# SYNTHESIS OF SEVERAL DERIVATIVES

## OF TRIFLUOROMETHYL ALKYL SULFONES

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Trifluoromethanesulfonylated compounds are widely used in organic synthesis owing to the unique and diverse properties of the trifluoromethanesulfonyl group [1-5]. This is one of the strongest electronegative substituents and a good leaving group. The starting substance for obtaining such compounds is usually trifluoromethanesulfonic acid [3, 6].

In the present communication we shall describe the synthesis of a number of aliphatic trifluoromethyl sulfones containing functional groups on the basis of other starting substances.

Triflouromethyl methyl sulfone (I) forms the stabilized  $\alpha$ -carbanion CF<sub>3</sub>SO<sub>2</sub>CH<sub>2</sub>, which is capable of being alkylated, of reacting with aldehydes and ketones, and of undergoing conjugated addition and acylation reactions [4]. We investigated several reactions of this carbanion. As its source we used trifluoromethane-sulfonylmethylmagnesium bromide (II). It is known [7] that II reacts with acetaldehyde to form 1-(trifluoromethanesulfonyl)-2-propanol (III) with a 37% yield. The conduction of this reaction at a low temperature (below -30°C) and the decomposition of the intermediate magnesium alkoxide by water made it possible to increase the yield of III to 93%.

$$\begin{array}{c} \mathrm{CF_{3}SO_{2}CH_{3} \rightarrow CF_{3}SO_{2}CH_{2}MgBr} \xrightarrow{\mathrm{1.\ CH_{3}CHO}} \mathrm{CF_{3}SO_{2}CH_{2}CHCH_{3}} \\ (\mathrm{I}) & (\mathrm{II}) & 0\mathrm{H} \\ (\mathrm{III}) & (\mathrm{III}) & 0\mathrm{H} \end{array}$$

When II is reacted with bromoacetone, the alkylation of II does not occur, and only the product of the addition of II at the C = O group of bromoacetone, viz., 1-bromo-3-trifluoromethanesulfony1-2-methy1-2-propanol (IV), forms.

$$\begin{array}{c} (\mathrm{II}) + \mathrm{BrCH}_{2}\mathrm{COCH}_{3} \rightarrow \mathrm{CF}_{3}\mathrm{SO}_{2}\mathrm{CH}_{2}\mathrm{C}(\mathrm{CH}_{3})\mathrm{CH}_{2}\mathrm{Br} \\ & \mathsf{I} \\ \mathrm{OH} \qquad (\mathrm{IV}) \end{array}$$

The oxidation of III by potassium bichromate in an acidic medium yields trifluoromethanesulfonylacetone (V),  $CF_3SO_2CH_2COCH_3$ . Ketone V does not form when acetyl chloride is reacted with II or  $(CF_3SO_2CH_2)_2Cd$  (ether, THF, +50 to -70°C).

We also studied the applicability of trifluoromethanesulfonylacetic acid (VI) as a starting compound for the synthesis of trifluoromethanesulfonyl derivatives, especially trifluoromethyl  $\alpha$ -nitroalkyl sulfones. Until recently, compounds having a CF<sub>3</sub>SO<sub>2</sub>-C-N fragment in the molecule had not been obtained [4]. The properties of VI were previously studied to a small extent in [7, 8].

Acid VI has a low stability and is easily decarboxylated in solutions at room temperature, being converted into sulfone I. For example, according to the PMR, TLC, and GLC data, acid VI completely decomposes over the course of 24 h in absolute methanol, acetonitrile, and acetone, its decarboxylation being more rapid, the higher is the basicity of the solvent. In acidic media VI is stable.

The ammonium salt of VI, which is obtained by reacting ammonia with an ethereal solution of VI, decomposes practically instantaneously, giving sulfone I, which does not react with ammonia under the present conditions. Compound VI is more stable in aqueous alkaline solutions, but under these conditions the optical density of the solution decreases appreciably after ~1 h (in 0.1 N KOH  $\lambda_{max} = 228$  nm,  $\varepsilon = 6000$ ).

