[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Mercuration of Benzene with Mercuric Nitrate

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Mercuric nitrate reacts readily with excess benzene to form phenylmercuric nitrate. The other product of this reaction is nitric acid which unfortunately oxidizes or otherwise decomposes the mercurated aromatic compound. This secondary reaction may be avoided by the use of a mixture of mercuric nitrate and mercuric oxide, the latter to form mercuric nitrate with the nitric acid. Water then becomes the second product in this reaction and, indeed, limits the yield, probably because the hydrate of mercuric nitrate formed therewith is insoluble in benzene. This effect in turn can be obviated by the use of Drierite (calcium sulfate); and under such conditions, and preferably in the absence of air, 80% of the mercuric nitrate or 54% of the total mercury enters into formation of phenylmercuric nitrate.

Absence of air has so far been desirable and in the early stages of the work was essential. For example, about twenty-five experiments were made in which benzene was allowed to react with mercuric nitrate under a variety of conditions, without mercuric oxide and Drierite, but all in the high-speed stirring apparatus in order to ensure maximum contact of the phases. No precaution was taken to exclude air. The products were amorphous yellow, brown or black powders of greater complexity than phenylmercuric nitrate, most with two, three or even four atoms of mercury—the high proportion probably from some occlusion of mercuric nitrate—per six carbon atoms or benzene ring, together with a very small amount of red colored material, soluble in hot water, that had a composition equivalent to one and a third phenylmercuric groups and one and a fifth nitro group per six carbon atoms. If the reactants were not added gradually to each other and if the temperature were not carefully controlled, the process easily got out of hand. When carbon dioxide was bubbled through the system, phenylmercuric nitrate was obtained for the first time, although afterwards not invariably; but if the carbon dioxide generator was placed at the outlet as well as the inlet in order to prevent back diffusion of air, phenylmercuric nitrate could be obtained from each reaction. Other instances of the effect of air on the more highly mercurated products that might have contained some occluded mercuric nitrate, were not lacking. A reaction that had gotten beyond control was discontinued. When the flask was disconnected from the stirrer and air admitted freely, a mild explosion followed. At another time a brown-colored amorphous product obtained as a residue from a large number of experiments was placed in a Soxhlet extractor and extracted with petroleum ether for five hours. It was then extracted with benzene. As the thimble was filling for the third time a vigorous exothermic explosion-like reaction occurred that pushed the condenser from the extractor and filled the room with a gray ash. The explosion was restricted to the area above the benzene layer in the thimble where air and benzene occurred together with the solid. Below the benzene liquid level the solid was unaffected. Whether this action by air is a direct one on the phenylmercuric nitrate or is an indirect one that assists the nitrogen oxides, which also undoubtedly have an important effect, was not determined. This aspect of the problem lost most of its attraction as soon as the value of mercuric oxide and Drierite was discovered, because, even in the presence of air, the yield and quality of the product were then very high (see Experiment 15, Table I).

A large part of the success in developing this new method of mercuration must be credited to the high-speed stirring apparatus, which kept the near-insoluble mercuric nitrate in intimate contact with benzene. For a while it was impossible to obtain any of this product unless the rate of stirring exceeded about 5000 r.p.m. After the use of mercuric oxide and Drierite had been introduced, the product could be obtained unless less special conditions, as, for instance, in a capped bottle in a shaking machine at room temperature. The yield was low; but at this comparatively low temperature, it was only a little better with the stirrer, possibly because of the reduced rate of reaction and possibly because of the lower solubility of mercuric nitrate in benzene.

Other modifications of the general principle used in this study can be employed. Mercuric acetate, for instance, in place of mercuric oxide gave a fair yield. Optimum conditions have in no sense been determined; yet the method of preparation is far better than the previous ones that used the reaction of nitrogen tetroxide with diphenylmercury in cold chloroform[1] or relied on extractions[2] with organic solvents from the dilute nitric acid solution of the commercial mixture of the nitrate and hydroxide, commonly referred to as phenylmercuric nitrate.

Phenylmercuric nitrate, as prepared by this reaction, is a beautifully crystalline compound that melts at 131–131.5°. It is converted easily to iodobenzene, phenylmercuric iodide and the basic salt by use of iodine, potassium iodide and a half equivalent of sodium hydroxide, respectively, reactions that establish the constitution. When stirred with aqueous sulfuric acid, it proved relatively insensitive toward cleavage of the car-

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(1) Pyman and Stevenson, *Pharm. J.*, **133**, 269 (1934).

