

pletely reduced mercury is just as effective as the salt itself.

TABLE II  
A COMPARISON BETWEEN THE CATALYTIC EFFECTS OF MERCURIC CHLORIDE AND FREE MERCURY SOLUTIONS OF IDENTICAL CONCENTRATIONS

Tube	Cc. HgCl <sub>2</sub>	Cc. re-duced	Cc. As <sub>2</sub> O <sub>3</sub>	Cc. SnCl <sub>2</sub>	Cc. HCl	Time for reduction	
						A	B
1	15	0	2	2	31	4:30	8:55
2	0	15	2	2	31	4:14	8:50
3	10	0	2	2	36	5:34	10:22
4	0	10	2	2	36	5:12	10:28
5	5	0	2	2	41	6:58	12:55
6	0	5	2	2	41	6:44	12:30
7	1	0	2	2	45	10:10	18:30
8	0	1	2	2	45	10:08	18:40
0	0	0	2	2	46	12:20	19:40

Preliminary investigation of some other reactions which have been called induced reactions show that they are catalytic just as the modified Bettendorff test is catalytic. The investigation of these reactions will be continued.

CHEMICAL LABORATORY  
IOWA STATE COLLEGE  
AMES, IOWA

RECEIVED FEBRUARY 6, 1939

### The Preparation of *m*-Bromophenol

By C. FREDERICK KOELSCH

The usual procedure involved in the replacement of an aromatic amino group by a hydroxyl group consists in warming an aqueous solution of the corresponding diazonium salt. This procedure, however, when applied to the preparation of *m*-bromophenol is quite unsatisfactory,<sup>1</sup> and the suggestion recently has been made<sup>2</sup> that this phenol is best obtained from *m*-bromoaniline through *m*-bromobenzenediazonium borofluoride and *m*-bromophenylacetate, the over-all yield in this series of three reactions being approximately 37.5%.

In the patent literature<sup>3</sup> it has been reported that *m*-bromophenol and the other *m*-halogenophenols can be prepared "in nearly quantitative yields" from *m*-halogenoanilines by the choice of the proper conditions for the hydrolysis of the corresponding diazonium sulfates. It has been found in this Laboratory that this patent claim is substantially true; by following the procedure described below one can obtain good yields (75-80%) of *m*-bromophenol rapidly and with a minimum expenditure of labor.

(1) Diels and Bunzl, *Ber.*, **38**, 1486 (1905).

(2) Smith and Haller, *This Journal*, **61**, 143 (1939).

(3) English Patent 200,714 (1922); *Chem. Zentr.*, **96**, II, 2297 (1925).

### Experimental

*m*-Bromoaniline (50 g.) is dissolved by boiling in a mixture of water (400 ml.) and sulfuric acid (50 ml.). The solution is then cooled to 10° and diazotized by the addition of sodium nitrite (21 g.) dissolved in a small amount of water. The resulting diazonium salt solution is run in a thin stream during fifteen to thirty minutes into a boiling mixture of water (300 ml.) and sulfuric acid (100 ml.) contained in a flask fitted with a dropping funnel, a steam inlet tube reaching to the bottom of the flask, and an efficient condenser set for downward distillation. During the addition of the diazonium salt solution the acid solution is heated so that its volume remains constant, and steam is passed in at such a rate that at the end of the addition approximately 1 liter of distillate has been collected. Steam distillation is then continued until 2-liters of distillate has been collected. To this is added sodium chloride (150 g.), and the phenol is extracted with ether, using portions of 200, 100, and 100 ml. The ether is removed from the combined extracts and the product is distilled under reduced pressure.

Eight runs<sup>4</sup> of 50 g. each of *m*-bromoaniline gave 330 g. of crude *m*-bromophenol boiling at 100-140° (20-30 mm.). Redistillation gave 313 g. (77.8%) of *m*-bromophenol which boiled at 125-130° at 25 mm.

Treatment of this 313 g. of product with sodium hydroxide and methyl sulfate gave 285 g. of *m*-bromoanisole, b. p. 100° at 20 mm.

(4) The last five of the eight batches were steam distilled from the accumulating sulfuric acid and sodium sulfate solution whose volume was allowed to increase somewhat during the successive runs. No drop in yield resulted from this procedure.

SCHOOL OF CHEMISTRY  
UNIVERSITY OF MINNESOTA  
MINNEAPOLIS, MINNESOTA

RECEIVED NOVEMBER 25, 1938

### The Melting Point of Barium Molybdate

By H. A. LIEBHAFSKY, E. G. ROCHOW AND A. F. WINSLOW

Barium molybdate, precipitated from an ammoniacal ammonium molybdate solution by adding aqueous barium chloride, washed until only a trace of chloride remained, charged into a platinum crucible that was placed in an electric furnace, then melted and cooled (7° per minute) in air, gave a cooling curve with a sharp break at 1480 ± 5° (platinum to platinum-10% rhodium thermocouple). This result confirms an earlier, less accurate, melting point determination, also made in air, in which an induction oil and an optical pyrometer were used. Attack of the platinum was absent or negligible, and there was no indication that the molybdate had been decomposed.

