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A Convenient Preparation of Arylthioynamines

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Synopsis. (2,2,2-Trifluoroethylthio)benzenes prepared from sodium thiolates and 2,2,2-trifluoroethyl *p*-toluenesulfonate reacted with 3 equiv of lithium dialkylamides in diethyl ether to give arylthioynamines in good yields. The present procedure gives good results with aliphatic sulfide.

Ynamines have received current interest as a versatile tool in organic synthesis.[1] Of particular interest are arylthioynamines{(arylthioethynyl)amines} which we call in short "thioynamines" since the arylthio groups can be utilized for further synthetic elaboration. However, little information has been available concerning the preparation and reactions of thioynamines.[2,3] In our previous paper, it has been shown that the equimolar reaction of (2,2,2-trifluoroethylthio)benzene with lithium diisopropylamide afforded the phenylthioynamine along with the difluorovinyl sulfide(**1**). This is in contrast to the exclusive formation of the difluorovinyl ether(**2**) with (2,2,2-trifluoroethoxy)benzene.[4]

$$PhX\text{-}CH{=}CF_2$$

1, X=S
2, X=O

Herein we wish to report a convenient preparation of various thioynamines **5** by the reactions of trifluoroethyl sulfides **4** with 3 equiv of various lithium dialkylamides.

$$\underset{\mathbf{3}}{TsOCH_2CF_3} \xrightarrow{NaSR} \underset{\mathbf{4}}{RSCH_2CF_3} \xrightarrow{LiNR'_2} \underset{\mathbf{5}}{RS\text{-}C{\equiv}C\text{-}NR'_2}$$

Sulfides **4** were obtained in 73—80% yields by the reactions of trifluoroethyl *p*-toluenesufonate(**3**)[5] with the corresponding sodium thiolate. The reactions of sulfides **4** with 3 equiv of lithium dialkylamides generated *in situ* from butyllithium and dialkylamines in diethyl ether at −78 °C for 3 h afforded thioynamines **5** in good yields except for **5c** (see Table); **5c** was obtained in 12% yield due to the partial decomposition during distillation. All thioynamines **5** were identified by their ^{1}H NMR and IR data (see Experimental part). The IR spectra show strong bands at 2120—2130 cm^{-1} due to the carbon-carbon triple bonds.

These thioynamines are stable on storage free from moisture for several weeks; however, they are quite susceptible to hydration affording the corresponding arylthio- or alkylthioacetamides.[6]

The present procedure gives good results both with aromatic and aliphatic sulfides and is more advantageous than the reported one[2] in the points of the easy availability of the starting materials and the simplicity of the procedures. The synthetic utility of the thioynamines is now under study.[7]

Experimental

All boiling points are uncorrected. NMR and IR spectra were recorded on a Varian EM390 spectrometer and a Hitachi 215 spectrometer, respectively.

Preparation of Trifluoroethyl Sulfides **4**. The reaction was carried out in the dark. Thiol (36 mmol) was added to a stirred suspension of sodium hydride (36 mmol) in DMF (40 ml). After the mixture was stirred at room temperature for 30 min, tosylate **3** (30 mmol) was added to the thiolate solution over a 10-min period and the mixture was stirred for an additional 1 h at room temperature. The mixture was then poured into water, and the aqueous solution was extracted twice with ether. The combined ethereal extracts were washed with a 5% aqueous NaOH and brine, dried over magnesium sulfate, and evaporated to leave crude **4**. Purification were effected by distillation under reduced pressure. Yields and boiling points are as follows; phenyl sulfide, 73%, 82—84 °C/25 mmHg (lit,[8] 62—63 °C/5.5 mmHg); *p*-tolyl sulfide, 80%, 95—97 °C/20 mmHg (lit,[9] 87 °C/12 mmHg); ethyl sulfide, 75%. 88—91 °C (lit,[10] 90 °C).

