BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39. 214—219 (1966)

The Reactions of *N*-Phenyl Ethanolamine with Imido Phosphites, Amido Phosphites and Amino Phosphines

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(Received March 2, 1965)

Various symmetrical and unsymmetrical triesters of phosphorous acid have been obtained by the reactions of phosphazo compounds with alcohols or phenols. When a phosphazo compound, amido phosphites or amino phosphine is treated with 2 mol. of *N*-substituted ethanolamine, the corresponding bis(β-aminoethyl) phosphites or phosphonite is obtained. On the other hand, when the same reaction is carried out with 1 mol. of the ethanolamine, cyclic phosphorous compounds are obtained in fairly good yields. Further, it has been found that the treatment of bis(β-anilinoethyl)phenyl phosphonite with phenyl isocyanate gives 2-phenylimino-3-phenyl-1, 3-oxazolidine.

The reaction of ethyl *N*-phenylimino phosphite (ethoxyphosphazobenzene) with benzaldehyde and ethanol has recently been reported to afford diethyl phosphite and benzilideneaniline.[1] In the present study, addition reactions of phosphazo compounds with active hydrogen compounds, such as amines, alcohols, phenols and aminoalcohols, were attempted. When *N*-phenylamino *N'*-phenylimino phosphine (I) was treated with an equimolar amount of aniline in boiling toluene, trisanilino phosphine (II), an addition compound, could not be obtained; rather, 53.8% of the starting material (I) was recovered, along with an unidentified product (Eq. 1):

$$\underset{\text{I}}{C_6H_5\text{-}N\text{=}P\text{-}NHC_6H_5} + C_6H_5NH_2 \not\longrightarrow \underset{\text{II}}{P(NHC_6H_5)_3} \qquad (1)$$

Ethyl dianilino phosphite (III), the expected addition compound, could not be obtained when I was treated with an equimolar amount of ethanol in boiling toluene, but triethyl phosphite and aniline were produced in 23.3 and 33.3% yields, and 21% of I was also recovered (Eq. 2):

$$\text{I} + \text{EtOH} - \begin{cases} \not\longrightarrow \underset{\text{III}}{(C_6H_5NH)_2P\text{-}OEt} \\ \longrightarrow (EtO)_3P + 2C_6H_5NH_2 \end{cases} \qquad (2)$$

On the other hand, the yield of triethyl phosphite was increased to 46% when 3 mol. of ethanol were used in the above reaction. In a similar manner, various trialkyl or triaryl phosphites were prepared by the reactions of 1 mol. of I with 3 mol. of alcohols or phenols (see Table I).

Similarly, unsymmetrical ethyl dialkyl or ethyl diphenyl phosphite was produced by the reaction of 1 mol. of ethyl *N*-phenylimino phosphite (IV) with 2 mol. of alcohols or phenol (Eq. 3). The results are summarized in Table II.

$$\underset{\text{IV}}{C_6H_5\text{-}N\text{=}P\text{-}OEt} + 2ROH \rightarrow (RO)_2P\text{-}OEt + C_6H_5NH_2 \qquad (3)$$

R=alkyl or phenyl

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[1] O. Mitsunobu and T. Mukaiyama, *J. Org. Chem.*, **29**, 3005 (1964).

TABLE I. THE REACTION OF *N*-PHENYLAMINO *N'*-PHENYLIMINO PHOSPHINE WITH ALCOHOLS AND PHENOLS

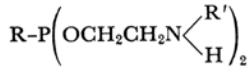
	Product			
Material	Phosphite	Yield, %	B. p., °C/mmHg	Aniline, Yield, %
EtOH	$(EtO)_3P$	45.8	52—63/26	94.7
n-BuOH	$(n\text{-}BuO)_3P$	77.6	90—91/1	64.6
C_6H_5OH	$(C_6H_5O)_3P$	81.5	117—136/0.05	86.0
p-Cl-C_6H_4OH	$(p\text{-}Cl\text{-}C_6H_4O)_3P$	78.2	119—146/0.08	78.6

