

REDUCTIVE REMOVAL OF MERCAPTO GROUPS FROM 1,3,4-THIADIAZOLES

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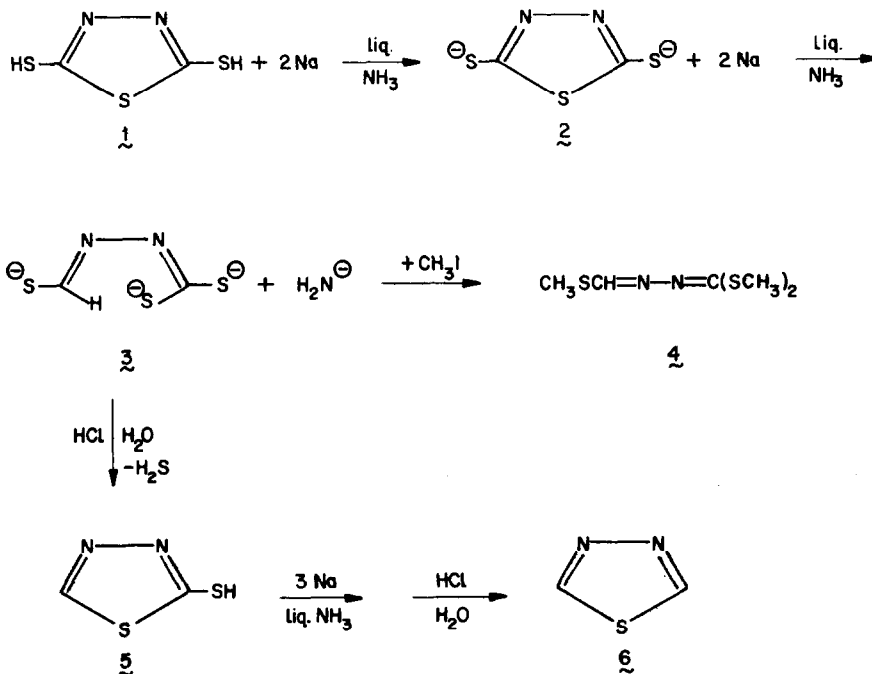
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In contrast to, for instance, 2,5-dimercapto¹- and 2-amino-5-mercapto-1,3,4-thiadiazole^{1,2}, which can be synthesized by simple procedures, substances such as 2-mercapto-1,3,4-thiadiazole and its parent compound^{3,4} can only be prepared by multistep procedures. We here report a simple method for the removal of mercapto groups from the 1,3,4-thiadiazole nucleus, which is based on the reductive cleavage⁵ of carbon-sulphur bonds in heterocyclic compounds with alkali metals in liquid ammonia.

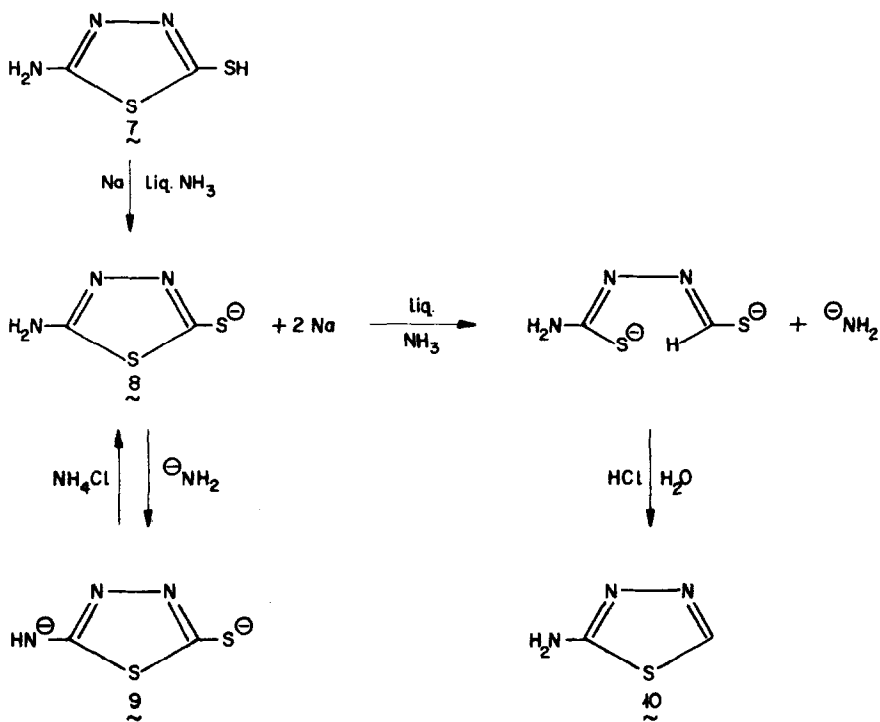
Treatment of a solution of 0.02 mol of 2,5-dimercapto-1,3,4-thiadiazole (1) in 200 ml of liquid ammonia* with four equivalents of sodium gave a quantitative yield of the trisodium salt 3 and sodium amide. The presence of 3 could be demonstrated by quenching the reaction mixture with methyl iodide. The PMR spectrum of the resulting product 4 showed the thioformamide proton as a singlet at low field, whereas the thiomethyl groups appeared as two singlets with a signal area ratio of 2. Apparently, two equivalents of sodium are needed to generate the 1,3,4-thiadiazolethiolate 2, which subsequently undergoes ring cleavage with the remaining two equivalents of sodium. Indeed, a separate experiment showed that 2, prepared from 1 and sodium amide, gave 3 after treatment with two equivalents of sodium. The trisodium salt 3 was isolated after evaporation of the ammonia; it showed a remarkable stability and could safely be stored for several months in a nitrogen atmosphere with exclusion of moisture. Acidification of an aqueous solution of 3 with concentrated HCl resulted in intramolecular cyclization and 2-mercapto-1,3,4-thiadia-

zole (5) was isolated in 61 % yield.



The parent 1,3,4-thiadiazole (6) was prepared in 60 % yield by reacting 2-mercapto-1,3,4-thiadiazole (5) with three equivalents of sodium, followed by acidification of the resulting salt as described above.

When 2-amino-5-mercapto-1,3,4-thiadiazole (7) was subjected to the same reaction conditions only two equivalents of sodium were consumed. Acidification of the salt, obtained after evaporation of the ammonia, yielded equal amounts of 2-amino-1,3,4-thiadiazole (10) and starting material. Here, too, the first equivalent of sodium is used to generate the corresponding thiolate (8). The second equivalent of sodium induces reductive ring cleavage of 8 with formation of sodium amide, which reacts with 7 or 8 to give the corresponding thiadiazole dianion 9, which is resistant towards ring opening. Apparently, replacement of S^\ominus by HN^\ominus increases the charge density of the thiadiazole nucleus to such an extent that further electron addition becomes an unfavourable process.



A higher conversion of **7** into **10** could be achieved when one equivalent of ammonium chloride was added to regenerate **8** from **9**, followed by addition of a third equivalent of sodium. Application of this procedure gave a conversion** of 75 % and a 62 % yield of 2-amino-1,3,4-thiadiazole (**10**).

REFERENCES AND FOOTNOTES

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- * The rate of sodium consumption decreases with increasing concentration of $\underline{1}$.
- ** Higher conversions can be attained by repeated NH_4Cl and sodium additions.