When melted in vacuum, the surface of the molybdate darkened, indicating partial decomposition, and some evaporation occurred; rough

observations show that its melting point in vacuum does not differ greatly from that in air.

RESEARCH LABORATORY  
GENERAL ELECTRIC COMPANY  
SCHENECTADY, NEW YORK RECEIVED FEBRUARY 23, 1939

### Study of the Reformatsky Reaction; Efficient Procedure for the Preparation of Bromoacetic Ester in Large Quantities

BY SAMUEL NATELSON AND SIDNEY P. GOTTFRIED

In the preparation of intermediates in certain synthetic studies, it was found necessary to prepare large quantities of the esters of dihydro- and tetrahydrophenylacetic acid. It was decided to proceed by means of the Reformatsky reaction.<sup>1</sup>

The procedures reported in the literature were repeated carefully. However, the yields were found to be poor and not suitable for the preparation of large quantities. A systematic study of the individual factors influencing the reaction was, therefore, initiated. Temperature, solvents, form of zinc or magnesium and methods of dehydration of the condensation product were studied. A procedure was developed wherein the reaction proceeds smoothly and gives good yields by controlling a few simple conditions.

The optimum temperature of the reaction mixture was found to be between 90–105°. At this temperature the reaction proceeds at a rapid rate, but not so rapidly as to become uncontrollable. The use of benzene alone as a solvent is not advisable except when the concentration of reactants is such as to raise the boiling point of the mixture to the required temperature. Numerous authors have employed conditions where a low boiling solvent or no solvent at all was used, but on checking their conditions we found that in the cases where the best yields were obtained the concentration of reactants was such as to give a temperature within the desirable range. A simple way of achieving and maintaining the desired temperature is to use as solvent, approximately a 1:1 mixture of benzene and toluene.

For best yield, smoothness of reaction, rapidity and convenience zinc is preferable to magnesium. The zinc used in the reaction should be in the form of zinc foil. This must be carefully scraped with sandpaper to cut through any impurities which may cover it. Cleaning the zinc by means of alkali is not recommended. The use of mossy zinc was found to be unsatisfactory, for it is not of

uniform thickness, difficult to clean and consequently uncertain in its reaction. Powdered zinc is not recommended for it is difficult to clean and hence occasionally the reaction is slow in starting. Once the reaction is started, it often becomes quite violent and is difficult to control. Copper-zinc couples have practically no advantage over zinc foil in our experience.

After the condensation product has been formed, and the zinc salt is hydrolyzed, it is sometimes a problem to dehydrate the resulting product. After trying numerous reagents such as potassium bisulfate, phosphorus pentoxide in various solvents, zinc chloride and sulfuric acid,<sup>2</sup> it was observed that the best method for obtaining good yields without decomposition is by the use of dry hydrogen chloride, hot or cold. The dehydration is usually quantitative. Numerous  $\beta$ -hydroxy esters can be dehydrated in this manner. Typical examples are the compounds obtained from the action of bromoacetic esters on cyclohexanones, the 1, 2 and 3-methylcyclohexanones, ethyl methyl ketone, methyl butyl ketone and 3,7-dimethyloctanal-1. In the terpene series a few cases were encountered where the dry hydrogen chloride polymerized the resultant product and was therefore of no use. In some cases, of course, it is not necessary to dehydrate the product formed, splitting out of water being spontaneous. An example of this type was encountered with the condensation of bromoacetic ester with methylcyclohexenone to form dihydroethylphenylacetate.<sup>3</sup>

An example of the recommended procedure is given below. These conditions have been applied by the authors and co-workers with consistent results to numerous aldehydes and ketones of various types. The yields rarely fall below 60% and are usually about 70%.

During these studies the authors had occasion to use large amounts of bromoacetic ester. A rapid and economical laboratory method for producing this compound in good yields was devised and is described herein. Acetic anhydride with pyridine makes an efficient catalyst for smooth bromination.

If the halogen carrier, pyridine, is omitted the bromination will take place, but the reaction here is from two to three times as long. Acetic an-

(2) Wallach and Salkind, *Ann.*, **314**, 153 (1901); Tetry, *Bull. soc. chim.*, [3], **27**, 600 (1902); DeFazi, *Gazz. chim. ital.*, [1], **45**, 555 (1915).

(3) Wallach, *Ann.*, **323**, 138 (1902).

(1) Wallach, *Ann.*, **343**, 287 (1905); **365**, 261 (1909).