

lates in bacteriological culture media can only be hypothesized at present, but they certainly must be taken into consideration.

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TRIMETHYL PHOSPHINE AND ITS SELENIDE.¹

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Received January 21, 1921.

In this paper the preparation of trimethyl phosphine and trimethyl phosphine selenide are described.

Trimethyl phosphine was first prepared by Cahours and Hofmann³ by the action of phosphorus trichloride on zinc methyl. They described it as a mobile, highly refractive liquid with an indescribable odor boiling between 40° and 42° and uniting with oxygen so readily that the substance fumes in the air and explodes easily. Later Hofmann⁴ prepared the substance by heating phosphonium iodide with various quantities of methyl alcohol in sealed tubes for 6 to 8 hours at 160–180°. He stated that this method is preferable to the zinc alkyl method in the ethyl series but not in the methyl because in the latter case the main product of the action is frequently the quaternary compound. Fireman⁵ claims that by substituting methyl ether for methyl alcohol in this reaction as complete a reaction can be brought about in less time and at lower temperatures, namely one to two hours at 120° to 140°.

Auger⁶ obtained a mixture of primary, secondary and tertiary phosphines when methyl iodide was treated with a solution of phosphorus in alcoholic sodium hydroxide containing water and when methyl iodide was heated at higher temperatures with phosphorus di-iodide, tribromide or trichloride.⁶ Apparently he did not obtain any better results for the preparation of trimethyl phosphine by the application of the Grignard reagent.⁷

Hibbert,⁸ however, using an excess of Grignard reagent and low temperatures has succeeded in isolating a very satisfactory yield (70%) of *tri-ethyl* phosphine as the carbon disulfide addition product.⁹

¹ Published by permission of Maj. Gen. W. L. Sibert, Director, C. W. S., U. S. Army.

² The authors wish to express their appreciation for the generosity shown by Dr. E. Emmet Reid, in offering the facilities of his laboratory for this work.

³ Cahours and Hofmann, *Ann.*, **104**, 29 (1857).

⁴ Hofmann, *Ber.*, **4**, 209, 373 (1871).

⁵ Fireman, *ibid.*, **30**, 1089 (1897).

⁶ Auger, *Compt. rend.*, **139**, 639 (1904).

⁷ Auger and Billy, *loc. cit.*, p. 597.

⁸ Hibbert, Dissertation "Ueber Additions produkte von Trialkyl-phosphinen-Arsinen und-Steibinen." See also *Ber.*, **39**, 160 (1906).

⁹ Application of this and of other methods of preparing the trialkyl derivatives of certain elements of Group V will be presented in a later paper.

The Preparation of Trimethyl Phosphine from Phosphonium Iodide and Methyl Alcohol.—The phosphonium iodide was prepared according to the directions of Hofmann.¹ For the conversion of this iodide into the tertiary phosphine the procedure of Hofmann² was followed with slight modification. This investigator found that when phosphonium iodide was treated with as little as one molecular quantity of methyl alcohol no primary or secondary phosphine could be detected though there was present phosphine and tetramethyl phosphonium iodide. This would indicate that the velocities of formation of the secondary and tertiary phosphines were relatively very high. Hofmann has shown that if the proportion is increased to three of methyl alcohol to one of iodide the main product of the reaction is the quaternary phosphonium iodide. Considering the foregoing it seemed advisable to use a relatively less amount of alcohol, say 2.5 to one of iodide, and heat at lower temperatures for longer periods of time.

The first experiments were carried out as follows. Ten g. of phosphonium iodide was placed in a bomb tube and then 5 g. of methyl alcohol contained in a smaller tube added, the bomb sealed and the contents mixed just before putting the bomb in the furnace. Three tubes were made. They were heated up slowly and finally kept at about 150° for 6 to 8 hours. On cooling they contained a magma of white crystals, and considerable compressed gas. The contents were dissolved in water and an excess of sodium hydroxide solution was added. An oily layer separated at the top of the solution. This was removed by means of a separating funnel, dried with a little solid potassium hydroxide and weighed, giving a yield of 30%. Other tubes with a volume of about 125 cc. were charged with 20 g. of the iodide and 10 g. of the methyl alcohol and heated for 25 hours at 130 to 140°, and a yield of about 35% obtained. A qualitative estimate of the effect of adding a few drops of methyl iodide seemed to indicate that this increased the yield slightly. In all cases a considerable quantity of tetramethyl phosphonium iodide was obtained but unfortunately the record of the percentage yield was not preserved. It appears that from this latter substance a further quantity of the tertiary phosphine could be obtained by converting it into the chloride and subjecting this to dry distillation. Collie³ has shown that tetramethyl phosphonium chloride (but not the iodide) when heated above 300° decomposed yielding trimethyl phosphine substantially quantitatively according to the following reaction,



The Preparation of Trimethyl Phosphine by the Action of Phosphorus Trichloride on Zinc Methyl.—Substantially the method described by Hofmann⁴ was followed.

A dropping funnel was inserted in a distilling flask containing a weighed amount of zinc methyl. The side arm was connected to a second distilling flask and to the side arm of the latter there was attached a U-tube, containing enough phosphorus trichloride to form a seal. The U-tube was connected to a large bottle through which a continuous stream of carbon dioxide was passing. Dry ether was added to the zinc methyl through

¹ Hofmann, *Ber.*, **6**, 286 (1873).

