(2)}$ 1.671(2), $N_{(2)}–N_{(3)}$ 1.317(3), $N_{(3)}–C_{(2)}$ 1.332(3), $C_{(2)}–C_{(1)}$ 1.398(4), $C_{(1)}–N_{(1)}$ 1.339(3), $N_{(1)}–N_{(2)}$ 1.319(3), $S_{(1)}–C_{(1)}$ 1.773(3), $S_{(1)}–C_{(3)}$ 1.748(3), $S_{(1)}–O_{(1)}$ 1.430(2), $S_{(1)}–O_{(2)}$ 1.426(2) Å; $C_{(1)}N_{(1)}N_{(2)}$ 102.5(2), $N_{(1)}N_{(2)}N_{(3)}$ 117.2$_{(2)}$, $N_{(2)}N_{(3)}C_{(2)}$ 103.1(2), $N_{(3)}C_{(2)}C_{(1)}$ 108.5(2), $C_{(2)}C_{(1)}N_{(1)}$ 108.7(2) deg.

The heterocyclic fragment $N_{(1-3)}C_{(1,2)}$ is planar, the maximum least squares deviation being 0.004 Å. Atoms $Cl_{(1)}$, $C_{(10)}$, and $S_{(1)}$ deviate from this ring plane by 0.06, -0.028, and 0.05 Å respectively. The dihedral angle between this ring and the tolyl ring $C_{(3)}$–$C_{(8)}$ is 80.47º.

Due to a very strong intermolecular $Cl_{(1)}^{\delta+}\ldots O_{(2)}^{\delta-}$ interaction (corresponding distance 2.740(2) Å) molecules of compound **3a** form infinite chains in the crystals (Fig. 2).

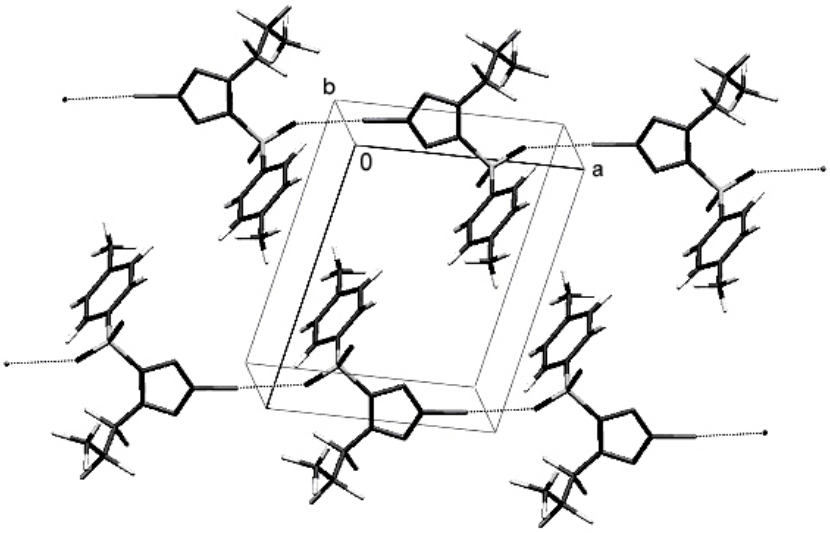


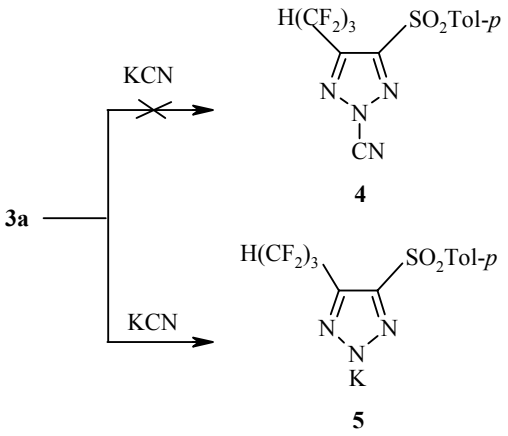
Fig. 2. Crystal packing in compound **3a.**

Attention was turned to the N–Cl bond length in compound **3a**. Analysis of the experimentally determined N–Cl bond lengths based on the Cambridge structural database (2005 version) showed that this bond length is decreased with increase in the electron-acceptor properties of the substituents R in the molecule R_2NCl. For example, the N–Cl bond lengths in N-chloroimides occur in the range 1.676-1.691 Å [7-9] while in N-chlorodialkylamines these lengths are 1.757-1.791 Å [10, 11]. The N–Cl bond length value obtained experimentally for compound **3a** (1.671(2) Å) agrees with the bond length (1.729 Å) determined through 6-31G type quantum-chemical calculations for compound **3a**. The values of the calculated atomic charge values point to a strong polarization of the N–Cl bond in the 1,2,3-triazole molecule **3a** (Millikan charge on atom $N_{(2)}$ -0.422 and the charge on the chlorine atom +0.478).

