NOTES

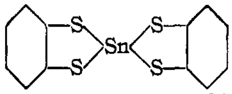
A Tin Derivative of Dithiocatechol

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 Chackladar[1] obtained a red solid, which they supposed to be the lactone of benzene-1-thiol-2-sulfonic acid. Hurtley and Smiles[2] 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 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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(1) P. C. Guha and M. N. Chackladar, *Quart. J. Indian Chem. Soc.*, **2**, 318–335 (1925).

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

Auto-Metalation with *m*-Tolylsodium

By Henry Gilman and H. A. Pacevitz

After carbonation of a reaction mixture of di-*p*-tolylmercury, sodium and benzene which had been allowed to stand for one month, Bachmann and Clarke[1] 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).

sodium, and is an interesting variation of the lateral metalation of toluene by ethylsodium which was first examined by Schorigin.[2]

Incidental to studies on interconversions by organometallic compounds, we have investigated procedures for the preparation of organoalkali compounds, particularly the benzylmetallic types.[3] One of the more interesting results is the conversion of *m*-tolylsodium to benzylsodium. *m*-Chlorotoluene and sodium in petroleum ether first give *m*-tolylsodium, as evidenced by the formation of *m*-toluic acid (free of phenylacetic acid) on carbonation. On refluxing the mixture, the *m*-tolylsodium is converted to benzylsodium. In the Bachmann–Clarke[1] migration with *p*-tolylsodium one may be dealing with an allylic rearrangement of the kind frequently observed with a variety of organometallic compounds. However, with *m*-tolylsodium it is difficult to account for the migration on the basis of an allylic rearrangement. Although mechanisms have not been proposed for the migrations cited, it is probable that the meta and para transformations proceed by different routes, if the relative rates of migration are criteria.

Experimental

A mixture of 12.7 g. (0.1 mole) of *m*-chlorotoluene, 5.7 g. (0.25 g. atom) of sodium sand and 100 cc. of petroleum ether (b. p., 85–100°) was heated to reflux temperature and then promptly cooled to room temperature. The reaction then proceeded spontaneously, and the temperature was kept between 35–40°. After two hours, the reaction mixture was black, and the evolution of heat ceased. Carbonation of an aliquot of the mixture by solid carbon dioxide yielded *m*-toluic acid as the only acid.[4] The remaining mixture was refluxed for six hours and then carbonated by pouring upon crushed solid carbon dioxide. From the resulting acids there was isolated a 5.3% yield of phenylacetic acid (mixed m. p.), but no *m*-toluic acid or phenylmalonic acid. A small quantity of clear, oily acidic material has not yet been identified.

With a twenty-hour period of refluxing, the yield of phenylacetic acid was 4.7%. However, with only a one-hour period of refluxing the yield of phenylacetic acid was 8.3%. It should be stated that carbonation after heating a mixture of *p*-chlorotoluene, sodium and petroleum ether yielded 65% of phenylacetic acid.[3]

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(2) Schorigin, *Ber.*, **41**, 2723 (1908).

(3) A detailed report on these studies by the authors together with Dr. Ogden Baine will be published shortly. An account of the reactions and their mechanisms was presented at the Eighth National Organic Symposium, St. Louis, Dec. 30, 1939.

(4) In a separate experiment where carbonation of the entire mixture was effected at this point, the yield of *m*-toluic acid was 84%.

Preparation of Borneol Glucuronide

BY HARVEY K. MURER AND LATHAN A. CRANDALL, JR.

We have had good success in the isolation of the zinc salt of borneol glucuronide by the method of Quick[1] and Pryde and Williams[2] from the urine of dogs fed borneol provided care is taken in the proper adjustment of acidity previous to the lead clarification of the urine.

In their preparation of the free glucuronide the zinc salt was dissolved in hot 3.4 *N* sulfuric acid, filtered and allowed to crystallize from the hot solution. The glucuronide was filtered off and washed with ice water and recrystallized from hot water for further purification. It is difficult to filter and wash this product in water, and several recrystallizations are necessary to obtain a pure product with subsequent loss in yield. Also uronic acids are destroyed by hot acid of this strength and some hydrolysis of the glucuronide takes place, giving rise to the difficulty of removing borneol from the product.

To avoid these difficulties the removal of the zinc was first attempted with hydrogen sulfide. The zinc salt was suspended in acetone. A slow but fairly good removal of zinc was accomplished but the product retained a strong odor of sulfide after several purifications from acetone.

The above use of acetone led to a simple method which has given good results in the preparation of large quantities of borneol glucuronide of good purity.

Two hundred grams of dry zinc borneol glucuronide is added with stirring to 800 ml. of warm acetone containing 14.7 ml. of concentrated sulfuric acid. The zinc sulfate and any unreacted zinc salt are easily centrifuged down and the clear acetone solution decanted. The centrifuge flasks and precipitate are washed once with 50 to 100 ml. of warm acetone, centrifuged and the clear solution added to the original. Fifty ml. of water is added to the acetone solution to allow for crystallization of the hydrate and to keep traces of zinc sulfate in solution. Crystals of fine needles will set the solution almost solid at room temperature. The product is filtered with suction, washed with cold acetone, and vacuum dried at 40°. The filtrate is easily concentrated and again cooled for crystallization without further addition of water, filtered and washed as before. A still

(1) A. M. Quick, *J. Biol. Chem.*, **74**, 331–341 (1927).

(2) J. Pryde and R. T. Williams, *Biochem. J.*, **27**, 1197–1204 (1933).