² Hofmann, *ibid.*, **4**, 209 (1871).

³ Collie, *J. Chem. Soc.*, **53**, 636 (1888).

⁴ Hofmann, *Ann.*, **104**, 29 (1857).

the dropping funnel and the flask cooled in an ice pack. The calculated quantity of phosphorus trichloride was then dropped slowly into the zinc methyl and the flask occasionally shaken. At the completion of the reaction, the ether was poured off from the white solid formed and the flask heated gently while a stream of carbon dioxide was passed through it in order to remove as much of the ether as possible. The solid was then treated carefully with an excess of an alkali solution and the trimethyl phosphine directly distilled over in a current of hydrogen. The distillate was treated with a little solid potassium hydroxide and redistilled. The product so obtained, usually boiling between 40° and 42° , was used in the preparative work.

When pure trimethyl phosphine is desired this method has one weakness, for it is difficult to prepare a product wholly free from ether. The last traces of ether are eliminated from the double salt of trimethyl phosphine and zinc halide only on prolonged warming in a current of oxygen-free gas, preferably carbon dioxide or hydrogen, and under these conditions notable quantities of the trimethyl phosphine may be lost due to the ready dissociation of the double salt. If the ether is not eliminated at this stage, it passes over into the trimethyl phosphine distillate, and on account of the nearness of their boiling points, its separation then is difficult.

In experiments where the zinc methyl was used without diluting it was found that the heat of the reaction vaporized an undue amount of the zinc methyl and that there was also a tendency for the double salt to form pockets inclosing some zinc methyl.

Indications are that the best procedure is to dilute the zinc methyl with one to two volumes of a high boiling inert solvent such as xylene.

Trimethyl Phosphine Selenide, $(\text{CH}_3)_3\text{P Se}$.—The selenide appears to have been prepared by Hofmann¹ though he states that his product melts at 84° whereas the pure product obtained by us melts at 140° (corr.).

The substance is very easily prepared by the direct action of the trimethyl phosphine on powdered, or better precipitated, selenium.

The following procedure is wholly satisfactory. Dilute the phosphine with 4 or 5 volumes of ether and add a slight excess of precipitated selenium. Stopper the container and allow to stand with occasional shaking until the pronounced odor of trimethyl phosphine has disappeared. This will take several hours. In the meantime needle crystals of the selenide will separate on the surface of the flask. Heat the ether to boiling to dissolve the selenide and filter from the excess of selenium. Evaporate the excess of ether and refrigerate. The selenide will crystallize in a mass of perfectly white needle crystals.

The product so obtained is quite pure. On standing particularly in the light and in contact with air it slowly turns pink and finally reddish colored. It is distinctly soluble in cold and markedly in hot ethyl alcohol. By slowly cooling its warm alcohol solution, it separates in long flat needles, which in one instance were over an inch long.

The substance was analyzed gravimetrically by weighing the precipitate of silver selenide obtained by adding an excess of standard silver

¹ Hofmann, *Ann.*, 104, 33 (1857).

nitrate solution, and volumetrically on the same sample by determining the excess of silver in the filtrate with thiocyanate.

Calc. for C_8H_7PSe : Se, 50.99. Found: gravimetrically, 51.11, 51.21; volumetrically, 50.64, 50.76.

The phosphorus analogue of choline has been prepared. This and other similar compounds of phosphorus, arsenic and antimony will be described in papers to be published later.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TUFTS COLLEGE.]

THE ADDITION OF AROMATIC AMINES TO BROMONITRO-STYRENE.

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Received January 22, 1921.

Introduction and Theoretical.

The α - β unsaturated nitro compounds contain a conjugate unsaturated system which makes their addition reactions of particular interest. The easiest and most convenient to prepare in quantity is nitro-styrene, $C_6H_5CH=CHNO_2$. Hence this compound was first chosen in an investigation of the addition of ammonia and substituted ammonias to unsaturated nitro compounds.¹ The sensitiveness of nitro-styrene, particularly the ease with which it polymerizes was found to restrict the scope of the reaction to those additions which took place readily. Those reactions in part have been reinvestigated with the bromo derivative of nitro-styrene, a substance which does not polymerize, and the limits more clearly defined.

Bromonitro-styrene was first prepared by Prieb's,² who assigned to it the structure $C_6H_5CBr=CHNO_2$ because of its solubility in aqueous alkali. Thiele³ later showed that the solubility in alkali is due to the formation of a salt through addition. He proposed $C_6H_5CH=CBrNO_2$ as the correct formula, based on the behavior of the potassium methylate addition product of bromonitro-styrene which reacts with bromine to form a compound that is insoluble in alkali.

A much more satisfactory proof of the correctness of Thiele's formula has been found in this research. One of the decomposition products resulting from the action of organic bases on bromonitro-styrene is bromonitro-methane, showing that bromine and the nitro group are held by the same carbon atom.

The first step in the reaction between bromonitro-styrene and organic

¹ *Dissertation*, Harvard University. This work was done under the direction of Professor Michael.

² Prieb, *Ann.*, **225**, 343 (1884).

³ Thiele and Haeckel, *ibid.*, **325**, 2 (1902).