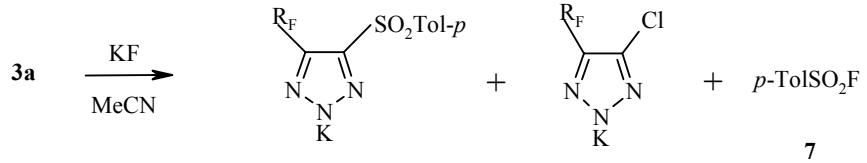
This bond polarization with marked concentration of negative charge on the heterocyclic nitrogen atoms (specifically $N_{(2)}$) has led to interesting features in the reaction of compound **3a** which are not characteristic of an N–Cl compound.

It is known [12] that N-chloro-1,2,3-benzotriazole reacts with KCN to give 1-cyano-1,2,3-benzotriazole.

By contrast, the reaction of the N–Cl-triazole **3a** with potassium cyanide is rather complicated and forms a mixture of compounds. However, the IR spectrum of this mixture following solvent (acetonitrile) removal shows the absence of an absorption band near to 2200 cm^{-1} and this points to the absence of a possible N–CN-triazole derivative **4** in the reaction products. At the same time the potassium salt of the triazole **5** is separated in 40% yield from the reaction mixture.

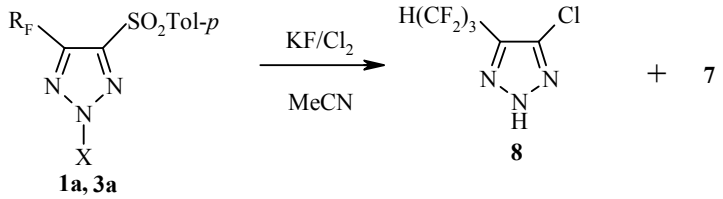


The triazole potassium salt **5** is formed in the same way by treating the triazole **3a** with KF in acetonitrile. In this case the potassium salt of the 4-chlorotriazole **6** and *p*-toluenesulfonyl chloride **7** are also found in the reaction mixture. The ratio of the potassium salts **5** and **6** is 1:1 in the reaction mixture.



$R_F = H(CF_2)_3$

When the reaction was carried out with an excess of chlorine and potassium fluoride (molar ratio of reagents triazole **3a**–KF–Cl_2 of 1:1.1:10) the 4-chloro-5-polyfluoroalkyl-1,2,3-triazole **8** was formed in 71% yield and *p*-toluenesulfonyl fluoride **7** in 76%. A similar result was obtained with the use of triazole **1a** in place of the N-chloro-compound **3a**.

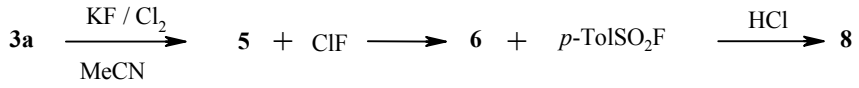


1a X = H, **3a** X = Cl, $R_F = H(CF_2)_3$

In order to understand the possible reaction course it was important to recall that formation of triazole **8** only occurs in the presence of potassium fluoride. Prolonged chlorination of compounds **1a** and **3a** in acetonitrile in the absence of potassium fluoride does not give compound **8**. Thus the ^{19}F NMR spectrum of the reaction mixture obtained when passing a tenfold molar excess of chlorine into a solution of compound **3a** in acetonitrile showed signals for the fluorine atoms of the starting triazole with insignificant in intensity signals for the fluorine nuclei of unidentified compounds. Signals typical of the triazole **8** were not observed.

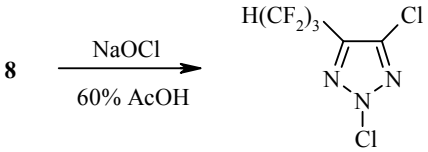
Bearing in mind the high polarization of the N–Cl bond in the molecule of triazole **3a** it can be proposed that reaction with potassium fluoride occurs by formation of chlorine fluoride. A similar proposal has been suggested earlier when studying the reactions of N-halosuccinimide with hydrofluoride salts [13, 14]. The

reaction of chlorine fluoride with the starting triazole occurs with cleavage of the C–SO_2Tol-*p* bond to form the sulfofluoride **7**. However, bearing in mind the high oxidative properties of the ClF molecule [15] and the fact that the reaction occurs in acetonitrile such an explanation may not be convincing. It appears more likely that compound **6** is formed as a result of reaction of the potassium salt of the triazole **5** with products of the reaction of ClF with acetonitrile. Hydrogen chloride and fluoride are possible products. In any case the first of these is indicated by formation of the NH-triazole **8** in the chlorination of the N-chlorotriazole **3a**.



