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Reactions of Trifluoromethanesulfonyl Azide with Aromatic Compounds

Nobumasa KAMIGATA,* Kazutoshi YAMAMOTO, Osamu KAWAKITA, Kiyoyuki HIKITA, Haruo MATSUYAMA, Masato YOSHIDA, and Michio KOBAYASHI
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo, 158

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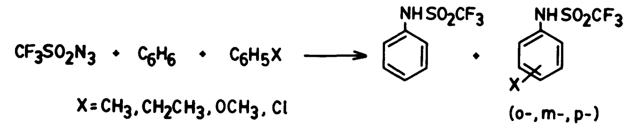
Synopsis. Thermolysis of trifluoromethanesulfonyl azide in solvents composed of 1:1 mixtures of benzene and substituted benzenes gives trifluoromethanesulfonanilide and substituted trifluoromethanesulfonanilides. The isomer ratios, the total rate ratios, and the partial rate factors for the sulfonamidation have been determined. By the intramolecular and intermolecular selectivities, the reaction mechanism involving trifluoromethanesulfonyl nitrene intermediate is discussed.

The thermal decomposition of sulfonyl azides in aromatic solvents was first reported by Curtius and Schmidt.[1] Abramovitch *et al.* studied the thermal reactions of methanesulfonyl azide with substituted benzenes and determined the isomer ratios, total rate ratios, and partial rate factors for the sulfonamidation.[2] We have studied the thermal reaction of trifluoromethanesulfonyl azide with monosubstituted benzenes since we have interest in the reactivities and selectivities of sulfonyl nitrenes possessing a strong electron-withdrawing group.

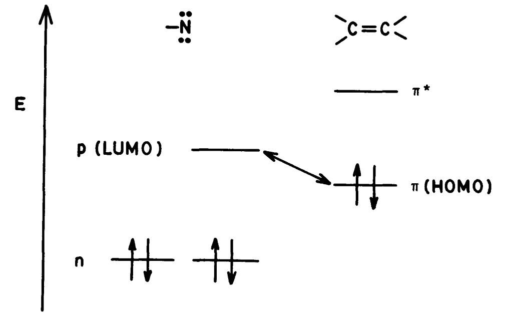
Thermal reactions of trifluoromethanesulfonyl azide in an equimolar mixture of benzene and substituted benzenes at 120 °C in a degassed sealed tube were carried out. The reaction products were trifluoromethanesulfonanilide and substituted trifluoromethanesulfonanilides which were analyzed on a silica-gel-column-packed HPLC using chloroform–ethanol as an eluent. The isomer ratio, the total rate ratios, and the partial rate factors for the trifluoromethanesulfonamidation were determined and the results are summarized in the Table together with those for sulfonamidation with methanesulfonyl azide.[2]



As shown in the Table, the partial rate factors for the trifluoromethanesulfonamidation of anisol are smaller than those for the methanesulfonamidation. Similar results were obtained in the sulfonamidation of toluene. Unfortunately, in the case of the sulfonamidation of toluene or ethylbenzene, ortho and meta or meta and para isomers of trifluoromethanesulfonanilides, respectively, could not be separated under various HPLC separating conditions. This implies that trifluoromethanesulfonyl nitrene intermediate formed by the thermolysis is more reactive and less selective than a methanesulfonyl nitrene. The fact that the total rate ratios for the trifluoromethanesulfonamidation of any substituted benzenes (especially that of chlorobenzene) are close to unity compared with methanesulfonamidation supports this interpretation. The trifluoromethanesulfonamidation has electrophilic nature since the total rate ratios are larger value in the electron-donating group (k_{OMe}/k, k_{Me}/k, and k_{Et}/k were 1.53, 1.12, and 1.10, respectively) and smaller value in the electron-withdrawing group (k_{Cl}/k=0.64). And also, no trifluoromethanesulfonamidation was observed in the reaction of triflazide with nitrobenzene. The ionic character indicates *the trifluoromethanesulfonyl nitrene reacts in* a singlet state.

$$CF_3SO_2N_3 \xrightarrow[-N_2]{} CF_3SO_2\underset{\cdot\cdot}{\ddot{N}}$$

According to the frontier molecular orbital theory, the electrophilic reactions of a singlet carbene with olefins are directed by the interaction with lowest unoccupied molecular orbital (LUMO) of the carbene and highest occupied molecular orbital (HOMO) of the olefin.[3] This conception could be applied in the reaction of electrophilic nitrene with olefins as shown below. Trifluoromethyl group should decrease the energy level of the LUMO (vacant p orbital) of the trifluoromethanesulfonyl nitrene in the singlet state compared with that of methanesulfonyl nitrene, thus the interaction of LUMO of trifluoromethanesulfonyl nitrene and HOMO of benzene becomes easier. Consequently, the trifluoromethanesulfonyl nitrene intermediate showed higher reactivities and lower selectivities (partial rate factors and total rate ratios are closer to unity) in the sulfonamidation of arenes compared with methanesulfonamidation.