TABLE II. THE REACTION OF ETHYL *N*-PHENYLIMINO PHOSPHITE WITH ALCOHOLS AND PHENOL

	Product			
Material	Phosphite	Yield, %	B. p., °C/mmHg	Aniline, Yield, %
EtOH	$(EtO)_3P$	72.6	75—78/40	98.5
n-PrOH	$(n\text{-}PrO)_2POEt$	50.0	79—81/15	170*
n-BuOH	$(n\text{-}BuO)_2POEt$	80.8	82—84/18	96.5
C_6H_5OH	$(C_6H_5O)_2POEt$	78.3	73—96/0.02	88.9

* In this case, the aniline fraction was contaminated with the phosphite.

TABLE III. THE SYNTHESIS OF BIS(β-AMINOETHYL)-PHOSPHOROUS COMPOUNDS


$$R\text{-}P\left(OCH_2CH_2N\begin{smallmatrix}R'\\ H\end{smallmatrix}\right)_2$$

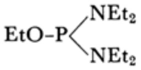
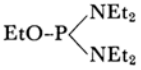
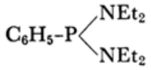
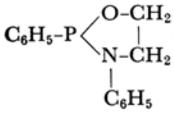
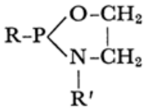
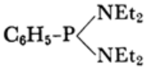
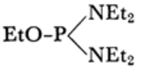
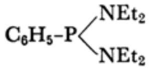
Starting material		Reaction condition			Product				
Phosphorous compound	Ethanolamine	Solvent	Time hr.	Temp. °C	R	R'	Yield %	B. p. °C/mmHg	Analysis N, %
 $EtO\text{-}P(NEt_2)_2$	$CH_3NHCH_2CH_2OH$	Toluene	4	110	EtO-	CH_3-	60.3	54—57/2	Found 12.50 Calcd. 12.50
 $EtO\text{-}P(NEt_2)_2$	$C_2H_5NHCH_2CH_2OH$	Toluene	7	110	EtO-	C_2H_5-	50.7	71—73/0.1	Found 11.35 Calcd. 11.11
EtO-P=N-Ph	$C_6H_5NHCH_2CH_2OH$	—	5	120	EtO-	C_6H_5-	32.6	99—101/0.005	Found 7.99 Calcd. 8.05
 $C_6H_5\text{-}P(NEt_2)_2$	$C_6H_5NHCH_2CH_2OH$	—	4	120	C_6H_5-	C_6H_5-	69.4	105—107/0.001	Found 7.45 Calcd. 7.37
 $C_6H_5\text{-}P\begin{smallmatrix}O\text{-}CH_2\\ N(C_6H_5)\text{-}CH_2\end{smallmatrix}$	$C_6H_5NHCH_2CH_2OH$	Xylene	4	140	C_6H_5-	C_6H_5-	31.4	124—126/0.03	Found 7.35 Calcd. 7.37

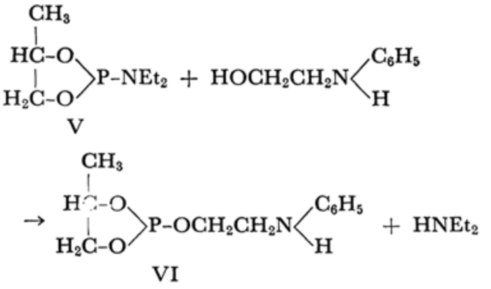
TABLE IV. THE SYNTHESIS OF 1, 3, 2-OXAZAPHOSPHOLIDINES


$$R\text{-}P\begin{smallmatrix}O\text{-}CH_2\\ N\text{-}CH_2\\ R'\end{smallmatrix}$$

