ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 9, pp. 1275–1279. © Pleiades Publishing, Inc., 2006.
Original Russian Text © L.M. Yagupol'skii, A.V. Bezdudnyi, Yu.L. Yagupol'skii, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 9, pp. 1297–1300.

Unusual Reactions of *N*-(Trifluoromethylsulfonylimino)di- and -trifluoromethanesulfinimidoyl Chlorides

L. M. Yagupol'skii, A. V. Bezdudnyi, and Yu. L. Yagupol'skii

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, ul. Murmanskaya 5, Kiev, 02094 Ukraine
e-mail: yurii@fluor-kiev.ua

Received August 2, 2005

Abstract—*N*-(Trifluoromethylsulfonylimino)di- and -trifluoromethanesulfinimidoyl chlorides $RS(=NSO_2CF_3)Cl$ (R = CF_3, CHF_2) react with potassium fluoride in 1,2-dimethoxyethane with formation of the corresponding *N*,*N*′-bis(trifluoromethylsulfonyl)fluoromethanesulfinimidamide potassium salts $RS(=NSO_2CF_3)NSO_2CF_3^-K^+$. Analogous methanesulfinimidoyl and fluoromethanesulfinimidoyl chlorides (R = CH_3, CH_2F) fail to react with KF under similar conditions. Treatment of trifluoromethanesulfenamides CF_3SNR_2 with *N*,*N*-dichlorotrifluoromethanesulfonamide $CF_3SO_2NCl_2$ leads to *N*,*N*-disubstituted *N*′-(trifluoromethylsulfonyl)trifluoromethanesulfinimidamides $CF_3S(=NSO_2CF_3)NR_2$. The reaction of *N*,*N*-dimethyl-*N*′-(trifluoromethylsulfonyl)trifluoromethanesulfinimidamide (R = CH_3) with gaseous hydrogen chloride in diethyl ether gives sulfinimidoyl chloride $CF_3S(=NSO_2CF_3)Cl$ which could not be obtained by imination of CF_3SCl.

DOI: 10.1134/S1070428006090041

We previously showed that replacement of an sp^2-oxygen atom by trifluoromethylsulfonylimino group ($CF_3SO_2N=$) at a carbon, sulfur, selenium, phosphorus, or iodine atom very strongly enhances the electron-acceptor power of such a substituent [1]. For example, in going from $–SO_2Cl$ to $–S(=O)(=NSO_2CF_3)Cl$ and $–S(=NSO_2CF_3)_2Cl$ (replacement of one or two oxygen atoms), the constant σ increases from 1.03 to 1.46 and 1.70, respectively; this effect is comparable to that produced by two or three nitro groups in the *ortho* and *para* positions to reaction center in benzene ring. Analogous replacement in an –S(=O)Cl group increases its σ_p value from 0.7 to 1.34 [2]. Thus introduction of an extremely strong electron-acceptor CF_3SO_2N group to the sulfur atom in such compounds reduces the negative charge on the chlorine atom and sharply changes their reactivity. Unlike benzenesulfonyl chloride, they do not react with ammonia with formation of amides but are reduced to sulfur(IV) derivatives like $PhS(=NSO_2CF_3)O^-NH_4^+$ and $[PhS(=NSO_2CF_3)NSO_2CF_3]^-NH_4^+$.

The chlorine atom in bis(trifluoromethylsulfonylimino) derivative $PhS(=NSO_2CF_3)_2Cl$ becomes so positive that this compound acts as a powerful chlorinating agent capable of chlorinating not only benzene but trifluoromethylbenzene to give, respectively, chlorobenzene and 1-chloro-3-trifluoromethylbenzene and sulfur(IV) compound $PhS(=NSO_2CF_3)NHSO_2CF_3$ [2]. An attempt to replace the chlorine atom by fluorine in *N*-(trifluoromethylsulfonyl)benzenesulfinimidoyl chloride $PhS(=NSO_2CF_3)_2Cl$ by the action of silver fluoride also resulted in reduction of the substrate to $[PhS(=NSO_2CF_3)NSO_2CF_3]^-Ag^+$ [2]. The corresponding reduction product was also obtained in the reaction of $CF_3S(=O)(=NSO_2CF_3)Cl$ with ammonia [3].

