DIMETHYL TRISULFIDE-$\underline{d}_6$

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SUMMARY

Dimethyl trisulfide-$\underline{d}_6$ was prepared in high purity and isotopic content. Methane thiol-$\underline{d}_3$ was generated by the base decomposition of the appropiate isothiouronium salt. Oxidation was mediated via bis-phthalimido sulfide with imidazole catalyst.

Introduction

As part of another investigation, we required a sample of dimethyl trisulfide-$\underline{d}_6$ ($\underline{1}$). A special feature of this work dictated

$$CD_3SSSCD_3$$

$\underline{1}$

that the amount of di-,tri-, and polysulfides be minimized. While there are many methods[1] by which aliphatic trisulfides may be prepared, the main objection to each procedure[1] is that they produce varying amounts of polysuflides as impurities (sometimes the main product). A further problem involving the target molecule is that the logical sulfur containing precursor is relatively difficult to handle (gas, odor) in addition to being the limiting reagent in the reaction.

A synthetic route which properly deals with the above difficulties is outlined below.

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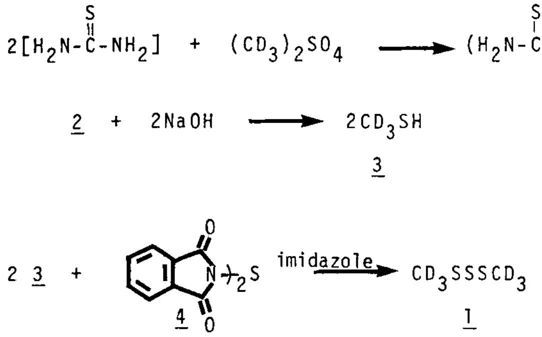

$$2[H_2N\text{-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-}NH_2] + (CD_3)_2SO_4 \longrightarrow (H_2N\text{-}\overset{\overset{\displaystyle SCD_3}{|}}{C}{=}NH)_2\cdot H_2SO_4$$

$$\underline{2} + 2NaOH \longrightarrow 2CD_3SH$$

Methane thiol-$\underline{d}_3$ (3) is generated in situ in one vessel, passed into a flask containing a pentane solution of bis-phthalimido sulfide (4). The latter reagent has served as an efficient sulfur-transfer reagent converting thiols to trisulfides[2]. In this system, a protium pilot run gave no product, however; the use of imidazole as a catalyst[3] afforded a modest yield of dimethyl trisulfide-$\underline{d}_6$(1)(21%).

This material was 98.7% deuterated(mass spectra)[4a] and >99% pure[4b]. A trace of dimethyl disulfide-$\underline{d}_6$ was found.

Experimental

Methyl isothiourea sulfate-S-d_6(2).- Thiourea(6.28 g, 82.5 mmol) was mixed with 3 ml of H_2O. To this was added 6.00g(45.4 mmol) of dimethyl sulfate-d_6. Within ca. 1 min an exothermic reaction was observed which required cooling with an ice-water bath. When the initial reaction subsided, the solution was refulxed for 1 hr. The mixture was cooled and 8 ml of ethanol added; insoluble material was filtered and washed with 2x3 ml of ethanol. The product was dried under vacuum affording 8.45g (72%) of a white solid mp 248d (lit.[5] 235d).

Dimethyl trisulfide-$\underline{d}_6$[5].- The thiouronium salt 2(8.39g, 29.5 mmol) and NaOH(2.36g in 12ml of D_2O, 59mmol) were placed in a round-bottom

50 ml flask. The flask was connected to an air condenser, Drierite drying-tube and finally to a pressure-resistant vessel cooled in a acetone/dry-ice bath. This vessel was attached to a trap of lead acetate solution to precipitate errant CD_3SH. The system was first flushed with nitrogen,then the initial flask heated for 2 hr at 50-60° (oil-bath temperature) and finally for 1 hr at reflux. After this, a clear liquid (CD_3SH) was observed in the cooled vessel. To this container was added sulfide 4 (3.24g, 10mmol), imidazole(1.36g, 20mmol) and 50 ml of pentane. The flask was sealed and stirred for 20 hr at room temperature. The solution was filtered and the filtrate washed with 10 ml of H_2O and dried over sodium sulfate. The resulting liquid was distilled through a short Vigreux column until the temperature reached 39°. Vpc analysis showed no trace of trisulfide in the distillate. The remaining liquid was transferred to a 5 ml flask and distilled through a minimum hold-up still. A forerun was obtained; 0.08g b_{16} 26-28°; the product distilled at b_{11} 60-61°; yield 0.27g (21%).

Acknowledgement

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References

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2. D.N. Harpp and D.K. Ash, *Intl. J. Sulfur Chem.*, **1**, 57 (1971); D.N. Harpp and T.G. Back, *Tetrahedron Lett.*, 1481 (1972).

3. Y. Abe, private communication. While in theory imidazole should be acting as a catalyst, this reaction proceeds more effectively using a molar amount.

4. (a) Mass spectra were recorded on an AEI-MS-902 spectrometer. Gas chromatography data were obtained on an F and M device.

5. The preparation was modified slightly from the procedure of P.R. Shildneck and W. Windaus, *Org. Syn, Coll. Vol II*, p. 411, John Wiley and Sons, N.Y., 1943.