(2) Schering-Kahlbaum, A. G., British Patent 446,703. *C. A.*, **30**, 6894 (1936).

bon–mercury bond possibly because of conversion to the sulfate. The nitrate radical is readily replaced by hydroxide, iodide, and sulfate radical. The compound is slowly decomposed in air and more rapidly affected if moistened with a little benzene. Within a week the dry powder usually changes from a benzene-soluble material to a benzene-insoluble one, frequently with darkening. The changes have not yet been examined but probably involve some hydrolysis to the basic nitrate and action of the nitric acid thereby formed and may involve oxidation. Phenylmercuric nitrate also dissolves readily in benzaldehyde but a chemical reaction ensues which eventually leads to reduction to metallic mercury. This and other interesting reactions of this compound are being studied.

Mercuric nitrate is a catalyst or aid in the nitration of aromatic compounds.[3] This action has been variously ascribed to an intermediate diphenylmercury,[4] to a complex[5,6] of undetermined composition, to the action of mercury nitrate as a carrier of the NO_2 group,[6] and to an intermediate addition compound corresponding to the addition product of mercury salts across double and triple bonds.[7] Also Darzen is credited[4] with the view that phenylmercuric nitrate is an intermediate. It is now clear that phenylmercuric nitrate forms with great ease, and that, unless special precautions are taken to keep the system free from nitric acid, air, and water, colored to gray-black secondary products result that contain large amounts of mercury, nitrogen, and oxygen. These by-products could easily be mistaken for active intermediates, whereas the phenylmercuric nitrate forms picric acid when treated with moderately strong nitric acid, although in small yield under the conditions employed.

Mercuration with mercuric nitrate is a very rapid and easy reaction, probably easier than nitration. This fact is indicated by experiment of Davis and co-workers[5] with 1.46 moles of 66% nitric acid, 0.26 mole of benzene and 0.26 mole of mercuric oxide. In this competitive reaction nitrobenzene can be regarded as the total product of primary nitration, since it undergoes no mercuration[3a] under the conditions of the experiment, and picric acid can be considered as derived from a primary mercuration. In spite of the four-fold excess of nitric acid and in spite of the disadvantage that mercuration should occur only in the acid phase, whereas nitration has been shown to occur in both phases,[8] the percentage yield (33%) of the picric acid was the same as that of nitrobenzene. In addition, the tarry by-products were undoubtedly the result of an initial mercuration. Davis[5] comments on the independent character that the mercuric nitrate action appears to have. Our own experiments in competitive reactions with a six-fold mole excess of nitric acid (66% strength) over mercuric nitrate indicated that tarry products formed in as large, if not larger, proportion than nitrobenzene. Some 2,4-dinitrophenol was isolated from the tar. With 33% acid no nitrobenzene was formed although mercuration occurred.

The easy control of the mercuration process, made possible by the use of mercuric oxide and a suitable drying agent under an inert atmosphere, and the cleanness with which the product separates offers the hope that this reaction will prove valuable for obtaining new derivatives of organic compounds. Further studies are in progress.

Experiments

Phenylmercuric Nitrate (by R. R. M.).—C. P. mercuric nitrate was stirred in a high-speed stirring apparatus[9] with thiophene-free benzene. The system was protected from air by a rapid stream of carbon dioxide, evolved from a bottle of the solid, that bubbled through concentrated sulfuric acid and then through benzene, the latter in order to replace the solvent lost from the reaction mixture as the gas passed through the flask. At the exit end the gases were passed through another flask that also contained solid carbon dioxide.

The temperature, time, rate of stirring and other important factors are recorded in the accompanying table. The respective improvements as mercuric oxide and Drierite were used can be seen readily in the column of yield. At the end of the reaction the mixture was filtered. When the filtrate had cooled to room temperature an equal volume of hexane was added. The mercuric nitrate precipitate was then recovered by filtration from a Buchner funnel. The crude material melted at 126 to 128°. When crystallized once, sometimes twice, from benzene it melted at 131–131.5° (cor.). The recorded value is 130–132°. The compound showed the correct composition.

Anal. Calcd. for $C_6H_5HgNO_3$: C, 21.2; H, 1.51; N, 4.12. Found: C, 21.1; H, 1.49; N, 4.14.

The compound is soluble in benzene, ethylene glycol and carbitol and is insoluble in water.

