enzyme on the phosphorus atom. In view of these findings, the α-isomer which shows the higher degree of inhibition and the higher entropy of activation is assigned the structure I and the β-isomer structure II. The conclusions expressed here are in agreement with results obtained from NMR spectrometric data.

RIVERSIDE, CALIF.

[A CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Phosphorus-Containing Monomers. I. The Synthesis of Vinyl Phosphines, Oxides, Sulfides, and Phosphonium Compounds

ROBERT RABINOWITZ AND JOSEPH PELLON

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Synthetic routes to a series of new vinyl phosphorus, nonester compounds are presented. Specifically the preparations of diphenylvinylphosphine, diphenylvinylphosphine oxide, diphenylvinylphosphine sulfide, diphenylmethylvinylphosphonium iodide, and diisobutylvinylphosphine oxide are described. The paths are general and suggest many analogous compounds. Preliminary polymerization work indicates that free radical polymerization of these monomers is difficult. They enter into copolymers; however, in a much smaller ratio than in the feed.

Very little information exists in the literature concerning vinyl phosphines and their derivatives.[1–4a] Two recent publications by Kabachnik and co-workers[5,6] describe convenient routes to a series of vinyl phosphines and vinyl phosphine oxides. In none of the above articles was any reference to polymerization or copolymerization uncovered. Furthermore, a search of the literature revealed no mention of vinyl phosphine sulfides.

It was the object of this work to prepare representative vinyl phosphines, oxides, sulfides, and phosphonium compounds in order to compare them as to polymerization reactivity with existing vinyl monomers.

Diisobutylvinylphosphine oxide and diphenylvinylphosphine oxide were synthesized by a combination of the following reactions:

$$R_2PCl + HOC_2H_5 \xrightarrow{(C_2H_5)_3N} R_2POC_2H_5 \quad (1)$$

$$R_2POC_2H_5 + BrCH_2CH_2Br \longrightarrow R_2P(O)CH_2CH_2Br \quad (2)$$

$$R_2P(O)CH_2CH_2Br + (C_2H_5)_3N \longrightarrow (C_2H_5)_3N{\cdot}HBr + R_2P(O)CH{=}CH_2 \quad (3)$$

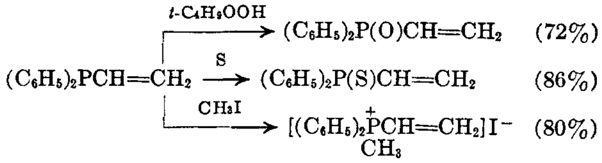
Yields, without any attempts at optimizing, were 62% in the diphenyl case and 21% for the dibutyl, both based on R_2PCl. In the diphenyl synthesis, some 1,2-ethanebis(diphenylphosphine oxide) was isolated. This is the product of the reaction of ethyl diphenylphosphinite with 2-bromoethyldiphenylphosphine oxide and can be kept at a minimum by use of a large excess of 1,2-dibromoethane.

The reaction of vinylmagnesium chloride with diphenylchlorophosphine was used to prepare diphenylvinylphosphine:

$$CH_2{=}CHMgCl + (C_6H_5)_2PCl \longrightarrow (C_6H_5)_2PCH{=}CH_2$$

In several experiments the yields varied from 15–40%. A variable amount of 1,2-ethanebis(diphenylphosphine oxide) was obtained from the pot residues after the distillation.

The diphenylvinylphosphine was used to prepare the corresponding sulfide and methylphosphonium iodide. It was also oxidized to the phosphine oxide, and this product was identical to the material prepared by dehydrobrominating 2-bromoethyldiphenylphosphine oxide.



$$(C_6H_5)_2PCH{=}CH_2 \xrightarrow{t\text{-}C_4H_9OOH} (C_6H_5)_2P(O)CH{=}CH_2 \quad (72\%)$$

$$(C_6H_5)_2PCH{=}CH_2 \xrightarrow{S} (C_6H_5)_2P(S)CH{=}CH_2 \quad (86\%)$$

$$(C_6H_5)_2PCH{=}CH_2 \xrightarrow{CH_3I} [(C_6H_5)_2\overset{+}{\underset{CH_3}{P}}CH{=}CH_2]I^- \quad (80\%)$$