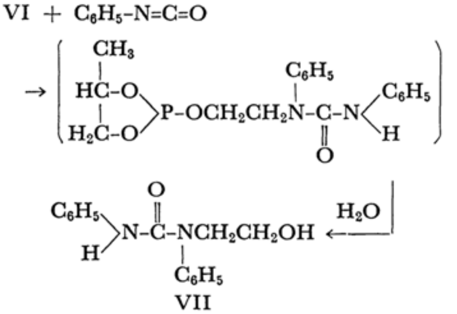
Starting material		Reaction condition			Product				
Phosphorous compound	Ethanolamine	Solvent	Time hr.	Temp. °C	R	R'	Yield %	B. p. °C/mmHg	Analysis N, %
 $C_6H_5\text{-}P(NEt_2)_2$	$C_6H_5NHCH_2CH_2OH$	Xylene	2.5	140	C_6H_5-	C_6H_5-	85	130—132/0.03	Found 5.88 Calcd. 5.76
 $EtO\text{-}P(NEt_2)_2$	$C_6H_5NHCH_2CH_2OH$	—	3	120	EtO-	C_6H_5-	84.3	88—91/0.02	Found 6.79 Calcd. 6.64
 $C_6H_5\text{-}P(NEt_2)_2$	$CH_3NHCH_2CH_2OH$	—	2.5	120	C_6H_5-	CH_3-	24.6	64—66/0.03	Found 7.83 Calcd. 7.74
$EtO\text{-}P{=}NC_6H_5$	$C_6H_5NHCH_2CH_2OH$	Toluene	5	110	EtO-	C_6H_5-	54.6	91—92/0.02	Found 6.70 Calcd. 6.64

It has recently been reported by Burgade[2] and Petrov et al.[3] that alcohols or phenols react with amido phosphites and amino phosphines to give the corresponding phosphites or phosphonites, with the elimination of the original amino groups.

In view of the finding that imido phosphites, amido phosphites or amino phosphines react with alcohols much more readily than amines, such phosphorous compounds may be expected to react with amino alcohols to form ω-aminoalkyl phosphites or phosphonites primarily. For instance, when 2-diethylamino-4-methyl-1, 3, 2-dioxaphospholane (V) is treated with an equimolar amount of *N*-phenyl ethanolamine in boiling toluene for 3 hr., β-anilinoethyl propylene phosphite (VI) is obtained in a 86% yield (Eq. 4):

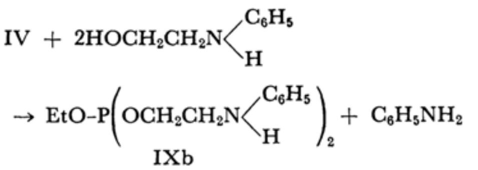

(4)

The structure of VI was confirmed by means of elemental analysis and a study of its infrared spectrum. The VI reacts with phenyl isocyanate to give a viscous oily product, the infrared spectrum of which shows the absorption at 1660 cm^{-1} due to the urea linkage. The liquid is readily hydrolyzed to give *N*-(β-hydroxyethyl)-*N*, *N'*-diphenyl urea (VII) in a good yield (Eq. 5):


(5)

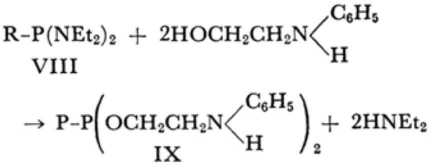
This fact shows that the nitrogen of the trivalent phosphorus-nitrogen bond is selectively replaced with the oxygen of the ethanolamine.

Further, when IV was treated with 2 mol. of *N*-phenyl ethanolamine while being refluxed in toluene for 5 hr., ethyl bis(β-anilinoethyl) phosphite (IXb) (b. p. 114—116°C/0.009 mmHg) was obtained in a 27% yield (Eq. 6):



$$\mathrm{IV} + 2\mathrm{HOCH_2CH_2N}{<}\begin{array}{l}\mathrm{C_6H_5}\\ \mathrm{H}\end{array} \rightarrow \underset{\mathrm{IXb}}{\mathrm{EtO\text{-}P}\left(\mathrm{OCH_2CH_2N}{<}\begin{array}{l}\mathrm{C_6H_5}\\ \mathrm{H}\end{array}\right)_2} + \mathrm{C_6H_5NH_2} \qquad (6)$$