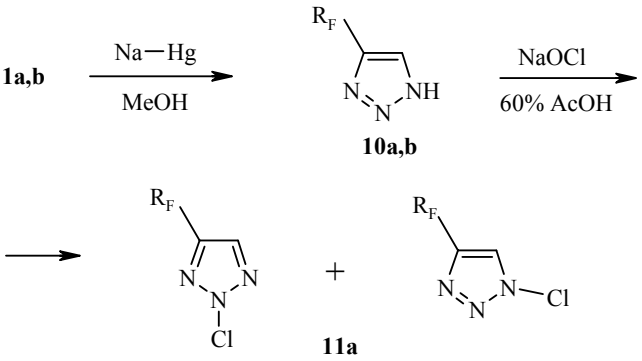
We are continuing to study the possible course of this reaction in our laboratories.

Similarly to triazoles **1a,s,** compound **8** reacts with sodium hypochlorite to give the N-chloro derivative **9** as the single regioisomer.



9

By contrast, the chlorination of compound **10a** (obtained by desulfonylation of triazole **1a** with sodium amalgam) gives the N–Cl-triazole **11a** as a mixture of two regioisomers. This is indicated by a double set of signals in the ^{1}H and ^{19}F NMR spectra of these compounds (see Experimental).

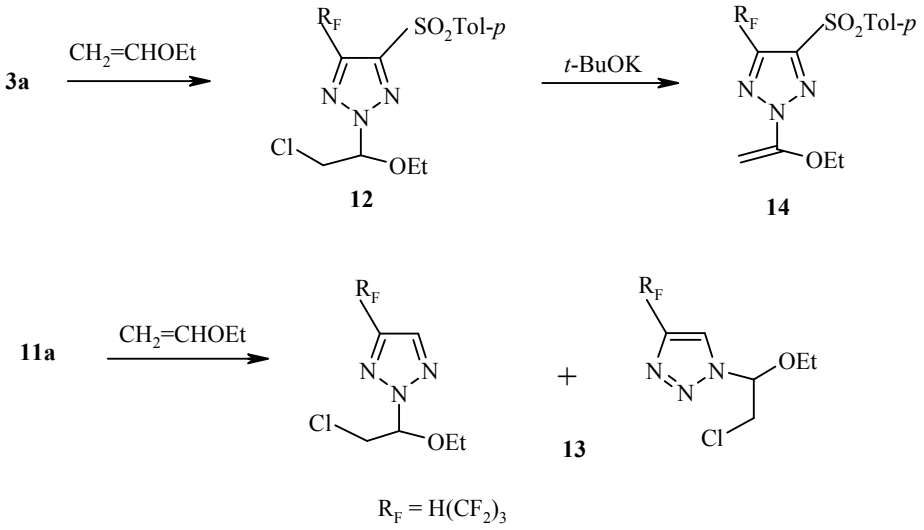


a $R_F = H(CF_2)_3$, **b** $R_F = CF_3$

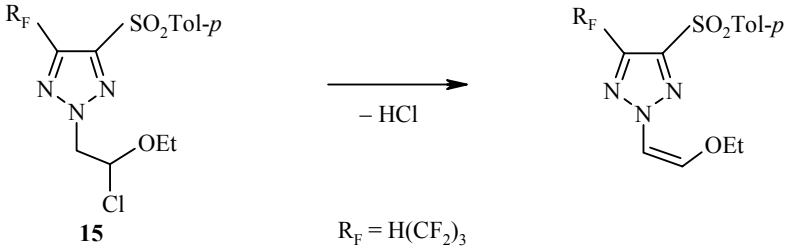
Evidently the most important influence on the regioselectivity of the chlorination reaction of the fluorinated triazoles is the presence of electron-acceptor substituents at position 4 (aryl(benzyl)sulfonyl group or chlorine atom).

The N-alkyl-substituted derivatives of the fluorinated triazoles **12** and **13** were formed on reaction of the N-chlorotriazoles **3a** and **11a** with vinylethyl ether.

For compound **3a** the addition reaction is regioselective and gives only the isomer **12**. When the regioisomers **11a** were used a mixture of compounds **13** was obtained in the same isomeric ratio.



