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Synthesis of Fluoroalkanesulfonyl Azides and their Reactions as Fluoroalkanesulfonyl nitrene Precursors

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Abstract Thermolysis or photolysis of the title compounds with cyclohexane, $Me_2C = CMe_2$, methyl sulfide and triphenyl phosphine gave the corresponding insertion or addition products via the perfluoroalkanesulfonyl nitrene intermediate.

It seems well established that many azides such as phenyl azide, azidoformate, alkane or aryl sulfonylazide etc, when decomposed thermally or under irradiation, react via nitrene intermediate R-N [1-5] (R: aryl, R'OCO, $ArSO_2$ etc). Trifluoromethanesulfonyl azide was first synthesized from the reaction of trifluoromethanesulfonic acid anhydride with sodium azide in 1965.[6] However, its reactions as the trifluoromethanesulfonyl nitrene precursor are little known, the only report was the reaction of $CF_3SO_2N_3$ with aromatic compounds.[7] In connection with our studies on the carbene and nitrene containing perfluoroalkanesulfonyl funtionality,[8,9] this note describes the reactions of perfluoroalkanesulfonyl azides ($\underline{1}$) as perfluoroalkanesulfonyl nitrene precursors.

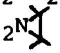
Compounds (1) were conveniently prepared by treatment of perfluoroalkanesulfonyl fluoride with sodium azide in methanol at room temperature[10], thus

$$R_FSO_2F + NaN_3 \xrightarrow[72\text{-}82\%]{CH_3OH,\ 20^\circ C,\ 8h} \underset{\underline{1}}{R_FSO_2N_3}$$

a: $R_f = C_4F_9$, b: $R_f = Cl(CF_2)_2O(CF_2)$; c: $R_f = I(CF_2)_2O(CF_2)_2$;
d: $Rf = H(CF_2)_2O(CF_2)_2$ e: $R_f = MeO_2CCF_2$

Perfluoroalkanesulfonyl azides ($\underline{1}$) are colourless liquids with a characteristic pungent odor. They are stable and can be stored at room temperature without change. The decomposition temperature is around 120°C. Under irradiation, $\underline{1}$ decomposed readily to give perfluoroalkanesulfonyl nitrene with the elimination of nitrogen. Several reactions studied are shown in Scheme 1.

Table 1 The reactions of azides 1

Reactants	Reaction condition	Products	Yield (%)^c
1d + cyclohexane	UV, 8h ^{a}	$R_fSO_2NHC_6H_{11}$ (2d)	52
		$R_fSO_2NH_2$ (6)	20
1d + $Me_2C = CMe_2$	UV, 8h ^{b}	R_fSO_2N (3d)	61
		$R_fSO_2NH_2$ (6)	16
1b + Me_2S	CH_2Cl_2, 25°C, 8h	$R_fSO_2N = SMe_2$(4b)	79
1c + Me_2S	CH_2Cl_2, 25°C, 8h	$R_fSO_2N = SMe_2$(4c)	82
1d + Ph_3P	Et_2O, 25°C, 2h	$R_fSO_2N = PPh_3$(5d)	66
		$R_fSO_2NH_2$ (6)	5

a. Cyclohexane is in excess b. $Me_2C = CMe_2$ is in excess

c. Isolate yield based on 1

Recently, Szonyi reported that, $R_FC_2H_4N{=}N{-}N{=}PPh_3$ was obtained from the reaction of $R_FC_2H_4N_3$ with PPh_3.[11] In our case, however, even the reaction was carried out at 0°C, N_2 was released immediately, when 1 was added to the solution of PPh_3 in Et_2O. Comparing with $R_FC_2H_4N{=}PPh_3$,[11] the product $R_FSO_2N{=}PPh_3$ (5) is more reactive,i.e; when it was exposured to air it decomposed readily to $R_FSO_2NH_2$ and Ph_3PO.

The structure of these new azides and the products were fully characterized by spectral data and microanalyses.

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