

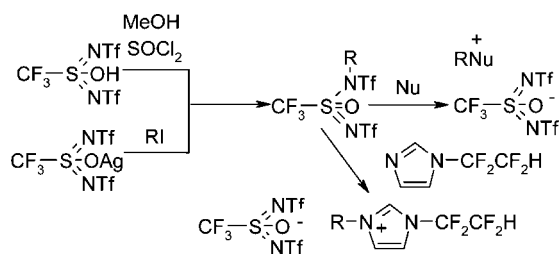
Alkyl Derivatives of  
Bis(perfluoroalkylsulfonylimino)  
trifluoromethanesulfonic Acid

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Received February 2, 2009



*N*-Methyl and *N*-ethyl derivatives of *N*-(trifluoromethylsulfonyl)-[*N'*-(trifluoromethylsulfonyl)-trifluoromethylsulfoximido] imides **2a,b** were prepared by alkylation of bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic acid **1** or its silver salt **1a**. It turns out that these imides are strong alkylating agents in spite of the fact that Me (Et) groups are attached to nitrogen atom. The alkylating activity of *n*-PrI, *i*-PrI, *n*-BuI, and *n*-AmI in the presence of silver salt of bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic acid **1a** was investigated.

Recently, the synthesis of bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic acid **1** through the condensation of *N*-(trifluoromethylsulfonyl)trifluoromethanesulfoximido fluoride with trifluoromethanesulfonamide was described by us.<sup>1</sup> Before this synthetic success, the calculations of deprotonation enthalpies predicted that the gas phase acidity of acid **1** is in excess of TfOH by 30 kcal/mol (i.e., more than 21 p*K*<sub>a</sub> units) and is approximately equal to HF-SbF<sub>5</sub>, which is known as "magic acid".<sup>2</sup>

Acid **1** can be represented as an analogue of trifluoromethanesulfonic acid in which both oxygen atoms are substituted by fragment =NTf. It was shown earlier that such replacement contiguous to C, P, S, and I centered groups caused

substantial increase of their electron-withdrawing properties<sup>3</sup> and considerable extension of the anionic charge delocalization in such a substituent. This also suggests that the strength of new bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic acid **1** must be considerably above the TfOH and HN(Tf)<sub>2</sub>, which are the strongest organic acids with the exception of the carborane acids.<sup>4</sup> Moreover, several reactive centers in the molecule are presented; therefore, our interest was an in-depth study of its properties to be compared with the above-mentioned acids.

Powerful methylating agents, such as trimethyloxonium salts,<sup>5</sup> methyl fluorosulfonate,<sup>6</sup> methyl trifluoromethane sulfonate,<sup>7</sup> and methyl nonafluoro-*n*-butanesulfonate,<sup>8</sup> are widely applicable. Methyl esters of very strong acids are commercially available, and other esters of these acids are easily prepared and have found uses in solvolytic studies of otherwise unreactive substrates.<sup>9</sup> Due to the excellent leaving group properties, alkyl perfluoroalkanesulfonates are one of the most powerful alkylating agents known, with the exception of the oxonium salts, capable of alkylating carbon, oxygen, and nitrogen centers. However, Meerwein salts have low solubilities, whereas methyl triflate as well as the somewhat less reactive but also less expensive methyl fluorosulfonate may well be the reagent of choice for methylation.<sup>10</sup> It has been reported on the basis of conductometric studies that acidities of currently used superacids, which determined the alkylating ability of their esters, are approximately equal but vary in different solvents: CF<sub>3</sub>SO<sub>2</sub>OH > HClO<sub>4</sub> > FSO<sub>2</sub>OH > H<sub>2</sub>SO<sub>4</sub> in acetic acid<sup>11</sup> and FSO<sub>2</sub>OH > ClSO<sub>2</sub>OH ~ CF<sub>3</sub>SO<sub>2</sub>OH ≫ HClO<sub>4</sub> in sulfuric acid.<sup>12</sup>

We now wish to report results of acid **1** alkylation, the synthesis of *N*-methyl and *N*-ethyl derivatives **2a,b**, and their alkylating ability toward different nucleophiles, as well as alkylation reactions by alkyl halides in the presence of silver salt of acid **1**.

