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Reaction of Trifluoromethanesulfonamide with Heterodienes under Oxidation Conditions

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Abstract—Reactions of trifluoromethanesulfonamide with divinyl sulfone, divinyl sulfoxide, divinyl sulfide, diphenyl sulfide, vinyl allyl and diallyl ethers was investigated in the presence of oxidation system *t*-BuOCl + NaI. The reaction with divinyl sulfone afforded a product of 1,5-heterocyclization, 2,6-diiodo-4-[(trifluoromethyl) sulfonyl]thiomorpholine 1,1-dioxide. The same product was obtained in the reaction with divinyl sulfoxide apparently due to its preliminary oxidation to sulfone. In reactions with divinyl sulfide and unsaturated ethers only the oxidation of substrates was observed accompanied with strong tarring; the products of a reaction with trifluoromethanesulfonamide were absent. With diphenyl sulfide a product was formed resulting from the oxidation at the sulfur atom [S(II) → S(IV)], *N*-(diphenyl-λ^4-sulfanylidene)trifluoromethanesulfonamide.

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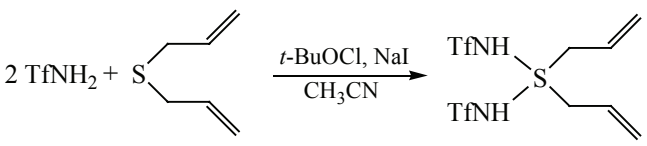
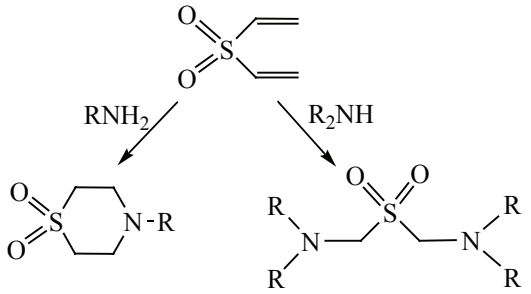
We formerly investigated the addition of trifluoromethanesulfonamide $CF_3SO_2NH_2$ ($TfNH_2$, triflamide) to a series of alkenes and dienes in the presence of an oxidation system *t*-BuOCl + NaI [1–6]. In contrast to the reaction with unfluorinated sulfonamides [7] aziridines were not found in the reaction with triflamide but depending on the nature of the substarate and the process conditions the formed products contained in various ratios their dimers, isomeric piperazines [1–3], the conjugate 1,2-addition products CH(NHTf)–CHX (X = TfNH, OH, Cl, I) [1–6], 9-heterobicyclo[4.2.1]nonanes [4]. The reaction of triflamide with heteroatomic unsaturated substrates was not investigated save our recent short communication on the formation of the product of oxidation at the sulfur atom in the reaction of triflamide with diallyl sulfide [8].

The unexpectedly easy oxidation of the sulfur atom [S(II) → S(IV)] and the inertness of the double bond in the diallyl sulfide were interpreted with the use of quantum-chemical calculations revealing that the HOMO of the diallyl sulfide molecule is localized on all olefin carbon atoms to less than 2% and to over 55% on the sulfur atom resulting in the ready oxidation of the latter [8].



The published data on λ^4-sulfanes containing S–N bonds are very scarce [9–13], only *S*,*S*-dialkylsulfodiimines $R_2S(NH_2)_2$ (R = Me, Et) are known formed in reaction of chloramines with dialkyl sulfides followed by the treatment with sodium ethylate [14].



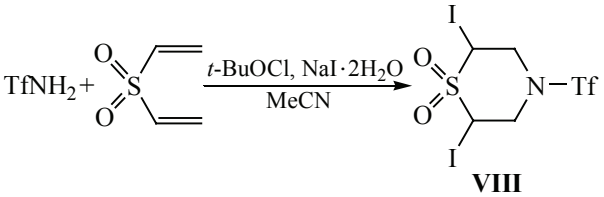
In extension of this research aiming at the investigation of the effect of the heteroatom nature and of the position of double bonds we report here on the study of triflamide (**I**) reactions with divinyl sulfone (**II**), divinyl sulfoxide (**III**), divinyl sulfide (**IV**), diphenyl sulfide (**V**), diallyl and vinyl allyl ethers (**VI, VII**). All reactions were carried out in acetonitrile at cooling in the presence of

the oxidation system *t*-BuOCl + NaI.

