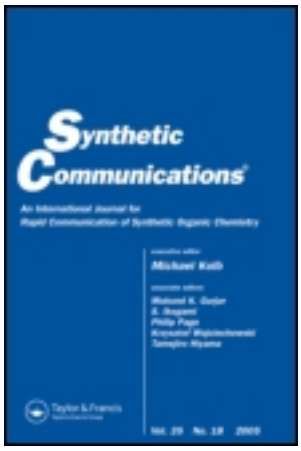

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A NOVEL SYNTHESIS OF SULFURIC ACID MONO-[2-(2-AMINO-ETHANESULFONYL)-ETHYL] ESTER FOR USE AS AN INTERMEDIATE IN THE PREPARATION OF REACTIVE DYES

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ABSTRACT

Sulfuric acid mono-[2-(2-amino-ethanesulfonyl)-ethyl] ester **8**, which is a key intermediate of reactive dyes was prepared in four steps in good overall yield under mild conditions from 2-aminoethanethiol and 2-bromoethanol.

Sulfuric acid mono-[2-(2-amino-ethanesulfonyl)-ethyl] ester **8** represents one of the important sulphatoethylsulphone intermediates (SES) in the synthesis of reactive dyes. Reactive dyes, which contain aliphatic SES are more water-soluble than those, which contain aromatic SES. An aliphatic SES requires a shorter dyeing time because of its water solubility. In addition, dyes prepared from such intermediates contain bonds which are relatively stable to acidic solutions and peroxide and survive the dyeing process well.

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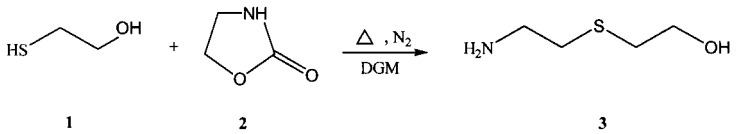
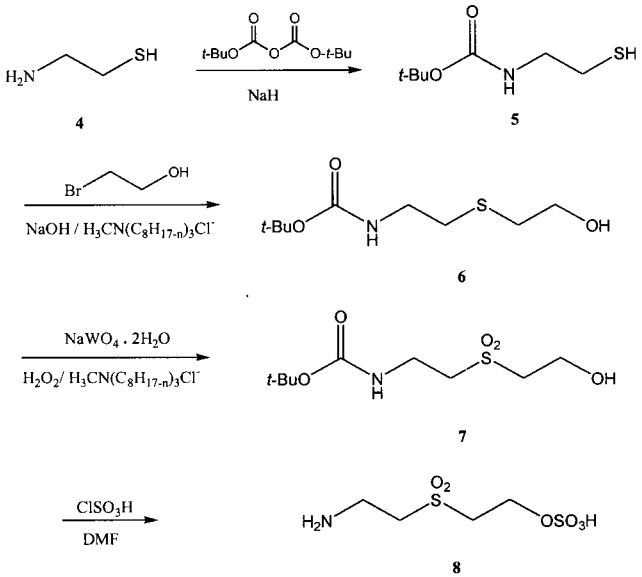
Only a limited number of synthetic routes to aliphatic SES have been reported. Of those, the synthesis of 2-(2-amino-ethylsulfanyl)-ethanol **3** has been reported in the patent literature (Scheme 1).[1] This method involves refluxing mercapto-ethanol and 2-oxazolidinon in DGM (diethylene glycol monomethyl ether) as a solvent. However, the procedure has some drawbacks in terms of reaction conditions. High temperature (180°C) is required and the yield of lactam byproduct, which is produced by oxidation in 19% yield, can be significant.



1 2 3

Scheme 1.

In this paper we report the development of a novel synthetic method for the synthesis of sulfuric acid mono-[2-(2-amino-ethanesulfonyl)-ethyl] ester **8**, which is summarized in Scheme 2.



4 5 6 7 8

Scheme 2.

Protecting 2-aminoethanethiol with di-*tert*-butyl dicarbonate gives compound **5** in nearly quantitative yield.[2–4] The purification of **5** is simple. The reaction mixture is concentrated and then passed through a pad of silica gel using a mixture of methanol and chloroform (1 : 9). Silica gel column chromatography allowed the isolation of compound **5** in reasonably pure form in 93% yield.

Compound **6** was obtained in 85% yield using a procedure wherein 2-bromoethanol was added to a rapidly stirred mixture of **5** in a suspension of aqueous sodium hydroxide/benzene at room temperature.[5] It should be noted that the use of methylene chloride as solvent was successful in this reaction but gave compound **6** in only 22% yield.

These two steps are very simple and efficient. The overall yield for the two steps is 80%.

The sulfone derivative of **6** (compound **7**) was produced in quantitative yield by oxidation with hydrogen peroxide in a mixture of methanol and water.[6,7] The reaction was performed under phase transfer conditions. Methyltri-*n*-octylammonium chloride (Aliquat 336) was used as the phase-transfer catalyst. This method involves shorter reaction times, milder reaction conditions, greater convenience and higher yields.[2,3] As a result, compound **7** was obtained very pure without any chromatographic purification, as evidenced by ^{1}H NMR. Both IR and ^{1}H NMR confirmed that the product obtained was sulfone and not the sulfoxide.

The desired product **8** was prepared via a series of simultaneous reactions, that is, deprotecting the *N*-amino compound by cleavage of the carbo-*tert*-butoxy group followed by the preparation of the sulfonate ester from the alcohol (compound **7**). The latter involved the use of chlorosulfonic acid and *N*,*N*-dimethylformamide as solvent.[8]

In conclusion the method described herein offers some distinct advantages, such as mild reaction conditions, ease of operation and moderate to good yields.

