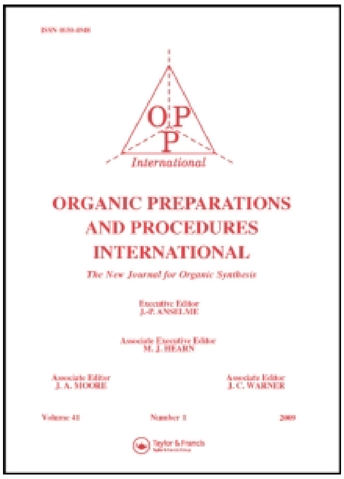

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ARYL N, N-DIFLUOROSULFONAMIDES[1]

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ARYL N, N-DIFLUOROSULFONAMIDES[1]

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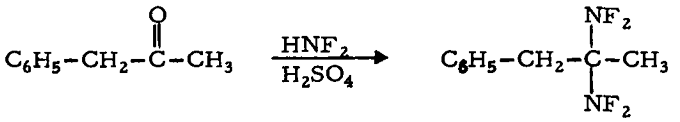
During our studies on the preparation of difluoramino compounds by the alkylation of difluoramine (HNF_2) in sulfuric acid,[2] certain aryl substrates gave diaryl sulfones and aryl N, N-difluorosulfonamides as well as the desired difluoramines.[3] For example, the preparation of 2, 2-bis(difluoramino)-1-phenylpropane (1) from phenylacetone and HNF_2 in 100% sulfuric acid gave the N, N-difluorosulfonamide 2 and the related sulfone 3 as well as 1. Unless the reaction time and temperature were controlled, 2 and 3 were the major reaction products.



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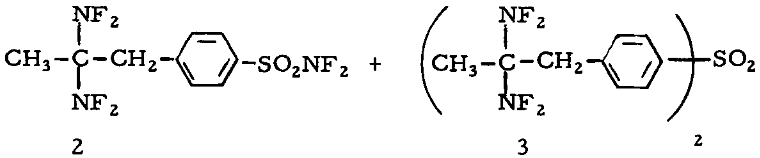


2

3

Benzene, toluene, and chlorobenzene were then exposed to HNF_2 in the presence of sulfuric acid to deliberately produce aromatic N, N-difluorosulfonamides. Only low yields of difluorosulfonamides were obtained; the table summarizes the results. Since the aryl N, N-difluorosulfonamides decompose in the presence of H_2SO_4 and liberate difluoramine, high conversions are probably not possible. In any event, no attempt was made to optimize the reaction conditions, or to determine the amount of diaryl sulfone accompanying the product.

Aryl N, N-Difluorosulfonamides

Ar=	M.P.	Yield %	Calculated				Found				^{19}F NMR ϕ[a]
			C	H	N	F	C	H	N	F	
C_6H_5	b	2[c]	37.3	2.61	7.25	19.7	37.3	3.15	7.26	19.5	-39.6
4-$CH_3C_6H_4$	34-36°	4[d]	40.6	3.41	6.76	18.3	40.3	3.40	6.54	18.6	-39.1
4-ClC_6H_4	62-63.5°	7[e]	31.6	1.77	6.15	16.7	31.5	2.42	6.04	16.3	-40.1

[a] ϕ Values are ppm from internal CCl_3F. [b] Liquid. [c] From 0.15 mole benzene, 0.17 mole HNF_2, 30 ml 30% fuming sulfuric acid, 60 ml CH_2Cl_2, 2 hr. reaction time at 15-25°. [d] Same conditions as c, 1 hr. reaction. [e] See Experimental Section.

Experimental

Melting points and boiling points are uncorrected. The ^{19}F NMR spectra were run in $CDCl_3$ at 40 MHz on a Varian 4300B spectrometer; ϕ values are parts per million from internal CCl_3F.

Reaction of Phenylacetone and HNF_2. - A solution of 10 g (75 mmoles) of phenylacetone in 30 ml of CH_2Cl_2 was added over 25 min to a mixture of 225 mmoles of HNF_2, 12 ml of 96% H_2SO_4, 16 ml of 30% fuming H_2SO_4 and 20 ml of CH_2Cl_2. The reaction temperature rose from 2 to 13° during the addition. After 15 min of stirring, excess HNF_2 was vented and the residue poured over ice. The CH_2Cl_2 extract was washed (H_2O and aqueous $NaHCO_3$), dried ($MgSO_4$) and concentrated. The residue, 7 g, was chromatographed on a silica gel column packed in pentane-CH_2Cl_2 (99:1). Elution with the same solvent gave 2,2-bis-(difluoramino)-1-phenylpropane, 1, 3.45 g (29%). The ^{19}F NMR spectrum had a peak at ϕ-27.9.

