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

PREPARATION OF PARA-TOLYL MERCURY COMPOUNDS[1]

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Since a number of the investigations in this Laboratory required large amounts of an aromatic mercury compound containing an unsubstituted hydrocarbon residue, the methods of preparing such substances were reviewed. The oldest method,[3] consisting of the action of sodium amalgam on an aryl bromide in the presence of ethyl acetate, proved troublesome and gave poor yields of a substance hard to purify. The more modern method[4] of treating an aromatic Grignard reagent with mercuric chloride was also found unsuitable. Direct mercuration of benzene[5] was unsatisfactory because it must be carried out under pressure and gives poor yields. A similar process with toluene[6] gives mixtures difficult to separate. It was finally decided to adapt as a means of preparation the reaction discovered by Peters[7] in which an aryl sulfinic acid reacts with mercuric chloride as follows: $R—SO_2H + HgCl_2 \longrightarrow R—HgCl + SO_2 + HCl$. The most readily available sulfinic acid is that of toluene, as it can be made from *p*-toluenesulfonyl chloride obtained as a by-product in the saccharin industry.[8] This preparation was modified by running the reaction between the chloride and zinc dust in water instead of alcohol and by isolating the product as the well-crystallized sodium salt instead of the free acid. It was soon found that the sodium salt gave better yields with mercuric chloride than did the free acid.

The change of *p*-tolylmercuric chloride to mercury ditolyl required a study of the reagents which cause the change, $R—HgX \longrightarrow R_2Hg$. As will be recalled, these are reagents all of which remove mercuric ions more

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[2] Part of the present work was done under a grant from the Research Board of the Public Health Institute of Chicago. Organic mercury compounds related to those studied are being investigated pharmacologically by Dr. A. S. Loevenhart of the University of Wisconsin under a similar grant.

[3] Dreher and Otto, *Ber.*, **2**, 542 (1869); *Ann.*, **154**, 94 (1870).

[4] Pfeiffer and Truskier, *Ber.*, **37**, 1127 (1904). Compare Marvel and his co-workers, THIS JOURNAL, **44**, 153 (1922); **45**, 820 (1923).

[5] Roeder and Blasi, *Ber.*, **47**, 2751 (1914).

[6] Dimroth, *ibid.*, **32**, 761 (1899). Steinkopf, *Ann.*, **413**, 329 (1917).

[7] Peters, *Ber.*, **38**, 2567 (1905). While the present work was in progress a paper appeared in which the reaction of Peters was used in a similar way. Kharasch and Chalkley, THIS JOURNAL, **43**, 611 (1921).

[8] The sulfonyl chloride used in this work was supplied by the Monsanto Chemical Co. of St. Louis at a nominal price.

completely than do the strong bases.[9] Among the substances tried in the present work were sulfide, stannite, thiosulfate, thiocyanate, and iodide solutions. At first it appeared that the best reagent was potassium thiocyanate,[10] but more extended experiments showed that the best yields of mercury ditolyl are obtained by refluxing pure tolylmercuric chloride for a long time with an excess of alcoholic sodium iodide.

The reactions involved in the preparations are as follows.

$$\text{I. } R{-}SO_2Cl \xrightarrow{Zn} (R{-}SO_2)_2Zn \xrightarrow{Na_2CO_3} R{-}SO_2Na.2H_2O$$

$$\text{II. } R{-}SO_2Na + HgCl_2 \longrightarrow R{-}HgCl + SO_2 + NaCl$$

$$SO_2 + 2\,H_2O + 2\,HgCl_2 \longrightarrow Hg_2Cl_2 + H_2SO_4 + 2\,HCl$$

$$\text{III. } 2\,R{-}HgCl + 4\,NaI \longrightarrow R_2Hg + 2\,NaCl + Na_2HgI_4$$

The yields in the three processes are about 80, 60 and 80%, respectively.

Experimental Part

Preparation of Sodium *p*-Toluene-sulfinate, $C_7H_7SO_2Na.2H_2O$.—Steam is passed into 4 liters of water in a 12-liter crock provided with a powerful brass stirrer. When the temperature reaches 70° the steam is turned off, 400 g. of 90 to 100% zinc dust is added at once, followed by 500 g. of powdered *p*-toluene-sulfonyl chloride gradually during about 10 minutes. The stirring is continued for about 15 minutes longer and then steam is passed into the mixture until the temperature reaches 90°. The mixture is treated with 350 cc. of 12 *N* sodium hydroxide solution and then with powdered soda ash in 50g. portions until strongly alkaline, when it is filtered by suction while hot. The cake of unchanged zinc dust and zinc compounds is washed by stirring with 750 cc. of water and passing steam into the mixture. The washings and the original filtrate are evaporated to about 1 liter in a large enameled dish. As the solution cools large, flat, transparent crystals of the sulfinate separate. The crystals are air-dried until efflorescence barely commences; yield, 80 to 90%. Careful acidification of the mother liquors with dil. hydrochloric acid gives about 15 g. of the free acid.

Preparation of *p*-Tolylmercuric Chloride, C_7H_7HgCl.—Three hundred cc. of water and 100 g. of powdered mercuric chloride are heated in a 2-liter Pyrex beaker. A solution of 80 g. of sodium *p*-toluene-sulfinate crystals in 200 cc. of boiling water is added cautiously to the hot mercuric chloride solution. A heavy curdy precipitate forms and sulfur dioxide is evolved rapidly. After the first frothing has ceased, 200 cc. of water is added and the mixture is boiled with occasional stirring until the sulfur dioxide evolution slackens. Then 200 cc. of water is added and the boiling is continued until no more sulfur dioxide is evolved. The hot mixture is filtered by suction and the residue is washed with water until the washings give no precipitate with sodium hydroxide. The filtrate and washings are treated with an excess of sodium hydroxide to change inorganic mercury compounds to the oxide. The crude tolylmercuric chloride is dried at 110°; yield, 65%. The recovered mercuric oxide corresponds to $^1/_4$–$^1/_3$ of the mercuric chloride used. The crude tolylmercuric chloride contains considerable calomel which must be removed before the preparation of mercury ditolyl. This is best accomplished by crystallization from boiling xylene. The extraction is troublesome unless carried out in a large extractor of the type recommended by H. T. Clarke.[11] This

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[9] THIS JOURNAL, **41**, 1850 (1919).

[10] Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., New York, **1921**, p. 181.

[11] Clarke, "Synthetic Organic Chemicals," Eastman Kodak Co., **1922**, p. 24.

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.

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

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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.