PREPARATION AND METHYLATION OF ALKALI METAL PHOSPHIDES

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Abstract—A sodium phosphide characterized as Na_3P by earlier workers has been demonstrated to be the major product resulting from the reaction of white phosphorus with sodium dispersion in inert organic media. Sodium phosphide and the mixed phosphide formed by reacting phosphorus with sodium–potassium alloy react readily with methyl halides in glyme solvents to give varying mixtures of tetramethylphosphonium- and trimethylphosphonium halides. These phosphonium salts have been converted to trimethylphosphine oxide and trimethylphosphine, respectively, to give overall yields of ca. 60 per cent of organophosphorus products under optimum conditions.

THE reaction of white phosphorus with sodium in a hydrocarbon reaction medium was first investigated by CAHOURS⁽¹⁾ in 1862 and a few years later by LETTS and COLLIE.⁽²⁾ These workers apparently assumed that sodium phosphide, Na₃P, was the product of the sodium–phosphorus reaction for two reasons. Firstly, a compound having this formula would be expected from a consideration of classical valence theory. Secondly, the formation of phosphonium salts on treatment of the phosphides with organic halides could be rationalized readily as resulting from Na₃P. Thus, treatment with benzyl chloride⁽²⁾

$$BNa + P \xrightarrow{\text{benzene or}} Na_{3}P \xrightarrow{RX} R_{4}PX + \text{``other products''}$$

afforded tetrabenzylphosphonium chloride in yields varying from 1 to 40 per cent. Tetramethyl- and tetraethylphosphonium iodides were obtained (yields not specified) from reactions with methyl and ethyl iodide, respectively.⁽¹⁾

However, the best known and well-established alkali metal phosphides, which are obtained from the reaction of the elements at high temperatures, have the formula M_2P_5 .⁽³⁾ In distinct contrast, there appears to be only one reliable claim⁽⁴⁾ in the literature for the preparation of a phosphide having the formula Na₃P from sodium and phosphorus under similar conditions. The basis for this claim rests mainly on the finding that the X-ray powder diffraction pattern of sodium phosphide is similar to the pattern exhibited by the known Na₃As.

More recently, a different approach has afforded one member of the alkali metal phosphide family having the formula M_3P . ISSLEIB and TZSCHACH⁽⁵⁾ have prepared Li₃P by an exhaustive metalation of phosphine with phenyllithium in diethyl ether.

$$PH_s + 3C_6H_5Li \longrightarrow PLi_s + 3C_6H_6$$

The reaction of elemental phosphorus with alkali metals in organic solvents appeared to warrant reinvestigation since M_3P compounds, if obtainable in high

⁽⁴⁾ G. BRAUER and E. ZINTL, Z. phys. Chem. B 37, 323 (1937).

⁽¹⁾ A. CAHOURS, Ann. 122, 329 (1962).

⁽¹⁾ E. A. LETTS and N. COLLIE, Proc. Roy. Soc. Edinburgh 11, 46 (1881).

⁽³⁾ J. R. VAN WAZER, Phosphorus and Its Compounds, pp. 133-44. Interscience, New York (1958).

⁽⁵⁾ K. ISSLEIB and A. TZSCHACH, Ber. Chem. Dtsch. Ges. 92, 1118 (1959).

yields, would have considerable potential as precursors to a variety of organophosphorus compounds. This is exemplified by the recent report⁽⁶⁾ of HORNER and co-workers who have demonstrated that the phosphides resulting from reactions of phosphorus trichloride with sodium and potassium dispersions in toluene afford phosphonium halides in yields varying from 25 to 62 per cent on treatment with organic halides.

$$PCl_{s} + 6M \xrightarrow{\text{toluene}} PM_{s} + 3MCl \xrightarrow{RX} R_{4}PX$$
$$M = Na, K$$

RESULTS

White phosphorus has been found to react with sodium and sodium-potassium alloy in inert hydrocarbon solvents at temperatures varying from 80 to 145°, and with high speed stirring, to give phosphides capable of reacting readily with alkyl halides in glyme* solvents. For example, these reactions afford methylphosphorus compounds in ca. 60 per cent overall yields under optimum conditions when methyl halides (chloride, bromide, and iodide) are used as the derivatizing agents.

$$3M + P \xrightarrow{80-145^{\circ}} M_{s}P \xrightarrow{CH_{s}X} (CH_{s})_{s}PX + (CH_{s})_{s}PHX \xrightarrow{NsOH} \begin{pmatrix} (CH_{s})_{s}P(O) \\ + \\ (CH_{s})_{s}P \end{pmatrix} 60\%$$

The results of this study demonstrate that sodium phosphide, Na_3P , is the major product of the sodium-phosphorus reaction in inert organic media under carefully controlled conditions. The most definitive evidence for the formation of sodium phosphide as the major product is afforded by X-ray powder diffraction data. A comparison of the X-ray powder diffraction data obtained by examination of the phosphide from a typical run with the data reported⁽⁴⁾ by BRAUER and ZINTL for the material they characterized as Na_3P reveals that the compounds are identical.