The reactions of divinyl sulfoxide and divinyl sulfone with amines are described in the literature. For instance, divinyl sulfone reacted with primary and secondary *N*-nucleophiles by the type of 1,5-heterocyclization or double 1,2-addition [15, 16].

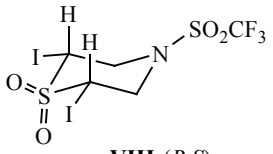
Divinyl sulfoxide reacted similarly furnishing 1,4-perhydrothiazine 1-oxides [17–19]. As to the reactions with sulfonamides, only the macrocycles formation was described in the reaction of divinyl sulfone with α,ω-bistosylamides in the presence of excess potassium carbonate [16].

The reaction of divinyl sulfone with triflamide under the oxidative conditions provided a single heterocyclization product, 2,6-diiodo-4-(trifluoromethylsulfonyl) thiomorpholine 1,1-dioxide (**VIII**).

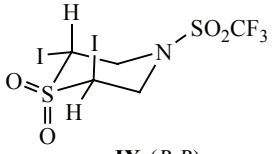


VIII

The composition and structure of compound **VIII** were proved by elemental analysis and IR, ^{1}H, ^{13}C, ^{19}F NMR spectroscopy. In the ^{1}H NMR spectrum three signals were observed characteristic of an *ABX* spin, where the upfield signal of the axial hydrogen atom of the CH_2 group at 3.9 ppm was split into a doublet of doublets with a large geminal and a large vicinal constants ($J_{ax–ax}$), and the downfield signal of the equatorial hydrogen atom of the CH_2 group at 4.4 ppm possessed a large geminal and a small vicinal constants ($J_{ax–eq}$). The signal of the CHI group at 5.4 ppm corresponds to the equatorial hydrogen atom since the bulky iodine atoms are located in the equatorial position. The ^{13}C NMR spectrum without decoupling from protons contains three signals: a doublet of the CHI group at 31.3 ppm and a triplet of the CH_2 group at 54.6 ppm, and also a quartet of the CF_3 group at 121.7 ppm.

