bath. The same conversion was also effected by dissolving II in concd. sulfuric acid and then pouring the solution onto ice.

*5,6-Dibromoacenaphthene.* The following modification of the bromination procedure described by Dashevskii and Karishin[11] was more satisfactory in our hands than the originally reported method.

Bromine (15.5 ml.) was slowly swept by a stream of nitrogen into a solution of 20 g. of acenaphthene in 120 ml. of 95% ethanol at reflux temperature. The mixture was refluxed an additional two hours; then the solvent was distilled and the residue chromatographed on a large silica gel column (solvent: 96 parts hexane, 4 parts benzene). Eight crystalline fractions (total, 8.4 g.) with similar infrared spectra were recombined and recrystallized several times from ethanol, yielding 4.0 g. (10%) of 5,6-dibromoacenaphthene; m.p. 138–140°; lit. m.p.[11] 140°; $\lambda^{KBr}$ 6.33, 7.40, 9.12, 11.6, 12.90 $\mu$. From subsequent chromatographic fractions was obtained a mixture (7.6 g.) of higher brominated products which was not further characterized. The NMR spectrum of 5,6-dibromoacenaphthene contained a single sharp peak at 97 c.p.s. (relative to tetramethylsilane) and a group of four peaks between 218 and 236 c.p.s. the total area of which was approximately equal to that of the 97 c.p.s. peak. This spectrum is consistent with the assignment of the two bromine atoms to the 5 and 6 positions in acenaphthene.

*Anal.* Calcd. for $C_{12}H_8Br_2$: C, 46.2; H, 2.58. Found: C, 45.6; H, 2.56.

*Reaction of 5,6-dibromoacenaphthene with butyllithium.* To 2.0 g. of 5,6-dibromoacenaphthene in 50 ml. of ether at 0° was added 40 ml. of 0.60*M* butyllithium. After the mixture had warmed to room temperature, it was stirred for 45 minutes and then carbonated. The spectrum of the crude 6-bromo-5-acenaphthenecarboxylic acid (1.08 g., 61%), which was isolated did not show any absorption in the 5.5–5.8 $\mu$ range either before or after sublimation, indicating the absence of the peri-dicarboxylic acid.[12] A sample recrystallized from ethanol melted at 285–290° (dec.); $\lambda^{KBr}$ 5.92, 7.78, 7.88, 8.98 $\mu$. It gave a positive halogen test (sodium fusion; Beilstein).

*Anal.* Calcd. for $C_{13}H_9BrO_2$: C, 56.3; H, 3.3; neut. equiv. 277. Found: C, 56.2; H, 3.2; neut. equiv. 279, 273.

*Reaction of 5,6-dichloroacenaphthene with magnesium.* 5,6-Dichloroacenaphthene, m.p. 168–170° was obtained in 40% yield by chlorination of acenaphthene with sulfuryl chloride by the procedure of Dashevskii and Petrenko.[13] Small portions of this dichloride (4.5 g. total) and *n*-butyl chloride (4.2 ml. total) in tetrahydrofuran were added alternately over a 90 minute period to 1.9 g. of magnesium turnings in tetrahydrofuran (20 ml. total at the end of the reaction) at the reflux temperature. After an additional nine hours of stirring the mixture was jetted onto Dry Ice. Hydrolysis and acidification afforded 2.8 g. (60%) of crude 6-chloro-5-acenaphthenecarboxylic acid; m.p. 185–195°; after three recrystallizations from ethanol it melted at 200–203°; neut. equiv. 225, 229. A pure sample, m.p. 222–224°, was obtained by chromatographing the crude material on silica gel (eluant, 95:5 benzene-ether).

*Anal.* Calcd. for $C_{13}H_9O_2Cl$: C, 67.1; H, 3.9. Found: C, 67.2; H, 3.7.

In another experiment, with 30% excess magnesium over that needed to react with dichloroacenaphthene (2 mole equivalents of magnesium) and butyl chloride, comparable results were obtained.

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(11) M. M. Dashevskii and A. P. Karishin, *Org. Chem. Ind.* (*U.S.S.R.*), **4**, 406 (1937).

(12) Like 1,8-naphthalic acid, 5,6-acenaphthenedicarboxylic acid dehydrates to the anhydride on heating [M. Freund and K. Fleischer, *Ann.*, **399**, 222 (1913)]. Acid anhydrides may be identified by the characteristic doublet in the 5.5–5.8 $\mu$ region in the spectrum; L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1954, p. 109.

