ium bromide (VII) prepared according to Pinck and Hilbert[9] and 0.50 g. (0.0026 mole) of 9-diazofluorene (I) dissolved in 30 ml. of ethanol was added dropwise with swirling approximately 2 ml. of aqueous 10% sodium hydroxide. A dark blue color characteristic of 1-(9-fluorenyl)pyridinium ylid (V)[9] appeared with the addition of each drop of base, and gradually changed to colorless upon swirling. Addition of the base required approximately 0.5 hr. and the mixture was allowed to stand for 15 min. before 0.81 g. (0.0023 mole, 87.4% yield) of fluorenone ketazine (VI, melting point and mixture melting point checked with an authentic sample) was recovered by filtration.

9-Diazofluorene (I) and Benzylidine Triphenylphosphorane (VIII).—To a stirred mixture of benzyltriphenylphosphonium bromide (10.8 g.) and 125 ml. of anhydrous benzene was added 10.6 g. of 14.98% by weight of butyllithium in hexane. A deep red color, characteristic of triphenylphosphorus ylids, developed immediately. This mixture was stirred for 15 min. and then 9-diazofluorene (I, 3.68 g.) was added. Stirring was continued overnight during which time the color changed from deep red to golden yellow. The reaction mixture was heated until it boiled and filtered hot, and 200 ml. of petroleum ether was added to the cooled benzene filtrate. A golden yellow precipitate of triphenylphosphine fluorenone azine (X) was filtered off, 2.3 g. (26.5%), m.p. 210–215°, lit.[15] m.p. 209–210°. Recrystallization from benzene gave an analytically pure sample which had m.p. 210–215°.

Anal. Calcd. for $C_{31}H_{23}N_2P$: C, 81.77; H, 5.06; N, 6.16; P, 6.88. Found: C, 81.68; H, 5.09; N, 6.26; P, 6.48.

The infrared spectrum was identical with that of an authentic sample.

The benzene–petroleum ether filtrate was reduced on a steam bath to a red oil which gave an orange-yellow solid upon being chilled in an ice–water bath. Recrystallization once from ethanol gave 1.2 g. (22.2%) of fluorenone benzalhydrazone (IX), m.p. 91–94°, lit.[16] m.p. 91–94°, mixture melting point with that of an authentic sample prepared according to Curtius and Kof[16] was undepressed.

9-Diazofluorene (I) and Pyridine N-Oxide (Table III).—A mixture of 3.00 g. (0.0156 mole) of 9-diazofluorene (I), 24 g. (0.25 mole) of pyridine N-oxide, and 30 ml. (or 60 ml.) of benzene was refluxed for 5 days. The reaction mixture was extracted with two 100-ml. portions of distilled water and two 15-ml. portions of 10% hydrochloric acid. The benzene layer (when applicable) was added to a suitable volumetric flask and diluted to the mark. An aliquot was then taken and evaporated to dryness on a steam bath under a stream of air. The ether-insoluble residue, fluorenone ketazine (VI, melting point and mixture melting point checked with an authentic sample), was recovered and the filtrate was evaporated to dryness in a sublimation apparatus. The residue was sublimed at a bath temperature of 85° (2–3 mm.) overnight to give fluorenone (IV, melting point and mixture melting point checked with an authentic sample). The total yield of fluorenone (IV) was calculated according to the following equation and is given in Table III: total volume of benzene solution in volumetric flask/ml. of aliquot × wt. of fluorenone sublimed = total wt. of fluorenone.

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[15] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 627 (1919).

[16] T. Curtius and K. Kof, *J. prakt. Chem.*, **86**, 113 (1912).

Phosphonium Salts. II. 2-Bromophenetole and Triphenylphosphorus as Novel Phosphonioethylation Precursors

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Triphenylphosphorus (I) and β-bromophenetole (II) in alcohol solvents gave high yields (45–88%) of the alkoxyethyltriphenylphosphonium bromides (IV). In nonhydroxylic solvents (and *t*-butyl alcohol) 1,2-ethylenebis(triphenylphosphonium bromide) (III) was obtained. Vinyltriphenylphosphonium bromide (V) was isolated (92%) and allowed to react with ROH, -SH, and -NH substrates.

Anionic, or Michael-type additions, have been observed with vinylsulfonium salts[1] and vinyldiphenylphosphine oxide.[2] Grayson and Keough[3] have recently shown that base-catalyzed reactions of vinyltributylphosphonium salts with compounds containing active hydrogens also undergo Michael-type additions (phosphonioethylations[3]) to give 2-substituted ethyl phosphonium salts. Wittig and Duffner[4] proposed vinyltriphenylphosphonium bromide (V) as an intermediate in the reaction of 1,2-ethylenebis(triphenylphosphonium bromide) (III) with lithium piperidide to give triphenyl(β-N-piperidinoethyl)phosphonium bromide, although the vinyl salt V was not isolated.

Pursuing our interest in the Wittig reaction,[5] we were led to undertake a study of the preparation of phosphorus salts of 2-substituted 1-bromoalkanes. The results of our studies of the reaction of triphenylphosphorus (I) with β-bromophenetole (II) in a variety of solvents showed this system to be a unique phosphonioethylation[3] precursor.