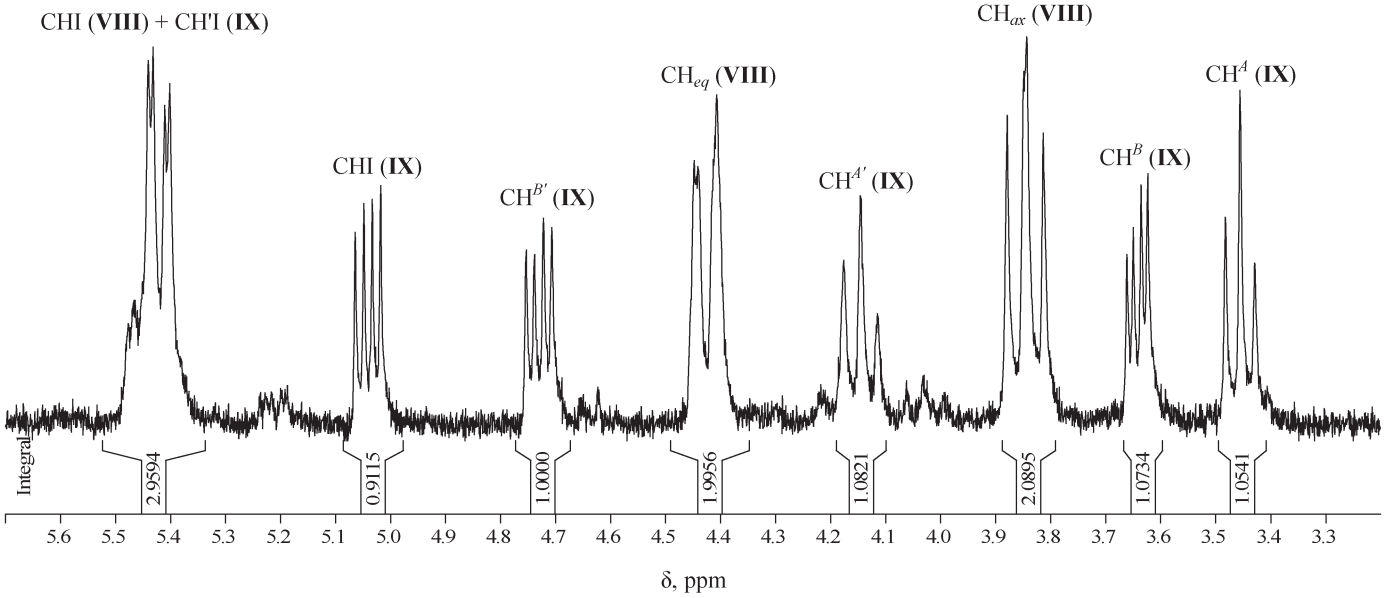


VIII-(*R*,*S*)



IX-(*R*,*R*)

In the reaction of triflamide with divinyl sulfoxide also oxide **VIII** was obtained, apparently due to the oxidation of divinyl sulfoxide to divinyl sulfone by the system *t*-BuOCl + NaI. We failed to detect the heterocyclization product of the proper divinyl sulfoxide, 2,6-diiodo-4-(trifluoromethylsulfonyl)thio-morpholine 1-oxide, but the careful analysis by column chromatography made it possible to isolate a fraction containing compound **VIII** and close to it in the structure compound **IX** in the ratio 2 : 1. The ^{1}H NMR spectrum of this mixture is presented in the figure.

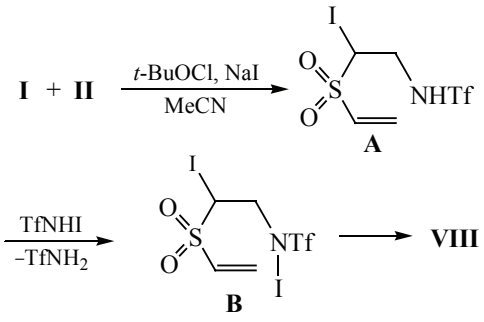


^{1}H NMR spectrum of a mixture of *S*,*R*- and (*R*,*R* + *S*,*S*)-diastereomers of 2,6-diiodo-4-(trifluoromethylsulfonyl)thiomorpholine 1,1-dioxide (**VIII, IX**), 2 : 1.

The presence of six separate signals in the spectrum of compound **IX** in contrast to three signals in the spectrum of compound **VIII** suggests that the reaction results in a mixture of *S*,*R*- and (*R*,*R*+*S*,*S*)-diastereomers of the heterocyclization product with the former compound prevailing. The main isomer apparently is conformationally rigid for both iodine atoms cannot be present in the axial position, whereas the minor isomer should be conformationally labile. Therewith the spin systems *ABX* and *A′B′X′* in molecule **IX** remain nonequivalent although in each system the coupling constants are averaged.

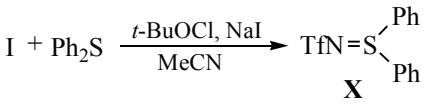
The heterocyclization mechanism of sulfone **II** is apparently analogous to that formerly assumed for the reaction with cyclodienes [6] and involves the reaction of CF_3SO_2NHI formed *in situ* at one double bond of the divinyl sulfone giving the intermediate adduct **A** with the subsequent attack of the second CF_3SO_2NHI molecule resulting in adduct **B**, which undergoes cyclization into compound **VIII**.

If the reaction of sulfoxide **III** with triflamide in the presence of *t*-BuOCl + NaI would proceed as the oxidation (**III**) → (**II**) and further along reaction (1), the spectra of the reaction mixtures would be identical. However the analysis of ^{1}H NMR spectra showed that even in the crude reaction product obtained from triflamide with sulfone **II** before chromatographic separation the signals of minor isomer **IX** were totally absent in contrast to the product of triflamide reaction with sulfoxide **III**. This shows that the reaction of sulfoxide **III** with triflamide is more complex and probably it involves the oxidation of sulfur atom not only in initial substrate **III** but also in one of the intermediate stages **A** or **B**.