Treatment of 60 g. of the product with 45 g. of iodine in ethylene glycol with a small amount of potassium iodide on a steam-bath gave iodobenzene, which, after being filtered, washed with 10% sodium hydroxide and dried, distilled at 184.5° and had a refractive index of 1.6196 at 20° and a density of 1.8310 at 20°. Magnesium and carbon dioxide converted this iodo compound to benzoic acid. Treatment of 10 g. of phenylmercuric nitrate in acetone with a small amount of potassium iodide for ten minutes gave an 80% yield of white satiny crystals of phenylmercuric iodide that melted at 264.5–266° (cor.). Treatment of 10 g. of the nitrate salt with 0.65 ml. of 10% sodium hydroxide in 65 ml. of water for two days at room temperature gave a product that was largely insoluble in benzene. The residue was very soluble in carbitol, from which it was recrystallized. This basic product melted at 175° with some decomposition.

Phenylmercuric nitrate (26 g.) was stirred in the high-speed stirring apparatus with 350 ml. of aqueous 3 *N* sulfuric acid at 35 to 40° for three hours either under an atmosphere of carbon dioxide or in the presence of air.

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(3) (a) Wolffenstein and Boeters, German Patent 194,883 (1908); *Ber.*, **46**, 586 (1913); (b) Kholevo and Eilington, *J. Applied Chem. U. S. S. R.*, **5**, 613 (1932); *C. A.*, **27**, 274 (1933).

(4) Desvergnes, *Chim. Ind.*, **22**, 451 (1926).

(5) Davis, Drake, Helmkamp and Young, THIS JOURNAL, **43**, 594 (1921); Davis, *ibid.*, **44**, 1588 (1922).

(6) Zakharov, *J. Chem. Ind.* (U. S. S. R.), **4**, 960 (1927); **8**, 30 (1930); *C. A.*, **22**, 3819 (1928); **25**, 4864 (1931).

(7) McKie, *J. Soc. Chem. Ind.*, **46T**, 261 (1927); Davis, "The Chemistry of Powder and Explosives," Vol. I, John Wiley and Sons, New York, N. Y., 1941, p. 162.

(8) Lewis and Suen, *Ind. Eng. Chem.*, **32**, 1095 (1940).

(9) Morton, Darling and Davidson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 734 (1942).

TABLE I

FACTORS IN THE PREPARATION OF PHENYLMERCURIC NITRATE BY MERCURATION OF BENZENE WITH MERCURIC NITRATE IN AN ATMOSPHERE OF CARBON DIOXIDE

Expt.	Benzene, ml.	$Hg(NO_3)_2$, g.	HgO, g.	Drierite, g.	Temp., °C.	Time, min.	R. p. m.	Yield G.	Yield %[a]
1	200	30	0	0	65	70	7900	2	6
2	200	30	0	0	60	90	5000	0.1	0.3
3	250	30	0	0	65	105	8000	2.6	10
4	200	60	0	0	65	120	8000	3.0	5
5	200	10	7	0	65	100	9800	6.5	62
6	600	45	20	0	65	105	9800	14	30
7	600	50	20	40	65	180	9800	25	48
8	600	50	20	70	65	180	9800	41.5	79
9	200	15	5	25	25	7 days	Shaken	3.5	22
10	200	15	5	25	25	120	9800	7	45
11	200	15	5	25	60	90	9800	12.5	80
12[b]	600	50	20	40	65	180	9800	19	36
13	200	30	27[c]	0	65	180	9800	6.5	24
14	225	32	26[d]	0	65	240	9800	6.6	20
15[e]	200	15	10	23	65	75	9800	9.4	58

[a] Yields calculated on the basis of the mercuric nitrate used. [b] The carbon dioxide was replaced by an atmosphere of nitrogen. The nitrogen was not previously dried by passage through concentrated sulfuric acid. [c] Mercuric acetate was used in place of the oxide. [d] An experiment approximately comparable with the preceding one but with mercuric oxide in place of the acetate. [e] Air previously dried by passage through concentrated sulfuric acid, was used in place of carbon dioxide. This experiment is approximately comparable to No. 11 except that more mercuric oxide was used in order to reduce the likelihood of the presence of traces of nitric acid. The reaction mixture was noticeably darker at the end of thirty minutes. The final product was slightly darker than the one prepared in the presence of carbon dioxide.

No benzene nor phenol was obtained. Some of the nitrate was unchanged. The remainder was hydrolyzed to a basic salt and, with longer stirring, to a compound soluble in water, probably the sulfate.

