Preparation and Chemistry of Some Pentasubstituted Phosphorus Compounds[1]

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Abstract: A series of trisubstituted phosphorus compounds have been allowed to react with diethyl peroxide. Materials with only phenyl and ethoxy groups bonded to phosphorus react to give pentasubstituted phosphorus compounds. The compound diphenyltriethoxyphosphorane undergoes pseudorotation at room temperature. At −60° pseudorotation has been slowed sufficiently so that two kinds of ethoxy groups are observed in the ^{1}H nmr spectrum. Dimethylphenylphosphine and trimethylphosphine react with diethyl peroxide to give substances which appear to be equilibrium mixtures of the pentasubstituted phosphorus compound and the phosphonium ethoxide. Various N,N-dialkylaminophosphines react with diethyl peroxide to give pentasubstituted compounds or the phosphine oxide. Products of the exchange of ethoxy groups for the N,N-dialkylamino groups are also observed.

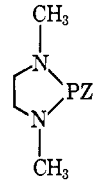
There are few general methods for the preparation of pentasubstituted phosphorus compounds. Various condensation reactions have been used with great success by Ramirez and his coworkers to prepare an exceedingly diverse variety of pentasubstituted phosphorus compounds in which the phosphorus is incorporated in one or more five-membered rings.[3] Pentaphenoxyphosphorane has also been prepared by this group.

It has been shown that diethyl peroxide reacts with acyclic and cyclic phosphites to give pentaoxyphosphoranes.[4] The reactions of triphenylphosphine and tributylphosphine with diethyl peroxide have been reported.[5] It was concluded that triphenylphosphine formed a stable pentasubstituted compound. The structure of the product from tributylphosphine was not nearly so clear. It was the purpose of the investigation to study the reactions of a wide variety of trisubstituted phosphines with diethyl peroxide. The major emphasis of this work has been to determine if pentasubstituted phosphorus compounds are formed and if so some information has been sought on their stability and their ability to undergo pseudorotation.[6]

Results

The compounds chosen for this study were **1–11**. Reaction of substances **1–3** with diethyl peroxide proceeded smoothly to give materials in solution with the following characteristics: (1) each reacted with benzoic acid to give ethyl benzoate and the phosphorus compound containing a phosphoryl group; (2) the ^{31}P nmr chemical shift of the major product was considerably more positive than that of the starting tricovalent phosphorus compound; and (3) the ^{1}H nmr spectra of the methylene protons consisted of two overlapping quartets which appeared as apparent quintets. The methyl protons of the compound from **1** were found as a triplet as were those of the compound from **2**. The methyl protons from the compound derived from **3** were found as a triplet which was further split by phosphorus into a sextet. All of the ethoxy groups in each substance showed equivalent methylene and methyl absorptions. The ^{31}P nmr data are collected in Table I and the ^{1}H nmr data are collected in Table II. The variable-temperature ^{1}H nmr spectra of these products have been investigated. The triphenylphosphine–diethyl peroxide product showed essentially no variation in its ^{1}H nmr spectrum between −60 and 120°. The compound from ethyl diphenylphosphinite and diethyl peroxide showed an interesting temperature variation in its ^{1}H nmr spectrum. At −60° one ethoxy group ab-

$(C_6H_5)_nP(OC_2H_5)_m$	$(C_6H_5)_nP(CH_3)_m$	$(C_6H_5)_nP[N(C_2H_5)_2]_m$
1, $n = 3$; $m = 0$	**4**, $n = 2$; $m = 1$	**7**, $n = 2$; $m = 1$
2, $n = 2$; $m = 1$	**5**, $n = 1$; $m = 2$	**8**, $n = 1$; $m = 2$
3, $n = 1$; $m = 2$	**6**, $n = 0$; $m = 3$	**9**, $n = 0$; $m = 3$