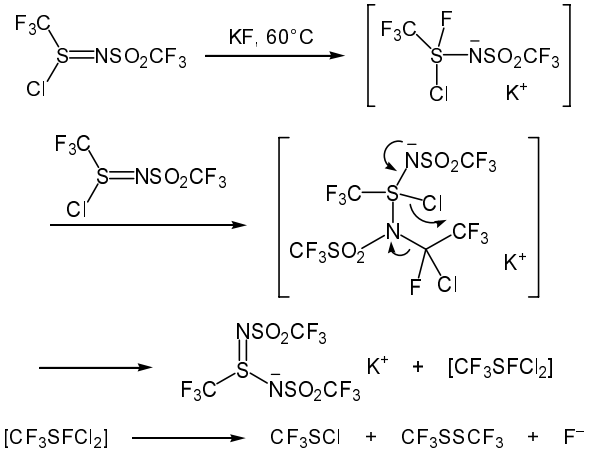
The fluorine atom is much more difficult to make positive, as compared to chlorine. Therefore, *N*-(trifluoromethylsulfonylimino)benzene- and -trifluoromethanesulfonimidoyl fluorides and even *N*,*N*′-bis(trifluoromethylsulfonylimino)benzenesulfonodiimidoyl fluoride $PhS(=NSO_2CF_3)_2F$ react with ammonia and amines to give the corresponding amides rather than sulfur reduction products [2].

The chlorine atom in *N*-trifluoromethylsulfonyl-substituted benzene- and trifluoromethanesulfinimidoyl chlorides is not as positive as in the corresponding sulfur(VI) derivatives. For example, the chlorine atom in $PhS(=NSO_2CF_3)Cl$ can be replaced by fluorine by the action of AgF, and the process is not accompanied by reduction of the sulfur atom [2]. Likewise, *N*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidoyl chloride $CF_3S(=NSO_2CF_3)Cl$ reacts with metal trimethylsilanolates (M = Li, Na, K) and trifluoro-

methanesulfonamide disilver salt, resulting in replacement of the chlorine atom without reduction [4, 5].

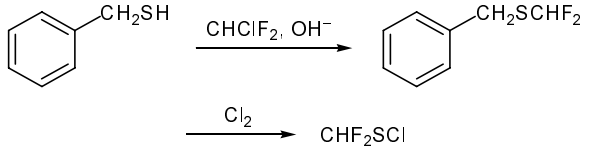
We revealed an interesting transformation while attempting to replace the chlorine atom in *N*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidoyl chloride $CF_3S(=NSO_2CF_3)Cl$ by fluorine via treatment with KF or AgF [5]. The products were *N*,*N*′-bis(trifluoromethylsulfonylimino)trifluoromethanesulfinimidamide salts (Scheme 1).

Scheme 1.



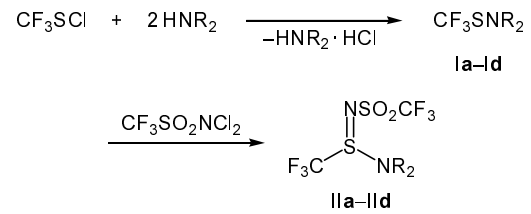
The goal of the present work was to elucidate how the electronic nature of the group attached to the sulfur atom affects the above reaction. We believed that inductive effect of this group is important; in combination with the electron-withdrawing effect of the CF_3SO_2N group, it ensures formation of a positive charge on the sulfur atom so that the latter becomes capable of taking up fluoride ion. As substrates we used *N*-trifluoromethylsulfonyl-substituted sulfinimidoyl chlorides of the general formula $RS(=NSO_2CF_3)Cl$ where R = CF_3 (σ_I = 0.39), CHF_2 (σ_I = 0.26), CH_2F (σ_I = 0.13), and CH_3 (σ_I = –0.08) [6]. Difluoromethanesulfenyl chloride was synthesized according to the procedure described in [7], by difluoromethylation of phenylmethanethiol in alkaline medium and subsequent chlorination (Scheme 2).