For confirmation of the structure of the addition products **12** and **13** the triazole **12** was dehydrochlorinated to give compound **14**. The ^{13}C NMR spectrum of this compound showed a signal at 79.78 ppm of carbon which was bonded to two hydrogen atoms and this was confirmed by an NMR experiment using APT. A CH_2= fragment is impossible in the composition of the dehydrochlorination product of the other possible isomer **15**.



EXPERIMENTAL

^1H, ^{19}F, and ^{13}C NMR spectra were measured on a Varian VXR-300 (300, 282, and 75 MHz respectively) with TMS as internal standard for ^1H NMR and C_6F_6 (δ = -162.9 ppm relative to CCl_3F) for ^{19}F NMR. Mass spectra were taken on an Agilent 1100 Series instrument fitted with a diode array and mass selective Agilent LC/MSD SL detector for chemical ionization at atmospheric pressure (APCI). IR spectra were recorded on a UR-20 instrument. Column chromatography was performed on grade 60A 70-230 silica gel. All of the solvent were initially purified and distilled by a standard method.

1,2,3-Triazoles 1a-c (General Method). Trimethylsilyl azide (6 mmol) was added dropwise with stirring to a solution of the corresponding sulfone **2a-c** [16] (3 mmol) and 1,4-diazabicyclo[2,2,2]octane (6 mmol) in benzene (15 ml) heated to 75ºC, refluxed for a further 1 min, cooled, and the solvent was evaporated *in vacuo*. The residue was dissolved in water (15 ml) and acidified with conc. HCl to pH 2-2.5. The oily compound **1a-c** produced slowly crystallized from water at room temperature.

5-(1,1,2,2,3,3-Hexafluoropropyl)-4-(*p*-tolylsulfonyl)-2H-[1,2,3]triazole (1a). Yield 86%; mp 51-52ºC (water). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.35 (2H, d, $^3J_{HH}$ = 8.0, C_6H_4); 7.89 (2H, dd, $^3J_{HH}$ = 8.0, C_6H_4); 6.27 (1H, tt, $^2J_{HF}$ = 52.1, $^3J_{HF}$ = 5.7, HCF_2); 2.44 (3H, s, CH_3). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): -107.80 (2H, m, CF_2); -131,35 (2F, m, CF_2); -137.95 – -138.11 (2F, dm, J_{FH} = 52.1, HCF_2). Found, %: C 38.65; H 2.40; N 11.28. $C_{12}H_9F_6N_3O_2S$. Calculated, %: C 38.61; H 2.43; N 11.26.

4-(*p*-Tolylsulfonyl)-5-trifluoromethyl-2H-[1,2,3]triazole (1b). Yield 82%; mp 150-151ºC (water). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.37 (2H, d, $^3J_{HH}$ = 8.0, C_6H_4); 7.93 (2H, d, $^3J_{HH}$ = 8.0, C_6H_4); 2.45 (3H, s, CH_3). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: -60.87 (3F, s, CF_3). Found, %: C 41.28; H 2.71; N 14.44. $C_{10}H_8F_3N_3O_2S$. Calculated, %: C 41.24; H 2.77; N 14.43.

4-Benzylsulfonyl-5-trifluoromethyl-2H-[1,2,3]triazole (1c). Yield 66%; mp 103-106ºC (water). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.19-7.32 (5H, m, C_6H_5); 4.59 (2H, s, $C\underline{H_2}C_6H_5$). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: -60.85 (3F, s, CF_3). Found, %: C 41.20; H 2.82; N 14.45. $C_{10}H_8F_3N_3O_2S$. Calculated, %: C 41.24; H 2.77; N 14.43.

N-chloro-1,2,3-triazoles 3a,b (**General Method**). NaOCl (8% solution in water, 1.39 mmol) was added dropwise with stirring to a solution of the triazole **1a,c** (1.34 mmol) in acetic acid (50%, 1 ml) at room temperature. The mixture was stirred for 3 h at room temperature, water (2 ml) was added, and the precipitated compound **3a,b** was filtered off. Compounds **3a,b** crystallized over 10-15 min at room temperature from the oily reaction mixture.

2-Chloro-5-(1,1,2,2,3,3-hexafluoropropyl)-4-*p*-(tolylsulfonyl)-2H-[1,2,3]triazole (3a).Yield 82%; mp 81-83ºC (a mixture of CCl_4–hexane, 2:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.47 (3H, s, CH_3); 6.27 (1H, tt, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 5.7, HCF_2,); 7.40 (2H, d, $^3J_{HH}$ = 8.0, C_6H_4); 7.92 (2H, d, $^3J_{HH}$ = 8.0, C_6H_4). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): -107.99 (2F, m, CF_2); -130.93 (2F, m, CF_2); -137.82, -137.98 (2F, dm, J_{FH} = 52.0, HCF_2). Found, %: C 35.33; H 2.01; Cl 8.69. $C_{12}H_8ClF_6N_3O_2S$. Calculated, %: C 35.35; H 1.98; Cl 8.70.