10, Z = OC_2H_5
11, Z = $N(CH_3)_2$

Table I. ^{31}P Nmr Spectral Results

Compound	$^{31}P^a$	Compound	$^{31}P^a$
$(C_6H_5)_3P$	+5	$(C_6H_5)_2PCH_3$	+28
$(C_6H_5)_3PO$	−28	$(C_6H_5)_2P(O)CH_3$	−27
$(C_6H_5)_3P(OC_2H_5)_2$	+54	$(C_6H_5)_2P(CH_3)(OC_2H_5)_2$	+47
$(C_6H_5)_2POC_2H_5$	−112	$C_6H_5P(CH_3)_2$	+47
$(C_6H_5)_2P(O)OC_2H_5$	−32	$C_6H_5P(O)(CH_3)_2$	−32
$(C_6H_5)_2P(OC_2H_5)_3$	+41	$C_6H_5P(CH_3)_2(OC_2H_5)_2$	+40
$C_6H_5P(OC_2H_5)_2$	−156	$(CH_3)_3P$	+62
$C_6H_5P(O)(OC_2H_5)_2$	+20	$(CH_3)_3PO$	−36
$C_6H_5P(OC_2H_5)_4$	+55	$(CH_3)_3P(OC_2H_5)_2$	+39

[a] All spectra were recorded in methylene chloride at 40.5 MHz; shifts are relative to 85% H_3PO_4.

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[2] Special Postdoctoral Fellow of the National Institutes of Health, 1967–1968.

[3] See F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968), for an up to date review.

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[5] D. B. Denney, D. Z. Denney, and L. A. Wilson, *Tetrahedron Letters*, 85 (1968).

[6] See F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968), for a timely discussion of pseudorotation in pentasubstituted phosphorus compounds.

Table II. ^{1}H Nmr Spectral Results of Ethoxy Groups[a]

Compound	Solvent	Temp, °C	^{1}H–CH$_2$	J	Multiplet	^{1}H–CH$_3$	J	Multiplet
$(C_6H_5)_3P(OC_2H_5)_2$	CS_2	R.T.	2.50	7	5	0.72	7	3
	CS_2	−50	2.46	7	5	0.72	7	3
	CH_2Cl_2	R.T.	2.54	7	5	0.72	7	3
	C_6H_5Cl	R.T.	2.61	7	5	0.76	7	3
	C_6H_5Cl	120	2.65	7	5	0.74	7	3
$(C_6H_5)_2P(OC_2H_5)_3$	CS_2	R.T.	3.35	7	5	0.99	7	3
	CS_2	−60	4.35 (1)	7	5	1.27 (1)	7	3
			2.78 (2)	7	5	0.81 (2)	7	3
	CS_2	−40	4.35		*b*	?		*b*
			2.78		*b*	0.81		*b*
	CD_2Cl_2	R.T.	3.40	7	5	1.00	7	3
	CD_2Cl_2	−60	4.39		*b*	1.22		*b*
			2.83		*b*	0.83		*b*
$C_6H_5P(OC_2H_5)_4$	CD_2Cl_2	R.T.	3.68	7	5	1.07	7	6[c]
	CD_2Cl_2	−60	3.67		*b*	1.07	7	*b*
$(C_6H_5)_2PCH_3(OC_2H_5)_2$	CH_2Cl_2	R.T.	2.64	7	5	0.73	7	3
	CH_2Cl_2	−60	2.57	7	5	0.75	7	3
	C_6H_5Cl	R.T.	2.68	7	5	0.78	7	3
	C_6H_5Cl	60	2.68	7	5	0.78		3
$C_6H_5P(CH_3)_2(OC_2H_5)_2$	CH_2Cl_2	R.T.	2.80		*b*	0.82	7	3
	CH_2Cl_2	−60	2.70	7	5	0.80	7	3
	C_6H_5Cl	R.T.	2.76	7	5 (?)	0.87	7	3
	C_6H_5Cl	100	2.80		*b*	0.82	7	3
$(CH_3)_3P(OC_2H_5)_2$	CH_2Cl_2	30	3.28	7	4	0.97	7	3
	CH_2Cl_2	−40	3.30		*d*	0.99	7	3

[a] All spectra were recorded at 100 MHz. [b] Broad absorptions were found under these conditions. [c] $J_{pH} = 1$. [d] Poorly defined quartet.

sorbed at 4.35 (CH_2) and 1.27 (CH_3) and the other two absorbed at 2.77 (CH_2) and 0.82 (CH_3). The product from diethyl phenylphosphonite and diethyl peroxide showed no important variation in its ^{1}H nmr spectrum on cooling to −60°.[7]

The reactions of compounds **4**–**6** with diethyl peroxide also proceeded smoothly to give in each case one major product. These products all reacted with benzoic acid to give ethyl benzoate and the appropriate phosphine oxide. The trend toward high upfield chemical shifts of the ^{31}P nmr absorptions of the products relative to the starting materials which was found with the products of the reactions of **1**–**3** was not followed in this series. The only product which absorbed at higher fields was that from **4**. The nmr spectral data are collected in Tables I and II.

