Anal. Calcd. for $C_{10}H_{13}NS$: C, 66.98; H, 7.31. Found: C, 66.98; H, 7.47.

Acknowledgment.—The authors are indebted to Dr. B. L. Appleton for pointing out the Taguchi method of resolution, to Dr. J. A. Montgomery and Dr. Y. F. Shealy for helpful discussions, and to Dr. W. J. Barrett and associates of the analytical section of this Institute for microanalyses and specific rotations.

The Cleavage of Methylenebis(diphenylphosphine) by Phenyl Azide

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In connection with some work on organophosphorus systems containing nitrogen, we have had occasion to study the reaction of polymethylenebis(diphenylphosphines) with phenyl azide. The isolation of *p*-phenylenebis(diphenylphosphinimine) from the reaction of 1,4-bis(diphenylphosphino)benzene with phenyl azide was reported recently.[2]

It was found that an ether–tetrahydrofuran solution of phenyl azide and 1,2-ethylenebis(diphenylphosphine) in 2:1 mole ratio evolved nitrogen to give a product which exhibited an elemental composition, molecular weight, infrared spectrum, and n.m.r. spectrum expected for 1,2-ethylenebis(diphenylphosphinimine) (I, eq. 1).

$$2PhN_3 + (Ph_2PCH_2)_2 \longrightarrow [Ph_2P(NPh)CH_2]_2\ (I) \qquad (1)$$

Hydrolysis of I produced 1,2-ethylenebis(diphenylphosphine) dioxide as expected (eq. 2).

$$[Ph_2P(NPh)CH_2]_2 + 2H_2O \longrightarrow [Ph_2P(O)CH_2]_2 + 2PhNH_2 \qquad (2)$$

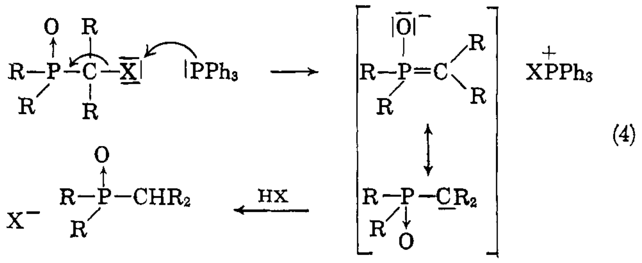
However, a 2:1 mole ratio of phenyl azide to methylenebis(diphenylphosphine) in ether did not lead to the isolation of a diphosphinimine. After a mildly exothermic slow gas evolution there occurred deposition of crystals of diphenylphosphinic acid anilide in 20.6% yield. The remaining solution gave more anilide when evaporated so that 78% was isolated. Column chromatography of the remaining sirup resulted in the isolation of methyldiphenylphosphine and its oxide in 64% yield as demonstrated by comparison with material produced from the reaction of lithium diphenylphosphide and methylchloride. Apparently the diphosphine was cleaved by phenyl azide (eq. 3).

$$(Ph_2P)_2CH_2 + PhN_3 \longrightarrow X \xrightarrow[H_2O]{air} Ph_2P(O)NHPh + Ph_2P(O)CH_3 \qquad (3)$$

The reaction was carried out under an atmosphere of prepurified nitrogen; therefore, the origin of the oxygen in the diphenylphosphinic acid anilide crystallizing out of the reaction solution poses a problem. Molecular oxygen and water were most probably present in very small amounts in the reagents and nitrogen used. Exposure to air after deposition of crystals and gas evolution had ceased did not cause any further gas evolution or precipitation. The significant fact, however, is that under similar reaction conditions essentially no cleavage of the ethylenebis compound occurred.

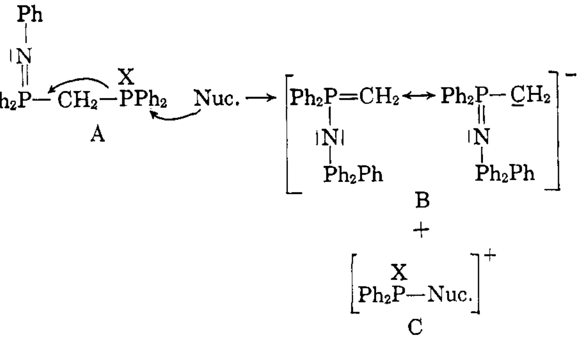
Although only 1 mole of phenyl azide appeared in the isolated products, an excess of azide helped in gaining cleavage. An equimolar solution of methylenebis(diphenylphosphine) and phenyl azide in ether evolved gas, but attempts at isolation of products resulted in the isolation of methylenebis(diphenylphosphine) dioxide (57%) and a small amount of diphenylphosphinic anilide. The presence of methyldiphenylphosphine oxide, determined by gas–liquid partition chromatography, presented further evidence that some cleavage of the diphosphine had occurred.