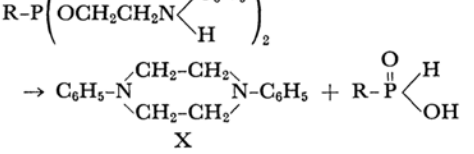
Similarly, when phenyl bis(diethylamino) phosphine (VIIIa) or ethyl bis(diethylamido) phosphite (VIIIb) was treated with 2 mol. of *N*-phenyl ethanolamine at 130°C for 4 hr., bis(β-anilinoethyl)phenyl phosphonite (IXa) or ethyl bis(β-anilinoethyl) phosphite (IXb) was obtained in a 69% or a 20% yield respectively (Eq. 7):



$$\underset{\mathrm{VIII}}{\mathrm{R\text{-}P(NEt_2)_2}} + 2\mathrm{HOCH_2CH_2N}{<}\begin{array}{l}\mathrm{C_6H_5}\\ \mathrm{H}\end{array} \rightarrow \underset{\mathrm{IX}}{\mathrm{P\text{-}P}\left(\mathrm{OCH_2CH_2N}{<}\begin{array}{l}\mathrm{C_6H_5}\\ \mathrm{H}\end{array}\right)_2} + 2\mathrm{HNEt_2} \qquad (7)$$

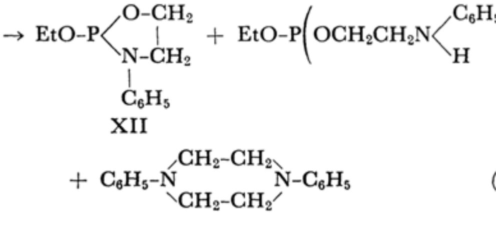
VIIIa: R=C_6H_5	IXa: R=C_6H_5
VIIIb: R=EtO	IXb: R=EtO

The resulting ethyl bis(β-anilinoethyl) phosphite or bis(β-anilinoethyl)phenyl phosphonite is rather unstable and is partly decomposed into *N*, *N'*-diphenyl piperazine (X) during distillation (Eq. 8):


(8)

The solvents, yields, and physical properties of the bis(β-aminoethyl) phosphites and phosphonite as well as the results of elementary analyses of these substances, are listed in Table III.

On the other hand, when VIIIa or VIIIb was reacted with an equimolar amount of amino alcohol, 2, 3-diphenyl-1, 3, 2-oxazaphospholidine (XI) or 2-ethoxy-3-phenyl-1, 3, 2-oxazaphospholidine (XII) was obtained in a fairly good yield. In the case of the reaction of 1 mol. of ethyl *N*-phenylimino phosphite with 1 mol. of *N*-phenyl ethanolamine, 2-ethoxy-3-phenyl-1, 3, 2-oxazaphospholidine and ethyl bis(β-anilinoethyl) phosphite were obtained in 55 and 21% yields respectively, along with a small amount of *N,N'*-diphenyl piperazine (Eq. 9): The results are summarized in Table IV.


(9)

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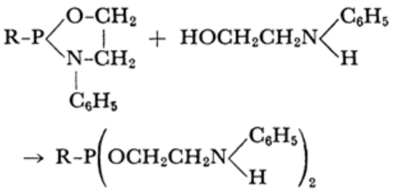
[2] R. Burgada, a) *Ann. Chim.* (*France*), 347 (1963); b) *Bull. soc. chim. France*, **1963**, 2335.

[3] K. A. Petrov, E. E. Nifantev, T. N. Lysenko and V. P. Evdakov, *Zh. Obshch. Khim.*, **31**, 2377 (1961).

The resulting cyclic phosphorous compounds may be expected to yield bis(β-aminoethyl) phosphite or phosphonite by the ring-opening addition of the other amino alcohol, as is shown in the following equation (10):



(10)

When 2, 3 - diphenyl-1, 3, 2-oxazaphospholidine was treated with an equimolar amount of *N*-phenyl ethanolamine in xylene, bis(β-anilinoethyl)phenyl phosphonite was obtained in a 31% yield; 15% of the cyclic phosphorous compound was also recovered.