The nature of the phosphides resulting from the reaction of alkali metals with phosphorus was found to be highly dependent on several factors. Firstly, chunk sodium metal, even above its melting point, gave incomplete reaction and appeared to convert white phosphorus to a complex polyphosphide stage. Therefore, this factor requires that a fine dispersion of the metal be used, preformed or formed in situ, to effect complete conversion of the phosphorus to Na₃P. Secondly, it was found necessary to heat the reaction mixture of sodium dispersion, phosphorus, and suspending medium for a minimum of 4 hr with high-speed stirring at ca. 100°. Higher temperatures and longer reaction times appeared to have little effect on the nature of the phosphides. Shorter reaction times gave incomplete reduction of the phosphorus and, as a consequence, led to very low conversions. Also, the complex polyphosphides obtained in this manner were found to react slowly with the methyl halides in glyme solvents. With sodium-potassium alloy, high speed stirring was not required and a lower reaction temperature was found to be satisfactory. Thirdly, the choice of the reaction medium for phosphide formation was found to be critical. Thus, the anomalous result observed when diglyme was used as the medium, i.e., the formation of a relatively large amount of trimethylphosphine, (see exp. 1 of Table) probably

[•] Glyme refers to monoglyme (1,2-dimethoxyethane) or diglyme [bis-(2-methoxyethyl)-ether].

⁽⁶⁾ L. HORNER, P. BECK and H. HOFFMANN, Ber. Chem. Dtsch. Ges. 92, 2088 (1959).

resulted from a reaction of sodium phosphide with the ether, either by α -metalation or by an elimination reaction. Reactions of this type have

 $Na_{s}P + CH_{s}OCH_{s}CH_{s}OCH_{s}CH_{s}OCH_{s} \longrightarrow Na_{s}PH + CH_{s}OCH_{s}CH_{s} + CH_{s}OCH_{s}CH_{s}O$

(2) NaOH (CH₃)₃P

precedence in the well-known attack of organometallic compounds on ethers.⁽⁷⁾ In accord with this proposal, only trace amounts of trimethylphosphine were obtained when inert reaction media such as benzene or octane were employed.

Lithium was found to be less satisfactory as a metal for the formation of alkali metal phosphides than either sodium or sodium-potassium alloy. In contrast to the latter elements, lithium dispersion reacted at a very slow rate with phosphorus. Thus, after 15 hr reaction time at 130°, only ca. two-thirds of the stoichiometric amount of lithium was consumed. Methylation of the resulting phosphide(s) in glyme solvents gave only trace amounts of methyl-phosphorus compounds.

Red phosphorus was found to be relatively inert to sodium dispersion at elevated temperatures. The inertness of red phosphorus may be due to its lesser degree of ring strain⁽⁸⁾ and its insolubility in organic solvents.

The nature of the solvent for the alkylation reaction was found to be a very significant factor. As the data in the table indicates, the phosphides were relatively inert to the methyl halides in hydrocarbon solvents, moderately reactive in a combination of hydrocarbon and glyme solvents, and very reactive in pure glyme. Since there appeared to be little difference in rates of reaction when monoglyme or diglyme was used, monoglyme, because of its low boiling point (83°), is recommended.

The reason for the large rate difference of methylation in going from hydrocarbon to glyme solvents is of interest. It may be speculated that the higher dielectric constant and cation solvating power⁽⁹⁾ of the glyme solvents, relative to hydrocarbon solvents, enable them to partially overcome the crystal lattice energy of the phosphide resulting in an enhanced polarization of the sodium-phosphorus bond.*



The rates of alkylation of the phosphides with methyl halides increased in the order expected for a reaction involving nucleophilic displacement at a saturated carbon atom, i.e., $CH_8Cl < CH_8Br < CH_8I$. However, the yields of methylphosphorus compounds obtained from alkylation with the three methyl halides were comparable.