Scheme 2.



Trifluoromethanesulfenyl chloride failed to react with *N*,*N*-dichlorotrifluoromethanesulfonamide on prolonged heating at 80°C. Therefore, we initially synthesized *N*,*N*-disubstituted trifluoromethanesulfenamides **Ia**–**Id** in which the sulfur atom is linked to electron-donor amino group. Compounds **Ia**–**Id** readily reacted with $CF_3SO_2NCl_2$ in methylene chloride to give *N*,*N*-disubstituted *N*′-(trifluoromethylsulfonyl)trifluoromethanesulfinimidamides **IIa**–**IId** (Scheme 3).

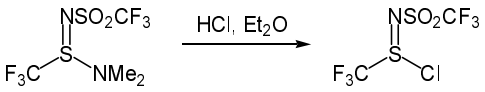
Scheme 3.



R = Me (**a**), Et (**b**), *cyclo*-C_6H_{11} (**c**); R_2N = morpholino (**d**).

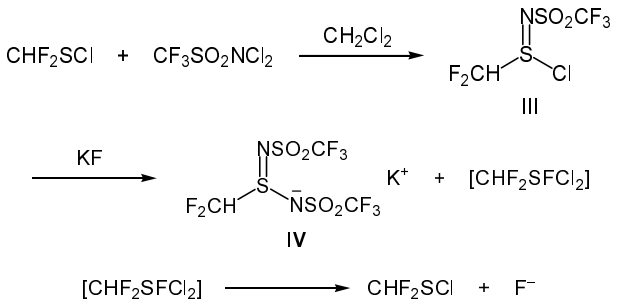
By treatment of *N*,*N*-dimethyl-*N*′-(trifluoromethylsulfonyl)trifluoromethanesulfinimidamide (**IIa**) with gaseous hydrogen chloride in diethyl ether we obtained the desired *N*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidoyl chloride $CF_3S(=NSO_2CF_3)Cl$ (Scheme 4).

Scheme 4.



Unlike CF_3SCl, difluoromethanesulfenyl chloride reacted with $CF_3SO_2NCl_2$ in methylene chloride at room temperature (reaction time 2 h; Scheme 5). Sulfinimidoyl chloride **III** thus obtained was heated with potassium fluoride in 1,2-dimethoxyethane for 10 h at 70–75°C. As a result, we isolated 42% of *N*,*N*′-bis(trifluoromethylsulfonyl) derivative **IV**. However, the reaction occurred at a considerably lower rate than with trifluoromethyl analog (4 h at 60°C; 89%) [5], and the yield was smaller. According to the ^{19}F NMR data, the reaction mixture also contained difluoro-

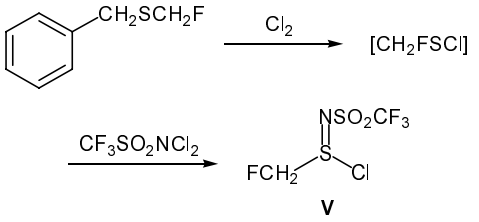
Scheme 5.



methanesulfenyl chloride (in the reaction with trifluoromethyl analog, trifluoromethanesulfenyl chloride was present in the reaction mixture).

Fluoromethanesulfenyl chloride was not reported previously. To prepare this compound, we synthesized fluoromethyl benzyl sulfide as described in [8, 9]; the subsequent chlorination gave fluoromethanesulfenyl chloride which was passed through a solution of *N*,*N*-dichlorotrifluoromethanesulfonamide. We thus obtained *N*-(trifluoromethylsulfonyl)fluoromethanesulfinimidoyl chloride (**V**) in a poor yield (12%) (Scheme 6). Neither compound **V** nor *N*-(trifluoromethylsulfonyl)methanesulfinimidoyl chloride $CH_3S(=NSO_2CF_3)Cl$ [10] reacted with KF on heating for 10 h in 1,2-dimethoxyethane, and the initial compounds were recovered from the reaction mixture.

Scheme 6.