The ^{1}H nmr spectrum of the product from **4** has a doublet for the methyl group bonded to phosphorus. The methylene hydrogens of the ethoxy groups appear as two overlapping quartets and the methyl hydrogens are found as a triplet.

The product from dimethylphenylphosphine and diethyl peroxide shows a doublet for the methyl protons of the PCH_3 group. The methylene protons of the ethoxy groups give a well-resolved quartet and the methyl protons are found as a triplet.

The variable-temperature spectra of these substances have been investigated. There is essentially no variation in the spectrum of the product from diphenylmethylphosphine and diethyl peroxide over the range −60 to 60°. The product from dimethylphenylphosphine and diethyl peroxide at −60° shows a fairly well-resolved quintet for the methylene protons of the ethoxy group. The same material in chlorobenzene rather than methylene chloride shows a very poorly resolved quintet for the methylene protons at room temperature which degenerates to a broad absorption at 100°.

The ^{1}H nmr spectrum at −50° of the product from trimethylphosphine and diethyl peroxide shows considerable broadening of the quartet of the methylene protons. The rest of the spectrum did not change.

Phosphines **7**–**9** also reacted smoothly with diethyl peroxide. In the case of **8** and **9** the only products were the corresponding phosphine oxides. In the case of **7** absorptions were found at +47, +43, −30, and −61 in the ^{31}P nmr spectrum after 3 days. The latter absorption is due to starting material and the absorption at −30 is due to $(C_6H_5)_2P(O)N(C_2H_5)_2$ and $(C_6H_5)_2P(O)OC_2H_5$. The absorption at +43 is the same as that found from the reaction of **2** and diethyl peroxide. When the reaction mixture was treated with benzoic acid, ethyl benzoate was formed, the absorption at −30 increased in intensity, and the absorptions at +47 and +43 disappeared.

Reaction of **10** with diethyl peroxide gave after 3 days a solution whose ^{31}P nmr spectrum showed a major absorption at +56. Starting material was still present and some of the oxide from **10** had formed. Two unidentified components were present. They had absorptions at −10.5 and +1. Addition of benzoic acid gave ethyl benzoate and mainly the material absorbing at −10.5.

Reaction of **11** with diethyl peroxide gave after 9 days a solution which contained **10**, **11**, and the oxide from **11**. There were also absorptions at −18.5, 49, and 56. Addition of benzoic acid yielded ethyl benzoate. A new absorption appeared in the ^{31}P nmr spectrum at −10 and those at +49 and +56 disappeared.

Discussion

It is believed that the compounds formed from **1**–**3** are pentasubstituted phosphorus compounds, **12**–**14**. The evidence for these structures is quite conclusive; thus the high-field absorption in the ^{31}P nmr spectra is highly indicative of a pentasubstituted phosphorus compound.[8] The ^{1}H nmr spectra show that the ethoxy

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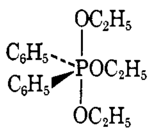
(7) Experiments at lower temperatures are now in progress in collaboration with Professor F. Jensen of the University of California.

groups are equivalent and that the methylene hydrogens are coupled to phosphorus. The formation of ethyl benzoate and the corresponding oxide on reaction with benzoic acid also supports the structural assignment.

The variation in the ^1H nmr spectrum of **13** with temperature can be explained in terms of inhibition of pseudorotation at −60°. The deshielding of one of the ethoxy groups and the shielding of the other two indicates that the favored structure at −60° is one in which two ethoxy groups are in apical positions and the other is in an equatorial position. The two apical ethoxy groups lie above and below the benzene rings and thus are in a shielding region. The equatorial ethoxy group lies in the same plane as the benzene rings and is therefore in a deshielding region.