The literature reveals that polymerization studies on vinylphosphorus compounds have been limited to esters of phosphorus acids. These compounds have a rather low tendency to homo- and copolymerize under free-radical conditions.[7–12]

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Preliminary polymerization studies indicate that the monomers described above are also difficult to homopolymerize under free-radical conditions. Copolymerization was chosen as a means to study further polymerization characteristics. Although the details will be reported at another time, it is sufficient to note that all of these monomers[13] enter into copolymers. However, the percentage of phosphorus in the polymer is always much lower than in the feed, thus following the trend observed with other vinylphosphorus monomers.[7–12]

EXPERIMENTAL

Preparation of diphenylvinylphosphine oxide. a. *Reaction of diphenylchlorophosphine with ethanol.* To a solution containing 27.4 g. (0.60 mole) of absolute ethanol, 54.5 g. (0.53 mole) of triethylamine, and 300 ml. of benzene in a 1-l., three necked flask fitted with a stirrer, thermometer, nitrogen inlet and outlet, and equilizing dropping funnel was slowly added 109.5 g. (0.495 mole) of diphenylchlorophosphine (distilled from a sample supplied by Victor Chemicals, b.p. 151–153° at 4.8 mm.). A white solid formed immediately The temperature was maintained between 20–30° with the aid of an ice bath. When the addition was half-complete an additional 100 ml. of benzene was added. Although the addition was completed in 15 min., the mixture was stirred for an additional 2 hr. and filtered. The triethylamine hydrobromide was washed with 300 ml. of benzene and air dried; the theoretical amount was recovered, 68.7 g. (0.50 mole). The combined filtrates were reduced in volume and fractionally distilled through a 1-ft., vacuum-jacketed, silvered Vigreux column. A total of 98.9 g. (0.43 mole, 87%) of distillate, ethyl diphenylphosphinite, was obtained, b.p. 121° (0.7 mm.).

Anal. Calcd. for $C_{14}H_{15}OP$: C, 73.0; H, 6.52; P, 13.47. Found: C, 73.21; H, 6.63; P, 13.33.

b. *Reaction of 1,2-dibromoethane with ethyl diphenylphosphinite.* Eastman Kodak White Label, distilled (b.p. 131–132°) 1,2-dibromoethane, 1440 g. (7.63 moles), was brought to reflux in a three necked, 1-l. flask fitted with a thermometer, dropping funnel, and 18-in. silvered, glass helix-packed column. A full reflux partial take-off head was attached to the column. A total of 89.95 g. (0.374 mole) of ethyl diphenylphosphinite was dropped into the refluxing 1,2-dibromoethane during a 30-min. period. During the first 2 hr. of refluxing, 36.7 g. (90%) of ethyl bromide distilled. Practically all the excess 1,2-dibromoethane was removed by distillation at reduced pressure. The final traces were separated by distilling the reaction mixture after 90 ml. of cumene was added as a chaser.

c. *Dehydrobromination of 2-bromoethyldiphenylphosphine oxide.* This resultant solution which contained cumene, 2-bromoethyldiphenylphosphine oxide, and perhaps some diphenylvinylphosphine oxide (from thermal dehydrobromination) was diluted with 400 ml. of toluene and 42 g. (0.415 mole) of triethylamine was slowly added. A small initial heat evolution was noted resulting in a cloudy solution. Further addition produced no heat.[14] When this solution was refluxed, a large amount of salt formed. An additional 5 g. of triethylamine was added to insure complete reaction. After 1 hr., 25 ml. of the mixture was distilled, b.p. 89–106°, indicating excess triethylamine had been present. The mixture was cooled and transferred to a 1-l. separatory funnel. When 200 ml. of water was added to the reaction flask to wash out the crystalline triethylamine hydrobromide, it was noted that a large amount of white insoluble solid was present.[15] This suspension was filtered. The filtrate was dried over sodium sulfate, reduced in volume to 250 ml., and diluted with 100 ml. of heptane. Upon cooling, 21.7 g. of crystalline solid was recovered, m.p. 110–140°. By reducing the volume of the mother liquor, another 2.4 g. was obtained. Five grams was recrystallized twice from boiling heptane (60 ml.) containing enough toluene to dissolve almost but not all the solid. A recovery of 3.8 g. of crystalline white solid was obtained, m.p. 115–117°, that was later identified as diphenylvinylphosphine oxide. The solid obtained from the suction filtration was extracted first with a boiling mixture of 250 ml. of heptane and 100 ml. of toluene, and then with 150 ml. of boiling toluene. From the former extract was obtained 11.6 g. of diphenylvinylphosphine oxide, m.p. 114–118°. From the latter extract, upon cooling to 0°, 14.9 g. of material was obtained, m.p. 110–182°. The mother liquor of this material yielded 4.34 g. of diphenylvinylphosphine oxide after standing in the cold for 3 days. This final mother liquor was reduced in volume to 50 ml. and was diluted with 150 ml. of heptane. Another 12.3 g. of diphenylvinylphosphine oxide, m.p. 115–117°, crystallized from this solution. A 5.0-g. sample of the fraction melting 110–182° was dissolved in boiling toluene. Upon cooling to room temperature a crystalline material separated and was collected, 1.1 g., m.p. 255–263°. Recrystallization from toluene gave 0.7 g., m.p. 262.5–263.5°. This was identified as 1,2-ethanebis(diphenylphosphine oxide) by comparison of its infrared spectrum to that of a known sample available at this laboratory.

