[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FAIRLEIGH DICKINSON UNIVERSITY]

Lithium Diphenylphosphide: A Convenient Source and Some Reactions

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Using the cleavage of triphenylphosphine by lithium in tetrahydrofuran as a source of lithium diphenylphosphide, a study was made of the reaction of this solution with benzyl halides. The nature of the products was found to depend upon the order of addition of the reagents. Inverse addition produced benzyldiphenylphosphine and dibenzyldiphenylphosphonium salts while normal addition gave rise to (1,2-diphenylethyl)diphenylphosphine. A method of selectively eliminating the phenyllithium is described.

Most of the methods employed in making alkali metal diphenylphosphides involve starting materials which are not readily available and are difficult to work with.[2–5]

A more convenient method of preparation has consisted of the cleavage of the available and easily handled triphenylphosphine by alkali metals in ethereal solvents.[6–9]

$$(C_6H_5)_3P + 2M \longrightarrow (C_6H_5)_2PM + C_6H_5M$$

Reinvestigation of the reaction of triphenylphosphine and lithium metal in tetrahydrofuran, studied by Wittenberg and Gilman[9] showed the reaction to proceed as described by these authors. Addition of dilute hydrogen peroxide produced diphenylphosphinic acid in over 90% yield.

$$(C_6H_5)_2PLi + C_6H_5Li + 2H_2O \longrightarrow C_6H_5H + (C_6H_5)_2PH + 2LiOH$$

$$(C_6H_5)_2PH + 2H_2O_2 \longrightarrow (C_6H_5)_2P(O)(OH) + 2H_2O$$

A phenyl to phosphorus bond was therefore quantitatively cleaved.

Upon addition of the tetrahydrofuran reaction solution to an excess of benzyl chloride in tetrahydrofuran, followed by refluxing and treatment with dilute hydrogen peroxide, benzyldiphenylphosphine oxide was obtained in 80% yield. This is not an unexpected result since lithium diphenylphosphide and phenyllithium in an excess of benzyl chloride would not be expected to interfere with each other. The reaction of alkali metal diaryl- or dialkylphosphides and alkyl halides to give tertiary phosphines is well known.[3]

It was felt that in order to extend the synthetic usefulness of this method of preparation of lithium diphenylphosphide, it would be desirable to eliminate selectively the phenyllithium produced. Since phenyllithium might be expected to be a stronger base than lithium diphenylphosphide,[10] *t*-butyl chloride, in an equimolar amount to the starting phosphine, was added to the reaction mass. An equimolar amount of benzyl chloride was then added to the solution and the reaction mass finally treated with dilute hydrogen peroxide. Benzyldiphenylphosphine oxide was isolated in 60% yield. No diphenylphosphinic acid could be isolated. These results may readily be explained by the following interpretation:

$$C_6H_5Li + (CH_3)_3CCl \longrightarrow (CH_3)_2C{=}CH_2 + LiCl + C_6H_5H$$

$$(C_6H_5)_2PLi + C_6H_5CH_2Cl \longrightarrow (C_6H_5)_2PCH_2C_6H_5 + LiCl$$

$$(C_6H_5)_2PCH_2C_6H_5 \xrightarrow{H_2O_2} (C_6H_5)_2P(O)(CH_2C_6H_5)$$

Added confirmation for this interpretation was sought by the attempted preparation of other derivatives of benzyldiphenylphosphine rather than attempting the isolation of this intermediate. When the stoichemetric amount of thiophosphoryl chloride was added to the reaction solution of triphenylphosphine and lithium, which had been treated with *t*-butyl chloride and subsequently refluxed for a period of time in the presence of benzyl chloride, a white crystalline solid melting at 162–163° and having a composition and infrared spectrum expected for benzyldiphenylphosphine sulfide was isolated. Benzyldiphenylphosphine sulfide was reported by Arbuzov as having been produced from the reaction of diphenylphosphinous chloride and benzyl mercaptan in ether solution in the presence of pyridine.[11] They reported, however, a melting point of 144–147° for their compound.

$$(C_6H_5)_2PCl + C_6H_5CH_2SH \longrightarrow (C_6H_5)_2P(S)(CH_2(C_6H_5)_2)$$

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[1] To whom inquiries regarding this article should be sent.