Anal. Calc'd. for $C_9H_{10}N_2F_4$: C, 48.65; H, 4.54; N, 12.61.
Found: C, 48.27; H, 4.46; N, 13.21.

The next fraction eluted from the column by pentane-CH_2Cl_2 (1:1) was 2, m.p. 53-55° after recrystallization from hexane. The ^{19}F NMR spectrum of 2 had peaks at ϕ-40.0 (SO_2NF_2) and at ϕ-28.2 [$C(NF_2)_2$].

Anal. Calc'd. for $C_9H_9F_6N_3O_2S$: C, 32.05; H, 2.69; N, 12.46.
Found: C, 32.20; H, 2.65; N, 12.21.

The next fraction eluted from the column (CH_2Cl_2) was 3, m.p. 167-169° (hexane-chloroform). The ^{19}F NMR had a single peak at ϕ-28.0; the ^1H NMR spectrum had peaks at 1.47δ ($-CH_3$), 3.40δ ($-CH_2$) and a multiplet centered at 7.68δ (A_2B_2, aromatic ring).

Anal. Calc'd. for $C_{18}H_{18}F_8N_4O_4S_2$: C, 42.7; H, 3.58; N, 11.06.
Found: C, 42.1; H, 3.82; N, 10.84.

Reaction of Chlorobenzene and HNF_2. - A mixture of 10 g (88 mmoles) of chlorobenzene, 125 mmoles of HNF_2, and 25 ml of 30% fuming sulfuric acid was stirred at 15-25° for 2.5 hrs. Excess HNF_2 was vented and the residue was poured on ice. The product was taken up in CH_2Cl_2 and washed (H_2O, aqueous $NaHCO_3$), dried ($MgSO_4$), and concentrated to 4 g of solid. Recrystallization of this material from hexane gave 4,4'-dichlorodiphenylsulfone, mp 148-149°, reported 148-149°.[4] The filtrate was chromatographed on silica gel. Elution with pentane $-CH_2Cl_2$ (2:1) gave 4-chlorophenyl-N, N-difluorosulfonamide, 1.44 g, mp 62-63.5°.

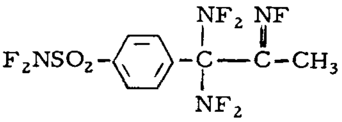
Reaction of Phenyl-N, N-difluorosulfonamide and Sulfuric Acid. - To 4 ml of solid 100% H_2SO_4 was added 0.58 g (3 mmoles) of phenyl-N, N-difluorosulfonamide in 1 ml of benzene. The mixture was frozen, degassed, and allowed to warm *in vacuo*. After 2 hrs at ambient temperature (stirring), the gases produced were pumped *in vacuo* through traps cooled to -80°, -110°, and -196°. The -110° trap contained 47 ml (STP), 2.1 mmoles of, by mass spectrum, 99.8% pure HNF_2.

References

1. This research was carried out under the sponsorship of the Advanced Research Projects Agency under U. S. Army Missile Command Contract DA-01-021-11909.

2. (a) W. H. Graham and J. P. Freeman, J. Org. Chem., 34, 2589 (1969); (b) J. P. Freeman, R. C. Petry, and T. E. Stevens, J. Am. Chem. Soc., 91, 4778 (1969); (c) T. E. Stevens, J. Org. Chem., 34, 2451 (1969).

3. During the preparation of 1,1-bis(difluoramino)-1-phenyl-2-fluoriminopropane[2b] from 1-diethylphosphato-1-difluoramino-1-phenyl-2-fluoriminopropane, HNF_2, and H_2SO_4, a small amount (1-2% yield) of a yellow oil that was undoubtedly i was obtained. This material was identified by elemental analysis and by its



i

^{19}F NMR spectrum which had peaks at ϕ-51.5 (C=NF), -40.5 (SO_2NF_2), and -30.4 [$C(NF_2)_2$].

4. H. Heymann and L. F. Fieser, J. Am. Chem. Soc., 67, 1982 (1945).

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