Anal. Calcd. for $C_{26}H_{24}P_2O_2$: C, 76.6; H, 5.59; P, 14.4; mol. wt., 430. Found: C, 76.6; H, 5.47; P, 13.9; mol. wt., 401.

A 4.0-g. sample of diphenylvinylphosphine oxide was recrystallized from a mixture of 70 ml. of heptane and 20 ml. of toluene. The recovered solid, 3.8 g., m.p. 116.5–118°, was analyzed.

Anal. Calcd. for $C_{14}H_{13}OP$: C, 73.9; H, 5.70; P, 13.6; Iodine no., 111.5. Found: C, 73.6; H, 6.20; P, 13.8; Iodine no., 109.5.

A total of 67.25 g. of crystalline material was recovered during this work-up. Approximately 60.8 g. of it was identified as diphenylvinylphosphine oxide, or a 71.5% yield based on ethyl diphenylphosphinite. This corresponds to an over-all yield of 62% based on diphenylchlorophosphine. At least 3.3 g. of the remaining 6.50 g. was 1,2-ethanebis-(diphenylphosphine oxide).

It must be emphasized that, in spite of the lack of knowledge of the solubility properties of the products, a 62% over-all yield was achieved. With this information available much of the labor described above can be eliminated, and an improved yield can be expected.

Preparation of diisobutylvinylphosphine oxide. a. *Chlorination of diisobutylphosphine.*[16] Into a solution of 116 g. (0.78 mole) of diisobutylphosphine in 300 ml. of dichloromethane maintained at −30° was bubbled 75 g. (0.76 mole) of phosgene. The phosgene had been passed through an air trap, sulfuric acid trap, and finally a mercury trap prior to entering the reaction mixture. A positive nitrogen pressure was maintained at all times over this magnetically stirred solution. An ice condenser was also attached to the three necked flask. When about 20% of the phosgene was added, a precipitate formed. An additional 200 ml. of dichloromethane was added, and no further precipitation was noted. When the addition was complete, the reaction mixture was allowed to warm to room temperature. A stream of nitrogen was bub-

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(13) No polymerization work on diphenylmethylvinylphosphonium iodide has been carried out as yet.

(14) The initial heat may have been due to dissolved hydrobromic acid in the solution.

(15) This white solid was later identified as mainly the desired product, diphenylvinylphosphine oxide. Since this is soluble in warm toluene, it would have been preferable and much simpler to filter the hot solution, thus removing only the triethylamine hydrobromide.