In the case of the nitration of VI by a mixture of  $H_2SO_4$  (d 1.84 and  $HNO_3$  (d 1.5) in 3:1 and 10:1 ratios at 20-60°C, by a mixture of 25% fuming sulfuric acid and  $HNO_3$ , and by 20% fuming  $HNO_3$  at 60-80°C in the pres-

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ence of solvents (CH<sub>2</sub>Cl<sub>2</sub>, HCCl<sub>3</sub>, CCl<sub>4</sub>) and without them, the reaction product is furoxan VII. It is stable in acidic media but readily decomposes under the action of even weak bases. In ethanolic solutions VII has characteristic absorption with  $\lambda_{max} = 270$  nm.

The formation of furoxans as a result of the nitration of sulfones is usually viewed as the result of the further conversion of the intermediately formed  $\alpha$ -mononitromethyl sulfone [9, 10]. Therefore, it might be postulated that in our case, too, trifluoromethyl nitromethyl sulfone (VIII) forms as an intermediate.



In order to obtain VIII, a search was made to find nitration conditions under which the conversion VIII  $\rightarrow$  VII is minimal. The formation of VII could be detected in the case of the nitration of VI by a 1:1 sulfuric acid—nitric acid mixture. For the purpose of selecting the optimal conditions for obtaining VIII, the amount of the nitrating mixture, the holding time, and the temperature were varied, and the reaction was conducted without solvents or in the presence of absolute CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub>.

The composition of the reaction products depends mainly on the temperature and the reaction time. At ~20°C the nitration process is extremely slow: After 5 h the yield of VIII is ~5%. A further increase in the time does not increase the yield of VIII. It only promotes the conversion of the latter into VII. Raising the temperature from 40 to 80°C simultaneously accelerates the formation of VIII and the conversion of VIII into VII. The optimal conditions for the synthesis of VIII are: ratio between  $H_2SO_4$  (d =1.84) and  $HNO_3$  (d =1.5) equal to 1:1 (by volume); tenfold excess of the nitrating mixture relative to VI, absolute  $CH_2Cl_2$  as the solvent, 40°C; time, 2.5 h. Under these conditions the yield of VIII is 50-65% (spectrophotometrically in 0.1 N KOH).

In order to destroy competitively formed furoxan VII, the reaction mixture was treated with dilute aqueous alkali. As a result, VI and VIII dissolved as salts of low stability in the aqueous solution, which was acidified at once, and VI and VIII were extracted by methylene chloride. Nitrosulfone VIII was recovered in the form of the ammonium salt VIIIa by applying NH<sub>3</sub> to this extract. At the same time, acid VI was converted into I, which remained in the solution. The yield of VIIIa was 34% (the purity was ~75%). Salt VIIIa can be stored for a long time without change, and it is soluble in water and practically insoluble in ethanol and acetone. It is not possible to isolate VIII from the reaction mixture in the form of the K salt with the use 5-10% aqueous solutions of KOH or  $CH_3OK$ , since the  $CF_3SO_2CHNO_2^{-}$  anion is unstable in strongly alkaline media.

The application of a saturated aqueous solution of CsF to a solution of VIIIa gave the water-insoluble cesium salt (VIIIb) with a ~70% yield. The analytically pure salt VIIIb has  $\lambda_{max} = 295$  nm and  $\epsilon = 13,000$  (H<sub>2</sub>O).

Acidification of an aqueous solution of VIIIa with 60% H<sub>2</sub>SO<sub>4</sub> in the presence of CH<sub>2</sub>Cl<sub>2</sub> gave VIII (00% yield). The structure of VIII was confirmed without isolating it from the solution by the data from PMR, <sup>19</sup>F NMR, and UV spectroscopy. In the individual state VIII is unstable; however, its solutions are suitable for work.

Thus, unlike the nitration of the monoester of malic acid in [11], in the case of the nitration of acid VI, one nitro group, rather than two, is introduced into the molecule.

In order to obtain a trifluoromethyl methyl sulfone containing several functional groups on one carbon atom, we carried out the sulfenylation of the Na salt of nitromalonic ester by trifluoromethanesulfenyl chloride and the oxidation of the trifluoromethanesulfenylnitromalonic ester (IX) obtained\* to trifluoromethanesulfonylnitromalinic ester (X).

