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SHORT COMMUNICATION

The Reactivity of a Thermally Unstable Perfluoroalkylsulfinyl Azide

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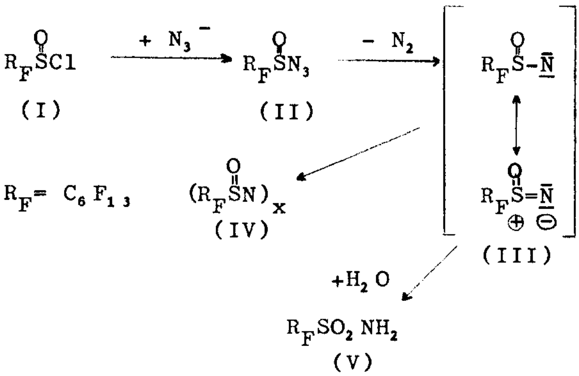
While sulfonyl azides are a well investigated class of compounds, rather less information is available to date on the chemistry of their sulfinyl analogues $RS(=O)N_3$. The only examples reported thus far are phenyl- and p-tolylsulfinyl azide [1,2], which have been shown to decompose at temperatures between -20 and 0°. In the present paper, we wish to describe the results obtained from attempts to prepare a F-alkylsulfinyl azide.

Based on the fact that the stability of azides is generally favoured by a high ratio of molecular weight to nitrogen, F-hexylsulfinyl chloride I was chosen as the starting material. When precooled solutions containing equimolar quantities of I and of tetraethylammonium azide [3] in dichloromethane were mixed at -50° in the cell of an infrared spectrometer, a strong band at 2122 cm^{-1} appeared instead of the original absorption due to the azide ion (2006 cm^{-1}). Subsequently, this new band, which can be assigned to the $\nu(as)$ N_3 vibration of $C_6F_{13}S(=O)N_3$ II, decreased to zero intensity over about a minute.

On adding I to solutions of the azide salt in dichloromethane, acetone or acetonitrile, at 0°C, effervescence occured from the evolution of nitrogen. A volumetric determination of the gas indicated that one mol of nitrogen was liberated per mol of R_F-compound. The same result was obtained using sodium azide, but the reactions were very slow due to the low solubility of this salt in the solvents employed. Product IV, isolated from such reactions, was a viscous, colorless oil, which analyzed as $C_6F_{13}NOS$. IV is believed to be a mixture of oligomers, presumably formed by self-condensations of a transient nitrene III, and held together by N-S=N linkages. Mass spectral analysis gave no molecular ion but showed significant fragments corresponding to $C_6F_{13}NOS^+$ and, mainly, $C_6F_{13}SO^+$.

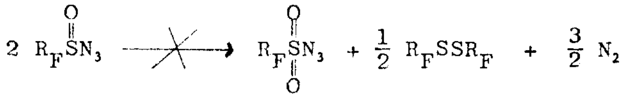
Reactions between I and the azide ion in the presence of water afforded substantial amounts of F-hexylsulfonamide V. The pathways leading to the formation of products IV and V are summarized in Scheme 1.



Scheme 1

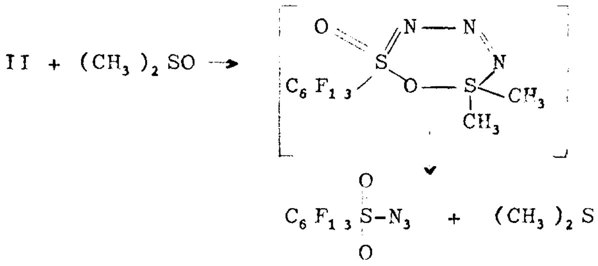
It appears that the sulfinylnitrene intermediate III, like the related species formed during the decomposition of arylsulfinyl azides [1] , is only a very weak electrophile. This may be inferred by its failure to undergo a Curtius type rearrangement. Moreover, when III was generated in a cyclohexene solution no product of insertion into the C=C bond could be detected.

The azide II did not show any tendency towards disproportionation into the sulfonyl azide and the bis(F-Alkyl)-disulfide (Scheme 2). By contrast, a reaction of this type had been a complicating sidepath [1,4] in the case of the arylsulfinyl compounds.



Scheme 2

However, F-hexylsulfonyl azide VI was obtained in good yield when the synthesis of II was carried out in dimethyl sulfoxide. This facile oxidation of II by DMSO probably takes place via an intermediate cycloadduct as shown in Scheme 3. It is interesting to note that arylsulfinyl azides, with regard to this reaction, behaved quite differently and formed sulfonyl sulfilimines [2,5] instead of sulfonyl azides.