Next, in order to prepare the corresponding urea derivatives of bis(β-aminoethyl) phosphorous compounds, the reaction of bis(β-anilinoethyl)phenyl phosphonite with 2 mol. of phenyl isocyanate was attempted. Contrary to our expectation, the urea could not be isolated, although 2-phenylimino-3-phenyl-1, 3-oxazolidine was obtained in a 58.5% yield. The unexpected oxazolidine formation may result in the subsequent decomposition of the initially-formed ureas. Futher study of this new synthesis of oxazolidine derivatives is now in progress.

Experimental

Materials.—Aminoalcohols and phenyl isocyanate were obtained commercially and purified by distillation. *N*-Phenylamino *N'*-phenylimino phosphine[4] (m. p. 246—248°C), ethyl phosphorodichloridite[5] (b. p. 48—50°C/80 mmHg), ethyl *N*-phenylimino phosphite[1] (b. p. 153—155°C/0.09 mmHg), phenyl phosphonous dichloride[6] (b. p. 59—61°C/2 mmHg) and 2-chloro-4-methyl-1, 3, 2-dioxaphospholane[7] (b. p. 75—76°C/50 mmHg) were prepared according to the methods in the literature.

The Preparation of Phenyl Bis(diethylamino) Phosphine.—A solution of phenyl phosphonous dichloride (179 g., 1.0 mol.) in 800 ml. of dry benzene was stirred, drop by drop over a period of 1.5 hr., into a solution of diethylamine (146 g., 2.0 mol.) and triethylamine (202 g., 2.0 mol.) in 300 ml. of dry benzene which had been cooled in an ice-water bath. The mixture was then stirred for another hour and subsequently heated to reflux. Triethylamine hydrochloride was removed by filtration. After the solvent had been removed under reduced pressure from the filtrate, the residue was distilled to give 217 g. (86.3%) of phenyl bis(diethylamino) phosphine (b. p. 123—125°C/0.2 mmHg).

Found: N, 11.08. Calcd. for $C_{14}H_{25}N_2P$: N, 11.10%.

By the same procedure, ethyl bis(diethylamido) phosphite was prepared in a 71.3% yield; b. p. 81—83°C/9 mmHg.

Found: N, 12.62. Calcd. for $C_{10}H_{25}N_2PO$: N, 12.73%.

The Preparation of 2-Diethylamino-4-methyl-1, 3, 2-dioxaphospholane.—A solution of diethylamine (75 g., 1.03 mol.) in 100 ml. of ligroin was vigorously stirred, drop by drop, into a solution of 2-chloro-4-methyl-1, 3, 2-dioxaphospholane (70 g., 0.5 mol.) in 300 ml. of ligroin which had been cooled in an ice-water bath. The mixture was then stirred for an additional 2 hr. at room temperature. Diethylamine hydrochloride was removed by filtration. After the solvent had been removed from the filtrate under reduced pressure, the residue was distilled to give 2-diethylamino-4-methyl-1, 3, 2-dioxaphospholane, (52 g., 59.1%; b. p. 67—68°C/6.5 mmHg).

Found: N, 7.85. Calcd. for $C_7H_{16}NPO_2$: N, 7.91%.

The Reaction of *N*-Phenylamino *N'*-Phenylimino Phosphine (I) (1 mol.) with Aniline (1 mol.).—A solution of aniline (1.86 g., 0.02 mol.) in 10 ml. of dry toluene was added to a solution of I (4.28 g., 0.02 mol.) in 10 ml. of dry toluene at room temperature. The mixture was then refluxed for 5 hr. After the solution had been cooled, the starting material was recovered as precipitates (2.30 g., 53.8%). The filtrate was concentrated under reduced pressure to give unidentified solids (2.09 g.; m. p. 139—169°C) which could not be purified further.

