avoids the filtration of hot xylene solutions. The mother liquors are used for further extractions; yield, about 90% of the crude product used; m. p., 230°.

Preparation of *p*-Mercury Ditolyl, $(C_7H_7)_2Hg$.—Forty g. of purified *p*-tolylmercuric chloride and 70 g. of sodium iodide (a 75% excess) are refluxed for 15 hours in 300 cc. of 95% alcohol in a 1-liter round-bottom Pyrex flask fitted with a reflux condenser and an efficient glass stirrer. All of the material does not go into solution at any time. The mixture is thoroughly cooled, filtered by suction, and the precipitate washed with water until the washings no longer react with hydrogen sulfide. The product is pure enough for most purposes, being contaminated only by traces of tolylmercuric iodide. It may be further purified by recrystallization from hot xylene. Its purity can be tested by the sodium fusion test for halogens; yield of purified product, 80%; m. p., 235°.

Summary

1. *p*-Tolylmercuric chloride and *p*-mercury ditolyl have been made readily available from *p*-toluene-sulfonyl chloride which is cheaply obtainable as a by-product of the saccharin industry.

2. The method of preparing sodium *p*-toluene-sulfinate has been improved.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

THE REACTION OF ORGANIC MERCURY COMPOUNDS WITH HALIDES. I. PARA-MERCURY DITOLYL AND SULFONYL HALIDES

BY FRANK C. WHITMORE AND NEAL THURMAN[1]

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The reaction of organic compounds of mercury with various halides other than those of metals has been the subject of many investigations. Chlorides of trivalent elements such as boron, phosphorus and arsenic react to give products of the general type, $R\text{-}ECl_2$, when heated with organic mercury compounds to about 150°. No satisfactory conclusions have been reached in the study of the reaction of alkyl and aryl halides with organic mercury compounds. The expected reaction with the formation of a lengthened carbon chain apparently does not take place. Acid halides do not react to form the expected ketones or similar products except in the case of the monomercurated thiophenes. The present paper is the first of a series in which these reactions will be taken up in some detail. The mercury compound used will be *p*-mercury ditolyl, as methods have been developed which make it the most readily available substance of the type, R_2Hg, in which **R** is an aromatic hydrocarbon residue.[2]

During the last few years mercury ditolyl has been treated with a number

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[1] Part of the present work was done under a grant from the Research Board of the Public Health Institute of Chicago.

[2] See preceding paper.

of reactive halides in this Laboratory. The first of these to give clean-cut results was *p*-toluene-sulfonyl iodide. Up to the present the only similar studies are those of Otto[3] who found that mercury diphenyl heated with benzene-sulfonyl chloride in benzene at 160° entered a complicated reaction forming small amounts of diphenyl-sulfone and phenylmercuric chloride. He also showed that mercury diphenyl heated with *p*-toluene-sulfonyl chloride in benzene at 120° for 15 hours gave a good yield of *p*-tolylmercuric chloride but only a trace of phenyl-tolyl-sulfone. It has been shown that the sulfonyl chlorides differ from the acyl chlorides in not reacting with mercurated thiophenes.[4]

In the present study it has been found that *p*-toluene-sulfonyl iodide when refluxed with *p*-mercury ditolyl in carbon tetrachloride for 50 to 90 hours reacts to give a good yield of *p*-ditolyl-sulfone, tolylmercuric iodide and mercuric iodide. The sulfonyl chlorides differ considerably from the iodides in this reaction. *p*-Toluene-sulfonyl chloride and benzene-sulfonyl chloride give no definite reaction with mercury ditolyl. Refluxing for from 50 to 90 hours in toluene or xylene gives various amounts of metallic mercury, calomel, mercuric chloride, organomercuric chlorides, tarry products, and always a large amount of unchanged material. No phenylmercuric chloride was obtained from the action of benzene-sulfonyl chloride with mercury ditolyl as might be expected from Otto's results.[3]

The difficulty in completing the reaction between toluene-sulfonyl iodide and mercury ditolyl made it seem possible that the reaction is reversible. However, such is not the case, as mercuric iodide does not react with tolylsulfone even on refluxing in carbon tetrachloride for 90 hours.

The study of the reaction of mercury ditolyl with a great variety of halides is being continued in this Laboratory.

Experimental Part

Preparation of *p*-Toluene-sulfonyl Iodide.—Thirty g. of pure sodium *p*-toluenesulfinate crystals is dissolved in 1.5 liters of distilled water at 20°. A saturated solution of 25 g. of iodine in 95% alcohol is prepared and added gradually to the sulfinate solution until a slight excess of iodine is present. The curdy yellow precipitate is filtered by suction, washed with cold water, and dried carefully on a porcelain plate at 50°; yield, 90%.

Reaction of *p*-Toluene-sulfonyl Iodide with *p*-Mercury Ditolyl

Preliminary experiments were run with these substances in boiling carbon tetrachloride and boiling toluene. Reaction occurred in both media, with sulfone formation. Carbon tetrachloride was chosen for the final runs, of which the following is typical.

Twenty-four g. of well-dried *p*-toluene-sulfonyl iodide, 300 cc. of carbon tetrachloride (b. p., 76–78°), and 16 g. of pure *p*-mercury ditolyl[2] are refluxed for 55 hours. The top of the condenser is provided with a tube leading into sulfate-free sodium hydroxide solution. Most of the solids in the reaction flask dissolve on heating. After about

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[3] Otto, *Ber.*, **18**, 246 (1885).

[4] Steinkopf and Bauermeister, *Ann.*, **403**, 59 (1914).