[2] K. Issleib and A. Tzschack, *Chem. Ber.*, 92, 1124 (1959).

[3] I. Issleib and D. Muller, *Chem. Ber.*, 92, 3175–3182 (1959).

[4] W. Kuchen and H. Buchwald, *Chem. Ber.*, 92, 227 (1959).

[5] F. G. Mann, I. T. Miller, and F. H. C. Stewart, *J. Chem. Soc.*, 2832 (1954).

[6] W. Rudorff and W. Muller, *Dissertation*, W. Muller Tubingen (1957).

[7] W. Kuchen and H. Buchwald, *Angew. Chem.*, 69, 307 (1957).

[8] K. Issleib and H. O. Frohlich, *Z. Naturforsch.*, 14b, 349 (1959).

[9] D. Wittenberg and H. Gilman, *J. Org. Chem.*, 23, 1063 (1958).

[10] As described in the literature,[8] diphenylphosphine was found to react with phenyllithium to produce lithium diphenylphosphide and benzene.

[11] A. E. Arbuzov and K. V. Nikonorov, *Zhur. Obshiche. Khim.*, 18, 2008 (1948).

The conversion of our sulfide to the corresponding oxide with alkaline peroxide lends support to the identity of our compound.

The production of benzyldiphenylphosphine sulfide can best be explained by assuming the preferential destruction of phenyllithium by the *t*-butyl chloride followed by the formation of benzyldiphenylphosphine. The phosphine then apparently exchanges sulfur with the thiophosphoryl chloride.[12,13]

$$(C_6H_5)_2PCH_2C_6H_5 + P(S)Cl_3 \longrightarrow (C_6H_5)_2P(S)(CH_2C_6H_5) + PCl_3$$

When the solution prepared by the addition of the mixture of phenyllithium and lithium diphenylphosphine to benzyl chloride was treated with thiophosphoryl chloride in the same manner as described above, an excellent yield of the same product was obtained.

Addition of the mixture of lithium diphenylphosphide and phenyllithium to benzyl bromide produced a phosphonium bromide which exhibited an infrared spectrum, a melting point, and an elemental composition expected for dibenzyldiphenylphosphonium bromide. Addition of benzyl bromide to the solution prepared by prior addition of *t*-butyl chloride gave the same product. Refluxing with dilute aqueous sodium hydroxide solution, under conditions found to convert benzyltriphenylphosphonium bromide (prepared by the reaction of triphenylphosphine and benzyl bromide in ether) to triphenylphosphine oxide and toluene, produced benzyldiphenylphosphine oxide.[14]

It can be assumed that benzyldiphenylphosphine was initially produced and that it then reacted with the excess benzyl bromide to produce the phosphonium salt.

$$(C_6H_5)_2PCH_2C_6H_5 + C_6H_5CH_2Br \longrightarrow (C_6H_5)_2P^{+}(CH_2C_6H_5)_2Br^{-}$$

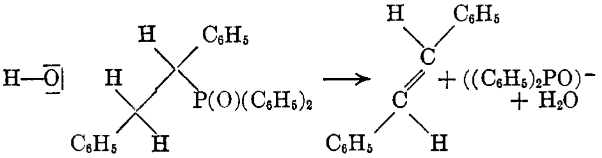
Interestingly, upon addition of excess benzyl chloride to the mixture of lithium diphenylphosphide and phenyllithium followed by refluxing and treatment with dilute hydrogen peroxide, only 25% of benzyldiphenylphosphine oxide (m.p. 192°) was obtained, the major product (57%) being a new phosphine oxide (I) (m.p. 220–221°). The infrared spectrum of I in chloroform solution was that expected for a tertiary phosphine oxide. Elemental analysis of I showed the composition to correspond to the formula $C_{26}H_{23}PO$.