The Reaction of *N*-Phenylamino *N'*-Phenylimino Phosphine (I) (1 mol.) with Ethanol (1 mol.).—A solution of ethanol (0.46 g., 0.01 mol.) in 5 ml. of dry toluene was added to a solution of I (2.14 g., 0.01 mol.) in 15 ml. of dry toluene at room temperature. The reaction mixture was then refluxed for 5 hr., after which time the reaction mixture was concentrated and the separated I (0.45 g., 21%; m. p. 234—241°C) was removed by filtration. The filtrate was fractionated in vacuo to give curde triethyl phosphite (0.39 g., 23.3%; b. p. 54—58°C/16 mmHg) and aniline (0.21 g., 33.3%; b. p. 34—39°C/3 mmHg). The infrared spectrum of triethyl phosphite was identical with that of an authentic sample.

The Reaction of *N*-Phenylamino *N'*-Phenylimino Phosphine (I) (1 mol.) with Ethanol (3 mol.).—In the same manner 3 mol. of ethanol (1.38 g., 0.03 mol.) was allowed to react with I (2.14 g., 0.01 mol.) thus producing triethyl phosphite (0.76 g., 45.8%; b. p. 52—63°C/26 mmHg) and aniline (1.76 g., 94.7%; b. p. 74—86°C/27 mmHg).

By a similar procedure, several trialkyl and triaryl phosphites were obtained, as Table I shows.

The Reaction of Ethyl *N*-Phenylimino Phosphite (IV) (1 mol.) with Ethanol (2 mol.).—A solution of ethanol (0.92 g., 0.02 mol.) in 10 ml. of dry benzene was added to a solution of IV(1.67 g., 0.01 mol.) in 10 ml. of dry beznene at room temperature. The reaction mixture was refluxed for 3 hr. After the solvent had been removed, triethyl phosphite (1.21 g., 72.6%; b. p. 75—78°C/40 mmHg) and aniline (0.91 g.,

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[4] H. W. Grimmel, A. Guenther and J. F. Morgan, *J. Am. Chem. Soc.*, **68**, 539 (1946).

[5] R. W. Young, K. H. Wood, R. J. Joyce and G. W. Anderson, ibid., **78**, 2126 (1956).

[6] B. Buchner and L. B. Lockhart, Jr., "Organic Syntheses," **31**, 88 (1951).

[7] H. J. Lucas, F. W. Mitchell, Jr., and C. N. Scully, *J. Am. Chem. Soc.*, **72**, 5491 (1950).

98.5%; b. p. 94—97°C/40 mmHg) were obtained by fractionation.

Similarly, some unsymmetrical phosphites were obtained, as is shown in Table II. In each case, a small amount of a mixture of various phosphites was formed by transesterification.

The Reaction of 2-Diethylamino-4-methyl-1, 3, 2-dioxaphospholane (V) (1 mol.) with *N*-Phenyl Ethanolamine (1 mol.).—A solution of V (10.62 g., 0.06 mol.) and *N*-phenyl ethanolamine (8.22 g., 0.06 mol.) in 20 ml. of dry toluene was refluxed for 3 hr. After the solvent and the evolved diethylamine had been removed under reduced pressure, the residure was distilled in vacuo, giving β-anilinoethyl propylene phosphite (12.5 g., 86.3%; b. p. 107—109°C/0.1 mmHg). Redistillation gave the pure phosphite (b. p. 107—109°C/0.1 mmHg).

Found: N, 5.89. Calcd. for $C_{11}H_{16}NPO_3$: N, 5.81%.

The Reaction of β-Anilinoethyl Propylene Phosphite (VI) (1 mol.) with Phenyl Isocyanate (1 mol.).—A solution of phenyl isocyanate (1.19 g., 0.01 mol.) in 10 ml. of dry toluene was added, drop by drop, to a solution (2.41 g., 0.01 mol.) of VI in 10 ml. of dry toluene. After an initial exothermic reaction had ceased, the reaction mixture was refluxed for 3 hr. After the solvent had then been removed under reduced pressure, an oily substance was obtained. The oily substance was solidified, with a slight heat liberation, by treatment with 5 ml. of water. The solid was filtered to give 2.46 g. (68.4%) of *N*-(β-hydroxyethyl)-*N*, *N*′-diphenyl urea (m. p. 80—83°C; recrystallized from ethyl acetate, m. p. 82—83°C).