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## A Novel Reaction Leading to (1,2-Diphenylethyl)diphenylphosphine

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A convenient method of preparation of lithium diphenylphosphide lies in the cleavage of readily available and easily handled triphenylphosphine by lithium metal in tetrahydrofuran.[2] The usefulness of this preparation depends upon the extent and nature of side reactions of the phenyllithium concurrently produced in the cleavage.

When an excess of benzyl chloride was added at reflux to a reaction solution of triphenylphosphine and lithium metal in tetrahydrofuran and the solution thus obtained treated with water and 3% hydrogen peroxide, a white solid shown to contain (1,2-diphenylethyl)diphenylphosphine oxide (I) in 55.0% yield and benzyldiphenylphosphine oxide[3] (II) in 25% yield was obtained.

Support for the structure assigned to compound I was obtained by fusion with sodium hydroxide to obtain diphenylphosphinic acid and a mixture of *trans*-stilbene and bibenzyl. The formation of bibenzyl can be explained in terms of the mechanism presented by Horner *et al.*[4] for the degradation of II. Stilbene production can be explained in terms of a beta elimination, while the *trans* nature of the product may be due to an "eclipsing effect" in the transition state if the elimination is assumed to proceed through an $E_2$ mechanism.

An alternate synthesis of I was accomplished by the reaction of phenyllithium and II to obtain ylid III which was then treated with benzyl bromide.[5] The product thus obtained was found to be identical to I in infrared spectrum of its chloroform solution and melting point. Mixed melting point determinations were undepressed.

$$(C_6H_5)_2P(O)(\underline{C}HC_6H_5) \qquad \text{(III)}$$

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(1) To whom inquiries regarding this article should be sent.

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

(3) A. E. Arbuzov and K. V. Nikonorov, *Zhur. Obshchei. Khim.*, **18**, 2008 (1948).

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

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When thiophosphoryl chloride was added to the reaction mixture of benzyl chloride with lithium diphenylphosphide and phenyllithium, a white solid consisting of (1,2-diphenylethyl)diphenylphosphine sulfide (IV) in about 60% yield and benzyl diphenylphosphine sulfide (V) in about 20% yield was obtained. Support for the structure assigned to IV comes from the fact that, upon treatment with 30% hydrogen peroxide in glacial acetic acid at 60° for thirty minutes, a quantitative yield of I was obtained. Rearrangement seems unlikely under these conditions.

This shows a common precursor to oxide and sulfide, namely: (1,2-diphenylethyl)diphenylphosphine (VI).

Incidental to this work was the discovery that the melting point of V is 162–163° and not 143–147° as reported by A. E. Arbuzov.[3] The assumption that our compound is benzyldiphenylphosphine sulfide is supported by its easy conversion with 3% hydrogen peroxide in dilute base to II.

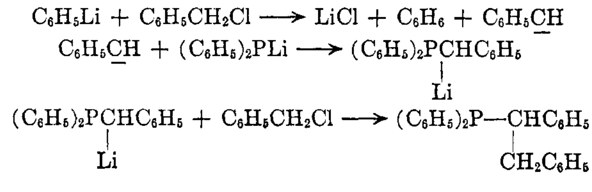
An obvious mode of formation of VI involves the attack of phenyllithium on the alpha hydrogen of the previously formed benzyldiphenylphosphine (VII) producing carbanion (VIII).

$$(C_6H_5)_2P\underline{C}H(C_6H_5) \qquad \text{(VIII)}$$

Nucleophilic displacement of chloride ion from benzyl chloride by VIII would lead to VI. This path requires that the rate of nucleophilic displacement by the diphenylphosphide ion on benzyl chloride and the rate at which phenyllithium reacts with benzyl chloride be such that some VII be produced in the presence of phenyllithium. It further assigns enough acidic character to the alpha hydrogen of VII for it to be abstracted by the phenyl carbanion.

When VII was treated with phenyllithium in refluxing tetrahydrofuran and benzyl chloride added, a small yield of I was obtained after oxidation with 3% hydrogen peroxide. This would indicate that the mechanism postulated above may account for the formation of VI.

Another possible mechanistic picture for the formation of VI can be put forward:



$$\begin{gathered}
C_6H_5Li + C_6H_5CH_2Cl \longrightarrow LiCl + C_6H_6 + C_6H_5\underline{C}H \\
C_6H_5\underline{C}H + (C_6H_5)_2PLi \longrightarrow (C_6H_5)_2P\underset{\displaystyle Li}{\underset{|}{C}}HC_6H_5 \\
(C_6H_5)_2P\underset{\displaystyle Li}{\underset{|}{C}}HC_6H_5 + C_6H_5CH_2Cl \longrightarrow (C_6H_5)_2P{-}\underset{\displaystyle CH_2C_6H_5}{\underset{|}{C}}HC_6H_5
\end{gathered}$$

This mechanism implies that although phenyl carbanion is a stronger base than diphenylphosphide ion,[6] the latter is a better nucleophile.