4-Benzylsulfonyl-2-chloro-5-trifluoromethyl-2H-[1,2,3]triazole (3b). Yield 89%; mp 142-144ºC (50% AcOH). ^{1}H NMR spectrum, δ, ppm: 7.37 (3H, m, C_6H_5); 7.24 (2H, m, C_6H_5); 4.59 (2H, s, $\underline{CH_2}C_6H_5$). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: -60.85 (3F, s, CF_3). Found, %: C 36.93; H 2.21; Cl 10.83. $C_{10}H_7ClF_3N_3O_2S$. Calculated, %: C 36.88; H 2.17; Cl 10.89.

Potassium Salt of 5-(1,1,2,2,3,3-Hexafluoropropyl)-4-(*p*-tolylsulfonyl)-2H-[1,2,3]triazole (5). KF (0.04 g, 0.7 mmol) was added to a solution of the triazole **1a** (0.26 g, 0.7 mmol) in acetonitrile (6 ml) at about 20ºC, stirred for 4 h, evaporated *in vacuo*, and the residue was washed with ether. Yield of salt 0.2 g (70%); mp 210ºC. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 7.73 (2H, d, $^3J_{HH}$ = 7.1, C_6H_4); 7.37 (2H, d, $^3J_{HH}$ = 7.1, C_6H_4); 7.17 (1H, tt, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 6.3, HCF_2); 2.36 (3H, s, CH_3). ^{19}F NMR spectrum (CH_3CN), δ, ppm (*J*, Hz): -102.72 (2F, m, CF_2); -130.44 (2F, m, CF_2); -136.90, -137.18 (2F, dm, J_{FH} = 52.0, HCF_2). Found, %: C 35.05; H 1.98; N 10.19. $C_{12}H_8F_6KN_3O_2S$. Calculated, %: C 35.04; H 1.96; N 10.21.

4-Chloro-5-(1,1,2,2,3,3-hexafluoropropyl)- 2H-[1,2,3]triazole (8). Calcinated KF (0.47 g, 8.09 mmol) was added to a solution of the corresponding triazole **1a** or **3a** (7.36 mmol) in acetonitrile (60 ml), stirred for 10 min, and a stream of chlorine was passed through at a rate of 1.3 g/h for 4 h at a temperature not exceeding 15ºC. The product was stirred for a further 3 h at 15ºC and filtered. The filtrate was evaporated *in vacuo* at 30-35ºC, benzene (50 ml) added, and washed with 0.5 M NaOH solution (0.5 molar, 2×30 ml). The combined aqueous extracts were acidified with conc. HCl to pH 2 and the oil produced was extracted with CH_2Cl_2 (2×30 ml). The organic layer was dried over Na_2SO_4, filtered, and solvent was removed *in vacuo* at 30-35ºC. The residue was distilled *in vacuo* collecting the fraction at 65-69ºC (0.06 mm Hg). Use of compound **1a** gave compound **8** (1.38 g, 74%) as a colorless oil. In the case of compound **3a** the yield of **8** was 1.32 g (71%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.19 (1H, tt, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 5.4, HCF_2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): -112.66 (2F, m, CF_2); -131.51 (2F, m, CF_2); -137.83, -138.11 (2F, dm, J_{FH} = 52.0, HCF_2). Mass spectrum, *m/z* (I_{rel}, %): 253.6 $[M+H]^+$ (100). Found, %: C 23.66; H 0.82; Cl 13.96. $C_5H_2ClF_6N_3$. Calculated, %: C 23.69; H 0.80; Cl 13.98.

2,4-Dichloro-5-(1,1,2,2,3,3-hexafluoropropyl)- 2H-[1,2,3]triazole (9). An aqueous solution of NaOCl (8%, 7.34 g, 7.89 mmol) was added dropwise with vigorous stirring to a solution of the triazole **8** (1 g, 3.94 mmol) in acetic acid (70%, 10 ml) over 1 min, stirred for 4 h, water (5 ml) added, and extracted with

CH_2Cl_2 (2×20 ml). The organic layer was separated, washed with water, dried with Na_2SO_4, and filtered. The filtrate was evaporated *in vacuo* at a bath temperature not above 35ºC to give compound **9** (1 g, 88%) as a colorless oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.15 (1H, tt, $^2J_{HF}$ = 52.1, $^3J_{HF}$ = 5.3, HCF_2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): -112.57 (2F, m, CF_2); –131.04 (2F, m, CF_2); -137.68, -137.96 (2F, dm, J_{FH} = 52.1, HCF_2). Found, %: C 20.82; H 0.38; Cl 24.64. $C_5HCl_2F_6N_3$. Calculated, %: C 20.85; H 0.35; Cl 24.62.