When the thiophosphoryl chloride treatment was applied to the solution prepared by the addition of benzyl chloride to the mixture of lithium diphenylphosphide and phenyllithium, a new tertiary phosphine sulfide (II) (m.p. 182–183°) was isolated as the major product. Elemental analysis showed the formula to be $C_{26}H_{23}PS$.

A solution of II in glacial acetic acid was treated with 30% hydrogen peroxide and I was produced.

It would seem, therefore, that a phosphine other than benzyldiphenylphosphine is produced upon addition of benzyl chloride to a mixture of phenyllithium and lithium diphenylphosphide. This phosphine reacts with dilute hydrogen peroxide to produce its oxide I or exchanges sulfur with thiophosphoryl chloride giving rise to the corresponding sulfide II.

Fusion of I with sodium hydroxide at 300° produced diphenylphosphonic acid, *trans*-stilbene, and 1,2-diphenylethane.[15] In view of the fact that similar treatment of benzyldiphenylphosphine oxide produced diphenylphosphinic acid and toluene, it seemed reasonable to assign the structure of (1,2-diphenylethyl)diphenylphosphine oxide to I.[15] The stilbene probably originates in a beta elimination of diphenylphosphine oxide, while the *trans* nature of this product may be due to an "eclipsing effect" in the transition state (if an S_N2 mechanism is assumed).



Benzyldiphenylphosphine oxide reacted with phenyllithium in tetrahydrofuran to produce yield III.[16]

$$(C_6H_5)_2P(O)\bar{C}HC_6H_5$$

III

Benzyl chloride was then added to III giving rise to I[16]. It, therefore, seems warranted to assign the structure of (1,2-diphenylethyl)diphenylphosphine oxide to I, (1,2-diphenylethyl)diphenylphosphine sulfide to II, and (1,2-diphenylethyl)diphenylphosphine to the precursor phosphine.

The origin of (1,2-diphenylethyl)diphenylphosphine can be visualized as involving the abstraction of an alpha hydrogen from the first formed benzyldiphenylphosphine by phenyllithium.

$$(C_6H_5)_2PCH_2C_6H_5 + C_6H_5Li \longrightarrow C_6H_5H + \underset{\text{IV}}{(C_6H_5)_2P\underset{-}{C}HC_6H_5}$$

Carbanion IV would then nucleophilically displace chloride ion from benzyl chloride producing (1,2-diphenylethyl)diphenylphosphine.

$$C_6H_5P\underset{-}{C}HC_6H_5 + C_6H_5CH_2Cl \longrightarrow (C_6H_5)_2P\underset{CH_2C_6H_5}{\underset{|}{C}}HC_6H_5$$

IV

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(12) H. B. Gottleib, *J. Am. Chem. Soc.*, **54**, 748 (1932).

(13) In unpublished work by F. Ramirez and A. Aguiar, it was found that triphenylphosphine will exchange sulfur with thiophosphoryl chloride.

(14) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, 1950, p. 104.

(15) L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, 91, 64 (1958).

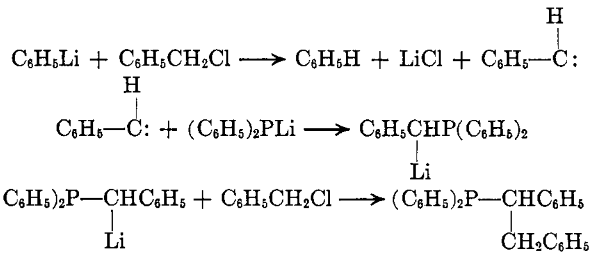
(16) L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, **92**, 2499 (1959).

This assumes that nucleophilic displacement of the chloride ion from benzyl chloride by the diphenylphosphide ion is fast enough, compared to the reaction of phenyllithium with benzyl chloride, to produce benzyldiphenylphosphine in the presence of phenyllithium. It also assigns some acidic character to the alpha hydrogen on benzyldiphenylphosphine.

When benzyldiphenylphosphine was treated with phenyllithium in refluxing tetrahydrofuran and benzyl chloride added to the resultant solution, a small amount of I was produced. It, therefore, seems possible that I could have arisen through such a path.