Reactions in the Presence of Air, Moisture and Nitric Acid. (By E. E. M. and R. E. E.).—These experiments were carried out in the same type of apparatus as was used in the previous series. At the beginning of the study the benzene was added dropwise to a suspension of mercuric nitrate in cyclohexane. Subsequently, the mercuric nitrate was added in small portions as a powder to excess benzene. The products were in general the same. A description of one experiment will suffice to illustrate the products. Thiophene-free benzene (20 ml. or 0.22 mole) was added dropwise to 35 g. (0.11 mole) of mercuric nitrate suspended in 100 ml. of cyclohexane in a high-speed stirring apparatus. The temperature was maintained at 65° and the reaction time was one hundred five minutes. The contents of the flask were then steam distilled and the hot residue filtered. The red purple powder that separated from the cooled filtrate showed the analysis: C, 14.9, 14.8; H, 0.97, 0.90; N, 7.21, 7.07; Hg, 53.4, 53.1; O, 23.9. The brown residue that remained on the filter was extracted successively with cold 3 *N* nitric acid (this strength acid was found to dissolve instantly the mixture of yellow basic nitrate and red mercuric oxide obtained by steam distillation of mercuric nitrate), alcohol and ether. The dried product weighed 12.4 g. and had the composition: C, 11.0, 10.2; H, 0.45, 0.52; N, 3.62, 3.55; Hg, 68.5, 68.6. This composition was equivalent to 2.3 atoms of mercury, 1.75 atoms of nitrogen and 7.2 atoms of oxygen per benzene ring. The amount of mercury corresponded to a 39% yield calculated on the original nitrate. Hydrolysis of either mercury-containing product with concentrated hydrochloric acid, removed the metal but yielded only tars or traces of crystals.

In one series of experiments, in which the mercuric nitrate was added to benzene, the benzene layer was reused twice in order to accumulate more of a crystalline compound. The benzene layer was then steam distilled (a little nitrobenzene was collected) and the aqueous layer in the distilling flask allowed to cool. Yellow crystals (0.5 g.) that melted at 144–145° were obtained. The composition (57.2% Hg, 2.92% N, 20.6% C and 1.44% H) corresponded with no simple compound. The crystals were soluble in 6 *N* sodium hydroxide but not in 6 *N* hydrochloric acid. Efforts to obtain crystals from the amorphous residue and to hydrolyze the material with hydrochloric acid or alkali produced no compound that had a melting point near that of a simple nitrophenol, although minute quantities of compounds melting near 200° were found in all these experiments.

Crystals could be obtained readily from experiments in which the protection of carbon dioxide was not perfect. Some of these crystals were phenylmercuric nitrate; others contained no mercury but had both phenolic and carboxylic groups. This mercury-free product appeared to be the result of a fortuitous combination of reactions that are now being studied separately. Always these products were accompanied by very much larger amounts of the grayish to black powder that contained high percentage of mercury and oxygen.

Four experiments were carried out in order to judge the comparative ease of mercuration and benzene. From 38 ml. of 66% nitric acid, 27 g. of mercuric nitrate and 10 ml. of benzene at 65° for sixty minutes in the high-speed stirring apparatus, a total of 4 g. of nitrobenzene was obtained. The remainder was a brown resinous product from which 1.2 g. of 2,4-dinitrophenol was sublimed. This material melted at 109° and was found identical with an authentic specimen. The experiment was repeated at 0° for a period of one and one-quarter hours. No nitrogen oxides were evolved at this low temperature as contrasted with copious evolution of gases at the higher temperature. The fumes were evolved, however, when the mixture was steam distilled at the end of the reaction. Two ml. of nitrobenzene was collected. The remainder was resinous material from which yellow crystals of crude 2,4-dinitrophenol were recovered by sublimation. Another experiment was made at a maximum temperature of 65° for one hour with 35 ml. of 33% nitric acid, 35 g. of mercuric nitrate and 10 ml. of benzene. No nitrogen oxide fumes were evolved. The product was a sticky brown to black tar. No nitrobenzene was found. In another identical experiment, except for a half hour at 60°, a red purple product (composition shown below) soluble in hot water and approximately similar to that already described was obtained but no nitrobenzene was found.

Anal. C, 12.6, 12.2; H, 0.42, 0.29; N, 3.53, 3.38; Hg, 68.0, 67.4.

Picric Acid (by R. M.).—Phenylmercuric nitrate (5 g.) was added to 25 ml. of concentrated nitric acid and 12.5 ml. of water. The mixture was heated on a steam-bath for five hours, after which it was diluted, cooled and extracted with ether. Evaporation of the ether extract left crude yellow crystals, which were dissolved in water and recovered by a second extraction with ether. Evaporation of this extract and three recrystallizations from benzene gave crystals that melted at 120°, a little low, but otherwise were identical with a known sample. Tarry products, similar to those observed in the preparation of phenylmercuric nitrate, were present in the nitrating mixture.