V

Thus we have revealed that the unusual transformation of *N*-(trifluoromethylsulfonyl)-substituted R-sulfinimidoyl chlorides into bis(trifluoromethylsulfonyl) derivatives $R(=NSO_2CF_3)NSO_2CF_3^- K^+$ on heating with potassium fluoride in 1,2-dimethoxyethane occurs only when the substituent R exerts a sufficient negative inductive effect. The reaction takes place when R = CF_3 or CHF_2 and does not when R = CH_2F or CH_3. Presumably, in the latter case, the positive charge on the sulfur atom is insufficient to ensure the first step, addition of fluoride ion, so that no subsequent addition of the second imidoyl chloride molecule is possible.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were measured on a Varian VXR-300 spectrometer at 299.94 MHz for ^1H and 282.2 MHz for ^{19}F using tetramethylsilane (^1H) and trichlorofluoromethane (^{19}F) as internal references. Methylene chloride was distilled first over phosphoric anhydride and then over calcium hydride. 1,2-Dimethoxyethane was distilled over metallic sodium. *N*,*N*-Dichlorotrifluoromethanesulfonamide was synthesized by the procedure described in [11]. Trifluoromethanesulfenyl chloride [12], *N*,*N*-dimethyltrifluoromethanesulfenamide (**Ia**) [13], and 4-(trifluoromethylsulfanyl)-morpholine (**Id**) [14] were prepared by known methods. All experiments were performed with careful protection from atmospheric moisture.

***N*,*N*-Diethyltrifluoromethanesulfenamide (Ib).** A solution of 0.73 g (10 mmol) of diethylamine in 15 ml of methylene chloride was cooled to –10°C, and 0.69 g (5 mmol) of trifluoromethanesulfenyl chloride was slowly passed through the solution. The mixture was stirred for 2 h, the precipitate was filtered off, and the filtrate was subjected to fractional distillation under atmospheric pressure. Yield 0.55 g (64%), colorless liquid, bp 78°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.14 t (6H, CH_3), 3.05 q (4H, CH_2). ^{19}F NMR spectrum ($CDCl_3$): δ_F –45.8 ppm, s (CF_3). Found, %: C 34.17; H 5.56; N 8.17. $C_5H_{10}F_3NS$. Calculated, %: C 34.67; H 5.82; N 8.09.

***N*,*N*-Dicyclohexyltrifluoromethanesulfenamide (Ic)** was synthesized in a similar way. After removal of the solvent under reduced pressure, the residue was recrystallized from pentane. Yield 51%, mp 62°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.5–1.4 m (12H), 1.6 m (8H), 2.0–2.2 m (2H). ^{19}F NMR spectrum ($CDCl_3$): δ_F –46.4 ppm, s (CF_3). Found, %: C 54.99; H 7.59; N 4.77. $C_{13}H_{22}F_3NS$. Calculated, %: C 55.49; H 7.88; N 4.98.

***N*,*N*-Dimethyl-*N′*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidamide (IIa).** A solution of 218 mg (1 mmol) of *N*,*N*-dichlorotrifluoromethanesulfonamide in 10 ml of methylene chloride was added dropwise to a solution of 145 mg (1 mmol) of *N*,*N*-dimethyltrifluoromethanesulfenamide in 10 ml of methylene chloride. The mixture was stirred for 10 h at room temperature, the solvent was distilled off under reduced preassure without heating, and the residue was extracted with pentane (3×10 ml). Removal of the solvent gave 173 mg (54%) of compound **IIa** with bp 85°C (10 mm). ^1H NMR spectrum ($CDCl_3$): δ 3.04 ppm, s (CH_3). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –67.08 s (3F, CF_3), –78.36 s (3F, CF_3). Found, %: C 16.59; H 2.26; N 9.76. $C_4H_6F_6N_2O_2S_2$. Calculated, %: C 16.44; H 2.05; N 9.59.

***N*,*N*-Diethyl-*N′*-(trifluoromethylsulfonyl)trifluoromethanesulfinimidamide (IIb)** was synthesized in a similar way from 173 mg of *N*,*N*-diethyltrifluoromethanesulfenamide and 220 mg of *N*,*N*-dichlorotrifluoromethanesulfonamide. Yield 202 mg (63%), bp 112°C (10 mm). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t (6H, CH_3), 3.48 q (4H, CH_2).