Scheme 3 (VI)

Compound VI is more stable than its known [6] homologue $CF_3SO_2N_3$ and can be distilled without noticeable decomposition.

Experimental

All reactions were performed under nitrogen. Infrared spectra were recorded on a Perkin-Elmer 325 spectrophotometer. ^{19}F NMR spectra were obtained using a Jeol C 60 instrument, at 56.45 MHz. The observed δ-values (ppm, upfield from e-CF_3COOH) are given in Table 1.

Table 1

Fluorine Nuclear Magnetic Resonance Data [+]

Compound		Chemical Shifts δ	
	1-CF_2	(2-5)-CF_2	CF_3
I	34.3(F_A),39.4(F_B) J F_AF_B= 230 Hz	43.3,44.5,45.4,49.2	4.4
IV	34.9 w, 41.0	42.6,43.8,44.5,48.3, 51.0 w	4.3
V	35.1	41.5,43.2,44.1,47.7	3.4
VI	31.5	41.6,43.5,44.4,48.2	4.2

[+] Spectra of I and VI were recorded without solvent, those of IV and V using DMSO solutions.

F-hexylsulfinylchloride I

A slow stream of hydrogen chloride was bubbled for 30 min through a stirred solution of N-Phenyl-perfluorohexylsulfinimin [7] (50 g, 109 mmol) in 200 ml of dry diethylether. The resultant precipitate of anilinium chloride was filtered off and the solvent evaporated. Distillation under reduced pressure afforded I (30.6 g, yield 69,7 %) as a colorless liquid (b.p. 66-67°/12 torr). Anal. Cl Calcd. (Found): 8.80 (8.9).

Preparation of $C_6F_{13}S(=O)N$ "oligomers" IV

In a carefully dried quartz flask connected to a mercury - filled bubbler, 40.26 g of I (0.1 mol) were added to a suspension of powdered sodium azide (6.5 g, 0.1 mol) in dry acetone (30 ml). Slow gas evolution was observed. After having been stirred for 60 h at 20°, the mixture was filtered and the acetone was removed in vacuo. The residue was dissolved in boiling F-(1-propylfurane); this solution was filtered and the solvent was removed at 10^{-2} torr to give IV (31 g, 81 %) as a sticky oil. Anal.

Calcd. for $C_6F_{13}NOS$ (Found): C 18.91 (19.0), F 64.81 (63.7), N 3.67 (3.62), S 8.41 (8.22).

F-hexylsulfonamide V

To 11.9 g of tetraethylammonium azide (69 mmol) in 100 ml of ether, containing 1 % of water, I (27.8 g, 69 mmol) was slowly added at 0° with vigorous stirring. The mixture was then stirred for 20 h at room temperature. On removal of solvent, the residue was repeatedly washed with water and dried in vacuo. Vacuum distillation of the resulting oily material through a short Claisen head gave a yellow crude product which was redistilled to afford 5.7 g (21 %) of colorless V (mp. 112°). Anal. Calcd. for $C_6H_2F_{13}NO_2S$ (Found): C 18.05 (18.4), H 0.50 (0.6), F 61.88 (61.5), N 3.50 (3.5), S 8.03 (8.0).
IR:νNH = 3350 cm^{-1}s, 3225 cm^{-1}m, 3110 cm^{-1}w.

F-hexylsulfonyl azide VI

0.1 mol of compound I (40.26 g) was added dropwise to a stirred suspension of sodium azide (6.5 g) in dry DMSO (100 ml) at 0°. The temperature was allowed to rise to 20° and the mixture was stirred for 20 h. Then it was filtered and, on addition of 50 ml of CF_2Cl_2, washed five times with 100 ml of water. The organic phase was dried over sodium sulfate and distilled to give 26.7 g (yield 63 %) of VI (b.p. 60-62°/12 torr). Anal. Calcd. for $C_6F_{13}N_3O_2S$ (Found): C 16.96 (17.0), F 58.10 (58.7), N 9.88 (9.3), S 7.54 (7.5).
IR: $\nu(as)N_3$ = 2152 cm^{-1}, vs.

Compound VI has also been obtained in 52 % yield from a displacement reaction of F-hexylsulfonylchloride (0.1 mol) with sodium azide (0.2 mol) in 100 ml of acetonitrile (20°, 24 h).

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