

2. Isatin has been condensed with *p*-bromoacetophenone to yield 2-phenyl-4'-bromocinchoninic acid.

3. 5,7-Dibromoisatin has been condensed with acetophenone and with *p*-methoxyacetophenone to yield, respectively, 6,8-dibromo-2-phenylcinchoninic acid and 6,8-dibromo-2-phenyl-4'-methoxycinchoninic acid.

NEW YORK CITY

[CONTRIBUTION NO. 195 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

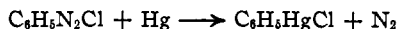
THE PREPARATION OF AROMATIC MERCURIC CHLORIDES FROM AROMATIC DIAZONIUM CHLORIDES

BY ROBERT E. McCLURE AND ALEXANDER LOWY

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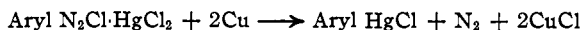
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In an investigation¹ by the authors upon the electrochemical reduction of benzenediazonium chloride to phenylhydrazine hydrochloride it was noted that another substance was formed when the mercury cathode was violently stirred. This product proved to be phenylmercuric chloride. A non-electrolytic experiment showed that the formation of the latter compound was purely a chemical reaction and may be represented by the following



This reaction appears somewhat similar to the Gattermann reaction and suggests the possible formation of an unstable phenylcupric halide. The nature of the reaction also suggested that other aromatic mercury compounds might be prepared in the same way. Further investigation confirmed this point of view and this paper describes the preparation of a number of these compounds.

Nesmejanow² prepared a number of aromatic mercury halides by the reaction



Experimental

It was evident in this type of reaction that the state of division of the mercury would be an important factor. A number of the usual types of stirrers were tried but even at high speed failed to give more than a small amount of the phenylmercuric chloride. An anchor-shaped stirrer, made from 4-mm. glass tubing with prongs drawn out to capillary fineness and with an opening at the base, gave good results. This stirrer was used in all the experiments described. The bottom of the stirrer was immersed in the mercury with the capillary tips extending into the solution. A fine spray of mercury was thrown from the tips by centrifugal action.

A Typical Experiment.—Five grams of redistilled aniline was dissolved in 30 cc. of concentrated hydrochloric acid and 50 cc. of water. The solution was cooled to 0°

¹ McClure and Lowy, *Trans. Am. Electrochem. Soc.*, **56**, 445-456 (1929).

² Nesmejanow, *Ber.*, **62B**, 1010 (1929).

and diazotized in the usual manner.³ The diazotized solution was made up to 200 cc. volume with distilled water. A 1.5-cm. layer of mercury was placed in a 600-cc. beaker and the solution added. The beaker was placed in an ice-bath and the temperature maintained below 5° throughout the entire experiment. The mercury and solution were stirred at 1000 r. p. m. Immediately after the stirrer was started a gray foam formed and gradually rose to the top of the beaker, persisting throughout the experiment. After four hours a test with alkaline β -naphthol showed that only a trace of the diazonium chloride remained. The stirring was stopped and the solution filtered through a Büchner funnel. The residue consisted of finely divided globules of mercury, which would not readily coalesce, and a fine grayish precipitate. The residue was boiled for several minutes with 100 cc. of water, which caused the mercury to coalesce. The precipitate was washed away from the mercury, filtered and dried by suction. After drying, the residue was extracted with several portions of hot acetone, 300 cc. in all. After two recrystallizations 8 g. of white leaf-like crystals was obtained. This product readily sublimed to white leaflets, melting point 251°, which agrees with that given in the literature for phenylmercuric chloride.⁴ The compound was further identified by treating with sodium iodide in cold acetone solution,⁵ the phenylmercuric iodide resulting: melting point 265°.⁶

A number of aromatic mercuric chlorides have been prepared by the same type of reaction. The apparatus used and the procedure were as described in the typical experiment. The results are given in Table I.

TABLE I

RESULTS OF EXPERIMENTS							
Amines diazotized, 5 g.	Product, -mercuric chloride	Solvent for purification	Yield, g.	Yield, %	M. p., °C.	M. p., °C. ⁴	
Aniline	Phenyl-	Acetone	8	45	251	251	
<i>p</i> -Toluidine	<i>p</i> -Tolyl-	Acetone	8	52	233	233.5	
<i>o</i> -Toluidine	<i>o</i> -Tolyl-	Ethanol	11	72	146	146	
2-Amino-1,4-dimethylbenzene	2,5-Dimethylphenyl-	Ethanol	9	64	182.5	183	
α -Naphthylamine	α -Naphthyl-	Benzene	2.5	20	188.5	189	

Instead of using the mechanically divided mercury produced by stirring, black precipitated mercury was used. This was precipitated from mercuric chloride by stannous chloride and carefully washed until free of chlorides. This was rapidly stirred with the benzenediazonium chloride and a 20% yield of phenylmercuric chloride was obtained.

Further work is being conducted upon this reaction at the present time.

Summary

1. A method for the preparation of aromatic mercuric chlorides by the action of finely divided mercury upon the corresponding aromatic diazonium chloride has been developed.

³ Gattermann, Ludwig, "Practical Methods of Organic Chemistry," MacMillan Co., New York, 1927, p. 237.

⁴ F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, 1921, p. 172.

⁵ Steinkopf, *Ann.*, 413, 313, 329 (1917).

⁶ F. C. Whitmore, Ref. 4, p. 174.

2. Phenylmercuric chloride, *o*- and *p*-tolylmercuric chlorides, 2,5-dimethylphenylmercuric chloride and α -naphthylmercuric chloride have been prepared by the above method.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SILICA GEL AS A CATALYST IN THE PREPARATION OF NITRILES¹

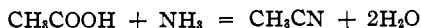
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Previous investigations have shown that silica gel is an excellent catalyst for certain dehydrating reactions involving organic compounds. Milligan, Chappell and Reid³ showed it to be an extraordinarily good esterification catalyst; Brown and Reid studied its application in the alkylation of ammonia and dehydration of alcohols⁴ and also in the alkylation of aniline.⁵

The catalytic dehydration of the nascent amide formed from acetic acid and ammonia, according to the equation



in the presence of thoria and alumina, has been studied by Van Epps and Reid.⁶ They found that an 85% yield of nitrile could be obtained at 500° with the better catalyst, alumina. They reported that no nitrile was obtained by passing ethyl acetate and ammonia over alumina, while Mailhe⁷ obtained nitriles from esters and ammonia with both thoria and alumina.

This reaction has been investigated in the presence of silica gel.

Results

We have found that silica gel is a more efficient catalyst than either thoria or alumina in the preparation of nitriles from acids and ammonia. Using acetic acid and an excess of ammonia, as the temperature of operation is raised the percentage conversion to acetonitrile increases until at 500–525° a maximum is reached (practically quantitative). Increasing the temperature to 550° results in a decreased yield and increasing it to 575° lowers the yield still further. It appears that operation at tempera-

¹ This and the two following papers, presented at the Atlanta meeting of the American Chemical Society, April, 1930, are extracted from a dissertation presented by James A. Mitchell to the Faculty of the Graduate School of Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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³ Milligan, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924).

⁴ Brown and Reid, *ibid.*, **28**, 1067, 1077 (1924).

⁵ Brown and Reid, *THIS JOURNAL*, **46**, 1836 (1924).

⁶ Van Epps and Reid, *ibid.*, **38**, 2128 (1916).

⁷ Mailhe, *Bull. soc. chim.*, [4] **23**, 232 (1918); *Ann. chim.*, [9] **13**, 213 (1920).