The preparation of 2-phenoxyethyltriphenylphosphonium bromide (IVf) was attempted by allowing triphenylphosphorus (I) and 2-bromophenetole (II) to react in a variety of nonprotonic solvents (Table I). The only products that were identifiable in these (and simple fusion) reactions were the unexpected 1,2-ethylenebis(triphenylphosphonium bromide) (III) and phenol.

$$\underset{\text{I}}{(C_6H_5)P} + \underset{\text{II}}{C_6H_5OCH_2CH_2Br} \xrightarrow[\text{and fusion}]{\text{nonprotonic solvents}} \underset{\text{III}}{\overset{-}{Br}(C_6H_5)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + C_6H_5OH \quad (1)$$

On employing methanol, ethanol, 1-butanol, benzyl alcohol, 2-propanol, or phenol as the solvent in the reaction of triphenylphosphorus (I) with 2-bromophenetole (II), the corresponding 2-alkoxy- or 2-phenoxyethyltriphenylphosphonium bromide (IV) was obtained in high yield (Table II).

The 2-phenoxyethylphosphonium bromide (IVf) decomposed readily, on heating in ethyl acetate (or ben-

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[1] W. von E. Doering and K. C. Schreiber, *J. Am. Chem. Soc.*, **77**, 514 (1955).

[2] M. I. Kabachnik, T. Y. Medved, Y. M. Polikarpov, and K. S. Yudena, *Izv. Akad. Nauk, SSSR Otd. Khim. Nauk*, **9**, 1584 (1962).

[3] M. Grayson and P. T. Keough, Abstracts of Papers, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 640.

[4] G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

[5] Paper I: E. E. Schweizer and R. Schepers, *Tetrahedron Letters*, **15**, 979 (1963).

TABLE I

REACTIONS YIELDING DISALT

$\overset{-}{Br}(C_6H_5)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}$ (III)

Precursors (mole)	Solvent	Reflux time, days	Yield of disalt III, %
1, $BrCH_2CH_2Br$ (0.09) + $(C_6H_5)_3P$ (0.018)	Ethanol (50 ml.)	1	94[a]
2, $CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}$ (0.003) + $(C_6H_5)_3P\cdot HBr$ (0.003)	Fuse at 120°	1.67	100
3, Same as 2	Ethyl acetate (25 ml.)	5	88
4, Same as 2	Chloroform (25 ml.)	5	100[b]
5, $C_6H_5OCH_2CH_2Br$ (0.1) + $(C_6H_5)_3P$ (0.1)	Fuse at 120°	2	28
6, $C_6H_5OCH_2CH_2Br$ (0.15) + $(C_6H_5)_3P$ (0.15)	Ethyl acetate[d] (200 ml.)	2	29
7, $C_6H_5OCH_2CH_2Br$ (0.05) + $(C_6H_5)_3P$ (0.05)	*t*-Butyl alcohol[d] (50 ml.)	2.5	24[c]
8, Same as 7	Benzene (150 g.)[e] + $C_6H_5OCH{=}CH_2$ (1.5 g.)	3	9
9, $C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}$ (0.003) + $(C_6H_5)_3P$ (0.003)	Benzene[d] (25 ml.)	2	Low
10, $C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}$ (0.003) + $(C_6H_5)_3P\cdot HBr$ (0.003)	Ethyl acetate (25 ml.)	5	63
11, $C_6H_5OCH_2CH_2Br$ (0.05) + $(C_6H_5)_3P$ (0.05) + $(C_6H_5)_3P\cdot HBr$ (0.05)	Ethyl acetate (150 ml.)	5	62[f]

[a] M.p. 297–300°, lit.[4] m.p. 308–315°. *Anal.* Calcd. for $C_{38}H_{34}Br_2P_2$: C, 64.06; H, 4.82. Found: C, 64.22; H, 4.66. [b] M.p. 305–315°. [c] Intractable residue also obtained. [d] No phenyl vinyl ether observed in the gas chromatographic analysis of the filtrate. [e] Gas chromatographic analysis of solvent system before and after reaction showed that the ratio of phenyl vinyl ether (VII) to benzene remained unchanged. [f] 76% based on recovered starting material.

$$\underset{\mathrm{I}}{(C_6H_5)_3P} + \underset{\mathrm{II}}{C_6H_5OCH_2CH_2Br} + ROH\ \text{solvent} \longrightarrow ROCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br} \qquad (2)$$

IVa, R = CH_3
b, R = C_2H_5
c, R = $CH_2(CH_2)_2CH_3$
d, R = $C_6H_5CH_2$
e, R = $CH(CH_3)_2$
f, R = C_6H_5

zene) solvent, to give better than 90% yield of vinyltriphenylphosphonium bromide (V). The salt (V) has recently been prepared and isolated (no yield given) by a unique route.[6]

$$\underset{\mathrm{IVf}}{C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)\overset{-}{Br}} \xrightarrow[\text{}]{\substack{\text{nonhydroxylic}\\ \text{solvent}}} \underset{\mathrm{V}}{CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + C_6H_5OH \qquad (3)$$

The phenoxyethylphosphonium salt (IVf) and the vinylphosphonium salt (V) both reacted readily on heating in alcohols to give the corresponding alkoxyethylphosphonium salts (IV). No basic catalysts were needed for any of the above mentioned reactions although reaction 4 was found to give higher yields when a catalytic amount of triphenylphosphorus (I) was present. The vinyl salt (V) gave essentially quantitative yields of the disalt (III, reaction 6) with triphenylphosphorus hydrobromide (VI).