Horner, *et al.*, have shown that halogen atoms α to a phosphorus carrying a positive charge are not readily displaced by a nucleophile but can be replaced by a proton in the presence of triphenylphosphine.[3] Nucleophilic attack on the partially positive α-halogen with the concurrent displacement of a resonance stabilized carbanion can be proposed as an explanation (eq. 4).



(4)

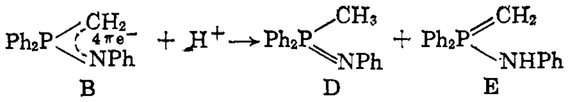
Methyldiphenylphosphine oxides are known to form anions in the presence of strong bases.[4,5] It is therefore reasonable to expect the monoimine or diimine of methylenebis(diphenylphosphine) (A) to cleave in the presence of a nucleophile (Nuc.) to give a resonance stabilized anion B (eq. 5).



(5)

X = NPh or a pair of electrons

The reaction of anion B with water (below) would result in a mixture of the N-phenylimine of methyldiphenylphosphine (D) and the tautomeric phosphinemethylene (E) (eq. 6). Further hydrolysis would be expected to lead to methyldiphenylphosphine oxide and aniline (eq. 7).



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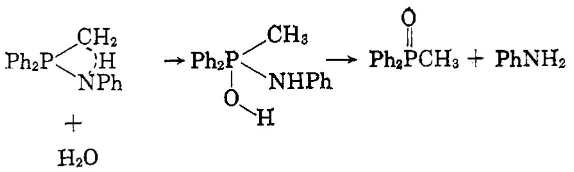
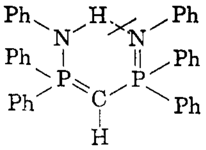

(7)

If the cleavage is due to instability of the diimine to water, cation C would be protonated diphenylphosphinic anilide. One might expect the methylenebis-(diphenylphosphinimine) to be more stable than the corresponding ethylenebis compound due to the possibility of intramolecular hydrogen bonding (structure 1).


Structure 1

Staudinger reported in 1921 that phenyl azide reacted with neither phosphorus trichloride nor phenylphosphonous dichloride.[6] In view of this fact it does not seem likely that phenyl azide should exhibit sufficient nucleophilicity to displace anion B from a tertiary phosphine. Phenyl azide can be seen to behave as an electrophile toward tertiary phosphines from the order of reactivity as reported by Staudinger: triethylphosphine > diethylphenylphosphine > triphenylphosphine.[7]

Spontaneous decomposition of monoimine A to give the products eventually seems unlikely. Support for this point of view is provided by the lesser extent of cleavage of the diphosphine in the reaction of equimolar amounts of methylenebis(diphenylphosphine) and phenyl azide.

Reaction of tertiary phosphines with phenyl azide have been reported to lead to phosphazides (in which the terminal nitrogen is bonded to the phosphorus) which then lose nitrogen producing phosphinimines[6,7] (eq. 8).

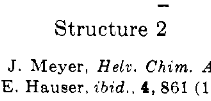
$$R_3P + PhN_3 \longrightarrow R_3P{=}\bar{N}{-}\bar{N}{=}\bar{N}{-}Ph \longrightarrow N_2\uparrow + R_3P = \bar{N}{-}Ph \quad (8)$$

Reaction of monimine A with another mole of phenyl azide would be expected to lead to a phosphinimine phosphazide which could lose nitrogen producing a diphosphinimine (eq. 9).

$$\underset{A}{Ph_2P(NPh)CH_2PPh_2} + PhN_3 \longrightarrow Ph_2P(NPh)CH_2P(N_3Ph)Ph_2 \longrightarrow [Ph_2P(NPh)]_2CH_2 \quad (9)$$

The possibility of intramolecular reaction of the phosphinimine phosphazide exists when the number of bridging methylene groups is such as to allow a favorable five- or six-membered cyclical intermediate (structure 2).