It is well-known that alkyl perfluoroalkanesulfonates are readily available via the reaction of alkyl halides with silver salts of the perfluoroalkanesulfonic acids. In order to prepare alkyl esters of bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic acid **1**, we carried out similar reactions of the silver salt of acid **1** with alkyl halides (MeI, EtI, *n*-BuI, *i*-BuI, *t*-BuI, *n*-PrBr, *i*-PrBr, *n*-AmI) at room temperature in different solvents (Et<sub>2</sub>O, benzene, CH<sub>2</sub>Cl<sub>2</sub>). Precipitation of silver halide was observed in all experiments, but only *N*-methyl and *N*-ethyl derivatives of *N*-(trifluoromethylsulfonyl)-[*N'*-(trifluoromethylsulfonyl)trifluoromethylsulfoximido]imides **2a,b** have

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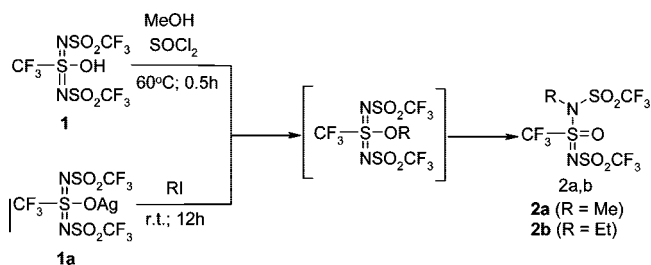
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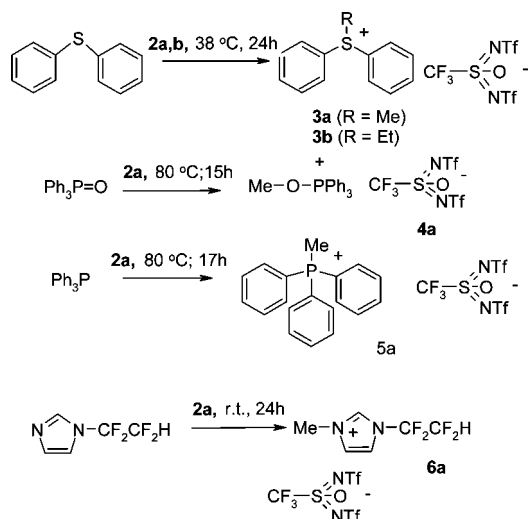
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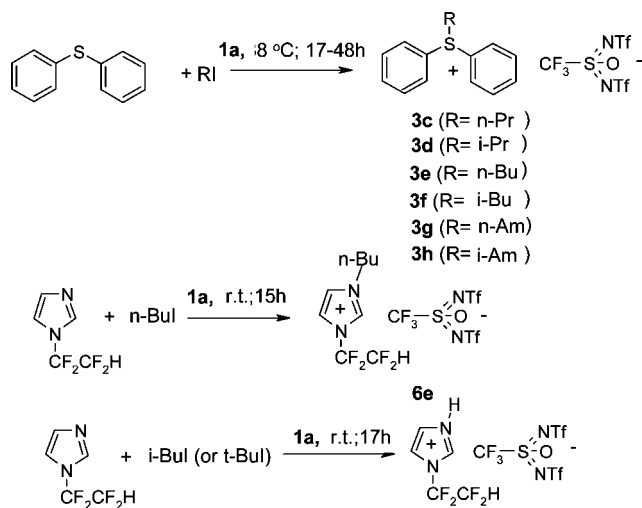
**SCHEME 1. Synthesis of *N*-Methyl and *N*-Ethyl Derivatives of *N*-(Trifluoromethylsulfonyl)-[*N'*-(trifluoromethylsulfonyl)-trifluoromethylsulfoximidoyl]imides **2a,b****



**SCHEME 2. Reactions of *N*-Methyl (**2a**) and *N*-Ethyl (**2b**) Derivatives of *N*-(Trifluoromethylsulfonyl)-[*N'*-(trifluoromethylsulfonyl)trifluoromethylsulfoximidoyl]imides with Nucleophiles**



**SCHEME 3. Reactions of Alkyl Halogenides with Nucleophiles in the Presence of Silver Salt **1a** of Bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic Acid**



been obtained with good yields in the cases of methyl and ethyl halides (Scheme 1).