4-Hexafluoropropyl(trifluoromethyl)-1,2,3-triazoles 10a,b (General Method). Sodium amalgam (3%, 125 g) was added with stirring to a solution containing the corresponding triazole **1a,b** (0.3 mol) and sodium hydrophosphate (17 g, 0.12 mol) in absolute methanol (150 ml) under an argon atmosphere and stirred for 72 h at 30ºC. The methanol solution was decanted and the mercury washed with methanol (2×70 ml). The combined methanol solutions were evaporated *in vacuo* and the residue was dissolved in water (200 ml). The aqueous solution was acidified with conc. HCl to pH 2-2.5, the oil produced was extracted with ether (4×100 ml), and the ether solution was dried over Na_2SO_4, filtered, and evaporated *in vacuo*. Compound **10a** was purified by distillation and **10b** by crystallization from $CHCl_3$.

4-(1,1,2,2,3,3-Hexafluoropropyl)-2H-[1,2,3]triazole (10a). Yield 56%; mp 26ºC, bp 65-67ºC (0.04 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 11.60 (1H, br. s, NH); 8.08 (1H, s, N=CH–); 6.19 (1H, tt, $^2J_{HF}$ = 52.1, $^3J_{HF}$ = 5.6, HCF_2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): –111.22 (2F, m, CF_2); -131.84 (2F, m, CF_2); -137.78, -138.04 (2F, dm, J_{FH} = 52.1, HCF_2). Found, %: C 27.43; H 1.35; N 19.19. $C_5H_3F_6N_3$. Calculated, %: C 27.41; H 1.38; N 19.18.

4-Trifluoromethyl-2H-[1,2,3]triazole (10b). Yield 60%; mp 78-79ºC ($CHCl_3$). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 14.80 (1H, br. s, NH); 8.45 (1H, s, CH). ^{19}F NMR spectrum (MeOH), δ, ppm: -57.88 (3F, s, CF_3). Found, %: C 26.31; H 1.45; N 30.69. $C_3H_2F_3N_3$. Calculated, %: C 26.29; H 1.47; N 30.66.

1(2)-Chloro-4-(1,1,2,2,3,3-hexafluoropropyl)-2H-[1,2,3]triazoles (11a). An aqueous solution of NaOCl (8%, 10 g, 10.74 mmol) was added dropwise with vigorous stirring at 15ºC to a solution of compound **10a** (1.5 g, 6.85 mmol) in acetic acid (60%, 6 ml), stirred for 5 h, water (4 ml) added, and extracted with CH_2Cl_2 (2×7 ml). The organic layer was washed with water (10 ml), dried over Na_2SO_4, solvent evaporated *in vacuo* at 30-35ºC, and the residue was distilled *in vacuo* collecting the fraction with bp 50-55ºC (0.3 mm Hg). Compound **11a** (0.9 g, 52%) was obtained as a colorless liquid as a mixture of isomers in the molar ratio 3:1. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J,* Hz) (mixture of isomers): 8.09 (1H, s, N=CH–); 7.96* (1H, s, N=CH–); 6.23 (1H, tt, $^2J_{HF}$ = 52.1, $^3J_{HF}$ = 5.4, HCF_2); 6.14* (1H, tt, $^2J_{HF}$ = 52.1, $^3J_{HF}$ = 5.4, HCF_2,). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz) (mixture of isomers): -111.66 (2F, m, CF_2); -111.88* (2F, m, CF_2); -131.87 (2F, m, CF_2); -131.45* (2F, m, CF_2); -137.60*, -137.89* (2F, dm, $^2J_{FH}$ = 52.1, HCF_2); -137.76, -138.0 (2F, dm, $^2J_{FH}$ = 52.1, HCF_2). Mass spectrum, *m/z* (I_{rel}, %): 218.0 $[M+H–Cl]^+$ (100), 199.0 $[M+H–Cl–F]^+$ (10). Found, %: C 23.65; H 0.84; Cl 14.00. $C_5H_2ClF_6N_3$. Calculated, %: C 23.69; H 0.80; Cl 3.98.

