ration of triphenylacetic acid and other derivatives, particularly those which form ether-soluble magnesium complexes.[10]

Summary

Conditions have been determined for the preparation of triphenylmethylmagnesium chloride in excellent yields.

AMES, IOWA

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

THE REACTION BETWEEN ALKALI METAL ALKYLS AND QUATERNARY PHOSPHONIUM HALIDES

BY D. D. COFFMAN AND C. S. MARVEL

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The question of whether or not phosphorus ever has a valence of five is still open. It is generally accepted that in the phosphonium salts its valence is four and that the negative ion is held by a polar valence to the phosphonium ion. Lewis[1] believes that phosphorus shares five pairs of electrons with five chlorine atoms in phosphorus pentachloride and has therefore a valence of five. Langmuir[2] has said that the valence of phosphorus in this compound is four and that one chlorine atom is held by a polar valence. Prideaux[3] has presented the idea that three of the chlorine atoms are attached to the phosphorus atom by means of true covalences whereas the remaining two are joined by singlet linkages. Sugden[4] has advanced experimental evidence favoring this view.

Staudinger and Meyer[5] attempted to prepare penta-alkyl phosphorus compounds by the action of zinc ethyl on tetra-ethylphosphonium iodide. However, at low temperatures no reaction was noted and at higher temperatures they obtained triethylphosphine, butane and zinc iodide. The same investigators[6] have prepared the compound $(C_6H_5)_3P{=}C(C_6H_5)_2$, called by them triphenylphosphinediphenylmethylene, in which all of the valences of phosphorus are satisfied by carbon atoms. This compound

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water-bath (60–80°). Then the addition of a volume of benzene in slight excess of that of the ether removed dissolves the reagent. For titration purposes it is merely necessary to make several marks on the reaction flask in order to measure subsequently the total volume of Grignard solution.

[10] Details will appear shortly on some general preparations involving triphenylmethylmagnesium chloride.

[1] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Company, New York, **1923**, p. 102.

[2] Langmuir, THIS JOURNAL, **41**, 919 (1919).

[3] Prideaux, *Chem. Industry*, **42**, 672 (1923).

[4] Sugden, *J. Chem. Soc.*, 1174 (1927).

[5] Staudinger and Meyer, *Helv. Chim. Acta*, **2**, 612 (1919).

[6] Staudinger and Meyer, *ibid.*, **2**, 635 (1919).

was prepared by combining triphenylphosphine with diazodiphenylmethane to give a phosphazine which lost nitrogen when heated.

$$(C_6H_5)_3P + (C_6H_5)_2CN_2 \longrightarrow (C_6H_5)_3{-}P{=}N{-}N{=}C(C_6H_5)_2 \longrightarrow (C_6H_5)_3P{=}C(C_6H_5)_2 + N_2$$

The phosphinemethylene resembled in many respects the tetramethyltriphenylmethylammonium, which was prepared previously by Schlenk and Holtz.[7] It is a brilliant red compound which is sensitive to air and moisture. With water it gives triphenylphosphine oxide and diphenylmethane, and with acids the corresponding phosphonium salt. Two of Staudinger's students, Lüscher[8] and Isler[9] have obtained some phosphinemethylenes by the action of molten potassium on quaternary phosphonium salts.

$$2R_3PBr{-}CHR_2 + 2K \longrightarrow 2R_3P{=}CR_2 + 2KBr + H_2$$

Only the compound containing five phenyl groups was stable enough for isolation in the pure form although certain others were formed in solution.