The optimal yield of IX (less than 45%) was obtained when the reaction was carried out in  $CCl_4$  and the  $CF_3SCl$  was purified to remove any traces of HF. When other solvents (ether,  $CH_2Cl_2$ ) were used or in the work with unpurified  $CF_3SCl$ , the yield of IX did not exceed 10%. The formation of IX was accompanied by the formation of nitromalonic ester (XI) (5-40% in  $CCl_4$ ), from which IX is removed by treating a toluene solution of the

<sup>\*</sup>On the basis of the absence of a characteristic absorption maximum in the short-wavelength region, O-sulfenvlation does not occur in this reaction.

panied by the formation of nitromalonic ester (XI) (5-40% in  $CCl_4$ ), from which IX is removed by treating a toluene solution of the reaction mixture with a 10% aqueous  $Na_2CO_3$ . Ester IX was scarcely hydrolyzed in the process.

Under the action of ethanolic alkali sulfide IX is quantitatively split at the  $S-C_{NO_2}$  bond to form the C (NO<sub>2</sub>) (COOEt)<sub>2</sub> anion. This reaction can be utilized for the quantitative determination of IX.

C-Sulfenylation of the anions of nitromethane and nitroacetic ester does not take place according to the PMR and  $^{19}$ F NMR data under conditions similar to the synthesis of IX.

It is known that  $\alpha$ -nitroalkyl sulfides are usually easily oxidized by 30% H<sub>2</sub>O<sub>2</sub> in acetic acid. Sulfide IX is not oxidized by 90% H<sub>2</sub>O<sub>2</sub> in acetic acid and can be isolated reversibly. By applying a stronger oxidizing agent, viz., trifluoroperacetic acid, to sulfide IX it was possible to obtain trifluoromethanesulfonylnitromalonic ester (X). The optimal yield of X (~ 50%) was obtained in CH<sub>2</sub>Cl<sub>2</sub> with the use of a tenfold excess of an equimolar mixture of H<sub>2</sub>O<sub>2</sub> and (CF<sub>3</sub>CO)<sub>2</sub>O (~ 20°C, 7h). The formation of X in the reaction was accompanied by the formation of XI, chloronitromalonic ester (XII), and an unidentified fluoride. Sulfoxides do not form as a result of the oxidation of IX (the band of >S=O at 1050 cm<sup>-1</sup> is absent in the Raman spectrum).

Compound X was not obtained in the individual state; however, its structure was proved by analyzing mixtures of various composition by <sup>19</sup>F NMR, PMR, UV, and Raman spectroscopy. The content of X in the mixtures was 70-75%. Sulfone X is hydrolyzed at the  $S - C_{NO_2}$  bond by applying 10% aqueous  $Na_2CO_3$  to a toluene solution of X.

The closest analog of the  $CF_3SO_2$  group is the  $CCl_3SO_2$  group. We studied the possibility of obtaining the trichloromethyl  $\alpha$ -nitroalkyl sulfones  $CCl_3SO_2C(NO_2)R^1R^2$  by reacting sodium trichloromethanesulfinate with  $\alpha$ -nitrocarbanions in the presence of  $I_2$  or potassium ferricyanide (in analogy to [10, 12, 13]). In both reactions it is not possible to obtain  $\alpha$ -nitro sulfones, and only products of the oxidative dimerization and oxidative nitration of the original  $\alpha$ -nitrocarbanion form. For example, in the reactions with the Na salt of 2-nitropropane the dimer (CH<sub>3</sub>)<sub>2</sub>C (NO<sub>2</sub>)C (NO<sub>2</sub>) (CH<sub>3</sub>)<sub>2</sub> and 2,2-dinitropropane (which were identified by TLC and PMR) form in a 0.7:1 to 2:1 mole ratio. The yield of the dimer in the reaction with  $I_2$  is equal to ~60%, and the yield in the reaction with  $K_3$ Fe (C N)<sub>6</sub> is ~40%. The same products form when  $I_2$  is reacted with (CH<sub>3</sub>)<sub>2</sub>CNO<sup>-</sup>Na<sup>+</sup> in DMFA.

During the reaction of  $\sum CNO_2^- + CCl_3SO_2^- + I_2$  (DMFA),  $CCl_3SO_2^- Na^+$  is destroyed with the formation of

NaCl in an amount equal to 70-95%. This is partially due to the instability of the  $CCl_3SO_2^{-}$  anion in DMFA (25-30% NaCl formed in the control experiment).