Decomposition of such an intermediate might lead to cleavage of a phosphorus to carbon bond, loss of nitrogen, and, after hydrolysis, to methyldiphenylphosphine oxide and diphenylphosphinic acid anilide. Although ethylenebis(diphenylphosphine) might form a seven-membered intermediate similar to that postulated in structure 2, cleavage to form ethyldiphenylphosphine is not favored by the possibility of 3d-2p overlap in the ejected fragment. Olefinic elimination apparently involves a higher energy of activation. The reported isolation of a diphosphinimine from the reaction of *p*-phenylenebis(diphenylphosphine) and phenylazide is not surprising, since no cyclic intermediate is possible.[2]


Structure 2

The mild conditions under which this cleavage occurs coupled with the general ease of preparation of substituted methylenebis(diphenylphosphine) make the reaction potentially useful in the synthesis of substituted tertiary phosphine oxides.

Experimental

Methylenebis(diphenylphosphine).—A solution of dichloromethane (8.5 g., 0.05 mole) in 50 ml. of tetrahydrofuran was added dropwise to a rapidly stirred, refluxing tetrahydrofuran solution of lithium diphenylphosphide prepared from 0.1 mole of triphenylphosphine.[8] The reaction mass was then refluxed in a nitrogen atmosphere for 0.5 hr. and cooled to room temperature; it was then added to 1000 ml. of water with stirring. The solid thus obtained was filtered off, water washed, and recrystallized from ethanol and water. After drying, the material weighed 17.3 g. (90% yield based on starting triphenylphosphine) and had m.p. 120–121°, lit. m.p. 122,[9] 120–121.5.[10]

The infrared spectrum was that expected for methylenebis-(diphenylphosphine). The Varian A-60 n.m.r. spectrum of a deuteriochloroform solution of this material exhibited a triplet at $\delta = 2.8$ p.p.m. and a set of aromatic peaks centering at $\delta = 7.25$ p.p.m. in a ratio of 1:10. The coupling constant was $J_{p\text{-CH}} = 1.5$ c.p.s. An internal standard of tetramethylsilane was used.

Oxidation of Methylenebis(diphenylphosphine).—A solution of the above compound in acetone was treated with 3% hydrogen peroxide until it became cloudy and then allowed to stand. Concentration of this acetone solution by slow evaporation at room temperature gave crystals which were filtered off and recrystallized from ethanol and water. This material exhibited phosphoryl peaks in the infrared and melted at 180–181°, lit.[11,12] m.p. 180–182°.

The Varian A-60 n.m.r. spectrum of a deuteriochloroform solution of this material showed a triplet centered at $\delta = 3.57$ p.p.m. with a coupling constant $J_{p\text{-CH}} = 15$ c.p.s. and phenyl hydrogens centered at 7.42 and 7.8 p.p.m. in the ratio of 1:10. An internal standard of tetramethylsilane was used.

Ethylenebis(diphenylphosphine).—Substitution of 1,2-dichloroethane for dichloromethane in the procedure described above led to ethylenebis(diphenylphosphine) in 80% yield based on starting triphenylphosphine. The material exhibited a melting point of 140–141°, lit.[10,13] m.p. 143–144°, and an infrared spectrum that fit the structure assigned. Since Issleib and Muller[9] report m.p. 159–161°, it was felt that other supporting evidence for the assigned structure was needed.

Anal. Calcd. for $C_{26}H_{24}P_2$: C, 78.4; H, 6.03; P, 15.55. Found: C, 79.9; H, 6.00; P, 15.15.

Determination of the Varian A-60 n.m.r. spectrum of a deuteriochloroform solution of this material revealed a case of "virtual coupling" in that a triplet at $\delta = 2.12$ p.p.m. and the phenyl complex centering at 7.25 p.p.m. in the ratio of 1:5 were observed. The coupling constant was $J_{p\text{-CH}} = 4.2$ c.p.s. All shifts are relative to an internal standard of tetramethylsilane.

Ethylenebis(diphenylphosphine) Dioxide.—The acetone–3% hydrogen peroxide oxidation of the above compound gave a new material exhibiting phosphoryl peaks in the infrared and having

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a melting point of 267–268.5°, lit. m.p. 276–278°,[14] 273–275°.[15] Issleib and Muller[9] reported m.p. 252–254°. Thus it was felt essential to obtain further support for the assigned structure.