Summary

Mercuric nitrate reacts readily with benzene, and if mercuric oxide and Drierite (calcium sulfate) are used in the mixture to prevent the secondary effects from nitric acid and water, and if air is excluded, the yields and quality of the phenylmercuric nitrate produced are very high.

Phenylmercuric nitrate is probably the intermediate when mercuric nitrate is used as a catalyst in nitration.

Mercuration appears to be a very rapid and easy reaction, probably faster under certain conditions than nitration.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 20, 1946

[COMMUNICATION NO. 1134 FROM THE KODAK RESEARCH LABORATORIES]

The Preparation of Polyvinylamine, Polyvinylamine Salts, and Related Nitrogenous Resins

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Introduction

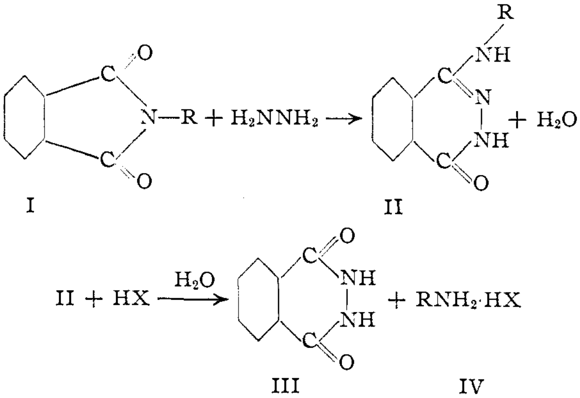
Polyvinylamine is not only of theoretical importance, but also of practical value, since it may be used as the starting material for the preparation of a variety of derived resins. Prior to the present work, a substantially pure polyvinylamine or its salts had not been prepared, though Hanford and Stevenson[1] isolated a polymer containing approximately 75% free amino groups and 25% incompletely hydrolyzed imide groups by hydrolysis of polyvinyl succinimide with concentrated hydrochloric acid at 700 pounds pressure and 180° for six hours.

After the work reported here had been completed, Jones, Zomlefer and Hawkins[2] published an account of their attempts to prepare polyvinylamine by a number of different methods. They state that "attempts at the hydrazine hydrolysis of polyvinyl phthalimide, hypobromite degradation of polyacrylamide and Beckmann rearrangement of polyvinyl methyl ketoxime did not meet with success." Their attempt to reduce polynitroethylene was also reported as unsuccessful.

The Gabriel synthesis[3] is often employed to produce primary amines but the conditions used are usually drastic, consisting in treating a substituted phthalimide with strong mineral acids or bases at relatively high temperatures, and often under pressure. These reaction conditions are not easy to carry out, especially on polymeric materials, and since the reactions are attended by side reactions, there is little hope of obtaining a pure polymeric product. In simple organic reactions, if even a small yield of the desired product is obtained it can be isolated and purified by distillation or crystallization. In polymer chemistry, these manipulations are not possible. To obtain a pure resin on a structural basis, the reaction must go to completion along the desired path; otherwise, residual or partially reacted groups will be a part of the molecule and cannot be physically removed therefrom. A number of attempts by us to prepare polyvinylamine by the usual technique of the Gabriel synthesis as well as the reported work of Hanford and Stevenson[1] have borne out these facts.

Such consideration led to the adoption of the hydrazine hydrolysis of polyvinyl phthalimide. Polyvinyl phthalimide was first treated with hydrazine hydrate to form a phthalhydrazide salt of polyvinylamine, as shown by VIII, from which phthalhydrazide and polyvinylamine hydrohalide were liberated. The latter was converted to polyvinylamine by treatment with alkali or to derived resins by reaction with the appropriate reagent. This method was used by Ing and Manske[4] for obtaining amines from simple non-polymeric nitrogen-substituted phthalimides. They often obtained nearly quantitative yields of the desired amine.

The supposed mechanism of the reaction is



$$\text{IV} + \text{NaOH} \longrightarrow \text{RNH}_2 + \text{NaX} + \text{H}_2\text{O}$$

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[1] Hanford and Stevenson, U. S. Patent 2,365,340.

[2] Jones, Zomlefer and Hawkins, *J. Org. Chem.*, **9**, 500 (1944).

[3] Gabriel, *Ber.*, **20**, 2224 (1887); **24**, 3104 (1891).

[4] Ing and Manske, *J. Chem. Soc.*, 2348 (1926).