An alternative path involves the reaction of the diphenylphosphide ion with *trans*-stilbene which might be produced from the reaction of phenyllithium and benzyl chloride. That this cannot account for the formation of I was shown by the fact that attempted reaction of these reagents resulted in quantitative recovery of *trans*-stilbene and diphenylphosphinic acid.

A more interesting possibility involves the formation of a carbene radical through attack of phenyllithium on benzyl chloride followed by reaction of the diphenylphosphide ion with the electrophilic radical.



$$C_6H_5Li + C_6H_5CH_2Cl \longrightarrow C_6H_5H + LiCl + C_6H_5\text{—}\overset{H}{C}:$$

$$C_6H_5\text{—}\overset{H}{C}: + (C_6H_5)_2PLi \longrightarrow C_6H_5\underset{Li}{CH}P(C_6H_5)_2$$

$$(C_6H_5)_2P\text{—}\underset{Li}{CH}C_6H_5 + C_6H_5CH_2Cl \longrightarrow (C_6H_5)_2P\text{—}\underset{CH_2C_6H_5}{CH}C_6H_5$$

This possibility is at present being investigated.

EXPERIMENTAL

Preparation of diphenylphosphinic acid. A suspension of 26.2 g. (0.1 mole) of triphenylphosphine,[17] 200 ml. of dry hydrofuran, and 1.4 g. (0.2 g.-atom) of lithium metal strips was stirred rapidly at room temperature under nitrogen. The solution became deep red and the temperature rose in 15 min. to a maximum of 55°. The stirring was continued for 1 hr. after the reaction mass had returned to ambient temperature to insure that practically no lithium was left. Cold water (40 ml.) was added dropwise, with rapid stirring and cooling. At 25°, 120 ml. of chilled, 3% aqueous hydrogen peroxide solution was added dropwise with rapid stirring and cooling. When the reaction mass returned to ambient temperature it was added to excess water and filtered to remove a small amount of dirty white solid. The basic filtrate was saturated with sodium chloride and ether extracted. The organic layer was then dried over calcium chloride and distilled, producing only tetrahydrofuran and benzene. Acidification of the water layer produced a crystalline white solid which after recrystallization from methanol, was identified as diphenylphosphinic acid (95%) by infrared spectral comparison and mixed melting point with a sample of this material prepared by the oxidative hydrolysis of diphenylphosphinous chloride (which was obtained by the thermal disproportionation of commercial phenylphosphonous dichloride).[18]

Preparation of benzyldiphenylphosphine oxide. To a reaction solution of triphenylphosphine and lithium metal in tetrahydrofuran, as prepared above, was added dropwise, with rapid stirring and cooling, a solution of 9.3 g. (0.1 mole) of *t*-butyl chloride in 50 ml. of tetrahydrofuran, in 10 min. and at 20°. An exothermic effect, accompanied by gas evolution and partial discharge of color was observed. The reaction mass was refluxed for 15 min. and a solution of 12.7 g. (0.1 mole) of benzyl chloride in 50 ml. of tetrahydrofuran was then added dropwise, with cooling and rapid stirring in 10 min. at 30°. The red color was discharged completely toward the end of the exothermic addition. After refluxing for 30 min., the suspension was added to a large excess of 3% hydrogen peroxide, allowed to stand overnight, filtered, water washed, dried at 100°, and ether-triturated producing 18 g. (62% yield) of white solid m.p. 191–192°. After recrystallization from ethanol and water the material was identified as benzyldiphenylphosphine oxide by spectral comparison and mixed melting point with an authentic sample prepared by the reaction of benzylmagnesium chloride and diphenylphosphinic chloride.[19]

Anal. Calcd. for $C_{19}H_{17}PO$: C, 78.08; H, 5.82. Found: C, 78.44; H, 5.85.

The aqueous filtrate was alkaline to litmus paper and did not give a precipitate upon acidification with hydrochloric acid.

Addition of the mixture of phenyllithium and lithium diphenylphosphide to benzyl chloride followed by oxidation with 3% hydrogen peroxide produced benzyldiphenylphosphine oxide in excellent yield.