We failed to obtain esters of acid **1** or *N*-alkyl imides **2** with propyl, butyl, or amyl halides or to detect them by NMR method, and the acid **1** was isolated in 70–80% yield as the major

product after workup. Probably, under these conditions, the competitive elimination reaction to olefins via carbocation formation becomes predominant.

It is highly probable that the reaction runs via generation of *O*-alkyl esters of bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonic acid, which are alkylating agents so powerful that they alkylate “themselves” through S=N double bond. The resulting *N*-methyl and *N*-ethyl derivatives **2a,b** are reasonably stable liquids at room temperature.

*N*-Methyl-*N*-(trifluoromethylsulfonyl)-[*N'*-(trifluoromethylsulfonyl)trifluoromethylsulfoximidoyl]imide **2a** can be prepared by reaction of acid **1** with methanol in the presence of thionyl chloride<sup>13</sup> with excellent yield (Scheme 1).

The imides **2a,b** have been tested as methylating agents toward S-, N-, and P-nucleophiles. It turned out that they have been sufficiently powerful alkylating agents, in spite of the fact that the alkyl group is connected with the nitrogen atom. Nucleophilic substitution reactions of *N*-alkyldi(trifluoromethanesulfonyl)amides with sodium, potassium salts,<sup>14</sup> methylation of *N*-methyl, *N*-ethyl imidazoles or pyridine,<sup>15</sup> as well as benzylation of alcohols<sup>16</sup> were reported. We found that imides **2a,b** react with diphenylsulfide, triphenylphosphine, and triphenylphosphate with good yields on warming. The imides **2a,b** react exothermically with *N*-methyl imidazole in methylene chloride at 0 °C, giving the products of imidazole ring splitting, while interaction with *N*-tetrafluoroethyl imidazole proceeds easily at room temperature with quantitative yield. The data are presented in Scheme 2 and Table 1.

It should be noted that imidazolium (**6**), sulfoxonium (**3**), and phosphonium (**5**) salts are stable liquids, kept at –20 °C for a few days without glass transition, and may be of interest as room temperature ionic liquids with a novel anion.

We investigated a possibility of propyl, butyl, amyl in situ carbocation generation for the reactions of acid **1** silver salt with corresponding alkyl halides and diphenylsulfide as a model substrate. It was found that direct alkylation of Ph<sub>2</sub>S using *n*-Pr, *i*-Pr, *n*-Bu, and *n*-Am halides in the presence of the silver salt **1a** affords high yields of the corresponding sulfonium salts **3c–e,g**, respectively (Scheme 3 and Table 2).

In the case of *i*-BuI and *t*-BuI, alkylation did not occur. If 1-(2,2,2-trifluoroethyl)imidazole was used as a model substrate, *n*-BuI produced 1-(*n*-butyl)-3-(1,1,2,2-tetrafluoroethyl)imidazolium bis-(trifluoromethylsulfonylimino)trifluoromethanesulfonate **6e** in good yield while 1-(*H*)-3-(1,1,2,2-tetrafluoroethyl)imidazolium bis(trifluoromethylsulfonylimino)trifluoromethanesulfonate **7** was the product of the reaction with *i*-BuI and *t*-BuI (Scheme 3).

Recently, we have prepared the unsymmetrical analogue of acid **1**, *N*-(trifluoromethylsulfonylimino)-*N'*-(nonafluoro-*n*-butylsulfonylimino)trifluoromethanesulfonic acid **8**.<sup>17</sup> It turned out that the reaction of acid **8** with methanol showed methylation on both NTf and NNf nitrogen atoms about pari passu formation of **9** (52%) and **10** (42%) with the traces of methylation through the S=O bond of triflic group **11** (6%), which was detected by NMR spectroscopy (Scheme 4).