10 hours red mercuric iodide begins to separate on the walls of the flask. At the end of 55 hours the mixture is cooled and filtered. The sodium hydroxide solution, treated with bromine, dil. hydrochloric acid and barium chloride, gives a very slight precipitate of barium sulfate, showing that a trace of sulfur dioxide is formed in the reaction.[3] The residue which is insoluble in cold carbon tetrachloride consists of about 7.5 g. of mercuric iodide, removed by repeated extractions with cold potassium iodide solution, and about 9 g. of a mixture of tolylmercuric iodide and unchanged mercury ditolyl which is very hard to separate. The carbon tetrachloride solution is evaporated under diminished pressure at about 50°. As the residue cools it crystallizes to a dark brown mass which contains, among other substances, free iodine, unchanged sulfonyl iodide, mercuric iodide, and a considerable amount of tolyl-sulfone. Recrystallization of the mixture from 50% alcohol gives 6 g. of the latter substance. Considering the great amount of unchanged substances recovered, this represents a very good yield of the sulfone. The identity of the *p*-tolyl-sulfone was proved by a sulfur analysis and melting-point determinations. *p*-Tolyl-sulfone made by the Friedel and Crafts reaction from toluene-sulfonyl chloride and toluene melted at 158°. The purest material obtained from the mercury reaction melted at 156–157°. Mixtures of the 2 products in 4 different proportions melted at 157–158° repeatedly. The carbon tetrachloride used was redistilled after the reaction and showed an unchanged boiling point. In one run a small amount of a low-melting solid was obtained which had the odor of *p*-tolyl iodide. The formation of this substance could be explained by the action of the tolylmercuric compounds with free iodine formed by the decomposition of the sulfonyl iodide.

Reaction of *p*-Toluene-sulfonyl Chloride and *p*-Mercury Ditolyl

In order to compare the activity of the sulfonyl chloride with that of the iodide, 10.2 g. of *p*-toluene-sulfonyl chloride and 7 g. of *p*-mercury ditolyl were refluxed with 50 cc. of carbon tetrachloride for 90 hours. The original substances were recovered unchanged and no trace of a sulfone or mercuric chloride could be found. The failure of the chloride to react is not surprising in view of the fact that the much more reactive iodide gives only an incomplete reaction.

Reaction of Benzene-sulfonyl Chloride and *p*-Mercury Ditolyl

No reaction took place between these substances on refluxing them in carbon tetrachloride for 100 hours. When the substances were refluxed in xylene they reacted but a large amount of tarry products was formed from which no pure organic substance could be isolated. Very small amounts of sulfur dioxide were evolved during the reaction. Considerable amounts of mercuric and mercurous chlorides as well as some metallic mercury were found in the mixture.

Running the reaction in boiling toluene for various lengths of time gave only slightly better results. The products were the same as in the xylene runs except that a small amount of an organic mercury compound melting at 230–232° was obtained in one run. This was apparently *p*-tolylmercuric chloride. In another run, 0.5 g. of phenyl-tolyl-sulfone was obtained.

***p*-Ditolyl-sulfone and Mercuric Iodide.**—These substances, refluxed in carbon tetrachloride for 90 hours, did not react.

Summary

1. *p*-Toluene-sulfonyl iodide, refluxed with *p*-mercury ditolyl in carbon tetrachloride, reacts partially to form tolyl-sulfone, mercuric iodide and tolylmercuric iodide. The yield of sulfone based on the material which reacts is almost quantitative.

2. p-Toluene-sulfonyl chloride does not react with p-mercury ditolyl under the above conditions.

3. p-Toluene-sulfonyl chloride and benzene-sulfonyl chloride react with p-mercury ditolyl at higher temperatures in toluene or xylene but give no more than traces of definite organic products.

4. No phenylmercuric chloride is obtained from the action of benzenesulfonyl chloride and p-mercury ditolyl.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. II. REDUCTION OF ALDEHYDES. ACTIVATION OF THE CATALYST BY THE SALTS OF CERTAIN METALS[1]

BY WALLACE H. CAROTHERS WITH ROGER ADAMS[2]

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Introduction

In a previous article by Voorhees and Adams[3] it was shown that a very active catalyst for use in hydrogenation of all types of organic compounds was produced by the fusion of chloroplatinic acid with sodium nitrate. The behavior of the catalyst in the reduction of aldehydes was particularly commendable in that it permitted the reduction of comparatively large amounts of material with relatively small amounts of platinum in a brief period of time and since the publication of the preliminary article, this catalyst has been used for reducing large amounts of various aldehydes to the corresponding alcohols. These results were especially gratifying in view of the fact that aldehydes, in spite of the ease with which they are reduced to alcohols by ordinary chemical methods, have been found to be difficult to reduce by hydrogen using ordinary platinum black as a catalyst. This fact has been noticed by several investigators.[4]

A catalyst so easily prepared as this, which allowed such rapid reduction of all types of organic compounds, particularly of compounds so difficult to reduce catalytically as aldehydes, merited further study. The discovery of the cause for its very great superiority in many respects over

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[1] Part of the chloroplatinic acid used in this investigation was purchased with the aid of a grant from the Bache Fund of the National Academy of Sciences. For this aid the authors are greatly indebted.

[2] This communication is an abstract of a thesis submitted by W. H. Carothers in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922).

[4] G. Vavon, *Compt. rend.*, **154**, 359 (1912). This investigator found it possible to reduce aldehydes and ketones to alcohols but he recommends the use of 12 g. of platinum for each gram molecule of aldehyde.