2-(2-Chloro-1-ethoxyethyl)-5-(1,1,2,2,3,3-hexafluororopyl)-4-(*p*-tolylsulfonyl)-2H-[1,2,3]triazole (12). Ethyl vinyl ether (0.24 g, 3.33 mmol) in $CHCl_3$ (1 ml) was added dropwise with stirring at 0ºC to a solution of the N-chlorotriazole **3a** (0.7 g, 1.72 mmol) in $CHCl_3$ (10 ml). The reaction mixture was stirred for 2 h at room temperature and the solvent was removed *in vacuo*. The residue was extracted with refluxing hexane (2×15 ml), the hexane solution cooled, and the precipitated crystals of compound **12** were filtered off. Yield 0.61 g (74%); mp 72-74ºC (hexane)). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.36 (2H, d, $^3J_{HH}$ = 8.0, C_6H_4); 7.90 (2H, d, $^3J_{HH}$ = 8.0, C_6H_4); 6.26 (1H, tt, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 5.6, HCF_2,); δ_X 5.80 (1H, dd, J_{AX} = 7.8, J_{BX} = 5.5, N–CH); δ_A 4.03 and δ_B 3.93 AB (2H, J_{AB} = 12.0, $^3J_{HAHX}$ = 7.8, $^3J_{HBHX}$ = 5.3, CH_ACH_BCl,); δ_A 3.64 and δ_B 3.47 ABX_3 (2H, J_{AX} = J_{BX} = 7.0, OCH_ACH_B); 2.45 (3H, s, $ArCH_3$); δ_X 1.15 (3H, t, J_{AX} = J_{BX} = 7.0, $CH_ACH_B\underline{CH_3}$). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): -108.56 (2F, m, CF_2); -131.66 (2F, m, CF_2); -137.93, -138.16 (2F, dm, $^2J_{FH}$ = 52.0, HCF_2). Found, %: C 40.06; H 3.39; Cl 7.37. $C_{16}H_{16}ClF_6N_3O_3S$. Calculated, %: C 40.05; H 3.36; Cl 7.39.

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* Isomer formed in larger amount.

1(2)-(2-Chloro-1-ethoxyethyl)-4-(1,1,2,2,3,3-hexafluoropropyl)-2H-[1,2,3]triazoles (13). Ethyl vinyl ether (0.125 g, 1.74 mmol) in $CHCl_3$ (1 ml) was added to a solution of the mixed regioisomers of **11a** (0.22 g, 0.87 mmol) in $CHCl_3$ (4 ml) at -40ºC, heated to room temperature, stirred for 1 h, and the solvent was evaporated *in vacuo*. The mixed isomers of compound **13** (0.254 g, 90%) were obtained as colorless oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz) (mixture of isomers in the molar ratio 3:1): 8.11 (1H, s, -CH=N); 7.96* (1H, s, CH=N); 6.28 (1H, tt, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 5.4, HCF_2); 6.14* (1H, tt, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 5.4, HCF_2,); δ_X 5.81 (1H, dd, J_{AX} = 7.7, J_{BX} = 5.3, N-CH); δ_X 5.80* (1H, dd, J_{AX} = 7.7, J_{BX} = 5.3, N–CH); δ_A 4.11* and δ_B 3.99* AB (2H, J_{AB} = 11.8, $^3J_{HAHX}$ = 7.7, $^3J_{HBHX}$ = 5.3, CH_ACH_BCl,); δ_A 4.01 and δ_B 3.97 AB (2H, J_{AB} = 11.8, $^3J_{HAHX}$ = 7.7, $^3J_{HBHX}$ = 5.3, CH_ACH_BCl); δ_A 3.71 and δ_B 3.52 ABX_3 (2H, J_{AX} = J_{BX}= 7.0, OCH_ACH_B); δ_A 3.64*, δ_B 3.47* ABX_3 (2H, J_{AX} = J_{BX} = 7.0, OCH_ACH_B); δ_X 1.24 (3H, t, J_{AX} = J_{BX} = 7.0, $CH_ACH_B\underline{CH_3}$); δ_X 1.18* (3H, t, J_{AX} = J_{BX} = 7.0, $CH_ACH_B\underline{CH_3}$). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz) (mixture of isomers): –111.19 (2F, m, CF_2); -111.92* (2F, m, CF_2); –132.10* (2F, m, CF_2); –132.38 (2F, m, CF_2); -137.77,* -138.05* (2F, dm, $^2J_{FH}$ = 52.0, HCF_2); -138.05, -138.26 (2F, dm, $^2J_{FH}$ = 52.1, HCF_2). Found, %: C 33.18; H 3.13; Cl 10.84. $C_{16}H_{16}ClF_6N_3O_3S$. Calculated, %: C 33.20; H 3.10; Cl 10.83.