Found: C, 69.92; H, 6.42; N, 11.23. Calcd. for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.94%.

The Reaction of Ethyl *N*-Phenylimino Phosphite (IV) (1 mol.) with *N*-Phenyl Ethanolamine (2 mol.).—A solution of IV (1.67 g., 0.01 mol.) and *N*-phenyl ethanolamine (2.74 g., 0.02 mol.) in 20 ml. of dry toluene was refluxed for 5 hr. After the solvent had been removed under reduced pressure, the residue was distilled, in vacuo giving aniline (0.19 g., 22%; b. p. 34—35°C/2 mmHg) and ethyl bis(β-anilinoethyl) phosphite (0.94 g., 27%; b.p. 114—116°C/0.009 mmHg); a tarry residue also remained. From this residue, *N*, *N*′-diphenyl piperazine (0.12 g.; m. p. 163—165°C) was extracted with boiling toluene; the residual substance gave an unidentified gray colored solid (m. p. 235°C).

The Reaction of Phenyl Bis(diethylamino) Phosphine (VIIIa) (1 mol.) with *N*-Phenyl Ethanolamine (2 mol.)—A mixture of VIIIa (5.04 g., 0.02 mol.) and *N*-phenyl ethanolamine (5.48 g., 0.04 mol.) was heated at 125—135°C (oil bath temperature) for 4 hr. After the diethylamine had been removed under reduced pressure, the residue was distilled in vacuo to give bis(β-anilinoethyl)phenyl phosphonite (5.27 g., 69.4%; b. p. 105—107°C/0.001 mmHg). Its infrared spectra showed absorption bands at 3350 (m), 1430 (m), 1175 (m), 1050(s), and 925(s) cm^{-1}.

Found: N, 7.45. Cacld. for $C_{22}H_{25}N_2PO_2$: N, 7.37%.

In a similar way, ethyl bis(β-anilinoethyl) phosphite, ethyl bis(β-ethylaminoethyl) phosphite and ethyl bis-(β-methylaminoethyl) phophite were prepared by the reactions of the corresponding ethanolamines with ethyl bis(diethylamido) phosphite (Table III).

The Reaction of Ethyl Bis(diethylamido) Phosphite (VIIIb) (1 mol.) with *N*-Phenyl Ethanolamine (1 mol.).—A mixture of VIIIb (22 g., 0.1 mol.) and *N*-phenyl ethanolamine (13.7 g., 0.1 mol.) was heated at 120—130°C (oil bath temperature) for 3 hr. The diethylamine was then collected in a trap cooled in an ice-water bath. The reaction mixture was distilled under reduced pressure to give 2-ethoxy-3-phenyl-1, 3, 2-oxazaphospholidine (17.79 g., 84.3%; b. p. 88—91°C/0.02 mmHg). Its infrared spectra displayed absorption bands at 1304(s), 1150(w), 1030(s), and 920(s) cm^{-1}.

Found: N, 6.79; mol. wt. (Ebulliometric) 218. Calcd. for $C_{10}H_{14}NPO_2$: N, 6.64%; mol. wt. 211.

In a similar way, 2, 3-diphenyl-1, 3, 2-oxazaphospholidine and 2-phenyl-3-methyl-1, 3, 2-oxazaphospholidine were prepared from phenyl bis(diethylamino) phosphine and the corresponding ethanolamines, as is shown in Table IV.

