

NOTES

A Tin Derivative of Dithiocatechol

BY HAROLD P. BROWN AND JAMES A. AUSTIN

In the preparation of dithiocatechol from *o*-benzenedisulfonyl chloride by reduction with tin and hydrochloric acid, Guha and Chackladar¹ obtained a red solid, which they supposed to be the lactone of benzene-1-thiol-2-sulfonic acid. Hurlley and Smiles² prepared dithiocatechol from the *o*-benzenedisulfonyl chloride by reduction with zinc dust and acid in the presence of alcohol and avoided the formation of the red solid. Repetition of the procedures described by both of these groups of workers verified the results which they had obtained. However, we cannot agree with the supposition of Guha and Chackladar with regard to the structure of the red solid which they obtained, but have found that it is a tin mercaptide.

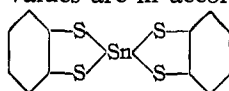
The mercaptide can be obtained from the reaction of stannic chloride with dithiocatechol. Also, the same product is obtained when stannous chloride solutions in contact with air react with dithiocatechol. The completeness of the reaction suggests the possible application of dithiocatechol to qualitative and perhaps quantitative determination of tin and certain other elements. Among the other metallic ions which have been found to react with the dithiocatechol are antimony, zinc, ferric ion, lead and thallium. The analytical possibilities of the reagent are being investigated.

When *o*-benzenedisulfonyl chloride is added gradually to a boiling mixture of tin and excess concentrated hydrochloric acid, a red solid soon appears. If the reaction mixture be distilled during the process of reduction, the formation of this red solid is minimized and oily droplets of dithiocatechol distil from the reaction mixture. However, sufficient tin chloride often carries over with the distillate to cause the formation of red solid particles. The use of a large excess of concentrated hydrochloric acid in the reducing media promotes the decomposition of the red solid. Redistillation of distillate containing the red solid

(1) P. C. Guha and M. N. Chackladar, *Quart. J. Indian Chem. Soc.*, **2**, 318-335 (1925).

(2) Wm. R. H. Hurlley and S. Smiles, *J. Chem. Soc.*, 1821-1828 (1926).

from concentrated hydrochloric acid yields pure dithiocatechol. The red mercaptide is insoluble in dilute mineral acid but soluble in alkali. When placed in concentrated hydrochloric acid, the color of the compound disappears and dithiocatechol separates. Addition of water or of alkali to the acid restores the color and precipitates the tin mercaptide. The solubility of the compound in alkali is similar to the solubility of stannic sulfide in alkali. The compound gradually darkens but does not melt below 250°. No traces of divalent tin could be detected in the compound. When stannous chloride reacts with dithiocatechol a yellow solid forms which may be a stannous mercaptide, but this is completely converted to the red stannic mercaptide by contact with air. A sample of the red complex obtained by the reduction of *o*-benzenedisulfonyl chloride with tin in concentrated hydrochloric acid was purified by dissolving in 4 *N* sodium hydroxide, filtering, reprecipitating with hydrochloric acid and drying at 110°. Analysis was accomplished by means of sodium peroxide fusion in a Parr bomb, the tin being precipitated from the alkali fusion mixture as stannic acid by means of nitric acid. The sulfur was precipitated from the filtrate as barium sulfate after elimination of the nitric acid. Analysis showed 29.44% tin and 31.88% sulfur. These values are in accord with the proposed structure



for which the calculated values are tin, 29.75% and sulfur, 32.14%.

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Auto-Metalation with *m*-Tolylsodium

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After carbonation of a reaction mixture of di-*p*-tolylmercury, sodium and benzene which had been allowed to stand for one month, Bachmann and Clarke¹ isolated benzoic acid (34%), *p*-toluic acid (30%) and phenylacetic acid (0.36%). The formation of phenylacetic acid establishes the migration of sodium from *p*-tolylsodium to benzyl-

(1) Bachmann and Clarke, *THIS JOURNAL*, **49**, 2096 (1927); see also, Ziegler, *Angew. Chem.*, **49**, 455 (1936).