Summary

1. The specific heats of tetryl, picric acid, trinitrotoluene, tetryl:-picric acid, tetryl:2 trinitrotoluene, have been measured over a range of temperature from 0° to 60° to 125°.

2. The values obtained indicate that Kopp's law does not hold for trinitrotoluene, tetryl or picric acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY, AND THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE DIRECT MERCURATION OF BENZENE AND THE PREPARATION OF MERCURY DIPHENYL[1]

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There are to be found in the literature ten reactions involving the formation of mercury diphenyl.[2] However, the preparation of a considerable quantity of the mercury diaryl by any one of these methods is unsatisfactory because of the low yield obtained. Phenylmagnesium bromide and mercuric chloride give a 44% yield,[3] while the action of 2.7% sodium amalgam on bromobenzene results in a 46% yield.[4] In the other eight reactions either the yields are not given, or the mercury diphenyl appears only in small amounts as a by-product. During the past year the author has had occasion to prepare considerable quantities of mercury diphenyl, and it was deemed advisable to develop a more satisfactory method of preparation.

An important general reaction of organic mercury compounds involves the transformation of $R\text{-}HgX$ to R_2Hg. Very few complications were met, so this process was selected for development. Of the many inorganic reagents capable of bringing about this change,[5] alkaline sodium stannite solution gave the best result: $2C_6H_5\text{-}HgX + Na_2SnO_2 + 2NaOH \longrightarrow (C_6H_5)_2Hg + Hg + 2NaX + Na_2SnO_3$. Mercury diphenyl and mercury are the only water-insoluble products formed, and they can easily be separated from each other. The reaction has been mentioned in an article on mercuration,[6] but quantitative data are lacking.

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[1] Presented at the Milwaukee meeting of the American Chemical Society, September, 1923.

[2] For a bibliography see Frank C. Whitmore, "Organic Compounds of Mercury," (American Chemical Society Monograph Series), Chemical Catalog Co., **1921**, pp. 163–164.

[3] Pfeiffer and Truskier, *Ber.*, **37**, 1127 (1904).

[4] Aronheim, *Ann.*, **194**, 148 (1878).

[5] Ref. 2, p. 40.

[6] Dimroth, *Ber.*, **35**, 2853 (1902).

Direct mercuration of benzene seemed to offer the simplest method of obtaining the desired C_6H_5-HgX. However, the reaction, $C_6H_5 + HgX_2 \rightleftharpoons C_6H_5\text{-}HgX + HX$, has heretofore been useless as a method of preparation of phenylmercuric derivatives because of the very low yield obtained. Benzene alone does not react with mercuric acetate at the boiling point, but when it is heated with the salt at 110° under pressure, compounds containing one and two acetoxymercuri groups are formed. The yield of mono-mercurated derivative does not exceed 10% of that calculated.

It has been pointed out that mercuration with mercuric acetate is a type of chemical action similar to hydrolysis.[7] Thus: $R\text{-}H + Hg(OAc)_2 \rightleftharpoons R\text{-}HgOAc + HOAc$; $HO\text{-}H + Hg(OAc)_2 \rightleftharpoons HO\text{-}HgOAc + HOAc$. In support of the analogy it is significant to note that mercuric salts which do not hydrolyze cannot be used for mercurations of this type. On the whole, however, the reversal of a mercuration cannot be accomplished as easily as that of an hydrolysis. It is evident that in the mercuration of benzene with mercuric acetate the reverse action does take place, because the removal of the acetic acid as soon as it is formed in the course of the reaction results in a greatly increased yield of phenylmercuric acetate even at the boiling point of benzene. The acid may be removed by neutralization with mercuric oxide or by the formation of an ester.[8] The latter method was adopted, for it was found that the presence of ethanol in the reaction mixture made possible an 80% yield of phenylmercuric acetate.

The transformation of phenylmercuric acetate to mercury diphenyl by means of an alkaline sodium stannite solution presented no difficulties. A 95% yield of the pure mercury diaryl was obtained.