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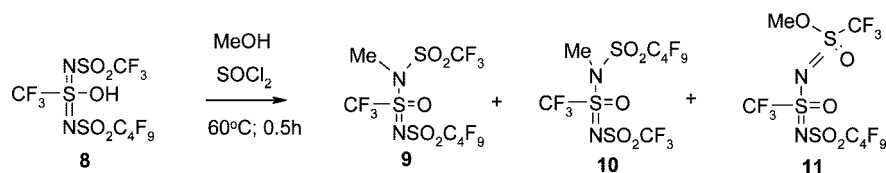
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**SCHEME 4. Synthesis of *N*-Methyl Derivatives of *N*-(Trifluoromethylsulfonylimino)-*N'*-(nonafluoro-*n*-butylsulfonylimino)trifluoromethanesulfonic Acid **8****



**TABLE 1. Reactions of *N*-Methyl (**2a**) and *N*-Ethyl (**2b**) Derivatives of *N*-(Trifluoromethylsulfonyl)-[*N'*-(trifluoromethylsulfonyl)trifluoromethylsulfoximidoyl]imides with Nucleophiles via Scheme 2**

N	alkylating agent	nucleophiles	$\tau$ (h)	$T$ ( $^{\circ}\text{C}$ )	product	isolated yield (%)
1	<b>2a</b>	$\text{Ph}_2\text{S}$	12	rt	<b>3a</b>	(10) <sup>a</sup>
2	<b>2a</b>	$\text{Ph}_2\text{S}$	24	38	<b>3a</b>	(97) <sup>a</sup> 89
3	<b>2b</b>	$\text{Ph}_2\text{S}$	12	rt	<b>3b</b>	(0) <sup>a</sup>
4	<b>2b</b>	$\text{Ph}_2\text{S}$	24	38	<b>3b</b>	(95) <sup>a</sup> 56
5	<b>2a</b>	$\text{Ph}_3\text{P}=\text{O}$	15	80	<b>4a</b>	(100) <sup>a</sup> 92
6	<b>2a</b>	$\text{Ph}_3\text{P}$	17	80	<b>5a</b>	(100) <sup>a</sup> 89
7	<b>2a</b>	1- $\text{CF}_2\text{CF}_2\text{H}$ -imidazole	24	rt	<b>6a</b>	(97) <sup>a</sup> 90

<sup>a</sup> The yield calculated on the basis of <sup>19</sup>F and <sup>1</sup>H NMR spectra data.

**TABLE 2. Reactions of Alkyl Halides with Nucleophiles in the Presence of Silver Salt of Bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic Acid **1a** via Scheme 3**

N	alkylating agent	nuc	$\tau$ (h)	$T$ ( $^{\circ}\text{C}$ )	product	isolated yield (%)
1	<b>1a</b> + <i>n</i> -PrI	$\text{Ph}_2\text{S}$	48	rt	<b>3c</b>	(0) <sup>a</sup>
2	<b>1a</b> + <i>n</i> -PrI	$\text{Ph}_2\text{S}$	19	38	<b>3c</b>	(72) <sup>a</sup> 45
					<b>3d</b>	(3.6) <sup>a</sup>
3	<b>1a</b> + <i>i</i> -PrBr	$\text{Ph}_2\text{S}$	48	38	<b>3d</b>	(94) <sup>a</sup> 50
4	<b>1a</b> + <i>n</i> -BuI	$\text{Ph}_2\text{S}$	17	38	<b>3e</b>	(80) <sup>a</sup> 68
					<b>3f</b>	(5) <sup>a</sup>
5	<b>1a</b> + <i>i</i> -BuI	$\text{Ph}_2\text{S}$	24	38	<b>3f</b>	0
6	<b>1a</b> + <i>t</i> -BuI	$\text{Ph}_2\text{S}$	14	38		0
7	<b>1a</b> + <i>t</i> -BuI	$\text{Ph}_2\text{S}$	14	140		0
8	<b>1a</b> + <i>n</i> -Aml	$\text{Ph}_2\text{S}$	19	38	<b>3g</b>	(85) <sup>a</sup> 83
					<b>3h</b>	(14) <sup>a</sup>
9	<b>1a</b> + <i>n</i> -BuI	1- $\text{CF}_2\text{CF}_2\text{H}$ imidazole	15	rt	<b>6e</b>	(91) <sup>a</sup> 84
10	<b>1a</b> + <i>i</i> -BuI	1- $\text{CF}_2\text{CF}_2\text{H}$ imidazole	18	rt	<b>7</b>	(91) <sup>a</sup> 84

<sup>a</sup> The yield calculated on the basis of <sup>19</sup>F and <sup>1</sup>H NMR spectra data.