(16) The diisobutylphosphine was prepared in this laboratory by free-radical addition of isobutylene to phosphine.

bled through while the system was warmed slightly, thus removing all the dichloromethane. Distillation of the reaction mixture gave 104 g. (76%) of diisobutylchlorophosphine, b.p. 63–65° (3.5 mm.).

b. *Reaction of diisobutylchlorophosphine with ethanol.* A procedure almost identical with that described above for the reaction of diphenylchlorophosphine with ethanol was used. The components were 27.7 g. (0.60 mole) of absolute ethanol, 60.5 g. (0.60 mole) of triethylamine, 97.5 g. (0.54 mole) of diisobutylchlorophosphine, and 400 ml. of benzene. Filtration of the reaction mixture gave 71.3 g. of triethylamine hydrochloride (96%). The benzene was removed from the filtrate under reduced pressure, and the residue, 94.8 g., was distilled through a 1-ft., vacuum-jacketed, silvered Vigreux column. The main fraction, after a forecut of 5 g., had a b.p. of 103° (39 mm.). The third and final fraction, 20 g., b.p. 103° (39 mm.) to 98° (2 mm.), was clearly a mixture. A 6-g. pot residue was obtained, which solidified quickly on standing.

c. *Reaction of 1,2-dibromoethane with ethyl diisobutylphosphinite.* The details of this step are the same as the corresponding reaction described above between 1,2-dibromoethane and ethyl diphenylphosphinite. The entire main cut of the distillation of ethyl diisobutylphosphinite was slowly added to 1300 g. (6.95 moles) of refluxing 1,2-dibromoethane. In 3 hr., a total of 20.9 g. of ethyl bromide (0.192 mole) had distilled, and no more was forming. After 2 hr. of further refluxing, the majority of the excess 1,2-dibromoethane was removed by distillation at atmospheric pressure, and the final traces eliminated by using cumene as a chaser at 100 mm. The final residue, 2-bromoethyldiisobutylphosphine oxide, was brown in color and solidified on standing.

d. *Dehydrobromination of 2-bromoethyldiisobutylphosphine oxide.* The above residue was diluted with 500 ml. of toluene. Although it did not dissolve, 60.0 g. (0.60 mole) of triethylamine was added (no heat evolution noted), and the mixture brought to reflux. Salt formation was apparent, and after 4 hr. the hot mixture was filtered. The salt obtained was water soluble and weighed 26.6 g. (0.146 mole). The volume of the filtrate was reduced to 75 ml., and this was distilled through a 1-ft., vacuum-jacketed, silvered Vigreux column. A total of 21 g. of diisobutylvinylphosphine oxide was obtained (21% based on diisobutylchlorophosphine), b.p. 122–123° (8 mm.), m.p. 18°.

Anal. Calcd. for $C_{10}H_{21}OP$: C, 64.0; H, 11.2; P, 16.5. Found: C, 63.7; H, 11.32; P, 15.4.

Preparation of diphenylvinylphosphine. To a tetrahydrofuran solution of 125 ml. of 2.1*M* vinylmagnesium chloride (purchased from Peninsular Chemresearch, Inc., Gainesville, Fla.) (0.26 mole) in a 500-ml., three necked flask equipped with a thermometer, water condenser, equilizing addition funnel, and nitrogen inlet was slowly added 65.5 g. (0.297 mole) of diphenylchlorophosphine. Heat was evolved, and the temperature was maintained between 40–50° by cooling. When approximately one half of the diphenylchlorophosphine had been added, no further heat evolution was noted. The remaining diphenylchlorophosphine was quickly added, and then an additional 125 ml. of the 2.1*M* Grignard solution dropped in. Heat evolution was again noted. Upon completion of the addition the reaction mixture was poured onto ice and, after standing for 2 hr., was acidified to neutrality with hydrochloric acid. This mixture was extracted with 500-, 200- and 200-ml. portions of chloroform; the extract dried over sodium sulfate, filtered, and reduced in volume. When the volume was about 325 ml., the solution bumped and approximately 80 ml. was lost. The volume was reduced to 125 ml., and this brown solution distilled through a 1-ft., vacuum-jacketed, silvered Vigreux column. A total of 19.8 g. (31.5%; 40% if the bumping loss is taken into account) of diphenylvinylphosphine was obtained, b.p. 117.5–119° (0.6 mm.).

Anal. Calcd. for $C_{14}H_{13}P$: C, 79.2; H, 6.12; P, 14.62. Found: C, 78.7; H, 6.23; P, 13.63.