Preparation of benzyldiphenylphosphine sulfide. After having treated the reaction solution of 0.1 mole of triphenylphosphine and 0.2 mole of lithium metal in 200 ml. of tetrahydrofuran with 0.1 mole of *t*-butyl chloride and 0.1 mole of benzyl chloride as described above, a solution of 17.1 g. (0.1 mole) of thiophosphoryl chloride in 50 ml. of tetrahydrofuran was added slowly to the rapidly stirring, cooled reaction mass. After the exothermic effect had subsided, the mass was refluxed for 1 hr. and left at room temperature overnight. The clear yellow solution was then poured into a large excess of cold water, filtered, water washed, and dried giving 18.0 g. (59%) of a slightly yellow solid which after recrystallization from 95% ethyl alcohol gave white crystalline solid melting at 162–163° which was essentially insoluble in carbon tetrachloride.

Anal. Calcd. for $C_{19}H_{17}PS$: C, 74.02; H, 5.52; P, 10.06; S, 10.39. Found: C, 74.02; H, 5.58; P, 10.52; S, 10.52.

A. E. Arbuzov and K. V. Nikonorov[11] have reported the preparation of benzyldiphenylphosphine sulfide by the reaction of diphenylphosphinous chloride and benzyl mercaptan in ether in the presence of pyridine. The melting point they report is 144–147°.

Addition of thiophosphoryl chloride to a reaction solution mixture prepared by addition of lithium diphenylphosphide and phenyllithium to benzyl chloride gave rise to the same product in good yield.

Oxidation of benzyldiphenylphosphine sulfide to benzyldiphenylphosphine oxide. To a refluxing solution of 1.0 g. of the above sulfide in 100 ml. of ethanol (95%) was added 50 ml. of a dilute solution of sodium hydroxide in 3% hydrogen peroxide. After refluxing for 3 hr. it was cooled to room temperature, filtered, water washed, and dried, giving rise to 0.3 g. of solid (m.p. 156–158°). An infrared spectrum of the chloroform solution was identical to that of the starting material. The filtrate was then allowed to stand for a few days and 0.6 g. of white crystals (m.p. 192.5–193.5°) came out. Mixed

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[17] Obtained from Metal & Thermit Corp., Rahway, N. J.

[18] C. P. Haber, D. L. Herring, and E. A. Lawton, *J. Am. Chem. Soc.*, **80**, 2116 (1958).

[19] D. C. Morrison, *J. Am. Chem. Soc.*, **72**, 4820–4821 (1950).

melting points and infrared comparison with an authentic sample of benzyldiphenylphosphine oxide showed these materials to be identical.

Preparation of dibenzyldiphenylphosphonium bromide. To a solution of lithium diphenylphosphide, prepared as described previously, a solution of 34.2 g. (0.2 mole) of benzyl bromide in 50 ml. of tetrahydrofuran was added dropwise at 40° in 10 min. The reaction mass was refluxed for 9.0 hr. and then filtered to give 20.0 g. (55.0%) of white solid (m.p. 219–225°).

After recrystallization from dilute hydrobromic acid the material melted at 252–254° and exhibited an infrared spectrum typical of a phosphonium salt. The nitric acid acidified solution of this compound gave an immediate precipitate when treated with aqueous silver nitrate solution.

Anal. Calcd. for dibenzyldiphenylphosphonium bromide: C, 69.79; H, 5.37; P, 6.95; Br, 17.81. Found: C, 69.35; H, 5.56; P, 6.87; Br, 17.81.

Addition of a mixture of phenyllithium and lithium diphenylphosphide to an excess of benzyl bromide produced the same compound in excellent yield.

Thermal decomposition of dibenzyldiphenylphosphonium hydroxide. A small sample of the above material was refluxed with dilute aqueous sodium hydroxide and a solid was recovered in good yield which was identical to benzyldiphenylphosphine oxide by mixed melting points and infrared spectrum comparison.