The anion of the salt  $CCl_3SO_2$   $Et_4N^+$ , which is obtained by reacting tetraethylammonium hydroxide with trichloromethanesulfinic acid, is not oxidized in water by  $K_3Fe(CN)_6$  over the course of 24 h (the values of  $\lambda_{max}$  and  $\varepsilon$  for this salt remain unchanged). When  $CCl_3SO_2Cl$  is reacted in absolute acetonitrile with the tetra-ethylammonium salt of dinitromethane, chlorodinitromethane forms (yield up to 40%, spectrophotometrically).

The results obtained show that reactions characteristic of aromatic compounds of the  $ArSO_2^{-}M^{+}$  and  $ArSO_2Hal$  types (introduction of an  $ArSO_2$  group [10, 12, 13]) do not occur with the corresponding  $CCl_3SO_2$  derivatives.

#### EXPERIMENTAL

Absolute solvents were used in the work; IR spectra were recorded on a UR-20 instrument and <sup>19</sup>F NMR spectra (relative to CF<sub>3</sub>COOH external reference) were recorded on an RS-56 spectrometer (56 MHz), the PMR spectra were recorded on Tesla BS-497 (100 MHz) and Varian DA-60-74 (60 MHz) spectrometers, and the UV spectra were recorded on a Specord UV-VIS spectrophotometer. The establishment of the individual compounds, as well as their identification were carried out by TLC and GLC. TLC conditions:  $1:10 \text{ CH}_3\text{COOH}:\text{CHCl}_3$  as the mobile phase, silufol from Kavalier (Czechoslovakia) as the adsorbent, development of the chromatograms by a KI solution of I<sub>2</sub> vapors.

Trifluoromethylmethyl sulfone (I), trifluoromethanesulfonylacetic acid (VI), and trifluoromethanesulfonylmethylmagnesium bromide (II) were obtained according to [7]. The Na salt of nitromalonic ester (XI)  $\lambda_{max} \approx 308 \text{ nm}, \epsilon \approx 13,000 \text{ in } H_2\text{O}$ ) was obtained by reacting ethanolic alkali with XI [14] and precipitation by ether (84% yield).

1-(Trifluoromethanesulfonyl)-2-propanol (III). An ethereal solution of II (26.8 mmole) was slowly added with stirring and cooling (-20 to -30°C) to a solution of 3.6 g of acetaldehyde in 20 ml of absolute ether. At the conclusion of the addition the mixture was stirred for 15 min at ~20°C (a light-yellow precipitate formed), 80 ml of ice water were added, and the ether layer was separated. The ether was washed twice with water and dried with MgSO<sub>4</sub>. The solvent was distilled off, and the residue was vacuum-distilled. This yielded 4.8g (93%) of III, bp 56-58°C (2 mm Hg). Found: F, 29.81%. Calculated for  $C_4H_7O_3SF_3$ : F, 29.68%. PMR spectrum ( $\delta$ , ppm): 1.55 (d, 3H, CH<sub>3</sub>, J<sub>1</sub> = 6 Hz), 3.65 (d, 2H, CH<sub>2</sub>, J<sub>2</sub> = 6 Hz), 4.27 S (1H, OH), 4.7 sextet (quartet triplet) (1H, CH, J<sub>1</sub> = 6, J<sub>2</sub> = 6 Hz). IR spectrum ( $\nu$ , cm<sup>-1</sup>, NaCl): 1120, 1200 (CF<sub>3</sub>), 1360 (SO<sub>2</sub>), 2970 (CH<sub>3</sub>), 3550 (OH); compare [7].