$$\underset{\mathrm{IVf}}{C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + ROH \longrightarrow \underset{\mathrm{IVb,c}}{ROCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + C_6H_5OH \qquad (4)$$

$$\underset{\mathrm{V}}{CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + ROH \longrightarrow \mathrm{IVa,e} \qquad (5)$$

$$\underset{\mathrm{V}}{CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + \underset{\mathrm{VI}}{(C_6H_5)_3P\cdot HBr} \longrightarrow \mathrm{III} \qquad (6)$$

One of the mechanisms considered possible for the formation of the disalt III, from β-bromophenetole (II) and triphenylphosphorus (I) involves a decomposition of β-bromophenetole (II) under the influence of triphenylphosphorus to phenyl vinyl ether (VII) and triphenylphosphorus hydrobromide (VI) followed by the reaction (6) to give the disalt III. However the following series of experiments do not support this reasoning.

(a) Phenyl vinyl ether (VII) was recovered unchanged when it was allowed to be present during the formation of the disalt from reaction 1 in benzene.

(b) No phenyl vinyl ether (VII) was observed as a product in the gas chromatograms of the solvents used in reactions 1, 2, or 4.

(c) Phenyl vinyl ether (VII) reacts rapidly with triphenylphosphorus hydrobromide (VI) giving 1-phenoxyethyltriphenylphosphonium bromide (VIII). The latter salt (VIII) does not yield the bisphosphonium salt (III) on heating with the hydrobromide VI in a solvent, although the comparable reaction with 2-phenoxyethyltriphenylphosphonium bromide (IVf) readily gives the disalt III, in good yield (see Table I). The 1-phenoxyethyl salt (VIII) also does not give 2-ethoxyethyltriphenylphosphonium bromide (IVb) when allowed to react in ethanol.

$$\underset{\mathrm{VII}}{C_6H_5OCH{=}CH_2} + \underset{\mathrm{VI}}{(C_6H_5)_3P\cdot HBr} \longrightarrow \underset{\mathrm{VIII}}{C_6H_5OCH(CH_3)P(C_6\overset{+}{H}_5)_3\overset{-}{Br}^-} \qquad (7)$$

$$\mathrm{VIII} + C_2H_5OH \xrightarrow{\;/\!/\;} \mathrm{IVb}$$

$$\mathrm{VIII} + \mathrm{VI} \xrightarrow{\;/\!/\;} \mathrm{III}$$

The following mechanism is, therefore, proposed for the phosphonioethylations observed.

$$\underset{\mathrm{II}}{C_6H_5OCH_2CH_2Br} + \underset{\mathrm{I}}{(C_6H_5)_3P} \longrightarrow \underset{\mathrm{IVf}}{C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} \qquad (8)$$

$$C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br} + B{:} \longrightarrow C_6H_5OCH_2\overset{-}{C}H{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br} + B{:}\overset{+}{H} \qquad (9)$$

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(6) D. Seyferth, J. S. Fogel, and J. K. Heeren, *J. Am. Chem. Soc.*, **86**, 307 (1964).

TABLE II

$$\mathrm{C_6H_5OCH_2CH_2Br + (C_6H_5)_3P + ROH \longrightarrow ROCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$$

ROH	Solvent[a]	Product, m.p., °C.	Products (yield, %)	Analysis, % Calcd. C	Analysis, % Calcd. H	Analysis, % Found C	Analysis, % Found H
	Phenol	138–141	$\mathrm{C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (100)	67.39	5.22	66.43	4.93
	Thiocresol	161–163	$\mathrm{C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (95)	67.39	5.22	67.02	5.18
	Thiophenol		$\mathrm{C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (74)				
	Glacial acetic acid		$\mathrm{C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (100)				
$\mathrm{CH_3OH}$	Methanol	207–209[d]	$\mathrm{CH_3OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (47)[b]	62.6	5.5	62.81	5.69
$\mathrm{CH_3CH_2OH}$	Ethanol	179–181	$\mathrm{CH_3CH_2OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (72)	63.6	5.83	63.76	6.16
$\mathrm{CH_3(CH_2)_3OH}$	1-Butanol		$\mathrm{CH_3CH_2CH_2CH_2OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (45)[c]				
			$\mathrm{\overset{-}{Br}(C_6H_5)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (6)				
$\mathrm{C_6H_5CH_2OH}$	Benzyl alcohol	176–177.5	$\mathrm{C_6H_5CH_2OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (52)	67.93	5.49	67.98	5.67
$\mathrm{CH_3CHOHCH_3}$	2-Propanol		$\mathrm{(CH_3)_2CHOCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (88)[c]				
			$\mathrm{Br(C_6H_5)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (5)				
$\mathrm{CH_3CHOHCH_3}$	2-Propanol + 0.5 mole of acetic acid per mole of β-Bromophenetole		$\mathrm{(CH_3)_2CHOCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (50)[c]				
			$\mathrm{\overset{-}{Br}(C_6H_5)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (42)				