In the hope of gaining further knowledge concerning the valence of phosphorus, the reactions of alkali metal alkyls with phosphonium salts have been investigated. Two alkali metal alkyls, lithium *n*-butyl and sodium triphenylmethyl, have been used. The first phosphonium salt studied was tetra-ethylphosphonium iodide. The reaction of this compound with sodium triphenylmethyl ran smoothly at ordinary temperatures. The color of the sodium triphenylmethyl faded and on working up the reaction mixture triphenylmethane, triethylphosphine and sodium iodide were obtained. This reaction is exactly analogous to the reaction between tetra-ethylphosphonium iodide and zinc ethyl reported by Staudinger and Meyer.[5] It is also analogous to the reactions of quaternary ammonium salts with alkali metal alkyls which have been studied by Hager with Marvel.[10]

Preliminary experiments with triphenylalkylphosphonium halides and alkali metal alkyls seemed to give colored solutions or colored insoluble compounds which resembled the phosphine methylenes. Accordingly, triphenyldiphenylmethylphosphonium bromide was prepared and treated with lithium *n*-butyl and with sodium triphenylmethyl. Both reagents produced triphenylphosphinediphenylmethylene in good yields. The reaction proceeds at room temperature and goes especially smoothly with lithium *n*-butyl.

The other phosphonium salts which were used were methyltriphenylphosphonium iodide, ethyltriphenylphosphonium iodide and *iso*propyltriphenylphosphonium bromide. These compounds reacted with an

[7] Schlenk and Holtz, *Ber.*, **49**, 603 (1916).

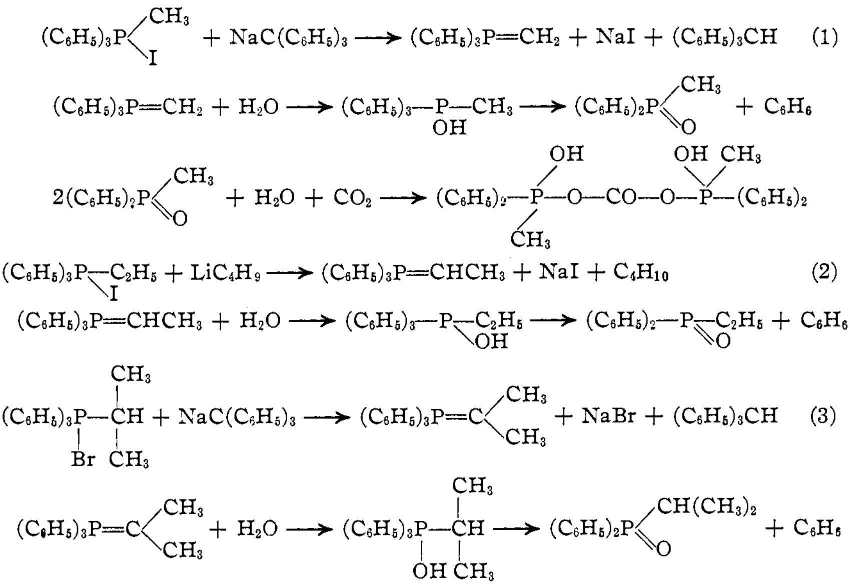
[8] Lüscher, Ph.D. "Thesis," Zurich, **1922**.

[9] Isler, Ph.D. "Thesis," Zurich, **1924**.

[10] Hager with Marvel, THIS JOURNAL, **48**, 2689 (1926).

ether solution of sodium triphenylmethyl or lithium *n*-butyl to give colored solutions which decolorized on exposure to moist air. The products isolated after decomposition were, respectively, a derivative of methyldiphenylphosphine oxide, ethyldiphenylphosphine oxide and *iso*propyldiphenylphosphine oxide. The formation of these compounds can best be explained by assuming that a phosphinemethylene is the first product of the reaction between the alkali metal alkyl and the phosphonium salt. When moist air is admitted to the reaction mixture the phosphinemethylene is converted to the quaternary phosphonium hydroxide, which then decomposes to the diphenylalkylphosphine oxide and benzene.[11]

The following equations illustrate the steps in these reactions



$$(C_6H_5)_3P\begin{smallmatrix}CH_3\\ I\end{smallmatrix} + NaC(C_6H_5)_3 \longrightarrow (C_6H_5)_3P{=}CH_2 + NaI + (C_6H_5)_3CH \qquad (1)$$

$$(C_6H_5)_3P{=}CH_2 + H_2O \longrightarrow (C_6H_5)_3{-}\underset{OH}{P}{-}CH_3 \longrightarrow (C_6H_5)_2P\begin{smallmatrix}CH_3\\ O\end{smallmatrix} + C_6H_6$$