Preparation of (1,2-diphenylethyl)diphenylphosphine oxide. A solution of 28.0 g. (0.22 mole) of benzyl chloride in 50 ml. of tetrahydrofuran was added dropwise in 15 min. at 35–40° to a rapidly stirred, cooled solution from the reaction of triphenylphosphine (0.1 mole) and lithium metal (0.2 g.-atom). The reaction mass was refluxed for 1 hr., cooled to room temperature and added to an excess of 3% hydrogen peroxide. After standing overnight, the suspension was filtered, water washed, and oven-dried to give 30.0 g. of a slightly yellow solid (m.p. 189–200°). After being ether triturated and dried, it was triturated with 400 ml. of 95% ethanol producing 21.0 g. (55.0%) of white solid (m.p. 211–214°). Repeated recrystallization from ethanol produced a solid melting at 221–222° and exhibiting an infrared spectrum which was similar to but not identical to that of $(C_6H_5)P(O)CH(C_6H_5)$

Anal. Calcd. for $C_{26}H_{23}PO$: C, 81.68; H, 6.02; P, 8.12; M.W., 382. Found: C, 81.76; H, 6.01; P, 8.35; M.W., 369.

The filtrate from the 95% ethanol trituration was reworked and produced 7.3 g. (25%) of benzyldiphenylphosphine oxide identified by melting point, infrared comparison, mixed melting point with an authentic sample.

Sodium hydroxide fusion of (1,2,-diphenylethyl)diphenylphosphine oxide. An intimate mixture of finely powdered (1,2-diphenylethyl)-diphenylphosphine oxide (36.8 g., 0.1 mole) and sodium hydroxide (8.0 g., 0.2 mole) was heated to 350° for 2 hr., the resultant mass was triturated with hexane and filtered.

A water solution of the residue (after filtration to remove a small amount of brown solid) was acidified with dilute hydrochloric acid producing 17.0 g. (78%) of diphenylphosphinic acid (identified by melting point, infrared spectrum comparison and mixed melting point determinations with an authentic sample).

After evaporation of the hexane from the hexane extract, 12.0 g. of a crystalline solid, m.p. 108–113°, remained. Chromatography on acid-washed alumina, using hexane as eluant, produced 8.0 g. (44%) of *trans*-stilbene and 4.0 g. (22%) of 1,2-diphenylethane, both identified by melting point, infrared spectrum comparison, and mixed melting point determinations with authentic samples of these compounds.

Preparation of (1,2-diphenylethyl)diphenylphosphine oxide from benzyldiphenylphosphine oxide. Phenyllithium was prepared in 50 ml. of ether from 15.7 g. (0.1 mole) of bromobenzene and 1.4 g. (0.2 g.-atom) of lithium metal ribbon. A suspension of 15.3 g. (0.052 mole) of benzyldiphenylphosphine oxide in 200 ml. of tetrahydrofuran was added. After the exothermic effect had subsided the yellow solution was refluxed for 45 min. A solution of 17.3 g. (0.1 mole) of benzyl bromide in 60 ml. of tetrahydrofuran was then added dropwise. After refluxing for 1 hr., the reaction mass was added to 1000 ml. of water and the precipitate filtered off. Triturated with cold 95% ethanol, gave 6.5 g. (34%) of white solid m.p. 209–211°. Recrystallization from ethanol and water produced a crystalline solid (m.p. 220–221°) exhibiting an infrared spectrum identical to that of the material produced by the addition of benzyl chloride to a mixture of lithium diphenylphosphide and phenyllithium. Mixed melting point determinations were undepressed.

Preparation of (1,2-diphenylethyl)diphenylphosphine oxide from benzyldiphenylphosphine. Phenyllithium was prepared from 8.42 g. (0.06 mole) of bromobenzene and 0.84 g. (0.12 g.-atom) of lithium metal in 100 ml. of ether. A solution of benzyldiphenylphosphine was prepared from 26.5 g. (0.1 mole) of triphenylphosphine, 1.4 g. (0.2 g.-atom) of lithium metal, 9.3 g. (0.1 mole) of *t*-butyl chloride and 7.6 g. (0.06 mole) of benzyl chloride in 300 ml. of tetrahydrofuran in the manner previously described. The phenyllithium was added to the benzyldiphenylphosphine maintaining the nitrogen atmosphere. After refluxing for 2 hr. at 56°, 7.6 g. (0.06 mole) of benzyl chloride was added and the mass refluxed for 5 hr. After returning to ambient temperature, the reaction mass was added to 1000 ml. of water containing one pint of 3% hydrogen peroxide. The dried precipitate weighed 28.4 g. (m.p. 161–170°). Acetone trituration followed by trituration with 95% ethanol gave a white solid 16.4 g. (m.p. 173–177°) which, after repeated recrystallization from ethanol and water had a melting point of 220–221° and an infrared spectrum identical to (1,2-diphenylethyl)diphenylphosphine oxide. Mixed melting point determinations were undepressed.