EXPERIMENTAL

Commercially available reagents were purchased from Aldrich and Acros Synthesis. ^{1}H NMR spectra (Bruker MSL 300 MHz) were recorded using TMS as an internal standard, and deuteriochloroform or deuterium oxide as solvents. IR spectra were recorded as thin films between sodium chloride plates or KBr disks on a Prospect-IR (MIDAC Co.). Preparative TLC was performed on silica gel plates (Merck, silica gel 60 F_{245}), and silica column chromatography were performed using Merck silica gel 60 (70–230 mesh ASTM).

(2-Mercapto-ethyl)-carbamic acid *tert*-butyl ester (5): To a stirred colorless solution of 2-aminoethanethiol hydrochloride **4** (9.8 g) in tetrahydrofuran (100 ml) at 0°C was added hexane washed sodium hydride (5.2 g, 60% in mineral oil). After 5 min, the bath was removed, the reaction mixture was allowed to warm to room temperature and stirred for 10 min further. The reaction mixture was then cooled to 0°C and neat di-*tert*-butyl dicarbonate (22.5 g) was added. After 20 min, the 0°C bath was removed. The reaction mixture was stirred for an additional 2 h at room temperature then quenched with an aqueous solution of sodium bicarbonate. The reaction mixture was poured into water and the resulting solution extracted with ethyl acetate. The combined organic layer was dried over magnesium sulfate, filtered and concentrated in vacuo to give essentially pure **5** (by T.L.C.) in quantitative yield. The product was further purified by column chromatography over a short column of silica gel; column inside diameter 25 mm, column length 400 mm and capacity of reservoir 500 ml (chloroform as eluent). Yield: 7.5 g (95%). IR (KBr): $\nu_{max} = 1520$ (-CO-N-), 1699 (-CO-), 2559.7 (-SH), 3356 (-NH-) cm^{-1}. ^1H NMR ($CDCL_3$): δ (ppm): 1.40 (9H, s, $-C(CH_3)_3$), 2.66 (2H, q, $-N-CH_2$), 3.31 (2H, q, $-S-CH_2$).

[2-(2-Hydroxy-ethylsulfanyl)-ethyl]-carbamic acid *tert*-butyl ester (6): In a typical preparation of the sulfide, compound **5** (2.48 g), sodium hydroxide (0.94 g), water (16 ml), methyltricapryl-ammonium chloride (~100 mg), 2-bromoethanol (1.79 g) and benzene (12.7 ml) were combined and stirred vigorously with a mechanical stirrer for 2 h at ambient temperature. The organic layer was then separated, washed with water, dried over magnesium sulfate, and evaporated on a rotary evaporator to give **6**, 3.1 g (85%) as colorless oil, which was used without further purification. IR (KBr): $\nu_{max} = 667$ (-S-), 1047 (-C-OH), 1520 (-CO-N-), 1693 (-CO-), 3354 (-NH-) cm^{-1}. ^1H NMR ($CDCL_3$): δ (ppm): 1.40 (9H, s, $-C(CH_3)_3$), 2.66, 2.80 (4H, t, $S-CH_2$), 3.31 (q, $-N-CH_2$), 3.75 (2H, t, $-CH_2$, -O).

[2-(2-Hydroxy-ethanesulfonyl)-ethyl]-carbamic acid *tert*-buyl ester (7): Compound **6** (7.52 g) was stirred in a mixture of water (15 ml) and methanol (40 ml), sodium tungstate dihydrate (34 mg) and methyltricapryl-ammonium chloride (~100 mg) was added at room temperature. A solution aqueous hydrogen peroxide (10 ml) was then added dropwise to this well-stirred clear solution at a rate such that the ensuing exotherm kept the reaction mixture at about 60°C. The reaction mixture was left for 2 h at room temperature. After completion of the reaction, the mixture was treated with 5% Pd/C (0.2 g) in order to decompose the remaining hydrogen peroxide. After evolution of oxygen had ceased, the solution was filtered and the solvent was then removed by evaporation under reduced pressure. The residue was extracted with ethyl acetate and the organic layer was separated, washed with water, dried over magnesium sulfate and evaporated

on a rotary evaporator to give a colorless liquid. Yield: 8.4 g (82%). IR (KBr): $\nu_{max} = 501$, 561, 1122, 1290 (-SO_2-), 1520 (-CO-N-), 1699 (-CO-), 3373 (-NH-) cm^{-1}. ^1H NMR ($CDCL_3$): δ (ppm): 1.49 (9H, s, -$C(CH_3)_3$), 3.28 (2H, t, -N-CH_2), 3.35, 3.66 (4H, t, q, -SO_2-CH_2), 4.12 (2H, t, -CH_2-OH).

Sulfuric acid mono-[2-(2-amino-ethanesulfonyl)-ethyl] ester (8): To a stirred solution of compound **7** (3.05 g) in DMF (9 ml) at 0–5°C, chlorosulfonic acid (1.82 g, 1.3 eq.) was added dropwise. When the addition was complete, the reaction mixture was allowed to react at 48°C. The resulting brown precipitate was filtered, washed with diethyl ether and dried in vacuo. An analytical sample was obtained in the form of off-white crystals by recrystallization by solution in water and precipitation with c-HCl to give compound **8**. Yield: 83%. m.p. 215–216°C. IR (KBr): $\nu_{max} = 590$, 1134, 1296 (-SO_2-), 1066 (-C-N-), 1197 (-OSO_3-) cm^{-1}. ^1H NMR (D_2O): δ (ppm): 3.44 (2H, t, -N-CH_2), 3.59 (4H, m, -SO_2-CH_2), 4.34 (2H, t, -CH_2-O-).

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