

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.<br>HgCl <sub>2</sub> | Cc.<br>re-<br>duced<br>HgCl <sub>2</sub> | Cc.<br>As <sub>2</sub> O <sub>3</sub> | Cc.<br>SnCl <sub>2</sub> | Cc.<br>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.

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### The Preparation of *m*-Bromophenol

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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.

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### The Melting Point of Barium Molybdate

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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