Anal. Calcd. for $C_{26}H_{24}O_2P_2$: C, 72.56; H, 5.58; P, 14.04. Found: C, 72.64; H, 5.58; P, 13.52.

The n.m.r. Varian A-60 spectrum of a deuteriochloroform solution of this material showed the methylene hydrogens as a doublet at δ = 2.6 p.p.m. with a $J_{p\text{-CH}}$ of 2.5 c.p.s. and phenyl hydrogens centered at 7.5 and 7.8 p.p.m. in the ratio of 1:5. All shifts are relative to an internal standard of tetramethylsilane.

Reaction of Ethylenebis(diphenylphosphine) with Phenyl Azide.—A slurry of 4.0 g. (0.01 mole) of ethylenebis(diphenylphosphine) in 175 ml. of anhydrous ether was brought to complete solution with 75 ml. of anhydrous tetrahydrofuran, then placed under a nitrogen atmosphere. Dropwise addition of 2.5 g. (0.021 mole) of phenyl azide in 23 ml. of anhydrous ether to the stirred reaction solution produced a slight exothermic reaction. Immediately after completion of the addition, the reaction mass was colored an opaque yellow. In a week, 3.15 g. of cubic crystals, m.p. 194–198°, separated. The filtrate was stripped of solvent on a steam bath just short of dryness, and an air stream was directed onto the remaining sirup for 15 hr. The residue was triturated with ether–pentane (50:50) which yielded 1.2 g. of a solid, m.p. 169–187°. Repeated recrystallization from anhydrous benzene gave an analytically pure sample, m.p. 196–198°.

Anal. Calcd. for $C_{38}H_{34}N_2P_2$: C, 78.7; H, 5.87; N, 4.83; P, 10.69. Found: C, 78.21; H, 5.96; N, 4.83; P, 10.55.

An over-all yield of 75% was therefore obtained. The infrared spectrum of a chloroform solution of the material showed absorption at 3.15 (w), 6.21 (s), 6.90 (m), 7.46 (s), 7.55 (s), 8.50 (m), 8.95 (s) and 9.53 μ (m). The Varian A-60 n.m.r. spectrum of a deuteriochloroform solution of this material showed a split peak at δ = 2.7 p.p.m. and a complex set of peaks between 6.7 and 7.9 p.p.m. The relative areas were 1:7.5, respectively. All shifts are relative to an internal standard of tetramethylsilane.

The residual oil from the work-up was shown to contain ethyldiphenylphosphine oxide by comparison of the retention time (on high temperature gas chromatography) with that of an authentic sample made from lithium diphenylphosphide and ethylbromide.[16] Comparison of proton n.m.r. spectra also showed them to be identical. This compound exhibits a 1,3-coupling of the P^{31} and the methyl hydrogens in that the latter show up as a quintuplet centered at δ = 1.18 p.p.m. The methylene hydrogens show up as a complex set centered at δ = 2.31 p.p.m. while the phenyl hydrogens appear as a complex centered at about 7.65 p.p.m. Integrated areas are in the expected ratio.

The Acid Hydrolysis of Ethylenebis(phenyliminodiphenylphosphine.—A purified sample of ethylenebis(phenyliminodiphenylphosphine), m.p. 196–198° (0.52 g., 0.897 mmole), was combined with 15 ml. of 4 *N* hydrochloric acid and enough 95% ethanol to just dissolve the solid at 75°. The temperature was maintained at 75° for 40 hr. and then cooled.

Fine white crystals (0.22 g.) of ethylenebis(diphenylphosphine) dioxide, m.p. 268–269°, crystallized from the reaction. Mixture melting point with an authentic sample prepared by direct oxidation of ethylenebis(diphenylphosphine) with 3% hydrogen peroxide showed no depression. Evaporation of the ethanol solvent of the reaction mixture on a steam bath gave a second crop of solid (0.06 g.), m.p. 263–268°, bringing the total yield to 73%. The remaining aqueous solution was evaporated almost to dryness on a steam bath with the aid of an air stream. Residual water was removed azeotropically with benzene. The tan powder which remained did not melt below 270°. A small sample of this material was sublimed at atmospheric pressure and 200° to give crystals of aniline hydrochloride, m.p. 197–199°. Mixture melting point with an authentic sample produced no depression. The bulk of the powder was dissolved in 15 ml. of water (a small amount of insoluble material was filtered and discarded), made basic with concentrated sodium hydroxide solution, and ether extracted. After drying the combined ether extracts over calcium oxide, the solvent was evaporated leaving 0.087 g. (52%) of a liquid whose infrared spectrum was identical with that of aniline.