$$2(C_6H_5)_2P\begin{smallmatrix}CH_3\\ O\end{smallmatrix} + H_2O + CO_2 \longrightarrow (C_6H_5)_2{-}\underset{CH_3}{\overset{OH}{P}}{-}O{-}CO{-}O{-}\overset{OH\ CH_3}{P}{-}(C_6H_5)_2$$

$$(C_6H_5)_3P\begin{smallmatrix}C_2H_5\\ I\end{smallmatrix} + LiC_4H_9 \longrightarrow (C_6H_5)_3P{=}CHCH_3 + NaI + C_4H_{10} \qquad (2)$$

$$(C_6H_5)_3P{=}CHCH_3 + H_2O \longrightarrow (C_6H_5)_3{-}P\begin{smallmatrix}C_2H_5\\ OH\end{smallmatrix} \longrightarrow (C_6H_5)_2{-}P\begin{smallmatrix}C_2H_5\\ O\end{smallmatrix} + C_6H_6$$

$$\underset{Br}{(C_6H_5)_3P}{-}\underset{CH_3}{\overset{CH_3}{CH}} + NaC(C_6H_5)_3 \longrightarrow (C_6H_5)_3P{=}C\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix} + NaBr + (C_6H_5)_3CH \qquad (3)$$

$$(C_6H_5)_3P{=}C\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix} + H_2O \longrightarrow \underset{OH}{(C_6H_5)_3P}{-}\underset{CH_3}{\overset{CH_3}{CH}} \longrightarrow (C_6H_5)_2P\begin{smallmatrix}CH(CH_3)_2\\ O\end{smallmatrix} + C_6H_6$$

There was no indication in any of the reactions studied that a penta-alkyl phosphorus compound analogous to the penta-alkyl nitrogen derivative of Schlenk and Holtz[7] had been obtained. Neither was there any evidence of penta-alkyl phosphorus compounds in which five equivalent valences were combined with the organic radicals. The phosphinemethylenes which are represented as intermediates in all of the above reactions are probably not compounds in which phosphorus has a valence of five but rather resemble the amine oxides and phosphine oxides in their structure.

In all the phosphonium salts thus far studied there has been one group which carried a hydrogen atom on the carbon attached to the phosphorus atom. Some compounds are now being studied where this is not true,

[11] Michaelis and Soden, *Ann.*, **229**, 315 (1885).

and preliminary results indicate that penta-alkyl phosphorus compounds may thus be obtained.

Experimental Part

Sodium triphenylmethyl solution in dry ether was prepared according to the general method of Schlenk and Holtz.[7] The modified reaction flask shown in Fig. 1 allows easy separation of the solution of the metallic alkyl from the excess amalgam and sodium chloride. Lithium *n*-butyl was prepared by the method of Hager and Marvel.[10] The triphenylphosphine was obtained by the method of Dodanow and Medox[12] and the phosphonium salts were prepared as described by Lüscher[8] and by Michaelis and Soden.[13] The apparatus used in the reactions was similar to that described by Hager and Marvel.[10]

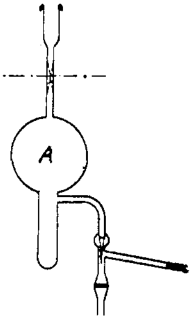


Fig. 1.

Lithium *n*-Butyl and Triphenyldiphenylmethylphosphonium Bromide.—The lithium *n*-butyl solution obtained by the action of 1.6 g. of di-*n*-butyl mercury and 0.5 g. of lithium in petroleum ether was run onto 5 g. of triphenyldiphenylmethylphosphonium bromide. The colorless salt immediately turned bright red. After two days the reaction flask was opened, the reaction mixture was filtered and the red reaction product was separated from the unreacted phosphonium salt and sodium bromide by dissolving it in dry benzene. After several crystallizations the product was dried in an atmosphere of nitrogen over phosphorus pentoxide. The yield was 0.8 g. The product melted at 172–174° and all of its properties agreed with those ascribed to triphenylphosphinediphenylmethylene by Staudinger and Meyer.[6] A mixture of this material and some made by the published method melted at 172–174°.