The pot residue was a brown solid, which appeared to be a mixture of a gum and a crystalline material. Trituration with acetone dissolved the gum leaving 2.5 g. of a tan solid, m.p. 200°. Two recrystallizations from toluene gave 1.6 g. of a material, m.p. 262–263°, which was identified by its infrared spectrum as 1,2-ethanebis(diphenylphosphine oxide) by comparison with the spectrum of this material which had been found as a product of the reaction of ethyl diphenylphosphinite with 1,2-dibromoethane. In other syntheses of diphenylvinylphosphine variable amounts of this dimer were found. From reactions involving 55.1 g. and 110.2 g. of diphenylchlorophosphine, 6.4 g. and 22.0 g., respectively, of 1,2-ethanebis(diphenylphosphine oxide) were found.

Oxidation of diphenylvinylphosphine. Addition of excess *t*-butyl hydroperoxide to a solution of 1.0 g. (0.00465 mole) in 3 ml. of benzene produced heat. Even after cooling and adding 15 ml. of heptane, no solid separated. The solvents were evaporated by heating at 100° using the water aspirator. The residue, which crystallized on standing, was recrystallized from a toluene-heptane mixture; 0.78 g. (73%) of solid was recovered. This was finally recrystallized from heptane containing a minimum of toluene; 0.55 g., m.p. 116–118.5° was obtained. It was identified as diphenylvinylphosphine oxide by comparison of its infrared spectrum to that of the sample described previously.

Reaction of diphenylvinylphosphine with sulfur. Preparation of diphenylvinylphosphine sulfide. To a solution of 3.175 g. (0.015 mole) of diphenylvinylphosphine in 10 ml. of benzene was added 0.480 g. (0.015 mole) of sulfur flowers. The temperature rose to 55° in 1 min. and dropped rapidly. A few particles appeared in the mixture and were removed by filtration. The benzene was evaporated at reduced pressure and the residue crystallized after standing 72 hr. at −10°. The solid was dissolved in ethyl ether. Petroleum ether (b.p. 30–60°) was added causing an oil to form. This crystallized at −10° and was collected, 2.62 g., m.p. 53–54°. An additional two fractions of material were isolated from the mother liquor, 0.32 g., m.p. 52–52.5°, and 0.13 g., m.p. 48–49°. This total of 3.07 g. (86%) of diphenylvinylphosphine sulfide was recrystallized from ether–petroleum ether; 2.1 g. was recovered, m.p. 53.3–54.9°.

Anal. Calcd. for $C_{14}H_{13}PS$: C, 69.0; H, 5.32; P, 12.70; S, 13.10. Found: C, 68.7; H, 5.4; P, 12.84; S, 13.24.

Preparation of diphenylmethylvinylphosphonium iodide. To 1.0 g. (0.00465 mole) of diphenylvinylphosphine was added 7 ml. of Eastman Kodak White Label iodomethane. The evolution of heat lasted for about 3 min; an oil layer floated to the top. Evaporation of the excess iodomethane left an immobile oil which failed to crystallize on standing. Trituration of a concentrated acetone solution of the oil with ether failed. The solvents were removed by evaporation whereupon trituration of the residue with benzene was successful. The yellow solid product was recrystallized from 20% acetone in benzene. The first crop, 1.2 g., was very slightly yellow. The second crop, 0.14 g., was obtained by adding toluene to the mother liquor and chilling. Thus a total of 1.34 g. of diphenylmethylvinylphosphonium iodide was obtained (80%). The combined 1.34 g. was recrystallized twice from dilute acetone in benzene yielding 0.91 g. of crystalline solid, m.p. 119–120°.

Anal. Calcd.: Iodine, 35.2%. Found: Iodine, 35.9%.

Polymerization studies. All polymerizations were carried out by adding the components to a heavy-walled, constricted test tube, degassing three times at −78°, and sealing. The tubes were allowed to thaw and then were placed in the appropriate oil bath.

A. *Diphenylvinylphosphine oxide.* A mixture of 1.0 g. of monomer, 3.0 ml. of benzene, and 15 mg. of azobisisobutyronitrile was heated at 70 for 4 days. No viscosity increase was noted. Precipitation into heptane gave a small amount of solid material, which softened between 100–140° and showed no vinyl absorption in the infrared.