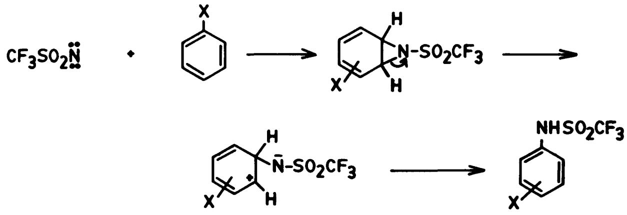
The isomer ratios of the trifluoromethanesulfonamidation were similar to those for the methanesulfonamidation. According to the mechanism for the methanesulfonamidation of arenes proposed by Abramovitch *et al.*,[2] a singlet sulfonyl nitrene adds to the aromatic ring giving aziridine, followed by opening of the three membered ring affording the final product *via* a carbonium ion intermediate. If we assume a similar mechanism for the trifluoromethanesulfonamidation as shown below, the ring opening will be directed by the stability of carbonium ion which is effected by the substituent X in the aromatic ring and does not depend on the group attached on the sulfonyl group (methyl or trifluoromethyl). Therefore, intramolecular selectivities (isomer ratios) of sulfonamidation of monosubstituted benzenes are quite similar in the cases of trifluoro-

Table 1. The isomer ratios, partial rate factors, and total rate ratios for the sulfonamidation of arenes in the thermolysis of sulfonyl azide at 120 °C

Sulfonyl Azide	Arene	Isomer Ratio (%) o-	m-	p-	Partial Rate Factor k_o/k	k_m/k	k_p/k	Total Rate Ratio k_x/k
$CF_3SO_2N_3$	$C_6H_5OCH_3$	53.1	3.5	43.5	2.43	0.16	3.99	1.53
$CH_3SO_2N_3$[2)]	$C_6H_5OCH_3$	55.5	1.2	43.3	4.23	0.09	6.6	2.54
$CF_3SO_2N_3$	$C_6H_5CH_3$	57.0[a)]		43.0	2.10[b)]		3.15	1.12
$CH_3SO_2N_3$[2)]	$C_6H_5CH_3$	65.4	2.4	32.2	3.65	0.13	3.59	1.86
$CF_3SO_2N_3$	$C_6H_5CH_2CH_3$	49.2	59.8[c)]		1.63	3.36[d)]		1.10
$CF_3SO_2N_3$	C_6H_5Cl	51.9	4.0	44.1	1.01	0.08	1.70	0.64
$CH_3SO_2N_3$[2)]	C_6H_5Cl	57.4	0.9	41.7	0.76	0.01	1.10	0.44

a) ortho+meta, b) k_{o+m}/k, c) meta+para, d) k_{m+p}/k

methanesulfonamidation and methanesulfonamidation.



Experimental

Materials. Trifluoromethanesulfonyl chloride was prepared from 25.0 g of trifluoromethanesulfonic acid treated with 50.0 g of phosphorus pentachloride at 100 °C. The volatile component was trapped by an ice-bath and distilled to give 24.0 g (85%) of trifluoromethanesulfonyl chloride: bp 33 °C. Trifluoromethanesulfonyl azide was prepared by dropping 8.4 g of trifluoromethanesulfonyl chloride into a slurry of 4.2 g of sodium azide in 60 cm^3 of acetonitrile with stirring at 0 °C and the mixture was stirred for additional 3 h. The organic layer was extracted with decalin, the extract washed with water and dried over anhydrous magnesium sulfate. Careful distillation of the extract gave 6.8 g (78%) of trifluoromethanesulfonyl azide: bp 45 °C/350 Torr (52.2 °C/444 Torr:[4)] 1 Torr=133.322 Pa); IR (neat) 1130, 1160, 1220, 1420, and 2150 cm^{-1}; Mass m/z 175 (M$^+$).

Preparation of Authentic Trifluoromethanesulfonimides. The general procedure described by Marvel *et al.* was used.[5)] To a dichloromethane solution of 2 molar equiv of the amine was added 1 equiv of trifluoromethanesulfonyl chloride in dichloromethane at 0 °C. The solution was stirred at room temperature for 3 h, and refluxed for 5 h. The reaction mixture was washed with 5% hydrochloric acid and water, then the organic layer was dried with anhydrous magnesium sulfate. Evaporation of the solvent left a residue which was subjected to Florisil column chromatography using benzene as eluent. The amide isolated was recrystallized from hexane.