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The chemical shifts of the hydrogens of the methylene and methyls of the ethoxy groups of **12** are very similar to those of the two apical ethoxy groups of **13** at −60°. A reasonable explanation for this behavior is that the ethoxy groups of **12** prefer to be in apical positions; however, pseudorotation can still be taking place.

The variable-temperature nmr spectra do indicate that the rate of pseudorotation is a function of the number of aryl groups bonded to phosphorus, there being a diminution in rate as the number of aryl groups increases. This finding is in agreement with earlier work.[2,9]

The compounds formed from **4**–**6** and diethyl peroxide show a variation in their spectral properties which are not always consistent with a pseudorotating pentasubstituted phosphorus compound. The substance **15** from diphenylmethylphosphine and diethyl peroxide is most easily formulated as a pentasubstituted phosphorus compound. Thus its ^{31}P and ^1H nmr spectra are most easily reconciled on this basis.

The materials, **16** and **17**, from dimethylphenylphosphine and trimethylphosphine cannot be simple pentasubstituted phosphorus compounds. Their properties can be rationalized in terms of an equilibrium between the pentasubstituted material and a phosphonium ethoxide. The variable-temperature ^1H nmr spectra of **16**

$$(C_6H_5)_nP(CH_3)_m(OC_2H_5)_2 \rightleftarrows (C_6H_5)_n\overset{+}{P}(CH_3)_mOC_2H_5 + C_2H_5O^-$$

16, $n = 1$; $m = 2$
17, $n = 0$; $m = 3$

in methylene chloride show that at −60° there is strong coupling between the methylene hydrogens of the ethoxy groups and the phosphorus. At ambient temperatures the protons of the methylene group do not show a well-defined coupling pattern. Such a behavior is consistent with an equilibrium between the pentasubstituted state and the phosphonium ethoxide. In chlorobenzene at ambient temperatures coupling is found between the protons and phosphorus. The coupling is much less pronounced at 100°. Ionization is probably not as facile in chlorobenzene as it is in methylene chloride and it is therefore not unreasonable that there should be a difference in these two solvents.

The ionization hypothesis also explains the relatively low chemical shift of **17** and the ^1H nmr spectrum of the methylene protons of the ethoxy group. These protons are found as a quartet at room temperature; *i.e.*, there is no coupling to phosphorus. The same behavior was noted with the material obtained from diethyl peroxide and tri-*n*-butylphosphine. If ionization is rapid enough, then loss of coupling to phosphorus is perfectly reasonable. At −60° the ^1H nmr absorption of the methylene hydrogens becomes "moundlike" which indicates that there has been a slowing in the rate of ionization.

The effect of structure on the ability of the materials to ionize is in complete accord with the ionization hypothesis. Thus as methyl groups are substituted for phenyl groups on phosphorus, ionization becomes more facile. The inductive donation of electron density to phosphorus plays a major role in the base strength of phosphines[10] and by the same effect stabilization of a positive charge on phosphorus should be more favorable when alkyl groups are substituted for phenyl groups. Clearly more work on these and other systems is required before the ionization hypothesis can be accepted as the only explanation for the behavior of these substances; however, at the moment it seems to be the best explanation. Recent studies by Ramirez and coworkers[11] have shown that cyclic five-membered ring phosphoranes which have nitrogen bonded to phosphorus often undergo ionization and in some cases both forms have been isolated. It has also been found that chlorophenylphosphoranes undergo ionization under suitable condition and that equilibrium mixtures of the pentasubstituted and tetrasubstituted compounds are often present in solution.[12]

The reactions of **7**–**9** with diethyl peroxide have not been studied in near the detail that those of **1**–**6** have. The products from **8** and **9** are the oxides. Whether a pentasubstituted intermediate is formed before the oxide is not clear.