<u>1-Bromo-3-trifluoromethanesulfonyl-2-methylpropanol (IV)</u>. After mixing and cooling to  $-10^{\circ}$ C, the ether solution was 0.02 M (II) and was slowly added to 2.75 ml of bromoacetone. The cooled portion was stirred, boiled for 5 h followed by addition of 10 ml water and 10% HCl at 0-5°C. The ether layer was separated and dried over MgSO<sub>4</sub>. The solution was heated and reduced in vacuo. Yield 3.6 g (63%) of IV, bp 72-74° (2 mm Hg). Found: Br 28.62; F 20.38%. C<sub>5</sub>H<sub>8</sub>O<sub>3</sub>SF<sub>3</sub>Br. Calculated: Br 28.10; F 20.00%. PMR spectrum ( $\delta$ , ppm): 1.63 s (3H, CH<sub>3</sub>), 3.54 s, 3.61 s, 3.65 s (5H, for CH<sub>2</sub>, CH<sub>2</sub>Br and OH). IR spectrum ( $\nu$ , cm<sup>-1</sup>, NaCl): 1120-1130 (CF<sub>3</sub>), 1200-1230 sh (CF<sub>3</sub>), 1150, 1370 (SO<sub>2</sub>), 3570 (OH).

<u>Trifluoromethanesulfonylacetone (V).</u> A mixture of 4.4 g of  $K_2Cr_2O_7$ , 46 ml water, and 9 ml conc.  $H_2SO_4$ was heated to 60°C, given an addition of a solution of 4 g of III in 13.5 ml of conc.  $H_2SO_4$ , held at that temperature for 1 h, cooled, extracted with  $CH_2Cl_2$ , washed with water (three 10-ml portions), and dried with MgSO<sub>4</sub>. The solvent was distilled off in a vacuum. This yielded 2.7 g (79%) of V. The substance was chromatographically pure, mp 36-37°C (from hexane), bp 70°C (4 mm Hg). PMR spectrum ( $\delta$ , ppm): 2.4 (s, 3H,  $CH_3$ ), 4.38 (s, 2H,  $CH_2$ ). IR spectrum ( $\psi$ , cm<sup>-1</sup>, NaCl): 1120, 1200 (CF<sub>3</sub>), 1350-1370 (SO<sub>2</sub>), 1720 (C=O), 2980 (CH<sub>3</sub>).

Bis (trifluoromethanesulfonyl)furoxan (VII). A 2-g portion of VI was slowly added with cooling  $(0-5^{\circ}C)$  and stirring to 4 ml of 20% fuming HNO<sub>3</sub>. After completion of the addition, the reaction mixture was held for 2 h at 10°C and 1 h at ~20°C, poured onto ice, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extract was dried with MgSO<sub>4</sub>. The solvent was distilled off, and the residue was vacuum-distilled. This yielded 1.2 g (33%) of VII, bp 65°C (3 mm Hg). Found: C 13.37; N 7.86%. Calculated for C<sub>4</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>F<sub>6</sub>: C 13.78; N 8.02%. UV spectrum (H<sub>2</sub>O, ethanol): 270 nm. <sup>19</sup>F NMR spectrum: -5.37 (s, 3F, CF<sub>3</sub>), -2.84 (s, 3F, CF<sub>3</sub>). IR spectrum  $(\psi, \text{ cm}^{-1}, \text{ NaCl})$ : 1040 (furoxan ring), 1235, 1115 (CF<sub>3</sub>), 1355 br (SO<sub>2</sub>), 1425 (O-N  $\rightarrow$  O).

Ammonium Salt of Trifluoromethyl Nitromethyl Sulfone (VIIIa). A solution of 0.2 g of VI in 4 ml of absolute  $CH_2Cl_2$  at 5-10°C was added with stirring to a mixture of 0.44 ml of conc.  $H_2SO_4$  and 0.44 ml of  $HNO_3$  (d = 1.5). The solution obtained was held at 40°C for 2.5 h, cooled to 0-5°C, and poured into 140 ml of 1.5% aqueous KOH. The aqueous layer was separated, 80 ml of  $CH_2Cl_2$  was added, cooled to 0-5°C, and given a dropwise addition of 2.5 ml of conc.  $H_2SO_4$ . The extract was separated, dried with MgSO<sub>4</sub>, concentrated to 10 ml, 2 ml of a saturated solution of NH<sub>3</sub> in absolute  $CH_2Cl_2$  at 0-5°C was added with stirring. The precipitated yellow salt was washed twice with  $CH_2Cl_2$  and dried over  $P_2O_5$ . This yielded 0.075 g (34%) of VIIIa. PMR spectrum ( $\delta$ , ppm): 6.18 (s,  $CH_2$ ). <sup>19</sup>F NMR spectrum (DMSO): -3.81 (s,  $CF_3$ ). IR spectrum ( $\nu$ , cm<sup>-1</sup>, KBr): 890, 1195, 1410 (NO<sub>2</sub>), 1170 br, 1380 br (SO<sub>2</sub>), 1120 (CF<sub>3</sub>), 3300 br (NH<sub>4</sub><sup>+</sup>).

