A Useful Preparation of Hexamethyldisilthiane[1]

David N. HARPP*, Kosta STELIOU

Department of Chemistry, McGill University, Montreal, Quebec, Canada

In our laboratory we have prepared several sulfur transfer reagents[2] that effectively deliver one or two atoms of sulfur to various heteroatoms.

$$2\ R^1{-}X{-}H\ +\ M{-}S_n{-}M \longrightarrow R^1{-}X{-}S_n{-}X{-}R^1\ +\ 2\ MH$$

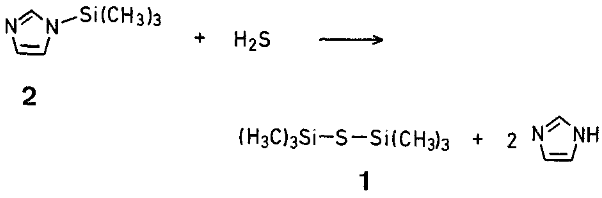
X = —NR²—, —NH—, S, O, n = 1,2,
M = phthalimide[2,3a], succinimide[2f,3b], imidazole[2f,3c,d], 1,2,4-triazole[2f], 1,2,3-benzotrizole[2f], benzimidazole[2f] moieties

However, the problem of transfering sulfur directly to carbon requires a somewhat different approach. Hexamethyldisilthiane (**1**) has been useful in this regard and while many methods have been employed for its preparation, almost all of the described procedures suffer either from low yields, difficult product isolation or require special apparatus[4].

$$(H_3C)_3Si{-}S{-}Si(CH_3)_3$$

1

The most convenient preparation reported to date appears to be the one described by Louis and Urry[4g]. They treat *N*-trimethylsilylimidazole (**2**) with hydrogen sulfide to effect the isolation of **1** in 68% yield.



The method reported here is a modification of this technique directly employing the less expensive and very convenient reagent hexamethyldisilazane (**3**)[5]. The reaction is performed in the presence of a catalytic (1%) amount of imidazole[6]; the desired product is formed in nearly quantitative yield. Furthermore, the reaction time is reduced to less than one-third (~4 h) of the time required by Louis and Urry. The product can be used without further purification.

$$\underset{\mathbf{3}}{(H_3C)_3Si{-}NH{-}Si(CH_3)_3} \xrightarrow{H_2S/1\%\ \text{imidazole}} \underset{\mathbf{1}}{(H_3C)_3Si{-}S{-}Si(CH_3)_3}$$

The reaction most probably involves the silylation of imidazole by hexamethyldisilazane which then reacts with hydrogen sulfide to regenerate imidazole and thus complete the cycle. The process is monitored by ^{1}H-N.M.R. spectroscopy by observing the disappearance of the singlet due to hexamethyldisilazane in favor of the one due to **1**, until the reaction is complete. It is important that hydrogen sulfide is bubbled into the system at a rate just sufficient enough to carry out the reaction and thus avoid massive formation of ammonium hydrogen sulfide [NH_4SH] and ammonium sulfide [$(NH_4)_2S$], which could be troublesome by clogging the condenser. Careful execution of the procedure as described readily and conveniently provides pure product in 96% yield.

Compound **1** was characterized by boiling point and infrared analysis in agreement with that previously reported[4c]. Further, treatment of **1** with benzyl bromide afforded dibenzyl sulfide in a yield of 87%.

Preparation of Hexamethyldisilthiane (1):

A 250 ml three-necked flask equipped with a water cooled condenser[7] was charged with hexamethyldisilazane (**3**; 80.7 g, 0.5 mol) and imidazole (1.0 g); the mixture was stirred and heated at 90–100° (oil bath temperature) which caused the imidazole to silylate. While maintaining this bath temperature, hydrogen sulfide was bubbled through slowly but continuously to prevent back pressure. The reaction was followed by ^{1}H-N.M.R. spectroscopy and was immediate. Complete reaction of hexamethyldisilazane with hydrogen sulfide (N.M.R.) to yield hexamethyldisilthiane (**1**) occurred within 4 h. The reaction mixture was allowed to reach room temperature while maintaining anhydrous conditions (drying tube on the condenser). Reagent **1** is a highly hygroscopic liquid which readily reacts with water to yield hexamethyldisiloxane and hydrogen sulfide, thus the reaction must be carried out in a well-ventilated, dry area. Precipitated imidazole as well as some ammonium hydrogen sulfide is filtered (dry nitrogen atmosphere) to yield a virtually pure (N.M.R.) product. Distillation or further purification was not found to be necessary; however, the compound distills as a clear liquid; yield: 85 g (96%) based on **3**; b.p. 160–165° at 760 torr, Lit.[4c,g] b.p. 162°/760 torr. The infrared spectrum of **1** compares favorably to that given in the literature[4c].