Reaction of lithium diphenylphosphide with trans-stilbene. Lithium diphenylphosphide was prepared from 13.1 g. (0.05 mole) of triphenylphosphine, 0.7 g. (0.1 g.-atom) of lithium metal and 4.64 g. (0.05 mole) of *t*-butyl chloride in 150 ml. of tetrahydrofuran as described previously.

Addition of 9.0 g. (0.05 mole) of *trans*-stilbene followed by refluxing for 1 hr. produced no color change. Addition to 1000 ml. of water containing 0.5 pint of 3% hydrogen peroxide produced 9.0 g. of *trans*-stilbene as shown by infrared spectrum comparison and mixed melting point determinations.

Acidification of the filtrate produced 8.0 g. of diphenylphosphinic acid by melting infrared spectrum comparison, and mixed melting point determinations with an authentic sample.

Preparation of (1,2-diphenylethyl)diphenylphosphine sulfide. The addition of benzyl chloride was carried out as described above, but instead of pouring into peroxide, 17 g. (0.1 mole) of thiophosphoryl chloride in 100 ml. of ether was slowly added. The reaction mass was allowed to stand for a few weeks and then filtered.

The residue was repeatedly recrystallized from ethyl alcohol and water producing 8.0 g. of white solid (m.p. 182–183°) with an infrared spectrum of a chloroform solution expected for a modified benzyldiphenylphosphine sulfide.

Anal. Calcd. for $C_{26}H_{23}PS$: C, 78.39; H, 5.78; P, 7.79; S, 8.04. Found: C, 77.92; H, 5.65; P, 8.15; S, 8.15.

The filtrate was stripped of solvent and the residual semisolid crystallized from ethyl alcohol and water to give more of this product, as well as some benzyldiphenylphosphine sulfide.

Oxidation of (1,2-diphenylethyl)diphenylphosphine sulfide. Treatment of the above sulfide with dilute hydrogen peroxide in base or sodium peroxide led to the quantitative recovery of the starting material as shown by melting points and infrared spectra.

A suspension of 5.0 g. of this solid in a mixture of 200 ml. of glacial acetic acid and 75 ml. (30%) of hydrogen peroxide was slowly heated to 90°. After standing at room temperature overnight, the solution was added to excess water and the suspension thus produced filtered. This produced (1,2-diphenylethyl)diphenylphosphine oxide by mixed melting point and infrared comparison.

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MADISON, N. J.

[CONTRIBUTION FROM THE PROCTOR & GAMBLE COMPANY, MIAMI VALLEY LABORATORIES]

The Thermal Reaction between Alkylating Agents and Phosphonate or Phosphate Esters

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The reaction between trimethyl phosphite and dodecyl bromide at 180–200° has been found to form methyl dodecyl methylphosphonate, I, in addition to the expected product, dimethyl dodecylphosphonate, II. I constitutes about 40% of the mixture. It has been established that I is formed by an alkyl exchange reaction between dodecyl bromide and dimethyl methylphosphonate, which is formed *in situ* by isomerization of trimethyl phosphite.

The alkyl exchange reaction has been shown to occur with phosphate as well as phosphonate esters, and thus appears to be a completely general reaction of aliphatic esters of organophosphorus acids. The reaction offers a new and convenient synthesis of mixed esters of phosphonic or phosphoric acids, of the type exemplified by I.