Cesium Salt of Trifluoromethyl Nitromethyl Sulfone (VIIIb). To a solution of 0.10 g of VIIIa in 1.5 ml of distilled water several drops of a saturated solution of CsF in water was added. The precipitated salt (VIIIb) was washed three times with CH<sub>2</sub>Cl<sub>2</sub> and dried in a vacuum over P<sub>2</sub>O<sub>5</sub>. This yielded 0.11 g (69%) of VIIIb, mp 137-138°C. UV spectrum (H<sub>2</sub>O):  $\lambda_{max}$  295 nm,  $\varepsilon = 13,000$ . Found: C 7.53; H 0.59; N 4.09; S 9.70; F 18.17%. Calculated for C<sub>2</sub>HNO<sub>4</sub>SF<sub>3</sub>Cs: C 7.40; H 0.34; N 4.10; S 9.86; F 17.58%. IR spectrum ( $\psi$ , cm<sup>-1</sup>, KBr): 890, 1195, 1410 (NO<sub>2</sub>), 1170, 1380 (SO<sub>2</sub>), 1120, 1200 (CF<sub>3</sub>), 3130 (CH).

<u>Trifluoromethyl Nitromethyl Sulfone (VIII)</u>. To a solution of 0.063 g of VIIIa in 2 ml of  $H_2O$  was added 17 ml of  $CH_2CI_2$  followed by 5 ml of 60%  $H_2SO_4$  at 0-5°C. The yield of VIII was 90% (spectrophotometrically in 0.1 N KOH/H<sub>2</sub>O). The  $CH_2CI_2$  layer was separated and dried with MgSO<sub>4</sub>. PMR spectrum: 5.91 (s,  $CH_2$ ). <sup>19</sup>F NMR spectrum (in  $CH_2CI_2$ ): -1.01 (s,  $CF_3$ ).

<u>Trifluoromethylsulfenylnitromalonic Ester (IX).</u> A 4.5-g portion of  $CF_3SC1$  [15] was bubbled into a suspension of 5 g of the Na salt of nitromalonic ester in 60 ml of absolute  $CCl_4$  with stirring and cooling (3 to  $-3^{\circ}C$ ) after it was passed through NaF dried before the beginning of the reaction for 2-3 h in a vacuum at 200-250°C. The mixture was stirred for 6 h at ~20°C, held for 48 h, and filtered. The solvent was removed, and the oil was dissolved in 20 ml of toluene, washed with 10% Na<sub>2</sub>CO<sub>3</sub> (four 20-ml portions) and water, and dried with MgSO<sub>4</sub>. The completeness of the removal of XI was verified by TLC. The toluene was distilled off, and the residue was distilled. This yielded 2.8 g (42%) of IX, bp 89-90°C (1 mm Hg). Found: C 31.1; H 3.18; N 5.28; S 10.2; F 19.92%. Calculated for  $C_8H_{10}NO_6SF_3$ , C 31.4; H 3.28; N.4.59; S 10.5; F 18.70%. IR spectrum ( $\nu$ , cm<sup>-1</sup>, NaCl): 854, 1300,

1590 (NO<sub>2</sub>), 1106, 1160 d, 1184 (CF<sub>3</sub>), 762 (S-CF<sub>3</sub>), 1722-1760 br (C=O), 1232 d, 1255 (COC), 3000 m (CH<sub>2</sub>CH<sub>3</sub>). PMR spectrum ( $\delta$ , ppm): 1.58 ( $\delta$ , 3H, CH<sub>3</sub>), 4.60 (q, 2H, CH<sub>2</sub>). <sup>19</sup>F NMR spectrum: -41.5 (s, CF<sub>3</sub>S).