Experimental Part

The Mercuration of Benzene.—A mixture of 80 cc. of benzene, 15 g. of mercuric acetate, and 20 cc. of 95% ethanol was refluxed on a steam-bath. Alcoholysis of the mercuric acetate took place as soon as heating was started. The yellow precipitate was dissolved by the addition of a few cubic centimeters of glacial acetic acid, and did not appear again during the course of the reaction. After five hours another 20cc. portion of ethanol was added. A very slow separation of mercurous acetate took place throughout the course of the heating. The amount was 1 g. over the entire period of 55 hours.

The solution was then filtered, and evaporated to dryness on a steam-bath under a hood. A jet of air was directed over the surface of the liquid in order to hasten the evaporation and to keep down the temperature, for phenylmercuric acetate is somewhat volatile at the boiling point of benzene. The residue was purified by crystallization from 95% ethanol; m. p., 149°; yield, 12.6 g., or 80%.

Mercury Diphenyl from Phenylmercuric Acetate.—An alkaline sodium stannite solution was prepared by the addition of 125 cc. of a cold 40% sodium hydroxide solution to 50 g. of stannous chloride dihydrate in 125 cc. of water. This was then added with

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[7] Ref. 2, p. 35.

[8] Ester formation suggested by Dr. W. H. Hunter, University of Minnesota.

vigorous mechanical stirring to 30 g. of phenylmercuric acetate in 300 cc. of water. Stirring was continued for an hour, and then the grayish-black precipitate of mercury diphenyl and mercury was filtered off on a Büchner funnel, washed well with water, and sucked as dry as possible.

The residue was extracted twice with 75cc. portions of acetone. Finely divided mercury ran through the filter papers, and it was necessary to amalgamate the metal with powdered zinc before a clear filtrate could be obtained. Water was added to the filtrate until a slight permanent turbidity was obtained. Crystals of mercury diphenyl formed very slowly on cooling, so enough water was added to precipitate all of the mercury compound. Filtered off and dried, it weighed 13.2 g., a yield of 95.6%. The colorless microcrystalline product melted at 124.5° (uncorr.) with preliminary softening.

Summary

1. The analogy between mercuration and hydrolysis has received further confirmation.

2. An 80% yield of phenylmercuric acetate was obtained by the *direct mercuration of benzene in the presence of ethanol.*

3. Mercury diphenyl in 95.6% yield was obtained from phenylmercuric acetate by means of sodium stannite.

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

TERTIARY-BUTYL ALCOHOL

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The usual laboratory methods for the preparation of tertiary-butyl alcohol involve the use of methylmagnesium iodide. As the use of this reagent in even moderately large scale operations is attended by considerable difficulty it seemed desirable to make a study of other methods for the preparation of the alcohol.

Wischnegradsky[1] has pointed out that a commercial grade of amylene is very readily dissolved, in part, when shaken with 50% sulfuric acid in a salt-ice bath. Attention has been drawn recently to the ease with which trimethyl ethylene may be converted into *tertiary* amyl alcohol by the preliminary formation of amyl sulfuric acid and subsequent neutralization.[2]

The boiling point of *iso*butylene (—6°) is so low, however, that the absorption of the liquid hydrocarbon has been carried out only in closed tubes.[3] Moreover, the *iso*butylene obtained by the dehydration of

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[1] Wischnegradsky, *Ann.* **190,** 332 (1878). No temperatures were noted, but it would seem certain from the emphasis laid on the use of a strong walled bottle and the rate of reaction that the temperature of the reacting mixture was considerably above that of the surrounding bath; 300 g. of amylene dissolved in 30 minutes.

[2] Adams, THIS JOURNAL, **40,** 1950 (1918).

[3] (a) Butlerow (Butleroff), *Ann.*, **180,** 246 (1876); (b) **189,** 48 (1877); Compare (c) Le Bel and Greene, *Bull. soc. chim.*, [2] **29,** 306 (1878).