B. *Diphenylvinylphosphine oxide.* One drop of di-*t*-butyl peroxide was added to a 1.0-g. sample of the monomer, and this mixture heated at 135°. After several hours some viscosity was noted, and in 24 hr. the tube contents were immobile. Isolation of the polymer revealed a material with an intrinsic viscosity of 0.020 at 30° in 2B alcohol,[17] mol. wt., 692. When this was repeated at one tenth the di-*t*-butyl peroxide level, again a glass was obtained, possessing an intrinsic viscosity 0.025. When the di-*t*-butyl peroxide concentration was decreased again by a factor of ten, the tube contents increased in viscosity only slightly indicating that the chains were too short to allow complete polymerization at that peroxide level.

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[17] Another homopolymer, formed by heating 2.13 g. of the monomer with one drop of di-*t*-butyl peroxide at 135° also had an intrinsic viscosity of 0.02 but a molecular weight of 1350.

[CONTRIBUTION FROM CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Oxidation of Secondary Phosphines to Secondary Phosphine Oxides[1]

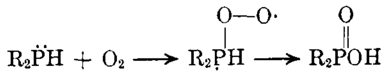
M. M. RAUHUT AND HELEN A. CURRIER

Received May 4, 1961

Oxidation of secondary phosphines by air under mild conditions has been found to give secondary phosphine oxides in good yields. Phosphinic acids were not found under the reaction conditions employed.

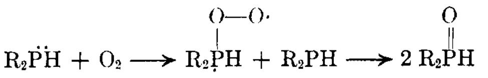
It has been reported that oxidation of secondary phosphines by nitric acid[2] or by air[3] proceeds vigorously[4], and that phosphinic acids are the products of such reactions.[2,3] Although secondary phosphine oxides have been considered possible intermediates in these oxidations, their isolation under the conditions employed has been thought to be impossible.[5]

In view of these results it is conceivable that air oxidation of a secondary phosphine might proceed directly to the corresponding phosphinic acid by an intramolecular oxygen shift.



$$R_2\ddot{P}H + O_2 \longrightarrow R_2\overset{O-O\cdot}{\overset{|}{P}}H \longrightarrow R_2\overset{O}{\overset{\|}{P}}OH$$

Alternatively, a secondary phosphine oxide might be formed as an intermediate, which under the conditions employed could oxidize further in a separate step to the phosphinic acid. If this latter mechanism is correct, one should be able to isolate the intermediate secondary phosphine oxides, since secondary phosphine oxides, obtained by other means,[6] have been found to be relatively stable toward oxidation.[7]

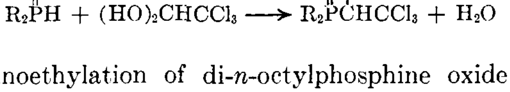


$$R_2\ddot{P}H + O_2 \longrightarrow R_2\overset{O-O\cdot}{\overset{|}{P}}H + R_2PH \longrightarrow 2\,R_2\overset{O}{\overset{\|}{P}}H$$

Accordingly, nine secondary phosphines were oxidized by air at moderate temperatures. In each case, the product obtained was found to be a secondary phosphine oxide (Table I). The reactions were run by simply exposing a small quantity of the phosphine to the atmosphere (Method A) or by passing dry air through a larger quantity of the phosphine dissolved in isopropyl alcohol (Method B). The crystalline oxides were characterized by elemental analysis, by infrared and NMR spectroscopy, and in several cases by the preparation of derivatives.

The oxidations were inhibited by hydroquinone as would be expected for a free-radical process. Unexpectedly, however, oxidation also failed to take place in benzene solution. This latter effect deserves additional study.

Di-*n*-butylphosphine oxide and diisobutylphosphine oxide were characterized by their reactions with chloral hydrate in refluxing isopropyl alcohol to give the corresponding 1-hydroxy-2,2,2-trichloroethylphosphine oxides.



$$R_2\overset{O}{\overset{\|}{P}}H + (HO)_2CHCCl_3 \longrightarrow R_2\overset{O}{\overset{\|}{P}}\overset{OH}{\overset{|}{C}}HCCl_3 + H_2O$$

Cyanoethylation of di-*n*-octylphosphine oxide in the presence of sodium ethoxide by the method of Miller, Bradley and Hamilton[8] gave (2-cyanoethyl)-di-*n*-octylphosphine oxide.

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(9) Melting points are uncorrected.