[a] Reaction time ranged from 2 to 5 days at reflux temperature or 100° whichever was lower. [b] Yield is 72% if based on recovered triphenylphosphorous. [c] Yield based on starting materials not consumed by the disalt III found. [d] O. Isler, M. Montavon, R. Ruegg, and P. Zeller [German Patent 1017163; *Chem. Abstr.*, **53,** 18,982*c* (1959); **53,** 13,412*g* (1958)] report m.p. 195–197°.

$$\mathrm{C_6H_5OCH_2\overset{-}{C}H{-}\overset{+}{P}(C_6H_5)_3Br^-} \longrightarrow \mathrm{C_6H_5O^- + \underset{V}{CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}} \qquad (10)$$

$$\mathrm{C_6H_5O^- + B{:}\overset{+}{H} \longrightarrow C_6H_5OH + B{:}} \qquad (11)$$

$$\mathrm{B{:} + C_2H_5OH \longrightarrow C_2H_5O^- + B{:}\overset{+}{H}} \qquad (12)$$

$$\mathrm{C_2H_5O^- + CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} \longrightarrow \mathrm{C_2H_5OCH_2{-}\overset{-}{C}H{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} \qquad (13)$$

$$\mathrm{C_2H_5OCH_2{-}\overset{-}{C}H\overset{+}{P}(C_6H_5)_3\overset{-}{Br} + B{:}H} \longrightarrow \mathrm{\underset{IVb}{C_2H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + B{:}} \qquad (14)$$

$$\mathrm{CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br} + (C_6H_5)_3P} \longrightarrow \mathrm{\underset{V}{[(C_6H_5)_3\overset{+}{P}{-}CH_2{-}\overset{-}{C}H{-}\overset{+}{P}(C_6H_5)_3]\overset{-}{Br}}} \qquad (15)$$

$$\mathrm{[(C_6H_5)_3\overset{+}{P}{-}CH_2{-}\overset{-}{C}H_2{-}\overset{+}{P}(C_6H_5)_3]\overset{-}{Br} + \underset{IVf}{C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}} \longrightarrow \mathrm{\underset{III}{\overset{-}{Br}(C_6H_5)_3\overset{+}{P}{-}CH_2{-}CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + C_6H_5\overset{-}{O}[CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3]} \qquad (16)$$

The mechanism proposed above, 8 through 16, suggests that high yields of the diphosphonium salt may be obtained by allowing equimolar quantities of triphenylphosphorus (I), β-bromophenetole (II), and triphenylphosphorus hydrobromide (VI) to react together. These expectations were fulfilled by carrying out this reaction in ethyl acetate; the disalt III, was obtained in 81% yield.

The disalt III, was prepared in 87% yield from 1,2-dibromoethane and triphenylphosphorus in ethanol, thus showing that the alkoxyethylphosphonium salts (IV) did not arise by the decomposition of disalt. The latter salts (IV) may be prepared readily from the disalt III, under the influence of a strong base (Table III).

$$\mathrm{\overset{-}{Br}(C_6H_5)_3\overset{+}{P}{-}CH_2CH_2{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br} + ROH} \xrightarrow{\mathrm{R\overset{-}{O}M^+}} \mathrm{\underset{IVa,c}{ROCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + (C_6H_5)_3P} \qquad (17)$$

The ready elimination of phenol from 2-phenoxyethyltriphenylphosphonium bromide (IVf), even under the conditions of recrystallization, made it impossible to prepare this salt in analytical purity from phenol solvent. However, when the phenol solvent was replaced by protonic solvents of greater acidity, such as thiophenols or acetic acid, high yields (74–100%) of the phenoxyethyl salt (IVf) could be obtained. Evidently traces of these solvents inhibited the decomposition of salt IVf prepared in this manner because analytically pure samples heated in ethyl acetate or ethanol did not give the expected vinyltriphenylphosphonium bromide (V) or the 2-ethoxyethyltriphenylphosphonium bromide (IVb). However, after repeated precipitations (five–seven times) from chloroform-ether, a lowering in melting point of salt IVf was noted and on refluxing in ethanol at this point a high yield

Table III

$$\bar{B}r(C_6H_5)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_6H_5)_3\bar{B}r + ROH + ROM \longrightarrow ROCH_2CH_2\overset{+}{P}(C_6H_5)_3\bar{B}r$$

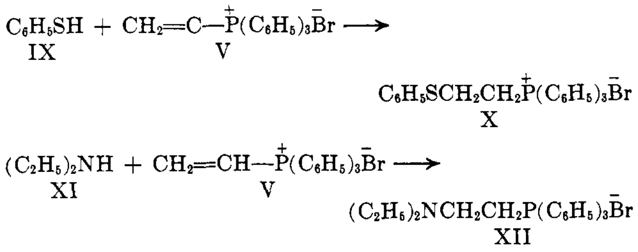
Salt III, mole	Alcohol (ml.)	Base (mole)	Reaction time, hr.	Product (yield, %)
0.02	Methanol (170)	Sodium methoxide (0.022)	12	$CH_3OCH_2CH_2\overset{+}{P}(C_6H_5)_3\bar{B}r$ (42)
0.025	1-Butanol (100)	Potassium *t*-butylate (0.0025)	40	$CH_3(CH_2)_3OCH_2CH_2\overset{+}{P}(C_6H_5)_3\bar{B}r$ (50)[a]

[a] 63% based on recovered disalt.