The Reaction of Methylenebis(diphenylphosphine) with 2 Moles of Phenyl Azide.—The diphosphine (2.98 g., 0.00776 mole) was dissolved in 250 ml. of anhydrous ether and to this was added 1.85 g. (0.0155 mole) of phenylazide in 30 ml. of anhydrous ether under a nitrogen atmosphere. A mildly exothermic reaction ensued, accompanied by slow gas evolution. The reaction solution was left standing for a week at room temperature. Large crystals (0.47 g.) slowly formed. The material was identified by its melting point (236–237°), infrared spectrum comparison, and mixture melting point with an authentic sample of diphenylphosphinic acid anilide.[17] The ethereal reaction solution was evaporated leaving a sirup from which 1.3 g. more of anilide, m.p. 235–237°, was obtained by ether trituration. The total yield of anilide isolated, therefore, was 78%. The triturate was stripped of solvent leaving 2.1 g. of a sirup which was chromatographed on a 1.5 × 37 cm. column of silica gel. Elution with *n*-hexane, benzene, and chloroform did not move the bands down the column. Elution with 750 ml. of chloroform saturated with water separated brown oils. When 100 ml. of chloroform–ethanol (10:1) was used as the eluent, 1.61 g. of a semicrystalline material was obtained. Recrystallization from cyclohexane yielded 1.07 g. of solid, m.p. 97–104°. Repeated recrystallization raised the melting point to 108–109°. The material showed a retention time identical with that of methyldiphenylphosphine oxide, lit.[12] m.p. 108–109°, synthesized from lithium diphenylphosphide and methyl chloride, on gas–liquid partition chromatographic analysis on silicone at 240°.[16] The Varian A-60 n.m.r. spectrum of a deuteriochloroform or carbon tetrachloride solution of this solid showed a complex signal centered around δ = 7.60 p.p.m. corresponding to the aromatic protons and a doublet centered at 1.9 p.p.m. (J = 14 c.p.s., relative to an internal tetramethylsilane standard) which could be assigned to the methyl protons. Therefore, it can be concluded that methyldiphenylphosphine oxide was produced in about 64% yield.

The Equimolecular Reaction of Methylenebis(diphenylphosphine) and Phenyl Azide.—A solution of 1.96 g. (0.00511 mole) of methylenebis(diphenylphosphine) in 250 ml. of anhydrous ether was treated with 0.61 g. (0.00512 mole) of phenyl azide in 15 ml. of anhydrous ether under nitrogen. Stirring was continued for 1 hr. after completion of the addition. The reaction mass was allowed to remain under nitrogen for 1 week. A small amount of solid material that had formed was filtered from the reaction solution and discarded. After evaporation, the ethereal solution yielded a sirup from which 0.50 g. of solid was obtained by trituration with ether–pentane (50:50). After the triturate had been stripped of solvent and allowed to stand 2 weeks, 0.55 g. of solid, m.p. 174–178°, was obtained by a similar trituration. The infrared spectra of both crops were identical with methylenebis(diphenylphosphine) dioxide, m.p. 184–185°, produced by a hydrogen peroxide oxidation of the parent biphosphine. The residual oil from the second triturate was chromatographed on a 12 mm. × 21 cm. column of silica gel eluted first with *n*-hexane and then with mixtures of *n*-hexane and benzene. The resulting fractions when combined gave 0.16 g. of methylenebis(diphenylphosphine) after one recrystallization from benzene–hexane; a total yield was 57%. Stripping the column with methanol–benzene (2:3) gave an oil which was shown to contain methyldiphenylphosphine oxide and benzene-phosphinic acid anilide by comparison of retention times with authentic samples using high temperature gas–liquid partition chromatography.[16] In addition, 0.05 g. of the anilide was isolated from the oil by recrystallization from methanol–water (m.p. 234–235°).

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