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NEW DERIVATIVES OF TRIFLUOROTHIAZYNE

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SUMMARY

Thiazyl trifluoride (trifluorothiazyne) reacts smoothly with various organolithium compounds at -78° producing S-substituted thiazynes. This method has been used not only to produce known compounds but, also to prepare several new mono and di-S-substituted thiazynes which contain carbon-sulfur bonds. Nuclear magnetic resonance studies on these compounds indicate that the difluorothiazyl group is more strongly electron-withdrawing than $-NO_2$, both inductively and resonantly.

INTRODUCTION

In 1974 we reported the first derivative of trifluorothiazyne, NSF_3, containing a carbon-sulfur bond. This difluorothiazyl compound was prepared by the reaction of perfluoropropene with trifluorothiazyne in the presence of a catalytic amount of cesium fluoride. [1] Glemser and co-workers have also prepared S-substituted derivatives of trifluorothiazyne by allowing it to react with suitable secondary amines or alcohols. [2] The trimethylsilyl analogs of these starting materials have also been shown to be excellent precursors for the S-substituted thiazyne derivatives. [3] Only one reaction of NSF_3 with an organoalkali compound has been reported in the literature. [4] Lithium bis-(trimethylsilyl)amide was shown to react with NSF_3 to produce not the expected thiazyl difluoride but a rearranged product.

$$NSF_3 + [(CH_3)_3Si]_2NLi \rightarrow LiF + (CH_3)_3Si\text{-}N{=}SF_2{=}N\text{-}Si(CH_3)_3$$

We now report that difluorothiazyl compounds containing carbon-sulfur bonds can be prepared by an analogous reaction.

RESULTS AND DISCUSSION

Since the preparation of a known compound would be a good test for this new method of preparation of thiazyl compounds we allowed lithium diethylamide, prepared from the reaction of diethylamine and *n*-butyllithium, to react with NSF_3. The characteristics of the product, diethylaminodifluorothiazyne (Et_2NSF_2N), were found to be the same as those reported by Glemser. [5] The first attempt to prepare new analogs,

$$NSF_3 + Ph_2NLi \rightarrow Ph_2NSF_2N + LiF$$

$$NSF_3 + 2Ph_2NLi \rightarrow (Ph_2N)_2SFN + 2LiF$$

produced different products, depending upon the ratio of the reactants. Lithium diphenylamide reacted with NSF_3 to produce Ph_2NSF_2N and the first known disubstituted thiazyl derivative, bis(diphenylamino)fluorothiazyne, $(Ph_2N)_2SFN$.

According to the following equations,

$$NSF_3 + PhLi \rightarrow PhSF_2N + LiF$$

$$NSF_3 + 2PhLi \rightarrow Ph_2SFN + 2LiF$$

the reactions of NSF_3 with organolithium compounds produce compounds containing S-C bonds. Trifluorothiazyne reacted with phenyllithium to form the second known thiazyl derivative containing a C-S bond. When the ratio of phenyllithium to NSF_3 was raised to 2:1, the disubstituted thiazyne, Ph_2NSF, was produced. *p*-Fluoro-, *m*-fluoro-, and *m*-trifluoromethylphenyldifluorothiazynes were also produced in the same way. The reaction of NSF_3 and p-phenylenedilithium produced the first known bis(difluorothiazyl) compound.

Several other reactions of NSF_3 with organolithium compounds were examined in order to investigate the scope of this reaction. Trifluorothiazyne reacted with alkyllithiums, but no products containing fluorine-sulfur bonds were found. This was probably due to the fact that the initial product, NSF_2CH_2R (R=H, n-C_3H_7), easily lost hydrogen fluoride and the resulting compound decomposed further. Mono-fluorothiazyne (NSF) and Ph_3SiF were isolated from the reaction of NSF_3 with Ph_3SiLi. Since the postulated intermediate, NSF_2SiPh_3, could easily decompose to form the strong silicon-fluorine bond in Ph_3SiF, the products obtained are reasonable. From the reaction of lithium phenylsulfide and trifluorothiazyne only diphenyl disulfide was isolated. Since NSF_3 can be reduced under certain conditions and since aryl sulfides are susceptible to oxidation, these products might be expected.

The Hammett σ_p, σ_m, σ_I, and σ_R values calculated from the ^{19}F nmr spectrum of the aryldifluorothiazynes show that the NSF_2- group is extremely electron-withdrawing.

Compound	^{19}F (C-F) shift (ppm)*
m-$FC_6H_4SF_2N$	+ 108.3
p-$FC_6H_4SF_2N$	+ 100.3

*Relative to Freon 11

Taft [6,7] showed that the σ_I can be determined from the ^{19}F magnetic resonance of m-substituted fluorobenzenes. From the value of σ_I, the

σ_p, σ_m, and σ_R can be calculated. Comparatives values are

Group	σ_R	σ_I	σ_p	σ_m
$-SF_2N$	0.27	0.80	1.07	0.94
$-SO_2CF_3$	0.26	0.75	1.01	0.88
$-NO_2$	0.21	0.56	0.77	0.67
$-SF_5$	0.09	0.56	0.65	0.61
$-CF_3$	0.10	0.41	0.51	0.46

While these values should not be considered as absolutes, they are still useful for indicating the trends which they reflect. It is interesting to note that the $-SF_2N$ group is a stronger electron-withdrawing group than $-SF_5$, $-CF_3$, and even $-NO_2$, both inductively and resonantly. The CF_3SO_2 group is very strongly electron-withdrawing, but not quite so strong as the SF_2N group.