M.S.: m/e calc for $C_6H_{18}SSi_2$ (**1**) 178.0668, found 178.0659.

Reaction of Hexamethyldisilthiane (1)[8] with Benzyl Bromide.

Under anhydrous conditions, **1** (2.0 g, 0.011 mol) was added to benzyl bromide (3.42 g, 0.02 mol). The solution was heated at 160° (oil bath). A white precipitate began to form but redissolved within a few minutes. The reaction was followed by N.M.R. spectroscopy which indicated complete consumption of benzyl bromide after 24 h. After allowing the solution to reach ambient temperature, absolute ethanol (20 ml) was added; an odor of hydrogen sulfide ensued. Flash evaporation provided a yellow solid (2.0 g) which was recrystallized in absolute ethanol to give dibenzyl sulfide; yield: 1.85 g (87%); m.p. 48–49°, m.m.p. 47–49°; the infrared spectrum was identical with that of an authentic sample[9].

We are greatful to the National Research Council of Canada and the Imperial Oil Company of Canada for financial support of this work.

Received: June 29, 1976

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[1] Organic Sulfur Chemistry Part XXIII. For part XXII, see D. N. Harpp, S. M. Vines, J. P. Montillier, T. H. Chan, *J. Org. Chem.* **42**, (1977), in press.

[2] (a) D. N. Harpp, D. K. Ash, *Int. J. Sulfur Chem.* **1**, 57 (1971).
(b) D. N. Harpp, T. G. Back, *Tetrahedron Lett.* **1971**, 4953.
(c) D. N. Harpp, D. K. Ash, *Int. J. Sulfur Chem. Part A*, **211** (1971).
(d) D. N. Harpp, T. G. Back, *Tetrahedron Lett.* **1972**, 1481.
(e) D. N. Harpp, T. G. Back, *J. Labelled Comp.* **11**, 95 (1975).
(f) D. N. Harpp, K. Steliou, T. H. Chan, unpublished results.

[3] (a) M. V. Kalnins, *Can. J. Chem.* **44**, 2111 (1966).
(b) J. Suzuki, private communication.
(c) L. Birkofer, P. Richter, A. Ritter, *Chem. Ber.* **93**, 2804 (1960).
(d) F. Feher, B. Degen, *Angew. Chem.* **79**, 690 (1967); *Angew. Chem. Int. Ed. Engl.* **6**, 703 (1967).

[4] (a) M. Schmeisser, W. Burgemeister, *Angew. Chem.* **69**, 782 (1957).
(b) E. W. Abel, *J. Chem. Soc.* **1961**, 4933.
(c) M. Fild, W. Sundermeyer, O. Glemser, *Chem. Ber.* **97**, 620 (1964).
(d) E. W. Abel, D. A. Armitage, R. P. Bush, *J. Chem. Soc.* **1964**, 2455.
(e) K. A. Hooton, A. L. Allred, *J. Inorg. Chem.* **4**, 671 (1965).
(f) K. Itoh, I. K. Lee, I. Matsuda, S. Sakai, Y. Ishii, *Tetrahedron Lett.* **1967**, 2667.
(g) E. Louis, G. Urry, *J. Inorg. Chem.* **7**, 1253 (1968).
(h) E. P. Lebedev, D. V. Fridland, V. O. Reikhsfeld, *Zh. Obshch. Khim.* **44**, 2784 (1974).
(i) E. P. Lebedev, V. A. Barburina, D. V. Fridland, S. V. Lebedev, *Zh. Obshch. Khim.* **45**, 1647 (1975).

[5] (a) L. F. Fieser, M. Fieser, *Reagents for Organic Synthesis* Vol. 1, J. Wiley and Sons, New York, N. Y. p. 427 (1967).
(b) Purchased from Silar Laboratories Inc., Watervliet, N. Y.

[6] Hexamethyldisilazane did not react in the absence of imidazole.

[7] There is a tendency for ammonium hydrogen sulfide to solidify on the condenser. To overcome this difficulty a second condenser may be used to replace the first when its surface area becomes saturated with the salt. Drying tubes during the reaction tend to slow the reaction considerably by absorbing the hydrogen sulfide; these are not necessary since positive pressure can be maintained by the hydrogen sulfide gas or by dry nitrogen. Ammonium hydrogen sulfide is removed by filtration and decomposition (ammonia + hydrogen sulfide) during distillation.

[8] This may be used directly without further purification from the previous preparation.

[9] C. Forst, *Justus Liebigs Ann. Chem.* **178**, 370 (1875).