In conclusion, *N*-methyl and *N*-ethyl derivatives of *N*-(trifluoromethylsulfonyl)-[*N'*-(trifluoromethylsulfonyl)trifluoromethylsulfoximidoyl]imides **2a,b** are formed upon alkylation of bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic acid **1** or its silver salt **1a**, and they turned out to be strong alkylating agents, in spite of the fact that the alkyl group is attached to the nitrogen atom. Alkylation of nucleophiles by *n*-PrI, *n*-BuI, and *n*-Aml in the presence of silver salt **1a** runs more selectively than probably arises from the formation of transitional complex with a voluminous anion.

### Experimental Section

All reactions were carried out in oven-dried glassware under nitrogen atmosphere, unless otherwise noted. All solvents and reagents were distilled immediately before use.

**Preparation of Silver Salt of Bis(trifluoromethylsulfonylimino)trifluoromethanesulfonic Acid (**1a**).** Silver carbonate (0.36 g, 1.3 mmol) was gradually added to aqueous solution of acid **1** (0.41 g, 1 mmol). The mixture was stirred for 15 h at rt and filtered, and water was removed in vacuo. The residue was dried for 25 h at 50  $^{\circ}\text{C}/0.04$  mmHg: Yield 0.43 g (85%); mp 105–108  $^{\circ}\text{C}$ ; decomposition started at 180  $^{\circ}\text{C}$ ; <sup>19</sup>F NMR (200 MHz, Et<sub>2</sub>O)  $\delta$  –79.2 (6F, s, 6F, CF<sub>3</sub>), –79.35 (3F, s, CF<sub>3</sub>). Anal. Calcd for C<sub>3</sub>F<sub>9</sub>AgN<sub>2</sub>O<sub>5</sub>S<sub>3</sub>: C, 6.94; F, 32.95; N, 5.39; S, 18.49. Found: C, 6.94; F, 32.94; N, 5.42; S, 18.9.

**Preparation of *N*-Methyl (**2a**) and *N*-Ethyl (**2b**) Derivatives of *N*-(Trifluoromethylsulfonyl)-[*N'*-(trifluoromethylsulfonylimino)trifluoromethylsulfoximidoyl]imides.**

**Method A:** Methyl or ethyl iodide (0.71 and 0.78 g, 5 mmol) was gradually added to a solution of silver salt **1a** (2 g, 4 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> with effective stirring and protection from moisture and light. The mixture was stirred for 12 h at room temperature, and AgI was filtered off. The solvent was removed in vacuo, and the residue was distilled: yields 1.07 g (65%) (**2a**) and 1.28 g (76%) (**2b**).

**Method B:** SOCl<sub>2</sub> (5 g, 42 mmol) was gradually added to the solution of acid **1** or **8** (0.8 or 1.12 g, 2 mmol) in methanol (1.12 g, 35 mmol) with stirring and protection from moisture. The mixture was refluxed until hydrogen chloride evolution ceased (0.5 h), and the product was isolated by distillation: yields 0.63 g (76%) (**2a**) and 1.02 g (89%) (**9–11**).

**Preparation of Bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonates (**3a,b**, **4a**, **5a**, **6a**).** The mixture of **2a** or **2b** (0.43 or 0.44 g, 1 mmol) and corresponding nucleophile (1 mmol) was heated with stirring and then was been reprecipitated from CH<sub>2</sub>Cl<sub>2</sub> by hexane. The temperature, time, and yields of salts are listed in Table 1.

**Preparation of Bis(perfluoroalkylsulfonylimino)trifluoromethanesulfonates (**3c–h**, **6e**, **7**).** The mixture of corresponding alkyl iodide (1 mmol) and diphenylsulfide or 1-(1,1,2,2-tetrafluoroethyl)imidazole (1 mmol) was gradually added to solution silver salt of acid **1** (0.52 g, 1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 mL). The mixture was refluxed, and the product was precipitated from CH<sub>2</sub>Cl<sub>2</sub> by hexane addition. The temperature, time, and yields of salts are listed in Table 2.

**Acknowledgment.** We thank Dr. T. M. Sokolenko (Institute of Organic Chemistry, National Academy of Sciences of Ukraine) for amiable supply of *N*-tetrafluoroethylimidazole, and V.V. Polovinko (Enamine Ltd., Kiev) for recording <sup>13</sup>C NMR spectra.

**Supporting Information Available:** Compound characterization, analytical data, and <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO900195K