EXPERIMENTAL

Trifluorothiazyne (NSF_3) was prepared according to the method of Clifford and Kobayashi by fluorination of N-fluoroformyl-S,S-difluorothiazene ($FC(O)N{=}SF_2$) with silver difluoride. The organolithium compounds were prepared from n-butyllithium and the appropriate halides at -78°. A special dropping funnel was constructed that would allow for the cooling of all reactants and for compatibility with vacuum line manipulations. All solvents were dried with appropriate drying agents. Nuclear magnetic resonance spectra were obtained on a JEOL PS-100 spectrometer at 100 mhz for ^{1}H and 94 mhz for ^{19}F. The ir spectra were obtained on a Beckman 20A-X infrared spectrophotometer, and mass spectra obtained with a Perkin-Elmer Hitachi RMU 7 mass spectrometer.

THE REACTIONS OF ORGANOLITHIUMS WITH NSF_3

In a typical experiment 5 mmol of trifluorothiazyne in 2 ml of diethyl ether were condensed into a flask attached to the special dropping funnel. The organolithium compound was introduced into the dropping funnel, degassed, and added dropwise to the NSF_3 solution at -78°. When the addition of the organometallic was complete, the solution was stirred for a half hour at -78° and then a half hour at room temperature. The highly volatile materials were then removed. The remaining solid was dissolved in ether and transferred to a heavier flask, filtered, and extracted three times with ether. The solvent was removed either by passing argon over it or by evaporation in vacuo. In a few cases only nmr data are available because the thermal instability of the products prevented further characterization. The spectral properties follow:

Diphenylaminodifluorothiazyne: ^{1}H nmr, 6.61-7.48 (m); ^{19}F nmr, -84.9 (bs)(S-F); ir, 1475, (N≡S), 750 (S-F), 700 (S-F).
Mass spectrum: m/e, %, ion: 46, 15.0, NS^+; 51, 61.5, SF^+; 65, 28.5, NSF^+, 70, 4.5, SF_2^+; 77, 51.0, C_6H_5; 84, 17.0, NSF_2^+, 91, 13.0, $N(C_6H_5)^+$, 13.0; 168, 100.0, $N(C_6H_5)_2^+$; 252, 8.0, $NSF_2NPh_2^+$.

Bis(diphenyl)aminodifluorothiazyne: ^{1}H nmr, 7.10-7.60 (m); ^{19}F nmr, -92.9 (bs)(S-F); ir, 150 (N≡S), 795 (S-F), 701 (S-F).

Phenyldifluorothiazyne: ^{1}H nmr, 6.80-7.80 (m), ^{19}F nmr, -97.5 (s) (S-F); ir, 1468 (N≡S), 750 (S-F), 690 (S-F).
Mass spectrum: m/e, %, ion; 46, 2.7, NS^+; 51, 28.9, SF^+; 65, 6.8, NSF^+; 70, 1.6, SF_2^+; 77, 100, 66 HS^+; 96, 38.6, $C_6H_5F^+$, 142, 13.7, $NSFPh^+$, 161, 43.6, NSF_2Ph^+.

Bis(diphenylamino)fluorothiazyne: ^{1}H nmr, 7.10-7.66 (m); ^{19}F nmr, -92.8 (bs) (S-F); ir, 150 (N≡S), 795 (S-F), 701 (S-F).

Phenyldifluorothiazyne: ^{1}H nmr, 6.80-7.80 (m), ^{19}F nmr, -97.5 (s) (S-F); ir, 1468 (N≡S), 750 (S-F), 690 (S-F).

Mass spectrum: m/e, %, ion; 46, 2.7, NS^{+}; 51, 28.9, SF^{+}; 65, 6.8, NSF^{+}; 70, 1.6, SF_2^{+}; 77, 100, $C_6H_5^{+}$; 96, 38.6, $C\ H\ F^{+}$, 142, 13.7 $NSFPh^{+}$; 161, 43.6, NSF_2Ph^{+}.

Diphenylfluorothiazyne: ^{1}H nmr, 7.15-7.95 (m), ^{19}F nmr, -102.9 (s) (S-F); ir, 1428 (N≡S), 740 (S-F), 680 (S-F).

p-Fluorophenyldifluorothiazyne: ^{1}H nmr, 7.19 (m) and 7.93 (m), ^{19}F nmr, 103.4 (S-F), 100.3 (C-F), ir, 1479 (N≡S), 728 (S-F), 715 (S-F), 690 (S-F).

Mass spectrum: m/e, %, ion; 141, 1.6, $NSC_6H_4F^{+}$; 160, 29.7, $NSF\ C_6H_4F^{+}$; 179, 76.6, $NSF_2C_6H_4F^{+}$.

m-Fluorophenyldifluorothiazyne: ^{19}F nmr, -109.0 (S-F), 108.3 (C-F).

m-Trifluoromethylphenyldifluorothiazyne: ^{19}F nmr, -113.4 (S-F).

p-Fluorophenyldifluorothiazyne: ^{1}H nmr, 6.9-8.1 (m), ^{19}F nmr, -98.9 (m) (S-F); ir, 1461 (N≡S), 829 (S-F), 688 (S-F).

REFERENCES

1 A. F. Clifford and J. S. Harman, J. Chem. Soc., Dalton, 571, 1974.

2 O. Glemser and W. Koch, F. Naturforsch., 23b, 745, (1968).

3 O. Glemser, J. Wegner, and R. Hofer, Chem. Ber., 105, 474, (1972).

4 O. Glemser and J. Wegner, Angew. Chem. Internat. Edit., 9 (4), 309, (1970).

5 O. Glemser, H. Meyer, and A. Haas, Chem. Ber., 98, 2049, (1965).

6 R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, J. Amer. Chem. Soc., 85, 709 (1963).

7 R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, J. Amer. Chem. Soc., 85, 3146 (1963).

8 A. F. Clifford and C. S. Kobayashi, Inorg. Chem., 4, 571 (1965).