Organic Electrosyntheses VI[1]. A Facile Preparation of 1,3-Thiazole

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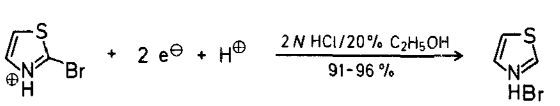
Thiazole is usually prepared by zinc-acetic acid reduction of the 2-bromo[2] or 2-chloro[3] derivative. Methanol or hypophosphite reduction of the 2-diazonium salt[4] gives only a moderate yield, and the older methods are not reliable[3]. The first method is reported to work well with a large excess of zinc powder, but requires a separation of thiazole by steam distillation from the zinc acetate formed. The present procedure is based on the polarographic results on halothiazoles by Laviron[5] and consists of electrolytic reduction of readily accessible 2-bromothiazole at −0.7 V (*vs* Ag/AgCl) in hydrochloric acid medium at a mercury electrode with cleavage of the C—Br bond in high yield:



Thiazole gives no polarographic wave in acid solution and is not further reduced under the experimental conditions. Thus, controlled potential conditions are not strictly necessary; however, the use of an electronic potentiostat is very convenient for laboratory work, enabling the electrolysis to be run in the absence of the operator. The use of hydrochloric acid both as a proton donor and supporting electrolyte greatly facilitates the work-up procedure, a simple evaporation, leaving the product thiazole as the hydrobromide salt wihout contamination from added reagents. The free base was obtained on a 0.2 mol scale in 88% yield by adding excess alkali, extracting with ether and fractionating.

Electrolytic Reduction of 2-Bromo-1,3-thiazole:

1,3-Thiazole Hydrobromide: The electrolyses were performed overnight in a conventional H-type cell[6] of approximately 400 ml cathodic volume surrounded by a water bath using a 100 V/10 A Juul Electronic potentiostat[7]. The 2-bromo-1,3-thiazole[2,4,8] (20.0 ml, 0.229 mol) was reduced at potentials more positive than −0.7 V *vs* Ag/AgCl in 2 *N* hydrochloric acid containing 20% ethanol; the same background solution was used in all three cell compartments. After reduction, the colourless catholyte was filtered, if necessary, and evaporated to dryness, leaving light brown crystals of crude 1,3-thiazole hydrobromide; yield: 36.4 g (96%); m.p. 186–187°.

Similar reductions of 2-bromo-1,3-thiazole (5.0 ml) in a smaller cell of approximate 175 ml of catholyte gave 8.60–9.10 g (91–96%) of crude hydrobromide. The evaporation was repeated twice with addition of absolute ethanol (25 ml); a little hydrobromic acid could be added to secure a total conversion to the hydrobromide. The salt was recrystallized from absolute ethanol (25 ml); yield: 7.65 g; m.p. 185–186°. The mother liquor was evaporated and the residue purified by dissolving in absolute ethanol (5 ml) and precipitated with anhydrous ether (25 ml) giving further 1.15 g of the hydrobromide, m.p. 185–186°; overall yield: 93.5%. Recrystallization from absolute ethanol/ether (1:1) m.p. 188–189°.

C_3H_4BrNS	calc.	C 21.69	H 2.47	Br 48.08	N 8.45	S 19.31
	found	21.59	2.51	48.20	8.31	19.24

1,3-Thiazole: To the crude hydrobromide (36.4 g) was added ether (100 ml) and 33% aqueous sodium hydroxide solution

(50 ml), the aqueous phase was extracted with further ether (25 ml), the combined ethereal solutions were dried over potassium hydroxide pellets and fractionated on a Vigreux column; yield: 17.1 g (88%); b. p. 117–118.5°; n_D^{25}: 1.5351; 98.5% pure by G. L. C. Redistillation: b. p. 117.5–118.5°; n_D^{25}: 1.5357[9]; 99.5% pure by G. L. C. (50°, 15% SE 30, Perkin-Elmer F 11).

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The value of n_D^{20}: 1.5969 given by Rosanow (Beilstein **27** I, 208 and cited by the Handbook of Chemistry and Physics, 1971 Ed.) seems to be erroneous. The Aldrich-Europe 1970 catalogue 15 states n_D^{20}: 1.5375.