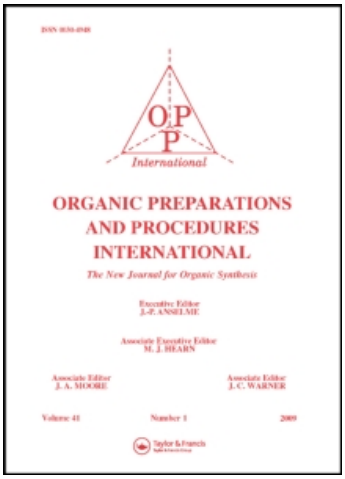


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# PREPARATION OF 2-HYDRAZINOBENZOTHIAZOLES BY EXCHANGE AMINATION

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# PREPARATION OF 2-HYDRAZINOBENZOTHIAZOLES BY EXCHANGE AMINATION

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We required a general method for the preparation of substituted 2-hydrazinobenzothiazoles II. Direct conversion of 2-aminobenzothiazoles I to II by exchange amination with hydrazine was an attractive approach in view of the general availability of 2-aminobenzothiazoles from oxidative cyclization of thioureas (Hugershoff reaction).[1] Such an exchange process had previously been reported,[2] but the procedure described gave poor yields of II unless the starting 2-aminobenzothiazole possessed a carboxyl sub-


I II

stituent in the benzenoid moiety.

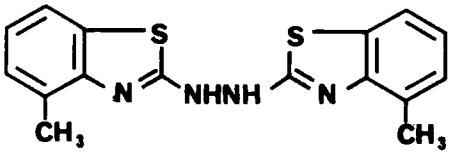
We have found that reaction of 2-aminobenzothiazoles with a hydrazine-hydrazine hydrochloride mixture in ethylene glycol solution (130-140°) affords the corresponding 2-hydrazinobenzothiazoles in excellent yields. Results for several examples are shown in Table I.

TABLE I

| R | Yield (%)[a] | mp (crude) | mp[b] |
|---|---|---|---|
| H | 90 | 194-198° | 196-198°[c] |
| 4-$CH_3$ | 93 | 165-168° | 167.5-169° |
| 5,6-$(CH_3)_2$ | 82 | 223-229° | 235-240°(dec.) |
| 4-$OCH_3$ | 89.6 | 215-220° | 224-226.5° |
| 6-$OCH_3$ | 90 | --- | 176-178°[d] |
| 6-$SCH_3$ | 92.5 | 173-176° | 178-180° |
| 4-Cl | 90.5 | 226-229° | 239-241° |

a) Based on weight of isolated crude product.
b) Recrystallized from ethanol.
c) Lit[6] mp 195°.
d) Lit[7] mp 168-169°.

The crude products were 90-95% pure (vpc analysis) and should generally be suitable for further processing without purification. Impurities included 2-4% starting material and lesser amounts of other by-products. The bis-hydrazobenzothiazole III was identified as a minor impurity in 2-hydrazino-4-methylbenzothiazole (II, R = 4-$CH_3$). Reaction of the desired




III

product II with a second molecule of starting material accounts for the formation of products of the type III.[3] Purification could easily be carried out by recrystallization from alcohol.

It should be noted that heterocyclic hydrazines are unstable to oxygen, particularly in the presence of base.[4] Reactions should be

carried out in an oxygen-free atmosphere and the products protected from direct exposure to air. The hydrazinobenzothiazoles described herein have been found to be stable for several months in tightly capped brown bottles.

## EXPERIMENTAL

General Procedure for the Preparation of 2-Hydrazinobenzothiazoles. To a suspension of 0.1 mole of the 2-aminobenzothiazole in 80 ml ethylene glycol is added 0.2 mole 85% hydrazine hydrate and 0.1 mole hydrazine monohydrochloride. The mixture is heated to 140° for 2 hr[5] in an atmosphere of nitrogen. The mixture is cooled to room temperature, water (80 ml) is added to complete precipitation, and the product filtered, washed with water, and dried. Yield and melting point data for specific examples are reported in Table I.



TABLE II

Elemental Analyses

| | Calculated | | | | Found | | | |
|---|---|---|---|---|---|---|---|---|
| II,R | C, | H, | N, | S | C, | H, | N, | S |
| 4-$CH_3$ | 53.61 | 5.06 | 23.44 | 17.89 | 53.84 | 4.98 | 23.17 | 17.68 |
| 5,6-$(CH_3)_2$ | 55.93 | 5.74 | 21.74 | 16.59 | 55.96 | 5.78 | 21.55 | 16.72 |
| 4-$OCH_3$ | 49.21 | 4.65 | 21.52 | 16.42 | 49.25 | 4.54 | 21.67 | 16.40 |
| 6-$SCH_3$ | 45.47 | 4.29 | 19.89 | 30.35 | 45.63 | 4.21 | 19.66 | 30.12 |
| 4-Cl | 42.11 | 3.03 | 21.05 | 16.06 | 42.30 | 3.13 | 20.82 | 16.11 |

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