The reaction of triflamide with divinyl sulfide in the presence of the system *t*-BuOCl + NaI proceeded with a strong tarring, we succeeded only to isolate the initial triflamide. The ^{1}H NMR spectrum after the workup of the reaction mixture also contained only the NH signal of triflamide.

In the reaction with diphenyl sulfide like in the reaction with diallyl sulfide [8] triflamide provided the product of the oxidation at the sulfur atom but in this case it possessed the sulfimine structure: *N*-(diphenyl-λ^4-sulfanylidene)trifluoromethanesulfonamide (**X**).



The composition and structure of amide **X** were proved by IR, ^{1}H, ^{13}C, ^{19}F NMR, and mass spectra, the latter also of high resolution. The most characteristic change in the ^{1}H NMR spectrum of compound **X** compared with the spectrum of the initial diphenyl sulfide was the downfield shift of all signals of aromatic protons by 0.3–0.4 ppm, and in the ^{13}C NMR spectrum, the downfield shift of C^p signal by 7 ppm and the upfield shift of C^i signal by 5 ppm. The main directions of the molecular ion fragmentation under the lectron impact were the rupture of the CF_3–SO_2 bond with approximately equal probability of the charge localization on both fragments, elimination of CF_3SO_2 and CF_3SO_2N groups as netral radicalx, and the formation of a phenyl cation.

Previously compound **X** was obtained by the oxidative imination of diphenyl sulfide under the treatment with precursors of trifluoromethylsulfonylnitrene like *N*,*N*-dichlorotrifluoromethanesulfonamide [20] or triflu oromethylsulfonylimino(aryl)-1-bromane [21]. Yet these procedures require preliminary preparation of reagents from triflamide whereas reaction (2) is a direct one-stage synthesis.

We failed to carry out the triflamidation of diallyl and allyl vinyl ethers under analogous conditions: In both cases strong tarring was observed. The lack of the triflamidation products in the reactions with divinyl sulfide, diallyl and allyl vinyl ethers is apparently due to the easier oxidation of these substrates compared with triflamide. In the NMR spectra of the reaction mixture obtained with diallyl ether the signals of the vinyl groups disappeared, and only the signals of OCH, OCH_2 groups were observed in the region 3.4–4.3 (^{1}H) and 43–71 ppm (^{13}C). The attempt to isolate the individual substances by column chromatography was unsuccessful.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer

Bruker IFS-113 from pellets with KBr. NMR spectra were registered on a spectrometer Bruker DPX-400 [operating frequencies 400 (^{1}H), 100 (^{13}C), 376 MHz (^{19}F)], chemical shifts are reported with respect to TMS (^{1}H, ^{13}C) and CCl_3F (^{19}F). Mass spectra taken in the electron impact mode (70 eV) were obtained on an instrument GC-MS TRACE DSQ II (Thermo Fisher Scientific GmbH). The precise masses were measured on an instrument Micromass Q-TOF$_{micro}$ (Waters) in the positive electrospray mode. The reaction progress was monitored by TLC on plates with silica gel 60 F-254, eluent–ether, 1 : 2.