^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –66.80 s (3F, CF_3), –78.51 s (3F, CF_3). Found, %: C 22.25; H 3.20; N 8.75. $C_6H_{10}F_6N_2O_2S_2$. Calculated, %: C 22.70; H 3.38; N 9.03.

***N*,*N*-Dicyclohexyl-*N'*-(trifluoromethylsulfonyl)-trifluoromethanesulfinimidamide (IIc)** was synthesized in a similar way from 281 mg of *N*,*N*-dicyclohexyltrifluoromethanesulfenamide and 238 mg of *N*,*N*-dichlorotrifluoromethanesulfonamide. Yield 216 mg (51%), decomposes at 195°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.5–1.6 m (12H), 1.7–1.95 m (8H), 2.1–2.7 m (2H). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –68.74 s (3F, CF_3), –78.77 s (3F, CF_3). Found, %: C 39.35; H 5.14; N 6.64. $C_{14}H_{22}F_6N_2O_2S_2$. Calculated, %: C 39.25; H 5.18; N 6.54.

4-[*N*-Ethyl-*S*-(trifluoromethyl)sulfinimidoyl]-morpholine (IId) was synthesized in a similar way from 187 mg of 4-(trifluoromethylsulfanyl)morpholine and 238 mg of *N*,*N*-dichlorotrifluoromethanesulfonamide. Yield 224 mg (67%), mp 42°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.50–3.70 m (4H, CH_2), 3.78–3.9 m (4H, CH_2). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –65.94 s (3F, CF_3), –78.58 s (3F, CF_3). Found, %: C 21.56; H 2.39; N 8.38. $C_6H_8F_6N_2O_2S_2$. Calculated, %: C 21.77; H 2.48; N 8.57.

***N*-(Trifluoromethylsulfonyl)trifluoromethanesulfinimidoyl chloride.** Gaseous hydrogen chloride was passed over a period of 15 min through a solution of 584 mg of sulfinimidamide **IIa** in 15 ml of diethyl ether. The mixture was filtered, the filtrate was evaporated, and the residue was distilled under reduced pressure (10 mm). Yield 290 mg (52%) [5].

***N*-(Trifluoromethylsulfonyl)difluoromethanesulfinimidoyl chloride (III).** A solution of 1.09 g (5 mmol) of *N*,*N*-dichlorotrifluoromethanesulfonamide in 5 ml of methylene chloride was slowly added to a solution of 0.59 g (5 mmol) of difluoromethylsulfenyl chloride in 10 ml of methylene chloride. The mixture was stirred for 2 h, the solvent was distilled off under reduced pressure, and the residue was distilled in a vacuum. Yield 1.1 g (82.7%), bp 78°C (12 mm). ^{1}H NMR spectrum ($CDCl_3$): δ 6.97 ppm, t (1H, CHF_2, $^2J_{HF}$ = 57 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –77.30 s (3F, CF_3), –102.85 d.d (1F, CF_2, $^2J_{FF}$ = 220, $^2J_{FH}$ = 57 Hz), –109.56 d.d (1F, CF_2, $^2J_{FF}$ = 220, $^2J_{FH}$ = 57 Hz). Found, %: C 8.93; H 0.77; N 5.57. $C_2HClF_5NO_2S_2$. Calculated, %: C 9.04; H 0.38; N 5.27.

***N*,*N'*-Bis(trifluoromethylsulfonyl)difluoromethanesulfinimidamide potassium salt (IV).** Dry powdered potassium fluoride, 123 mg (2.15 mmol), was added to a solution of 573 mg (2.16 mmol) of compound **III** in 20 ml of anhydrous 1,2-dimethoxyethane, and the mixture was stirred for 10 h at 70–75°C. The precipitate was filtered off, the solvent was distilled off from the filtrate under reduced pressure, and the residue was treated with benzene until a solid crystallized. The solvent was separated by decanting, and the residue was dried under reduced pressure. Yield 42%, mp 102°C. ^{1}H NMR spectrum (DMSO-d_6): δ 6.84 ppm, t (1H, CHF_2, $^2J_{HF}$ = 54 Hz). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –79.23 s (6F, CF_3), –118.55 d (2F, CHF_2, $^2J_{HF}$ = 54 Hz). Found, %: C 8.33; H 0.96; N 6.65. $C_3HF_8KN_2O_4S_3$. Calculated, %: C 8.65; H 0.24; N 6.73.