<u>Oxidation of IX.</u> A 20.3-ml portion of  $(CF_3CO)_2O$  was added to 3.16 ml of 90%  $H_2O_2$  in 48 ml of absolute  $CH_2Cl_2$  at 0-5°C with stirring, and then a solution of 4 g of IX in 48 ml of absolute  $CH_2Cl_2$  was added, and the mixture was stirred for 7 h at ~20°C and poured into ice water. The organic layer was washed with water and dried with MgSO<sub>4</sub>, the solvent was driven off, and the residue (3g) was fractionated. The fraction with by 96°C. (1 mm Hg) (1.6 g) contained 73% X, 15% XII, 7% fluoride, and 5% XI. <sup>19</sup>F NMR spectrum: -15.6 (s, CF<sub>3</sub>) (X), -12.0 (s, fluoride). Raman spectrum: 1120  $\psi_S$  SO<sub>2</sub>), 1350\*  $\psi_{as}$  SO<sub>2</sub>), 1355  $\psi_{as}$  NO<sub>2</sub>), 1350\*  $\psi_S$  NO<sub>2</sub>), 1108  $\psi_S$  CF<sub>3</sub>), 1775 (C = O), 1155 (C - O - C), 1465 (CH<sub>2</sub>CH<sub>3</sub>). Compounds XII and XI were identified by GLC. The presence of a C (NO<sub>2</sub>) (COOEt)<sub>2</sub> fragment in X was demonstrated by hydrolysis of a toluene solution of a mixture of X, XI, and XII under the action of 10% aqueous Na<sub>2</sub>CO<sub>3</sub> with spectrophotometric monitoring according to the <sup>-</sup>C (NO<sub>2</sub>) (COOEt)<sub>2</sub> anion. Under these conditions XII and IX are not hydrolyzed.

<u>Tetraethylammonium Salt of Trichloromethanesulfinic Acid.</u> a) Tetraethylammonium hydroxide was obtained by shaking (3-5 h) 30 g of silver oxide with a solution of 30 g of  $Et_4 NI$  in 300 ml of absolute methanol, the mixture was filtered, and benzene was added to a volume of 1 liter. The content of the hydroxide was determined by titration with benzoic acid.

b) A solution of 21.8 mmole of  $CCl_3SO_2H$  [16] in 7 ml of absolute  $CH_3OH$  was given a dropwise addition of 98.6 ml (20.7 mmole) of a solution of  $Et_4NOH$  with stirring at 0-5°C. After 20 min, the reaction mixture was given an addition of ~21iter of ether and cooled, and the salt precipitating was filtered, washed with ether, and dried in a vacuum over NaOH. This yielded 4.1 g (63%) of  $Et_4NSO_2CCl_3$ , mp 140-142°C (with decomposition). Found: C 34.98; H 7.37; N 4.39; S 9.84; Cl 32.65%. Calculated for  $C_9H_{20}NO_2SCl_3$ : C 34.56; H 6.44; N 4.47; S 10.25; Cl 34.01%. UV spectra (nm): in  $H_2O \lambda'_{max} = 238$  ( $\varepsilon = 2240$ ), in abs.  $CH_3CN \lambda'_{max} = 248$ ,  $\lambda''_{max} = 273$ . PMR spectrum ( $\delta$ , ppm, acetone-d<sub>6</sub>): 1.37 (t.t., 3H, CH<sub>3</sub>), 3.33 (q, 2H, CH<sub>2</sub>), i.e., (CH<sub>3</sub>CH<sub>2</sub>)<sub>4</sub>N. IR spectrum ( $\nu$ , cm<sup>-1</sup>, KBr): 765, 785, 1045, 1080, 1142, 1189, 1264, 1320, 1380, 1409, 1470-1480, 2958, 2999-3000, compare [17].

### CONCLUSIONS

1. The nitration of trifluoromethanesulfonylacetic acid results in the formation of trifluoromethyl nitromethyl sulfone and its conversion product, viz., bis (trifluoromethanesulfonyl) furoxan.

2. The reaction of nitromalonic ester with trifluoromethanesulfenyl chloride yields trifluoromethanesulfenylnitromalonic ester, and its oxidation yields trifluoromethanesulfonylnitromalonic ester.

3. The reaction of trifluoromethanesulfonylmethylmagnesium bromide with bromoacetone results in the addition of the former to the carbonyl group.

#### LITERATURE CITED

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\*Superposition of bands of SO<sub>2</sub>  $(\nu_{as})$  and NO<sub>2</sub>  $(\nu_{s})$ .