(67%) of the desired ethoxyethylphosphonium salt (V) was obtained. The conversion of the analytically pure phenoxy salt IVf to the desired ethoxy salt IVb was also accomplished by adding a catalytic amount of triphenylphosphorus (I).

All the alcohols used as solvents gave respectable yields of the alkoxyphosphonium salts (IV) as shown in Table II. However, when *t*-butyl alcohol was used as solvent (Table I) only the diphosphonium salt (III) could be isolated. Furthermore, when *t*-butyl alcohol was allowed to reflux with the vinyltriphenylphosphonium bromide (V), it did not react and, in fact, *t*-butyl alcohol was found to be an ideal solvent for carrying out recrystallizations of salt V. This lack of reactivity may possibly be attributed to steric inhibition or low acidity.

Thiophenol (IX) and diethylamine (XI) both gave the respective adducts X and XII with the vinyltriphenylphosphonium bromide (V) in quantitative yields (Table II), indicating that the ability of the salt V is certainly equivalent to or better than that of the vinyltributylphosphonium bromide in phosphonioethylation reactions as described by Grayson and Keough,[3] since present reactions did not require the use of added basic catalysts.[7]



$$\underset{\text{IX}}{C_6H_5SH} + \underset{\text{V}}{CH_2{=}C{-}\overset{+}{P}(C_6H_5)_3\bar{B}r} \longrightarrow \underset{\text{X}}{C_6H_5SCH_2CH_2\overset{+}{P}(C_6H_5)_3\bar{B}r}$$

$$\underset{\text{XI}}{(C_2H_5)_2NH} + \underset{\text{V}}{CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\bar{B}r} \longrightarrow \underset{\text{XII}}{(C_2H_5)_2NCH_2CH_2P(C_6H_5)_3\bar{B}r}$$

Recently Rauhut, *et al.*,[8] have shown that the reaction of triphenylphosphorus (I) with 2-chloroethylacetate, in the absence of a solvent, yields 2-ethylenebis(triphenylphosphonium chloride), suggesting a reaction path similar to that described herein. It is interesting to note that when equimolar quantities of triphenylphosphorus (I) and β-bromophenetole (II) were allowed to react in isopropyl alcohol contaminated with a 0.5-*M* quantity of acetic acid (Table II), a 42% yield of the disalt was obtained with only a 50% yield of the 2-isopropoxyethyltriphenylphosphonium bromide (IVe) based on the remaining starting material.

The effect of steric hindrance, acidity, and nucleophilicity on the ability of protonic substrates to undergo Michael-like additions are under investigation.

Experimental

The experiments given are not necessarily the ones that afford the highest yields of an individual salt, but the ones which illustrate a procedure for separating the products obtained. The names of the compounds produced are followed by a "table" reference when they characterize a general reaction procedure.

All melting points were uncorrected and obtained on a Fischer-Johns melting point apparatus. The gas chromatographic analyses (v.p.c.) were obtained on a 6-ft. Dow 710 silicon-on-firebrick column. The infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer; the n.m.r. spectra were obtained on an A-60 Varian analytical n.m.r. spectrometer.

Reagents.—Triphenylphosphorus, obtained from Metal and Thermit Chemicals, Inc., Rahway, N. J., was purified by recrystallization from anhydrous ether. The β-bromophenetole was obtained from Fisher Scientific Co., Philadelphia, Pa., and was used as purchased. Anhydrous, reagent grade solvents were employed in all cases.

2-Phenoxyethyltriphenylphosphonium Bromide (IVf, Table II).—Forty grams of β-bromophenetole and 52.4 g. of triphenylphosphorus were heated at 90° for 48 hr. in 400 g. of phenol. The solution was stirred into 2500 ml. of anhydrous ether and agitated until white crystals formed. The mixture was filtered, washed throughly with hot anhydrous ether, and after drying (60° under reduced pressure) gave an essentially quantitative yield (92 g.) of the phenoxy salt (IVf), m.p. 138–141°. Attempts at crystallization from cold chloroform–tetrahydrofuran lowered the melting point of the salt with the appearance of phenol in the crystallizing solvent (by v.p.c.) indicating decomposition of the salt (IVf). For analysis see Table II. The infrared and n.m.r. spectra were identical with those of the analytically pure sample prepared in thiocresol solvent (Table II).

The n.m.r. spectra of the analytical sample of salt IVf made from thiocresol in deuteriochloroform follow: centered at τ 2.3, aromatic multiplet, weight 15.3, assigned to the triphenylphosphorus phenyls; at τ 2.9 and 3.5, aromatic multiplet and a split doublet assigned to the phenoxy phenyl, weight 2.9 and 2, respectively; at τ 5.5, aliphatic multiplet, weight 3.9, assigned to the methylene hydrogens.

Vinyltriphenylphosphonium Bromide (V).—Three grams of the recrystallized 2-phenoxytriphenylphosphonium bromide (IVf) obtained in the previous experiment was allowed to stir under reflux for 48 hr. in 25 ml. of ethyl acetate. The mixture was cooled, poured into 50 ml. of anhydrous ether, and filtered. The residue was treated once more exactly as described above. The white crystalline residue was washed with tetrahydrofuran and then ether. Drying under reduced pressure gave 2.2 g. (92%) of vinyltriphenylphosphonium bromide (V), m.p. 189–190°.