* Van Wazer has concluded from the available X-ray data that the bonds from the phosphorus in Na₂P are primarily covalent with some ionic character; see Reference (3).

- ⁽¹⁾ R. G. JONES and H. GILMAN, Org. Reactions 6, 351 (1951); K. ZIEGLER and H. G. GILBERT, Ann. 567, 185 (1950).
- (8) L. PAULING and M. SIMONETTA, J. Chem. Phys. 20, 29 (1952), state that red phosphorus is thermodynamically more stable than white phosphorus by 4.4 kcal/g atom.
- (1) H. D. ZOOK and T. J. RUSSO, J. Amer. Chem. Soc. 82, 1258 (1960).

Treatment of the reaction mixtures obtained from methylations of sodium (potassium) phosphide with sodium hydroxide gave trimethylphosphine oxide, and, in most instances, varying amounts of trimethylphosphine. From one reaction, in which only two moles of methyl iodide per mole of sodium phosphide was added, a small amount (0.4 per cent) of tetramethyldiphosphine (isolated as the disulphide) was obtained.

The trimethylphosphine oxide arises from the well known base catalyzed decomposition of tetramethylphosphonium hydroxide:⁽¹⁰⁾

 $(CH_3)_4PX + NaOH \longrightarrow (CH_3)_4POH \frac{NaOH}{\Delta} (CH_3)_3P(O) + CH_4$

The trimethylphosphine must result from a precursor unstable to base since the phosphine could not remain unquaternized in the presence of excess methyl halide. This suggests that the bulk of the trimethylphosphine liberated on treatment with base arises from neutralization of the corresponding hydrogen halide salt, $(CH_3)_3PHX$. Indeed, the presence of trimethylphosphonium halide as a reaction product was substantiated by infrared and nuclear magnetic resonance spectral analyses. The proton required for the formation of trimethylphosphonium halide was probably abstracted from the alkylation solvent by sodium phosphide or either of the partially methylated phosphides, CH_3PNa_2 or $(CH_3)_2PNa$.

The origin of the small amount of tetramethyldiphosphine is not known. However, it may be speculated that the diphosphine is formed directly from tetrasodiodiphosphide which, in turn, results from incomplete reaction of phosphorus with the alkali metal(s) or from one of several possible halogen-metal interchange reactions.

$$Na_{s}P + CH_{s}I \longrightarrow Na_{s}PI + CH_{s}Na$$

EXPERIMENTAL

General

Extreme care was exercised in these reactions due to the toxicity and pyrophoric nature of phosphorus and trimethylphosphine. Therefore, all manipulations of reactants, intermediates, and products were performed under an atmosphere of dry, oxygen-free argon and in a well ventilated hood. Due care was also exercised in dismantling equipment because of the possibility of residual phosphines.

Under normal operating procedure, the effluent gases during the alkylation step were passed through the following sequence of traps: (1) mineral oil, (2) empty, (3) ethanol-methyl iodide solution, (4) dilute nitric acid, and (5) dilute silver nitrate. This precaution prevented any gaseous phosphines from escaping into the atmosphere.

The ether solvents, i.e., monoglyme (1,2-dimethoxyethane), diglyme [bis-(2-methoxyethyl)-ether], and tetrahydrofuran, were distilled from either calcium hydride or lithium aluminum hydride under an atmosphere of argon immediately before use.

Water was removed from white phosphorus in one of two ways; (a) azeotroping with the solvent used for phosphide formation, i.e., benzene or toluene, or (b) successive washings with ethanol, benzene, and ether.

Unless stated otherwise, the mixture of phosphorus, sodium, and solvent was heated to the melting point of sodium (97.5°) before the high speed stirrer (Talboys) was started.

The quantity of trimethylphosphine oxide obtained was determined by either direct weighing, gas phase chromatography, or potentiometric perchloric acid titration in acetic anhydride.⁽¹¹⁾

⁽¹⁰⁾ G. W. FENTON and C. K. INGOLD, J. Chem. Soc. 2342 (1929).

⁽¹¹⁾ D. C. WIMER, Analyt. Chem. 34, 873 (1962).

The accompanying Table 1 summarizes the results of several reactions in which experimental variations were investigated in attempts to increase the per cent conversion of white phosphorus to methyl-phosphorus compounds (trimethylphosphine oxide and trimethylphosphine). Experiment (1) of this section is typical of the techniques employed in the reactions.