The reaction of **7** does give a pentasubstituted phosphorus compound which is assigned the structure **18** on the basis of its large positive ^{31}P chemical shift and also its reaction with benzoic acid. Exchange of diethylamino groups with ethoxy groups occurs in the reaction system and a mixture of products is formed. The exchange probably involves ethanol which is formed during the reaction.

$$(C_6H_5)_2P[N(C_2H_5)_2](OC_2H_5)_2$$

18

The compound **10** gives a pentasubstituted phosphorus compound; however, it is quite unstable and it decomposes readily to tetracovalent phosphorus compounds. Reaction of **11** yields a pentasubstituted phosphorus compound, **19**, ^{31}P + 49, along with products

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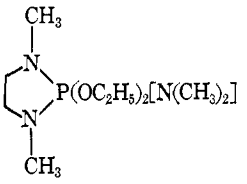

19

formed by exchange. Once again the compound **19** is quite unstable and it decomposes readily to tetracovalent phosphorus compounds.

The relative instability of the compounds with amino nitrogen bonded to phosphorus is not unexpected. Amino nitrogen can stabilize a positive charge on phosphorus and therefore enhance dissociation to phosphonium salts which can undergo further decomposition to tetracovalent phosphorus compounds.

Experimental Section

Materials. The starting phosphines were prepared by standard techniques or purchased when possible. Their ^1H and ^{31}P nmr spectra agreed with literature values.

Reactions. Equimolar quantities (*ca.* 5 × 10^{-3} mol of the phosphine and diethyl peroxide) were allowed to react in methylene chloride. Usually the reactants were cooled to at least 0° before mixing. The reactions were monitored by ^1H and ^{31}P nmr spectroscopy. In those studies in which other solvents were used the methylene chloride was evaporated at room temperature *in vacuo* and the residue was dissolved in the appropriate solvent. Benzoic acid was added to each reaction mixture and the formation of ethyl benzoate was demonstrated by glpc.

Vinylic Cations from Solvolysis. I. The Trianisylvinyl Halide System[1]

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Abstract: Solvolysis of trianisylvinyl chloride (**1**-Cl) and bromide (**1**-Br) and of 1-anisyl-2,2-diphenylvinyl bromide (**7**) in 80% ethanol follows a first-order course in the substrate, is independent of the concentration of added sodium hydroxide, and is only slightly dependent on that of added *p*-toluenethiolate ion. The solvolysis of **1**-Br is 1.75 times faster than that of α-bromo-*p*-methoxystyrene, excluding the addition–elimination mechanism. The similar rates for **1**-Br and **7** point to the absence of β-aryl participation. The Grunwald–Winstein *m* values of 0.34–0.53 and the $k_{1\text{-Br}}/k_{1\text{-Cl}}$ value of 58 at 120° are discussed in terms of intermediate vinylic cations in the solvolysis. The reactivity difference between α-bromostyrene and α-phenylethyl bromide is entirely due to activation energy difference. Vinylic and saturated cations are compared.

Vinylic cations were studied very little until recent years. Lately, they were suggested as intermediates in electrophilic additions to allenes and acetylenes (eq 1),[2] in the deamination of vinylamines,[3] or in the reaction of 2-oxazolidones in basic solution[4] or vinyltriazenes in acidic solution[5] (eq 2). Ions with contributing vinylic cation structures were observed by nmr,[6] and solvolysis products of acetylenic sulfonates may arise from vinylic cations formed by triple bond participation.[7]

Solvolytic formation of vinylic ions (eq 3) was studied even less. This may be due to the belief that vinyl halides are not easily solvolyzed, although the only evidence is the inertness of simple vinyl halides toward alcoholic silver nitrate.[8] The solvolysis of a vinylic halide may be more difficult than that of a saturated one owing to the partial carbon–halogen double bond in the former,[9] but the relative values were not determined.

$$\mathrm{RC{\equiv}CR} + \mathrm{H^+} \longrightarrow \mathrm{R\overset{+}{C}{=}CHR'} \xrightarrow{+X^-} \mathrm{RCX{=}CHR'} \quad (1)$$

$$\mathrm{R_2C{=}CR'N{=}NHAr} + \mathrm{H^+} \longrightarrow \mathrm{R_2C{=}\overset{+}{C}R'} \xrightarrow{+X^-} \mathrm{R_2C{=}CR'X} \quad (2)$$

$$\mathrm{RR'C{=}CR''Hal} \xrightarrow{-\mathrm{Hal}} \mathrm{RR'C{=}\overset{+}{C}R''} \xrightarrow{+X} \mathrm{RR'C{=}CR''X} \quad (3)$$

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