2,6-Diiodo-4-(trifluoromethylsulfonyl)thiomorpholine 1,1-dioxide (VIII). To a solution of 2 g (13 mmol) of triflamide, 5.85 g (39 mmol) of NaI, and 1.35 mL (13 mmol) of divinyl sulfone in 80 mL of CH_3CN was added dropwise 4.5 mL (39 mmol) of *t*-BuOCl under argon, in the dark, at cooling to 4°C. The reaction mixture was maintained for 24 h, the solvent was distilled off at a reduced pressure, the residue was dissolved in ethyl ether, and washed with $Na_2S_2O_3$ solution. The extract was dried with $CaCl_2$ and evaporated in a vacuum, the residue (2.59 g, 38%) was purified by column chromatography on silica gel (0.063–0.200 mm), eluents hexane and ether–hexane, 1 : 1. The reaction product was recrystallized from chloroform. Yellowish crystals, mp 275°C. IR spectrum, ν, cm^{-1}: 3009, 2963, 2955, 1629, 1450, 1386, 1201, 1132, 1075, 934, 597. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 3.86 d.d (1H, CH^A, ^2J 14.1, ^3J 12.2 Hz), 4.44 d.d (1H, CH^B, ^2J 14.1, ^3J 3.4 Hz), 5.43 d.d (1H, CHI, ^3J 12.2, 3.4 Hz). ^{13}C NMR spectrum (CD_3CN), δ, ppm: 31.28 d (CHI, *J* 165.3 Hz), 54.64 t (CH_2, *J* 152.6 Hz), 121.69 (CF_3, *J* 319.9 Hz). ^{19}F NMR spectrum (CD_3CN), δ, ppm: –76.33. Found, %: C 12.31; H 1.45; I 49.54; N 2.83; S 12.11. $C_5H_6F_6I_2NO_4S_2$. Calculated, %: C 11.57; H 1.17; I 48.90; N 2.70; S 12.36.

Reaction of triflamide with divinyl sulfoxide. To a solution of 2 g (13 mmol) of $CF_3SO_2NH_2$, 5.85 g (39 *mmol*) of NaI, and 1.3 mL (13 mmol) of divinyl sulfoxide in 80 mL of CH_3CN was added dropwise 4.5 mL (39 mmol) of *t*-BuOCl in the dark, at cooling to 4°C. The reaction mixture was maintained for 24 h, the solvent was distilled off at a reduced pressure, the residue was dissolved in ethyl ether, and washed with $Na_2S_2O_3$ solution. The extract was dried with $CaCl_2$, evaporated in a vacuum, the residue (2.10 g) was twice subjected to column chromatography on silica gel in order to remove tarry impurities, eluents hexane and ether–hexane, 1 : 1. We obtained 0.8 g of triflamide and 150 mg of yellowish powder of compound **VIII** identical to the above described.

***N*-(Diphenyl-λ^4-sulfanylidene)trifluoromethanesulfonamide (X).** To a solution of 2 g (13 mmol) of triflamide, 5.85 g (39 mmol) of NaI, and 2.3 mL (13 mmol) of diphenyl sulfide in 80 mL of CH_3CN was added dropwise 4.5 mL (39 mmol) *t*-BuOCl under argon, in the dark, at cooling to 6°C. The reaction mixture was maintained for 24 h, the solvent was distilled off at a reduced pressure, the residue was dissolved in ethyl ether, and washed with $Na_2S_2O_3$ solution. The extract was dried with $CaCl_2$ and evaporated in a vacuum, the residue (2.58 g, 59%) was twice subjected to column chromatography on silica gel in order to remove tarry impurities, eluents hexane and ether–hexane, 1:1. We obtained 200 mg of triflamide and 500 mg of light yellow analyticqally pure compound **X**. Yellow crystals, mp 98°C (2-PrOH). IR spectrum, ν, cm^{-1}: 3099, 3067, 1585, 1478, 1450, 1338, 1220, 1175, 1143, 1009, 995. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 7.63 m (3H, H^{m+p}), 7.95 m (2H, H^o). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 121.3 q (CF_3, *J* 322.6 Hz), 128.0 (C^o), 131.4 (C^m), 134.2 (C^p), 136.7 (C^I). ^{19}F NMR spectrum (CD_3CN): δ –77.82 ppm. Mass spectrum, *m/z* (I_{rel}, %): 333 (100) [*M*]$^+$, 264 (85) [*M* – CF_3]$^+$, 200 (95) [*M* – Tf]$^+$, 186 (90) [Ph_2S]$^+$, 77 (70) [Ph]$^+$, 69 (65) [CF_3]$^+$. Found [*M*]$^+$ 333.0104. $C_{13}H_{10}F_3NO_2S_2$. Calculated *M* 333.0105.

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