Trifluoromethanesulfonanilide. Mp 65.5—66.0 °C (66—67 °C[6)]); IR (KBr) 1140, 1200, 1360, and 3300 cm^{-1}; NMR ($CDCl_3$) δ=6.52 (1H, s) and 7.37 (5H, s); Mass m/z 226 (M$^+$+1).

o-*Trifluoromethanesulfontoluidide.* Mp 55—56 °C; IR (KBr) 1140, 1190, 1360, and 3280 cm^{-1}; Mass m/z 239 (M$^+$).

m-*Trifluoromethanesulfontoluidide.* Mp 64.5—65.5 °C; IR (KBr) 1145, 1210, 1360, and 3280 cm^{-1}; Mass m/z 240 (M$^+$+1).

p-*Trifluoromethanesulfontoluidide.* Mp 42.5—43.5 °C; IR (KBr) 1140, 1210, 1355, and 3290 cm^{-1}; Mass m/z 239 (M$^+$).

N-(o-*Ethylphenyl)trifluoromethanesulfonamide.* Mp 61—62 °C; IR (KBr) 1140, 1210, 1360, and 3260 cm^{-1}; NMR ($CDCl_3$) δ=1.18 (3H, t, J=7.2 Hz), 2.58 (2H, q, J=7.2 Hz), and 7.00 (4H, s); Mass m/z 254 (M$^+$+1).

N-(m-*Ethylphenyl)trifluoromethanesulfonamide.* IR (KBr) 1140, 1215, 1365, and 3295 cm^{-1}; NMR ($CDCl_3$) δ=1.18 (3H, t, J=7.8 Hz), 2.55 (2H, q, J=7.8 Hz), 6.41 (1H, s), and 6.8—7.6 (4H, m); Mass m/z 253 (M$^+$).

N-(p-*Ethylphenyl)trifluoromethanesulfonamide.* Mp 33—34 °C; IR (neat) 1145, 1215, 1365, and 3300 cm^{-1}; NMR ($CDCl_3$) δ=1.17 (3H, t, J=7.2 Hz), 2.55 (2H, q, J=7.2 Hz), 6.58 (1H, s), 7.09 (4H, s); Mass m/z 254 (M$^+$+1).

o-*Trifluoromethanesulfonanisidide.* Mp 60—61 °C; IR (KBr) 1150, 1205, 1370, and 3300 cm^{-1}; Mass m/z 255 (M$^+$).

m-*Trifluoromethanesulfonanisidide.* Mp 64.5—65.5 °C; IR (KBr) 1140, 1195, 1380, and 3170 cm^{-1}; Mass m/z 255 (M$^+$).

p-*Trifluoromethanesulfonanisidide.* Mp 39.5—40.0 °C; IR (KBr) 1150, 1210, 1375, and 3300 cm^{-1}; Mass m/z 256 (M$^+$+1).

N-(o-*Chlorophenyl)trifluoromethanesulfonamide.* Mp 74.5—75.5 °C; IR (KBr) 1140, 1215, 1370, and 3270 cm^{-1}; Mass m/z 262 and 260 (M$^+$+1).

N-(m-*Chlorophenyl)trifluoromethanesulfonamide.* Mp 76.5—77.5 °C; IR (KBr) 1140, 1210, 1360, and 3270 cm^{-1}; Mass 261 and 259 (M$^+$).

N-(p-*Chlorophenyl)trifluoromethanesulfonamide.* Mp 50—51 °C; IR (KBr) 1135, 1215, 1410, and 3320 cm^{-1}; Mass m/z 261 and 259 (M$^+$).

The Reaction of Trifluoromethanesulfonyl Azide with Substituted Benzenes. A solution of trifluoromethanesulfonyl azide (105 mg, 0.6 mmol) in benzene (2.34 g, 30 mmol) and monosubstituted benzene (30 mmol) was heated at 120 °C in a degassed sealed tube for 24 h. The reaction mixture was subjected to Florisil column chromatography using hexane-ethyl acetate as eluent to remove the resinous by-product. The trifluoromethanesulfonanilide and substituted trifluoromethanesulfonanilides formed were analyzed by HPLC using silica-gel column and chloroform-ethanol as eluent. The isomer ratios and partial rate factors for the trifluoromethanesulfonamidation were determined. The overall yield of the amidation based on the trifluoromethanesulfonyl azide used was 50—80%. The results are summarized in Table 1.

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