Anal. Subs. 0.2087: CO_2, 0.6645; H_2O, 0.1158. Calcd. for $C_{31}H_{25}P$: C, 86.91; H, 5.85. Found: C, 86.83; H, 6.16.

Sodium Triphenylmethyl and Triphenyldiphenylmethylphosphonium Bromide.—An ether solution of 0.0027 mole of sodium triphenylmethyl was added to 1.2 g. (0.002 mole) of the phosphonium salt. After shaking for a few minutes the solution lost its color and a red precipitate of the phosphinemethylene appeared. After one day the reaction flask was opened and the reaction mixture was filtered. From the precipitate triphenylphosphinediphenylmethylene melting at 171–173° was obtained. From the ether solution triphenylmethane (m. p. 91–92°) was isolated. Its identity was established by a mixed melting-point determination with known triphenylmethane.

Sodium Triphenylmethyl and Triphenyl-*iso*propylphosphonium Bromide.—An ether solution of 0.003 mole of sodium triphenylmethyl was added to 1.2 g. of triphenyl-*iso*-propylphosphonium iodide. The reaction mixture was allowed to stand for about forty-eight hours. During this time the color of the solution changed slightly and no longer was that of the original solution. When the reaction mixture was opened to the air the color was almost instantly discharged. The insoluble salts were removed by filtration. The filtrate was evaporated, the residue was dissolved in benzene and to the concentrated solution was added some petroleum ether (b. p. 40–60°). This gave a precipitate which after recrystallization from benzene and petroleum ether melted at 142–143°. Analysis of the product showed it to be diphenyl-*iso*propylphosphine oxide.

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[12] Dodanow and Medox, *Ber.*, **61B**, 907 (1928).

[13] Michaelis and Soden, *Ann.*, **229**, 295 (1885).

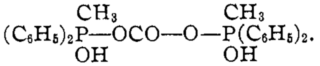
Anal. Subs., 0.1144: CO_2, 0.3092; H_2O, 0.0734. Calcd. for $C_{21}H_{22}PO$: C, 73.77; H, 6.97. Found: C, 73.71; H, 7.12.

From the benzene–petroleum ether mother liquors, triphenylmethane (m. p. 91–92°) was isolated.

Sodium Triphenylmethyl and Triphenylmethylphosphonium Iodide.—An ether solution containing 0.01 mole of sodium triphenylmethyl was added to 4 g. (0.01 mole) of triphenylmethylphosphonium iodide. The deep red color of the solution was discharged and at the end of three weeks a light orange colored solution remained. On exposure to the air, this color disappeared almost entirely. Moist carbon dioxide was passed into the solution and a white precipitate separated. The precipitate was removed by filtration. From the filtrate triphenylmethane (m. p. 91.5–92°) was obtained.

The precipitate produced by the carbon dioxide was purified by solution in chloroform, followed by precipitation with dry ether. In this way a compound melting at 109–111° with evolution of gas was obtained. This compound was very soluble in alcohol. When treated with acids it liberated carbon dioxide.

Anal. Subs., 0.2442: CO_2, 0.5886; H_2O, 0.1291. Calcd. for $C_{27}H_{28}P_2O_6$: C, 65.59; H, 5.67. Found: C, 65.74; H, 5.86.

The properties and analysis of this compound indicated that it was the basic carbonate of diphenylmethylphosphine oxide,  $(C_6H_5)_2\overset{CH_3}{\underset{OH}{P}}\text{—OCO—O—}\overset{CH_3}{\underset{OH}{P}}(C_6H_5)_2$.

Lithium *n*-Butyl and Triphenylethylphosphonium Iodide.—A petroleum ether solution containing 0.025 mole of lithium *n*-butyl was added to 10 g. (0.024 mole) of triphenylethylphosphonium iodide. In a short time the solution took on an orange color. After the reaction flask had stood for four days it was opened and water vapor was admitted. The color disappeared at once. Most of the petroleum ether was evaporated and the residue was extracted with benzene. Some unreacted phosphonium salt and the lithium iodide were undissolved. Addition of petroleum ether to the benzene solution precipitated an oil which slowly crystallized. This product was recrystallized from alcohol and water and again from benzene and petroleum ether. It then melted at 118–119.5°. It was shown to be ethyldiphenylphosphine oxide since the melting point (119–120°) was unchanged when mixed with an authentic specimen of this compound.