2-(1-Ethoxyvinyl)-5-(1,1,2,2,3,3-hexafluoropropyl)-4-(*p*-tolylsulfonyl)-2H-[1,2,3]triazole (14). A suspension of potassium *tert*-butylate (0.16 g, 1.42 mmol) in THF (2 ml) was added to a solution of compound **12** (0.61 g, 1.27 mmol) in a mixture of *tert*-butanol and THF (1:1) cooled to -4ºC, stirred at room temperature for 6 h, water (5 ml) added, and extracted with ether (3×10 ml). The ether extract was washed with water, dried over Na_2SO_4, filtered, and the solvent evaporated *in vacuo*. A brown oil was produced (0.5 g) which was purified chromatographically to give compound **14** (0.11 g, 20%) as a colorless oil with R_f 0.6 (Silufol UV-254, chloroform, visualized using iodine vapor). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.36 (2H, d, $^3J_{HH}$ = 8.0, C_6H_4); 7.93 (2H, d, $^3J_{HH}$ = 8.0, C_6H_4); 6.32 (1H, tt, $^2J_{HF}$ = 52.2, $^3J_{HF}$ = 5.6, HCF_2); 5.03 (1H, d, $^2J_{HH}$ = 4.4, CH_2=C); 4.30 (1H, d, $^2J_{HH}$ = 4.4, CH_2=C); 4.08 (2H, q, $^3J_{HH}$ = 7.0, $O\underline{CH_2}CH_3$); 2.44 (3H, s, CH_3); 1.43 (3H, t, $^3J_{HH}$ = 7.0, $OCH_2\underline{CH_3}$). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): -107.83 (2F, m, CF_2); -131.27 (2F, m, CF_2); -137.85, -138.06 (2F, dm, $^2J_{FH}$ = 52.2, HCF_2). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 151.77 (=C–O); 149.26 ($C_{(4)}$–SO_2); 146.09 ($\underline{C}_{Ar}$–CH_3); 136.66 (t, $^2J_{CF}$ = 33.1, $\underline{C}_{(5)}$–CF); 136.33 ($\underline{C}_{Ar}$–SO_2); 130.14 ($2C_{Ar}$); 128.91 ($2C_{Ar}$); 114-106 (m, CF_2CF_2); 107.95 (tt, J_{CF} = 254.0, $^2J_{CF}$ = 30.0, HCF_2); 79.78 (CH_2=); 66.80 ($\underline{CH_2}$–CH_3); 21.78 ($C_6H_5\underline{CH_3}$); 14.04 (CH_2–$\underline{CH_3}$). Mass spectrum, *m/z* (I_{rel}, %): 443.0 $[M+H]^+$ (100), 372.0 $[M+H–CH_2=C–OC_2H_5]^+$ (80). Found, %: C 43.31; H 3.40; N 9.50. $C_{16}H_{15}F_6N_3O_3S$. Calculated, %: C 43.34; H 3.41; N 9.48.

X-ray Structural Investigation of Single Crystal of Compound 3a (0.31×0.49×0.52 mm), grown from CCl_4–hexane (2:1). Carried out at room temperature on an Enraf-Nonius CAD-4, automatic four circle diffractometer (CuKα radiation, λ = 1.54178 Å, 2θ/ω scanning to θ_{max} = 68º, spherical segment $0 \le h \le 10$, $-11 \le k \le 10$, $-13 \le l \le 12$). In all, 3145 reflections were collected of which 2942 are symmetrically independent (R_{int} = 0.02). Crystals of **3a** are triclinic, *a* = 8.935(6), *b* = 9.167(7), *c* = 10.830(7) Å, α = 104.65(6), β = 101.83(5), γ = 101.55(6)º, *V* = 809.7(11) Å^3, *M* = 407.72, *Z* = 2, d_{calc} = 1.67 g/cm^3, μ = 40.530 cm^{-1}, *F*(000) = 408.000, space group $P\bar{1}$ (*N* 2). The structure was solved by a direct method using the least squares approximation in a full matrix anisotropic approximation employing the CRYSTALS program package [17]. In the refinement 2597 reflection were used with $I > 3\sigma(I)$ (226 refinement parameters, number of reflections per parameter 11.5). The positions of more than 60% of the hydrogen atoms were revealed directly from the electron density difference map and the remainder were placed geometrically and included in the refinement with fixed thermal and positional parameters. The Chebyshev weighting scheme [18] was used in the refinement with the parameters 4.10, 0.423, and 2.67. The final values of the difference factors were R = 0.056 and R_W = 0.061, GOF = 1.080. The residual electron density from the Fourier difference series amounted to -0.47 and 0.35 e/Å^3. Calculation of the absorption in the crystal was achieved using the azimuthal scanning method [19]. The full set of X-ray structural data for compound **3a** has been deposited in the Cambridge structural database (reference CCDC 602440).

* Isomer formed in larger amount.

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