A sample obtained from a similar reaction was shown to be analytically pure, m.p. 189–190°, lit.[3] m.p. 185–187°.

Anal. Calcd. for $C_{20}H_{18}BrP$: C, 65.05; H, 4.91. Found: C, 64.99; H, 4.93.

The n.m.r. spectra of the analytically pure sample obtained in deuteriochloroform follow: centered at τ 2.2, an aromatic multiplet which overshadowed the —CH of the vinyl group, weight 16; centered at τ 3.62, a sextet with a span of 10.2 p.p.m., weight 1.96, ascribed to the vinyl =CH₂ group.

1,2-Ethylenebis(triphenylphosphonium bromide) (III, Table I). A. From β-Bromophenetol (II) and Triphenylphosphorus (I).—Thirty grams of β-bromophenetole (II) and 39 g. of triphenylphosphorus (I) were refluxed with stirring in 200 ml. of ethyl acetate for 48 hr. Phenol was observed as the only by-product by v.p.c. (gas phase chromatography) from the decanted solvent. The tarry residue was washed and stirred with acetone until white crystals remained. The disalt III, 15.5 g. (29%) recovered, m.p. 275–285°, was recrystallized once from dioxane

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[7] It is recognized that, as the referee pointed out, diethylamine, triphenylphosphorus, and the thiophenoxide ion (the latter from dissociation of thiophenol) are all good bases.

[8] M. M. Rauhut, G. B. Borowitz, and H. C. Gillham, *J. Org. Chem.*, **28**, 2565 (1963).

with a trace of water. The pure product had m.p. 295–300°. The mixture melting point and infrared spectra were identical with that of the authentic sample prepared from 1,2-dibromoethane (Table I).

B. From Vinyltriphenylphosphonium Bromide (V) and Triphenylphosphorus Hydrobromide.—Triphenylphosphorus hydrobromide (1.3 g.) and 1.2 g. of vinyltriphenylphosphonium bromide (V) were stirred and refluxed for 5 days in 25 ml. of ethyl acetate. The product was filtered, washed with ether, and dried to give 2.2 g. (88%) of the disalt III, m.p. 300–305°. Mixture melting point and infrared spectra were identical with that of the authentic sample.

2-Isopropoxyethyltriphenylphosphonium Bromide (IVc, Table II).—Triphenylphosphorus (I, 13.1 g.) and 10.1 g. of β-bromophenetole (II) were placed in a solvent system prepared from 50 ml. of 2-propanol and 1.5 g. of glacial acetic acid and allowed to reflux for 4 days. The solution was poured into 400 ml. of anhydrous ether. The solvent was decanted from the viscous yellow precipitate and the precipitate was triturated with 400 ml. more of ether yielding, after filtration and drying, 15.3 g. of light yellow crystals, m.p. 200–215°. The solvent showed phenol as the only volatile product (v.p.c.). The crystals were refluxed with agitation in 100 ml. of acetone. The mixture was filtered giving 7.4 g. (42%) of 1,2-ethylenebis(triphenylphosphonium bromide) (III), m.p. 305–308°, mixture melting point and infrared spectra identical with that of an authentic sample.

The acetone filtrate was treated with ether and gave 6.1 g. (50% based on starting material left after disalt formation) of 2-isopropoxyethyltriphenylphosphonium bromide (IVe), m.p. 198–201°; infrared spectra and mixture melting point were identical with the analytical sample (Table IV).

TABLE IV

$$\underset{\mathrm{V}}{\mathrm{CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}} + \mathrm{RXH} \longrightarrow \underset{\mathrm{IVa,e,\ X,\ XII}}{\mathrm{RXCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}}$$

RXH (ml.)	Reaction time, days	Temp., °C.	Product (yield, %)
Methanol (20)[a]	0.833	Reflux	$\mathrm{CH_3OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (100)
Isopropyl alcohol (25)[a]	2	Reflux	$\mathrm{(CH_3)_2CHOCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (88)[b]
Thiophenol (25)[a]	1	90	$\mathrm{C_6H_5SCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (100)[c]
Diethylamine (20)[a]	3	Reflux	$\mathrm{(CH_3CH_2)_2NCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (100)[d]
t-Butyl alcohol (25)[a]	1	Reflux	No reaction[e]

[a] Reactions run with (0.0027 mole) salt $\mathrm{CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$. [b] *Anal.* Calcd. for $C_{23}H_{26}BrOP$: C, 64.34; H, 6.10. Found: C, 64.15; H, 5.98. M.p. 198–202°. [c] *Anal.* Calcd. for $C_{26}H_{24}BrPS$: C, 65.13; H, 5.05; Br, 16.68. Found: C, 65.32; H, 4.99; Br, 16.49. [d] *Anal.* Calcd. for $C_{24}H_{29}BrNP$: C, 65.16; H, 6.61; Br, 18.07. Found: C, 64.95; H, 6.62; Br, 18.27. M.p. 178–182°. [e] No reaction, salt $\mathrm{CH_2{=}CH{-}\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ recovered quantitatively unchanged.