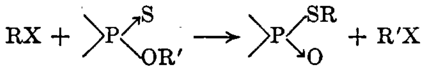
The relative reactivity of alkyl halides in the alkyl exchange reaction is RI > RBr > RCl. The relative reactivity of esters is phosphinate > phosphonate > phosphate. This information provides support for the concept that the reaction involves nucleophilic displacement by phosphoryl oxygen on the alkylating agent.

A classical method for the preparation of aliphatic phosphonates, $RPO(OR')_2$, is the "mixed" Michaelis-Arbuzov reaction between an alkylating agent and a trivalent phosphorus ester[1]:

$$RX + (R'O)_3P \longrightarrow RPO(OR')_2 + R'X; \quad X = \text{halide, tosylate, etc.}$$

The permissible structural variations in RX and in the phosphorus ester have been studied extensively, and the generally accepted mechanism involves nucleophilic attack of the phosphorus atom on the alkyl halide as the primary step.

The fact that an alkylating agent can react with *pentavalent* organophosphorus esters is not so generally recognized, although there are a few scattered references to such reactions. Pistschimuka and others[2] have investigated the reaction between alkyl halides and thiophosphoryl esters. The alkyl halide and the ester exchange substituents according to the general scheme[3]: The R group of the



$$\mathrm{RX} + {>}\mathrm{P}{<}\begin{matrix}\mathrm{S}\\ \mathrm{OR'}\end{matrix} \longrightarrow {>}\mathrm{P}{<}\begin{matrix}\mathrm{SR}\\ \mathrm{O}\end{matrix} + \mathrm{R'X}$$

halide always attaches to sulfur, and the ether-like oxygen becomes a coordinately bonded oxygen. Related reactions in the oxygen series have been reported only recently. Among these are the reaction of 2-bromoethyl acetate with methyl methylphenylphosphinate, which yields the 2-acetoxyethyl ester of the phosphinic acid,[4a] and the reactions of 1,3-dibromopropane with phosphite or phosphonite esters,[4b] which yield cyclic phosphonate or phosphinate esters, respectively. Examples of the alkyl exchange reaction between phosphonate esters and various alkylating agents have also appeared recently in the Russian literature.[4c] Ref. 4a quotes other examples of thermal reactions of 2-chloroalkyl phosphonate and phosphate esters, which can be viewed as alkyl exchange reactions, and to a copper-catalyzed exchange reaction. The latter, one might guess, would differ mechanistically from the purely thermal reactions considered in this paper.

RESULTS

In this paper it is shown that *O*-alkyl groups of simple aliphatic phosphonate or phosphate esters react with suitable alkylating agents to undergo an alkyl exchange reaction at high temperatures. This reaction has proved to be a useful synthesis of mixed esters of phosphonic or phosphoric acids, and has also been shown to occur as a side reaction in certain Michaelis-Arbuzov reactions.

Although Harwood and Grisley[4a] were the first to report a well documented case of the alkyl exchange reaction involving the phosphoryl rather than the thiophosphoryl group, their study was

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[1] G. M. Kosolapoff, *Organophosphorus Compounds*, Wiley, New York, 1950, p. 121.

[2] P. Pistschimuka, *J. für prakt. Chem.* (2), **84**, 746 (1911); *J. Russ. Phys.-Chem. Soc.*, **44**, 1406 (1912); *Chem. Zentr.*, **84**, I, 1581 (1913); A. J. Burn and J. I. G. Cadogan, *Chem. & Ind.* (London), 591 (1961).

[3] The term "alkyl exchange reaction" is used in this paper to describe this general reaction.

[4] (a) H. J. Harwood and D. W. Grisley, Jr., *J. Am. Chem. Soc.*, **82**, 423, 6429 (1960). (b) A. Y. Garner, U. S. Patent **2,916,510**, December 8, 1959; U. S. Patent **2,953,591**, September 20, 1960. (c) A. N. Pudovik, A. A. Muratova, T. I. Konnova, T. Feoktistova, and L. N. Levkova, *Zhur. Obshchei, Khim.*, **30**, 2624 (1960); *Chem. Abstr.*, **55**, 15332 (1961).