Preparation of Thioynamines **5**; *General Procedure*. The reaction was carried out under nitrogen. A 2.0 M solution of butyllithium (22.5 ml) in hexane was added to a mixture of sulfide **4** (15 mmol) and dialkylamine (45 mmol) in diethyl ether (30 ml) cooled in a dry ice-acetone bath. The mixture was then stirred for 3 h, and allowed to stand at room temperature. The mixture was poured into a 5% aqueous sodium hydrogencarbonate solution, and the aqueous mixture

TABLE. PREPARATION OF THIOYNAMINES **5**

	Thioynamine[a]	Yield (%)	Bp (°C/mmHg) lit[c]
5a	$C_6H_5S\text{-}C{\equiv}C\text{-}N(C_2H_5)_2$	91	108—113/2 (110—115/0.01)
5b	$C_6H_5S\text{-}C{\equiv}C\text{-}N(i\text{-}C_3H_7)_2$	70	154—156/5
5c	$C_6H_5S\text{-}C{\equiv}C\text{-}N(CH_2)_5$	12[d]	128—132/1
5d	$p\text{-}H_3C\text{-}C_6H_4S\text{-}C{\equiv}C\text{-}N(C_2H_5)_2$	78	124—127/0.04 (80—83/0.01)
5e	$p\text{-}H_3C\text{-}C_6H_4S\text{-}C{\equiv}C\text{-}N(i\text{-}C_3H_7)_2$	87	140—142/3
5f	$C_2H_5S\text{-}C{\equiv}C\text{-}N(C_2H_5)_2$	83	110—112/20 (65—70/0.1)

a) Hydration occurred too readily to give reliable elemental analyses. The purities could be checked by IR and NMR spectra (Ref. 6) since the hydration product was the only contaminant. b) Yields refer to the isolated thioynamine after distillation. c) See Ref. 2. d) See the text. The ^{1}H NMR spectrum of crude **5c** showed that it was practically pure.

was extracted twice with ether. The combined ethereal extracts were washed with brine, dried over potassium carbonate, and evaporated to leave crude **5**. Purification was done by distillation under reduced pressure. Yields and boiling points are given in Table and $\nu_{C\equiv C}$ in IR (liq film) and ^1H NMR (CCl_4) data are as follows; **5a**, 2130 cm^{-1}, $\delta=1.0$—1.3 (2t, 6H), 2.8—3.2 (2q, 4H), 6.8—7.3 ppm (m, 5H); **5b**, 2120 cm^{-1}, $\delta=1.2$ (d, 12H), 3.1 (sep, 2H), 6.9—7.4 ppm (m, 5H); **5c**, 2125 cm^{-1}, $\delta=1.3$—1.8 (m, 6H), 2.8—3.3 (m, 4H), 6.7—7.4 ppm (m, 5H), **5d**, 2120 cm^{-1}, $\delta=1,2$ (t, 6H), 2.3 (s, 3H), 3.0 (q, 4H), 7.0—7.3 ppm (m, 4H); **5e**, 2120 cm^{-1}, $\delta=1.2$ (d, 12H), 2.3 (s, 3H), 2.8 (sep, 2H), 6.8—7.2 ppm (m, 4H); **5f**, 2125 cm^{-1}, $\delta=1.2$ (t, 6H), 1.3 (t, 3H), 2.4 (q, 2H), 2.9 ppm (q, 4H),

References

1) J. Ficini, *Tetrahedron* **32**, 1449 (1976); H. G. Viehe, *Angew. Chem. Int. Ed. Engl.*, **6**, 767 (1967).

2) S. Y. Delavarenne, H. G. Viehe, *Tetrahedron Lett.*, **1969**, 4761.

3) R. Gompper, S. Mentsch, G. Seybolt, *Angew. Chem. Int. Ed. Engl.*, **14**, 704 (1975).

4) T. Nakai, K. Tanaka, N. Ishikawa, *Chem. Lett.*, **1976**, 1263.

5) F. G. Bordwell, W. T. Brannen, Jr., *J. Am. Chem. Soc.*, **86**, 4645 (1964). Available from Aldrich Chem. Co., Inc., Milwaukee, Wisconsin 53233, U.S.A.

6) The IR spectra of the acetamides showed strong carbonyl absorptions at 1640 cm^{-1} and the NMR exhibited sharp singlets around δ 3.6 ppm due to the *S*-methylene protons.

7) Recently we developed a new method for the stereospecific synthesis of conjugated dienamides via additions of allylic alcohols to thioynamines **5** followed by the [3,3] sigmatropic rearrangement; T. Nakai and H. Setoi, Abst. No. 1T03, 36th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1977.

8) J. Hine, R. G. Ghirardell, *J. Org. Chem.*, **23**, 1550 (1958).

9) T. Nakai, K. Tanaka, N. Ishikawa, *Nippon Kagaku Kaishi*, **1976**, 1888.

10) R. C. Terrell, T. Veciardi, J. F. Vitcha, *J. Org. Chem.*, **30**, 4011 (1965).