Sodium phosphide

Typical preparation and methylation. A mixture of 3.1 g (0.1 g atom) of white phosphorus, 6.9 g (0.3 g atom) of sodium, and 125 ml of toluene was heated to the melting point of sodium (pot temperature = 125°) and high-speed stirring was started. A reaction occurred immediately as evidenced by the liberation of heat and formation of a finely divided black solid. Stirring at 125° was continued for 4 hr.

Subsequent to cooling to room temperature, the toluene was removed by filtering the mixture through a Grignard flask having a sintered glass filter into a flushed, dry receiver. To facilitate this separation, the argon source to the receiver was clamped off and the receiver was cooled in a Dry Ice-acetone bath.

To the solid residue there was then added 125 ml of diglyme, followed by the dropwise addition of an excess (0.66 mole) of methyl bromide over a 2 hr period. (The methyl bromide was contained in a Dry Ice-acetone jacketed addition funnel and, consequently, was added as a liquid.) An immediate reaction occurred as evidenced by the liberation of heat and formation of a white solid.

Following the completion of the addition; the mixture was treated successively with 75 ml of ethanol (caution!) and 50 ml of water. The ethanol and water were then distilled into a receiver containing 10 ml of a mixture of ethanol and methyl iodide (50:50). Evaporation of the water and ethanol from the receiver left 0.2 g of tetramethylphosphonium iodide, m.p. 358° (dec.) (lit.⁽¹³⁾ m.p. > 360°).

Subsequent to the addition of 8 g (0.2 mole) of sodium hydroxide and 50 ml of ethanol to the residue, the mixture was heated to co-distill ethanol and trimethylphosphine into a receiver containing methyl iodide. The insoluble tetramethylphosphonium iodide that formed was filtered and dried [1.9 g (9 per cent), m.p. > 360° (dec.)]. An infrared spectrum of the compound was superimposable on that of an authentic sample. The sample exhibited a proton n.m.r. absorption at 8.0 τ (doublet, J = 15 c/s) in deuterium oxide.

The residue in the flask was heated under vacuum (1.5 mm) for ca. 7 hr to sublime 5.5 g (59 per cent) of trimethylphosphine oxide, m.p. 138–140° (sealed capillary) [lit. m.p. 140–141°]. The trimethylphosphine oxide had proton and phosphorus n.m.r. adsorptions at 8.4τ (doublet, J = 14 c/s) and -48.8 p.p.m. (rel. to 85 per cent H₃PO₄), respectively, in deuterium oxide.

Preparation at room temperature. A dispersion of 2.4 g (0.08 g atom) of white phosphorus, 5.2 g (0.023 g atom) of sodium dispersion, and 100 ml of toluene was stirred at room temperature for 8 hr.

The reaction product(s) was then treated successively with 50 ml of tetrahydrofuran, 35 ml of methyl bromide, and 71 g (0.5 mole) of methyl iodide, with no visual sign of reaction. Some reaction did occur after standing for two days as evidenced by the formation of a yellow-orange insoluble material. To the reaction mixture there was then added 50 ml of diglyme and stirring was continued for 2 hr.

Filtration of the mixture afforded a solid that evolved phosphine(s) when treated with water. (The phosphine(s) were detected by pulling the gaseous sample through a tube containing silica gel impregnated with a silver nitrate.) An undetermined amount of red, amorphous material, having a phosphine-like odour, was observed to be present at this time.

Distillation of the water left a solid residue that appeared to contain a small amount of tetramethylphosphonium halide (as evidenced by an infrared spectrum of the material). No attempt was made to isolate this salt.

Preparation using magnetic stirrer. A mixture of 0.8 g (0.026 g atom) of phosphorus, 1.72 g (0.075 g atom) of sodium, and 70 ml of toluene was stirred at ca. 100° for 2 hr. During this time a finely divided black insoluble compound was formed. Subsequent to cooling to room temperature, ca. 0.8 g (~45 per cent) of the sodium was recovered. The remainder of the reaction mixture was treated with 21.4 g (0.15 mole) of methyl iodide and heated to 90° (oil-bath temperature) for 3 hr, cooled and stirred at room temperature for 4 days.

⁽¹²⁾ W. VON E. DOERING and A. K. HOFFMANN, J. Amer. Chem. Soc. 77, 521 (1955).