2-Ethoxyethyltriphenylphosphonium Bromide (IVb, Table V).—2-Phenoxyethyltriphenylphosphonium bromide (IVf) (4.63 g., prepared in phenol) and 0.26 g. of triphenylphosphorus (I) were placed in 25 ml. of absolute ethanol and allowed to reflux 40 hr. The solution was poured into 400 ml. of dry ether with stirring, and white crystals precipitated. Filtration and thorough washing of the residue gave 3.0 g. (72%) of pure 2-ethoxyethyltriphenylphosphonium bromide (IVb), m.p. 179–181°. Phenol was found as the only volatile product of the reaction (v.p.c.). Mixture melting point and infrared spectra were identical with an authentic sample prepared from 2-bromoethyl ethyl ether and triphenylphosphorus in acetonitrile (87% yield), m.p. 179–181°, and with the analytical sample (Table II).

TABLE V

$$\underset{\mathrm{IVf}}{\mathrm{C_6H_5OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}} + \mathrm{ROH} \longrightarrow \mathrm{ROCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}} + \mathrm{C_6H_5OH}$$

Salt IVf, mole	Solvent (ml.)	Product (yield, %)[a]
0.0065[b]	Ethanol (25)	$\mathrm{CH_3CH_2OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (52)
0.01[b,c]	Ethanol (25)	$\mathrm{CH_3CH_2OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (72)
0.01[d]	Ethanol (25)	$\mathrm{CH_3CH_2OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (67)
0.01[c,e]	Ethanol (25)	$\mathrm{CH_3CH_2OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (45)
0.0032[b]	1-Butanol (25)	$\mathrm{CH_3(CH_2)_3OCH_2CH_2\overset{+}{P}(C_6H_5)_3\overset{-}{Br}}$ (97)[f]

[a] Obtained after refluxing solution 40 hr. [b] Phenoxy salt (IVf) prepared in phenol solvent. [c] With triphenylphosphorus (I), 0.001 mole added as catalyst. [d] Phenoxy salt (IVf) prepared in acetic acid followed by repeated precipitations from chloroform–ether (six times). [e] Phenoxy salt (IVf) prepared in thiocresol. [f] *Anal.* Calcd. for $C_{24}H_{28}BrOP$: C, 65.01; H, 6.37. Found: C, 65.24; H, 6.37. M.p. 170–174°.

2-Thiophenoxyethyltriphenylphosphonium Bromide (X, Table IV).—One gram of vinyltriphenylphosphonium bromide (V) was placed in 25 ml. of thiophenol and allowed to stir for 24 hr. at 90°. The reaction mixture was poured into 300 ml. of anhydrous ether with vigorous stirring to give 1.4 g. of white crystals, m.p. 137–142°. Recrystallization from chloroform–tetrahydrofuran–ether solvent system gave 1.3 g. (100%) of analytically pure 2-thiophenoxyethyltriphenylphosphonim bromide (X), m.p. 148–149° (Table IV).

2-*n*-Butoxyethyltriphenylphosphonium Bromide (IVc, Table III).—Commercial potassium *t*-butoxide (2.8 g.), 17.8 g. of 1,2-ethylenebis(triphenylphosphonium bromide) (III), and 100 ml. of 1-butanol were added to a flask in a drybox. The mixture was heated and stirred under a nitrogen blanket at 90° for 40 hr. The mixture was cooled and filtered; 3 g. of potassium bromide was recovered. The mixture was quenched with ether and the crystalline product was extracted with hot acetone; the residue was washed thoroughly with ether and dried, affording 4.3 g. of the disalt III starting material; melting point, mixture melting point and infrared spectra were identical with that of an authentic sample.

The acetone extracts were combined and treated with ether to give 5.5 g. (50%) of 2-butoxyethyltriphenylphosphonium bromide, m.p. 160–165°. Two recrystallizations from 1-butanol–ether gave the analytically pure sample, m.p. 170–172°; mixture melting point and infrared and n.m.r. spectra showed this sample to be identical with the sample obtained by allowing β-bromophenetole (II) and triphenylphosphorous (I) to react in 1-butanol (Table II).

1-Phenoxyethyltriphenylphosphonium Bromide (VIII).—Six grams of phenyl vinyl ether (VII) was added with stirring to a mixture of triphenylphosphorus hydrobromide (VI) in 100 ml. of dry acetone. The hydrobromide (VI) immediately went into solution with the evolution of heat. The reaction was allowed to stir at room temperature for 4 hr., and the solvent was evaporated on a rotary evaporator. The brown gummy residue was triturated with petroleum ether (b.p. 30–60°). Filtration gave 22.0 g. (94.5% yield) of 1-phenoxyethyltriphenylphosphonium bromide (VIII), m.p. 102–110°. On recrystallization three times from chloroform–ether, analytically pure, very hygroscopic white crystals were obtained, m.p. 132–135°.

Anal. Calcd. for $C_{26}H_{24}BrOP$: C, 67.39; H, 5.22. Found: C, 67.49; H, 5.31.

The n.m.r. spectrum in $CDCl_3$ follow: centered at τ 2.23, 2.67, and 2.96, two aromatic multiplets and a doublet somewhat overlapped, assigned to the phenoxy and triphenylphosphorus phenyls and the tertiary proton, weight 21 ± 2; centered at τ 8.24, a split doublet, weight 3, assigned to the C-methyl protons.