***N*-(Trifluoromethylsulfonyl)fluoromethanesulfinimidoyl chloride (V).** Fluoromethyl benzyl sulfide, 3.12 g (0.02 mol), was placed in an ampule equipped with a Teflon seal, the ampule was cooled to –45°C, and 1.42 g (0.02 mol) of dry chlorine was condensed thereto. The mixture was kept for 30 min at –40°C and allowed to warm up to room temperature, and gaseous products were passed through a solution of 2.18 g (0.01 mol) of *N*,*N*-dichlorotrifluoromethanesulfonamide in 20 ml of methylene chloride. The mixture was stirred for 2 h at room temperature, the solvent and excess *N*,*N*-dichlorotrifluoromethanesulfonamide were distilled off under reduced pressure (water-jet pump), and the residue was distilled in a vacuum. Yield 0.59 g (12%), bp 85°C (10 mm). ^{1}H NMR spectrum ($CDCl_3$): δ 5.29 ppm, d (2H, CH_2F, $^2J_{HF}$ = 46 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm –78.4 s (3F, CF_3), –198.6 t (1F, CH_2F, $^2J_{HF}$ = 46 Hz). Found, %: C 10.02; H 1.09; N 5.79. $C_2H_2ClF_4NO_2S_2$. Calculated, %: C 9.70; H 0.81; N 5.66.

REFERENCES

1. Yagupol'skii, L.M., Popov, V.I., Pavlenko, N.V., Maletina, I.I., Mironova, A.A., Gavrilova, R.Yu., and Orda, V.V., *Zh. Org. Khim*., 1986, vol. 22, p. 2169.
2. Garlyauskajte, R.U., Sereda, S.V., and Yagupolskii, L.M., *Tetrahedron*, 1994, vol. 23, p. 6891.
3. Garlyauskajte, R.U., Bezdudny, A.V., Michot, C., Armand, M., Yagupolskii, Y.L., and Yagupolskii, L.M., *J. Chem. Soc., Perkin Trans. 1*, 2002, p. 1887.
4. Yagupolskii, Y.L., Bezdudnyi, A.V., and Yagupolskii, L.M., *J. Fluorine Chem*., 2002, vol. 115, p. 129.

5. Yagupol'skii, Yu.L., Haas, A., Savina, T.I., Bezdudnyi, A.V., and Yagupol'skii, L.M., *Russ. J. Org. Chem*., 1999, vol. 35, p. 1766.
6. Yagupol'skii, L.M., Il'chenko, A.Ya., and Kondratenko, N.V., *Usp. Khim*., 1974, vol. 43, p. 64.
7. Moore, G., *J. Org. Chem*., 1979, vol. 44, p. 1708.
8. Paquette, L., Wittenbrok, L., and Schreiber, K., *J. Org. Chem*., 1968, vol. 33, p. 1080.
9. Lange, U. and Senning, A., *Chem. Ber*., 1991, vol. 124, p. 1879.
10. Garlyauskaite, R.Yu., Bisskii, G.V., and Yagupol'skii, L.M., *Russ. J. Org. Chem*., 1998, vol. 34, p. 1117.
11. Nazaretyan, V.P., Radchenko, O.A., and Yagupol'skii, L.M., *Zh. Org. Khim*., 1974, vol. 10, p. 2460.
12. Tullock, C.W. and Coffman, D.D., *J. Org. Chem*., 1960, vol. 25, p. 2016.
13. Emeleus, H.J. and Nabi, S.N., *J. Org. Chem*., 1960, vol. 25, p. 1103.
14. Kolasa, A. and Lieb, M., *J. Fluorine Chem*., 1995, vol. 70, p. 45.