	Other	Trace organo- phosphorus polymer trace (CH ₃) ³ PH											Trace of polyorgano- phosphorus compound(s)		Trace (CH ₂) ₂ PHI	
Yield of	Trimethyl- phosphine	24	1	1	٢	e	11	0	٢	0	0	15	7	И	1	0
	Trimethyl- phosphine oxide	Trace	59	63	53	48'	52	46	22	36	59	~50'	54'	55	33	trace
	Methyl ^ø halide	CH,I	CH ₈ Br	CH3CIA	CH	CH ₃ Br	CH	CH ₃ Br	CH ₃ Br	CHI	CH ₃ Br	CH ₃ Br	CH ₃ Br	CH _a Br	CH ₈ Br ^A	CH ₃ Br ⁴
	Alkylation solvent	Diglyme	Diglyme	Diglyme	Diglyme	Monoglyme	Monoglyme	Diglyme	Diglyme	(1) benzene ^r (2) monoglyme ^e	Monoglyme	Monoglyme	Monoglyme	Monoglyme	Monoglyme	Monoglyme*
Column for	phosphide formation	Diglyme 125° 2·5 hr	Toluene	Toluene 125°. 4 hr	Toluene 125° 4 hr	Octane 125°. 4 hr	Octane 125° 4 hr	Octane 125°, 10 hr	Toluene 125°. 5 hr	Benzene 80°. 3 hr	Benzene 80°. 3 hr	Benzene 80°, 6 hr	Benzene 80°. 8-5 hr	Benzene 80°, 7 hr	Decalin 145°. 7 hr	Benzene 80°, 4 hr
	siometry	3 Na	3 Na	3 Na	3 Na	3 Na	3 Na	3 Na	2 Na	3 Na/K	3 Na/K	3 Na/K	3 Na/K	3 Na/K	3 Na/K	2 Na/K
	Stoiche	pa,e	Pa,c	Pa,0	Å	Po, e	p,4	₽¢,4	Pa,o	Å.	Å	፟፟፟፟	å	ሏ	ፈ	2
	Exp.	Ð	(2)	(2)	(4)	(2)	(9)	6	(8)	(6)	(10)	(11)	(12)	(13)	(14)	(15)

(a) Water azeotroped from phosphorus.

Phosphorus dried by successive washings with ethanol and benzene.
Phosphorus dried by successive washings with ethanol and benzene.
Soldium and phosphorus heated to 97.5° (melting point of sodium) and high speed stirrer was started.
Phosphorus and preformed sodium dispersion heated to melting point of phosphorus (44°) and stirring was started.
Phosphorus and preformed sodium dispersion heated to melting point of phosphorus (44°) and stirring was started.
No reaction occurred in this solvent.
Excess methylating reagent used unless stated otherwise.
Methyl iodide was added to insure complete reaction after initial alkylation with halide specified.
Yield of trimethylphosphine oxide was determined by a potentiometric perchloric acid titration in acetic anhydride.
The trimethylphosphine oxide was hydrated and therefore an accurate yield was not obtained.

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TABLE 1,---PHOSPHORUS-ALKALI METAL(S)-METHYL HALIDES REACTIONS

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The color of the reaction mixture during this time changed from black to orange-red. Subsequent to the addition of 25 ml of diglyme and an additional 24 hr of stirring, the reaction mixture was treated with wet diglyme (1 ml $H_2O/15$ ml diglyme). Some amorphous red substance (presumably a mixture of red phosphorus and polyphosphorus hydrides) was recovered by filtration. Concentration of the filtrate afforded more amorphous material that was not worked up.

Derivatization with methyl iodide and sulphur (isolation of tetramethyldiphosphine disulphide). A mixture of 4.6 g (0.15 g atom) of phosphorous, 10.35 g (0.45 g atom) of sodium, 100 ml of toluene, and 85 ml of decalin was heated to ca. 110°, and the high speed stirrer was started and continued for 4 hr (pot temperature constant at 135°). Following a transfer of the reaction mixture to a Grignard flask having a sintered glass filter, the solvents were removed by filtration and replaced with 100 ml of monoglyme. The dropwise addition of 42.6 g (0.3 mole) of methyl iodide to the finely divided black phosphide(s) resulted in an exothermic reaction and the formation of a white, insoluble solid. Subsequent to the complete addition, approximately 40 per cent of the solution was filtered into a receiver containing 2.4 g (0.075 mole) of sulphur in 20 ml of benzene. A white solid formed immediately. The mixture was then stirred 18 hr at room temperature and 6 hr at gentle reflux. The reaction mixture was then treated with 10 ml of dilute hydrochloric acid and filtered to give 0.2 g (0.4 per cent) of crude tetramethyldiphosphine disulphide, melting over the range, 215-235°. Recrystallizations from ethanol and tetrahydrofuran narrowed the melting point to 232-234°. An admixed melting point determination with an authentic sample⁽¹⁸⁾ gave no depression. An infra-red spectrum of the compound was superimposable on that of an authentic sample. Also, the retention times of the compound obtained above and tetramethyldiphosphine disulphide on a 20 per cent Apiezon-Fluoropak vapour phase chromatography column were identical. Separation and concentration of the organic layer afforded 1.43 g of solid melting over the range 105-152°. Attempts to purify this material by recrystallizations from several solvents failed. An infrared spectrum of the material had absorption bands at 7.8 μ (P-CH₃) and 13.4, 13.7 μ (P-S).