The possibility of addition of the phosphide ion to *trans*-stilbene which might be formed from the reaction of phenyllithium and benzyl chloride is ruled out by the observation that attempted reaction of these compounds has resulted in quantitative recovery of *trans*-stilbene and diphenylphosphinic acid (from the initially produced diphenylphosphine by subsequent oxidation).

The possibility, that what is occurring is a Wittig rearrangement of dibenzyldiphenyl phosphonium chloride, is considered unlikely since even when the lithium diphenylphosphide solution is added to an excess of benzyl bromide, dibenzyldiphenyl phosphonium bromide is precipitated out of solution only after several hours of refluxing. Since the bromide ion is a better leaving group than chloride ion it seems unlikely that any dibenzyldiphenyl phosphonium chloride is formed under the conditions used.

Further work is being carried out on the mechanistic path and the synthetic applications of this reaction.

## EXPERIMENTAL

*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. After being triturated with ether and dried, it was triturated with 400 ml. of 95% ethanol producing 21.0 g. (55.0% and m.p. 211–214°) of solid. Repeated recrystallization from ethanol produced a solid melting at 221–222° and exhibiting an infrared spectrum typical of a tertiary phosphine oxide.

*Anal.* Calcd. for $C_{26}H_{23}PO$: C, 81.68; H, 6.02; P, 8.12; mol. wt., 382. Found: C, 81.76; H, 6.01; P, 8.35; mol. wt., 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, and 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

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[6] This is shown by the fact that phenyllithium reacts with diphenylphosphine to give benzene and lithium diphenylphosphide.

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. Trituration 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 *tert*-butyl chloride, and 7.6 g. (0.06 mole) of benzyl chloride in 300 ml. of tetrahydrofuran.[7] 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 *tert*-butyl chloride in 50 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 identified by 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 benzyl diphenylphosphine 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 benzyl diphenylphosphine 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. of 30% 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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[7] Described in a forthcoming paper.

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## Preparation of 2,1,3-Benzothiadiazoles Using Dimethylformamide-Sulfur Dioxide Reagent[1]

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2,1,3-Benzothiadiazoles have been prepared by treatment of *o*-phenylenediamines with thionyl chloride,[2] *N*-sulfinylaniline,[3] and with sulfurous acid under pressure.[4]

In the latter method Hinsberg reported that *o*-phenylenediamine could be converted to 2,1,3-benzothiadiazole by heating with sulfurous acid at 180° for five to six hours and that there was no reaction under milder conditions. We have investigated the use of solutions of sulfur dioxide in dimethylformamide in place of sulfurous acid and have found this to be a convenient method for preparing 2,1,3-benzothiadiazole, 5-methyl- and 5-chloro-2,1,3-benzothiadiazole, and 2′,3′-naphtho-2,1,3-thiadiazole in yields of 15–40%. While the yields are not high, the method has the convenience of being carried out in ordinary, open apparatus at temperatures of 70–115° and of being easy to work up.

From 3,3′-diaminobenzidine no bis-2,1,3-benzothiadiazole was obtained but 5-(3′,4′-diaminophenyl)-2,1,3-benzothiadiazole was isolated in 2.5% yield. This compound is of particular interest since it represents an important type of starting material for preparing certain heterocyclic analogs of steroids.

### EXPERIMENTAL[5]

*2,1,3-Benzothiadiazoles.* To 70 ml. of a saturated solution of sulfur dioxide in dry dimethylformamide was added 0.03

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[1] This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF 49(638)-49. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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[3] A. M. Khaletskiĭ, V. G. Pesin, and Chi-Chun Chao, *Doklady Akad. Nauk S.S.S.R.*, **106**, 88 (1956), *Chem. Abstr.*, **50**, 13885c (1956), V. G. Pesin, A. M. Khaletskiĭ, and Chi-Chun Chao, *Zhur. Obshcheĭ Khim.*, **27**, 1570–5 (1957), *Chem. Abstr.*, **52**, 3790i (1958).

[4] O. Hinsberg, *Ber.*, **22**, 2895 (1889).

[5] Melting points were determined with the Fisher-Johns apparatus and are corrected.