Reaction of 1-Phenoxyethyltriphenylphosphonium Bromide (VIII) with Triphenylphosphorus Hydrobromide.—One gram of triphenylphosphorus hydrobromide and 1.35 g. of the salt VIII were allowed to reflux in 20 ml. of benzene for 24 hr. No phenol was observed, with v.p.c., of the solvent. On quenching with ether and decanting, the sirupy product was washed with cold water. Concentration of the water showed no solubility of the product in water. On heating the sirupy product to reflux in water it became soluble.

Formation of the disalt III would produce phenol. The disalt III is highly soluble in cold water. Thus this material (salt VIII) could not be an intermediate in the reaction.

Reaction of 1-Phenoxyethyltriphenylphosphonium Bromide (VIII) with Ethanol.—One gram of the disalt VIII was refluxed 24 hr. in 20 ml. of ethanol. Ether was added and a trace of gummy sirup precipitated. This material was intractable and could not be crystallized to yield 2-ethoxyethyltriphenylphosphonium bromide (IVb). The solvent showed phenol to phenyl vinyl ether in a 2:1 ratio.

None of the 2-ethoxy salt (IVb) was found and phenyl vinyl ether (VII) was observed, with v.p.c. of the solvent system. The ether VII was not observed in the solvent system from the reactions of the 2-phenoxy salts (IVf); thus, it is felt that the 1-phenoxy salt (VIII) cannot be an intermediate in our reaction.

Nucleophilic Substitution at the Pyridazine Ring Carbons. III. Alkoxide Exchange[1]

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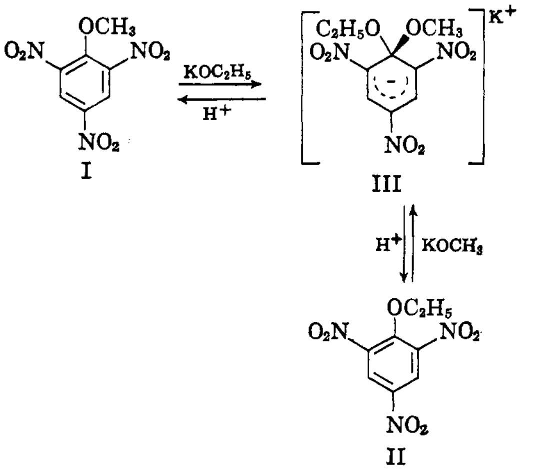
The phenomenon of alkoxide exchange in the mono-, di-, and bisalkoxypyridazines has been experimentally established. It has been utilized in a novel synthesis of monoalkoxypyridazines. A general method for the preparation of nonbisdialkoxypyridazines is described.

Meisenheimer[3] has established that ethers of strongly acidic phenols can be attacked at the benzene ring carbon by alkoxides. Thus, when 2,4,6-trinitroanisole (I) is treated with potassium ethoxide, the corresponding phenetole (II) is produced. Compound II can be reconverted to I by treatment with excess potassium methoxide. In addition, an isolable adduct (III) is obtained which is identical for both reactions. This gives convincing evidence for the route of the reaction.[4] The success of this exchange is attributed to the positive nature of the benzene ring carbon attached to the ether oxygen and the subsequent attack by the nucleophilic reagent.

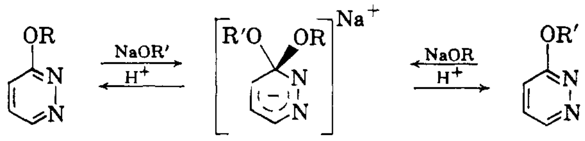


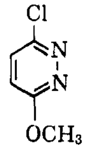
I

III

II

In the light of recent work in this laboratory concerning nucleophilic attacks at the pyridazine ring carbons,[5-7] it seemed of interest to attempt to extend alkoxide exchange to the field of pyridazines. A possibility that such an exchange might occur in the pyridazine ring system is found in the experimental section of a paper by Steck and Brundage.[8] They reported that when 3-chloro-6-methoxypyridazine (IV), the purity of which had not been elucidated, was treated with an equivalent amount of sodium 2-diethylaminoethoxide (V), a halogen-containing oil was formed. This oil was a mixture which was shown to contain some 3,6-bis(2-diethylaminoethoxy)pyridazine (VI) by formation of the known bismethiodide derivative.





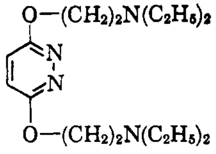
IV

$(C_2H_5)_2N—(CH_2)_2ONa$

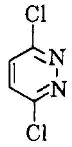
V

$(CH_3)_2N—(CH_2)_2ONa$

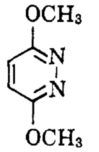
VII



VI



VIII



IX

The work of Steck was repeated using sodium 2-dimethylaminoethoxide (VII) in place of V. It became evident in the preparation of 3-chloro-6-methoxypyridazine (IV) using the traditional route that the product contained up to 20% impurities as shown by g.l.c. analysis. The contaminants occurred in equal amounts and were 3,6-dichloropyridazine (VIII) and 3,6-dimethoxypyridazine (IX). Hence, elemental analysis would agree with the desired product IV, and would not reveal the presence of a mixture containing IV along with equal parts of VIII and IX. If Steck

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[3] J. Meisenheimer, *Ann.*, **323**, 205 (1902).

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[6] P. Coad and R. Coad, *ibid*., **28**, 1919 (1963).

[7] P. Coad, R. Coad, and C. Wilkins, *J. Phys. Chem.*, in press.

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