Attempted reaction of red phosphorus with sodium

A mixture of 1.55 g (0.05 g atom) of red phosphorus 3.45 g (0.15 g atom) of sodium, and 100 ml of toluene (distilled from calcium hydride immediately before use) was heated to ca. 100° and stirring was started (Talboys high-speed stirrer). No reaction occurred during 2 hr at 100° or 8 hr at room temperature. No attempt was made to recover the starting materials.

Reaction of lithium, phosphorus and methyl iodide

A mixture of 3.03 g (0.098 g atom) of phosphorus, 2.1 g (0.3 g atom) of lithium dispersion (from 3.5 g of 60 per cent lithium-paraffin dispersion) and 50 ml of octane was stirred at gentle reflux for 16 hr. From the purple-black reaction mixture ca. 40 ml of solvent and some of the unreacted lithium (*ca.* 10 per cent recovered) was removed.

To the residue there was added 50 ml of monglyme, followed by the dropwise addition of 69 g (0.48 mole) of methyl iodide. An immediate reaction occurred as evidenced by the liberation of heat and formation of white insoluble compounds. An infra-red spectrum of some of the white solid formed at the base of the addition funnel revealed it to be mainly tetramethylphosphonium iodide with a trace of trimethylphosphonium iodide.

Subsequent to removal of the solvents, the solid remianing was heated (ca. 180°) with 8.0 g (0.2 mole) of sodium hydroxide under vacuum. The distillate obtained was shown to be free of trimethylphosphine oxide by infra-red spectral analyses and gas phase chromatography. An infra-red spectrum of the residue indicated that trimethylphosphine oxide had not been formed and that phosphonium salt(s) remained. The residue was dissolved in water and thoroughly extracted with chloroform. Concentration of the chloroform extracts afforded no methylphosphorus compounds. The aqueous layer on concentration gave a residue that contained small amounts of phosphonium salts. No attempt was made to isolate these compounds.

Typical preparation of sodium-potassium phosphide and methylation

To a three-necked 250 ml flask, equipped with magnetic stirrer and condenser, and containing 1.65 g (0.053 g atom) of phosphorus dispersed in 80 ml of dry benzene, there was added 5.5 ml (158 meq.) of sodium-potassium alloy (16.4 meq. Na/ml, 12.3 meq. K/ml) over 0.5 hr at room

⁽¹³⁾ H. NIEBERGALL and B. LANGENFELD, Ber. Chem. Disch. Ges. 95, 64 (1962).

temperature. An exothermic reaction occurred with the formation of a black solid. Subsequent to an additional 0.5 hr of stirring, the reaction mixture was heated to gentle reflux for 8.5 hr. The mixture was then cooled to 20°, 80 ml of monoglyme was added, and an excess of methyl bromide (51 g, 0.55 mole) was added dropwise during a 1 hr period, resulting in a mildly exothermic reaction. The reaction mixture, after standing overnight, was cautiously treated with 30 ml of ethanol resulting in some gas evolution. Subsequent to the removal of ca. three-fourths of the solvents by distillation, 6 g (0.15 mole) of sodium hydroxide and 75 ml of ethanol was added. The volatile components were then distilled into a receiver containing methyl iodide. Tetramethylphosphonium iodide (0.23 g, 2 per cent), m.p. 330–360° (dec.), was obtained on evaporation of the fraction. The original reaction flask was heated to 200° under 5 mm vacuum to sublime trimethylphosphine oxide, 25.4 meq. (48 per cent), as determined by potentiometric perchloric acid titration.⁽¹¹⁾ The distillation residue was dissolved in sufficient hydrochloric acid to give a saturated acidic solution. Extraction with chloroform afforded a solid that was sublimed to give an additional 0.28 g (3 meq., 5.7 per cent) of trimethylphosphine oxide, m.p. 137–140°.⁽¹⁰⁾

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