The Reaction of Ethyl *N*-Phenylimino Phosphite (IV) (1 mol.) with *N*-Phenyl Ethanolamine (1 mol.).—A solution of IV (16.7 g., 0.1 mol.) and *N*-phenyl ethanolamine (13.7 g., 0.1 mol.) in 200 ml. of dry toluene was refluxed for 5 hr. After the solvent had been removed, the residue was fractionated into four major fractions. Fraction 1: aniline (5.77 g., 62.2%; b. p. 58—64°C/6 mmHg). Fraction 2: 2-ethoxy-3-phenyl-1, 3, 2-oxazaphospholidine (11.48 g., 54.6%; b. p. 91—92°C/0.02 mmHg). (This fraction shows an infrared spectrum identical with that of the 2-ethoxy-3-phenyl-1, 3, 2-oxazaphospholidine obtained in the above experiment). Fraction 3: ethyl bis(β-anilinoethyl) phosphite (3.59 g., 20.6%; b. p. 117—119°C/0.03 mmHg). (Its infrared spectra shows absorption bands at 3350(m), 1270(s), 1150(m), 1020(s), 900(s) cm^{-1}. Fraction 4: 6.58 g., b. p. 131—151°C/0.006 mmHg. This fraction was partly solidified. The fraction was extracted with boiling toluene. After the extract had been cooled, *N*, *N*′-diphenyl piperazine (0.89 g., m. p. 163—165°C) was obtained. Recrystallization from toluene raised the melting point to 166—167°C, and the melting point was undepressed on admixture with an authentic sample.

Found: C, 79.63; H, 8.09; N, 11.96. Calcd. for $C_{16}H_{18}N_2$: C, 80.67; H, 7.57; N, 11.77%.

The Reaction of 2, 3-Diphenyl-1, 3, 2-Oxazaphospholidine (XII) (1 mol.) with *N*-Phenyl Ethanolamine (1 mol.)—A solution of XII (2.84 g., 0.01 mol.) and *N*-phenyl ethanolamine (1.53 g., 0.01 mol.) in 7 ml. of dry xylene was refluxed for 4 hr. After the solvent had been removed, the residue was fractionated into two fractions. Fraction 1: 0.65 g. (42.2%); b. p. 82—84°C/0.005 mmHg. (The infrared spectrum of the product was identical with that of *N*-phenyl ethanolamine). Fraction 2: 3.07 g., b. p. 104—110°C/0.008 mmHg. After this substance had stood in a refrigerator, 0.43 g. (15%) of XII (m. p. 75—77°C) was recovered. After the XII had been removed by filtration, the residue was distilled to give 1.39 g. (31%) of bis(β-anilinoethyl)phenyl phosphonite (b. p. 124—126°C/0.03 mmHg).

The Reaction of Bis(β-anilinoethyl) Phenyl Phosphonite (IXa) with Phenyl Isocyanate.—A solution of phenyl isocyanate (2.38 g., 0.02 mol.) in 10 ml. of dry toluene was stirred, drop by drop, into a solution of IXa (3.80 g., 0.01 mol.) in 10 ml. of dry toluene at room temperature. After an initial exothermic reaction had ceased, the reaction mixture was refluxed for 3 hr. The solvent was removed under reduced pressure, and an oily substance was obtained. After the oily substance had been stored for several days at room temperature, a small amount of a white crystalline compound was precipitated. When 5 ml. of 99.5% ethanol was added to the mixture, a white crystalline compound (1.44 g., 58.5%; m. p. 115—116°C) was again obtained. This crystalline compound was purified by recrystallization from ethanol (m. p. 117—118°C). The compound was identical in its infrared spectrum with that of an authentic 2-phenylimino-3-phenyl-1, 3-oxazolidine[8] and with the results of the elemental analysis.

Found: C, 75.60; H, 6.11; N, 11.83. Calcd. for $C_{15}H_{14}N_2O$: C, 75.63; H, 5.83; N, 11.76%.

The authors wish to thank the Bridgestone Tire Co., Ltd., especially, its General Director, Mr. Kunio Yasutake, for permission to publish this work; they wish also to acknowledge the helpful advice given by Mr. Yoshitake Kubota and the late Mr. Koshiro Fujiwara.

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8) H. Nohira, Y. Nishikawa and T. Mukaiyama, This Bulletin, **37**, 797 (1964).