When sodium triphenylmethyl was used with triphenylethylphosphonium iodide, there was some difficulty in isolating a pure phosphine oxide.

Sodium Triphenylmethyl and Tetra-ethylphosphonium Iodide.—Preliminary experiments demonstrated that sodium triphenylmethyl solutions in ether reacted with tetra-ethylphosphonium iodide to give colorless products. Dry carbon dioxide had no effect on the reaction mixture. Water in contact with the ether solutions was neutral, showing that no basic oxide was present.

An ether solution of 0.01 mole of sodium triphenylmethyl was added to 2.7 g. (0.01 mole) of tetra-ethylphosphonium iodide. On opening the reaction flask a strong odor of triethylphosphine was noted. To a portion of the filtered ether solution was added an aqueous solution of zinc iodide in an attempt to isolate the double salt which Hofmann[14] reports as having a melting point of 99°. A small quantity of a solid melting at 82–88° was obtained. A second portion of the ether solution was treated with ethyl iodide and the quaternary phosphonium salt separated. This melted at 270–278°. Triphenylmethane (m. p. 91–92°) was isolated from another portion of the ether solution. Attempts to identify the ethylene which must also have been produced were not successful.

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[14] Hofmann, *Ann. Supl.*, **1**, 1 (1861).

Summary

1. Alkali metal alkyls react with quaternary phosphonium halides at room temperature.

2. Tetra-ethylphosphonium iodide and sodium triphenylmethyl give at once colorless products and the reaction is apparently analogous to that between alkali metal alkyls and quaternary ammonium salts.

3. Triphenylalkylphosphonium halides react with alkali metal alkyls to give colored products, apparently identical with the phosphinemethylenes of Staudinger, as the primary products of the reaction. The products isolated from several different reactions of this type are easily explained as decomposition products of the intermediate phosphinemethylenes.

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[Contribution from the Chemical Laboratory of Iowa State College]

THE REACTION BETWEEN SULFOCHLORIDES AND ORGANOMAGNESIUM HALIDES

By Henry Gilman and Robert E. Fothergill

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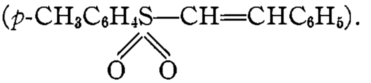
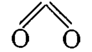
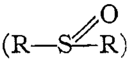
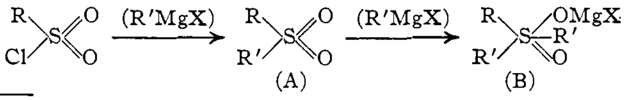
Introduction

In connection with studies on the electronic interpretation of the ethylenic linkage, Gilman and Peterson[1] reported a complete reaction between ethylmagnesium bromide and di-*p*-tolyldisulfonethylene. In order to throw some light on the nature of that reaction it was advisable to study a simpler conjugated system of the same type, namely, styryl-*p*-tolylsulfone  (p-$CH_3C_6H_4SO_2$—$CH{=}CHC_6H_5$). With this in view, we set out to prepare the sulfone from *p*-toluenesulfochloride and styrylmagnesium bromide. The indifferent success attending this synthesis prompted a more general investigation of the reaction between sulfochlorides and RMgX compounds.

Earlier studies of this reaction were made by Hepworth and Clapham[2] and by Wedekind and Schenk.[3] Hepworth and Clapham[2] proposed the following reactions to account for the sulfones  (R—SO_2—R), sulfoxides  (R—SO—R) and sulfides (R—S—R) isolated by them from the reaction between benzenesulfochloride and some RMgX compounds.

 (I)

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[1] Gilman and Peterson, This Journal, **48**, 423 (1926).

[2] Hepworth and Clapham, *J. Chem. Soc.*, **119**, 1188 (1921).

[3] Wedekind and Schenk, *Ber.*, **54**, 1604 (1921).