Pentaphenoxyphosphorane

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Abstract: Attempts to prepare pentaphenoxyphosphorane by the procedures described by Anschütz, *et al.*, in 1927 and by Zhmurova and Kirsanov in 1959 failed. These procedures led to mixtures of dichlorotriphenoxyphosphorane, $(C_6H_5O)_3PCl_2$, and other materials. Authentic pentaphenoxyphosphorane, $\delta^{31}P$ +85.6 ppm *vs.* H_3PO_4, was made in two stages: (1) 1 mol of phosphorus pentachloride was added to a hexane solution containing 5 mol of γ-collidine; (2) the resulting adduct was treated with a benzene solution containing 5 mol of phenol. Both reactions were carried out at 0°. Treatment of pentaphenoxyphosphorane with hydrogen chloride gave dichlorotriphenoxyphosphorane and phenol. The course of the reactions of phosphorus pentachloride with phenol and with triphenyl phosphite, under various experimental conditions, was studied by means of ^{31}P nuclear magnetic resonance spectrometry.

In 1927, Anschütz[2] and his coworkers described the first preparation of pentaphenoxyphosphorane (**2**), a new type of organic compound with pentavalent phosphorus. The synthesis involved two steps: (1) the reaction of 3 mol of phenol with 1 mol of phosphorus pentachloride at 140° to give dichlorotriphenoxyphosphorane (**1**), (2) the reaction of dichlorotriphenoxyphosphorane (**1**) with 2 additional mol of phenol at 25° to give the assumed pentaphenoxyphosphorane (**2**). The melting point given was 46–52°; elemental analysis and molecular weight were provided.

$$3C_6H_5OH + PCl_5 \longrightarrow \underset{\mathbf{1}}{(C_6H_5O)_3PCl_2} + 3HCl$$

$$\underset{\mathbf{1}}{(C_6H_5O)_3PCl_2} + 2C_6H_5OH \longrightarrow \underset{\mathbf{2}}{[(C_6H_5O)_5P]} + 2HCl$$

The preparation of dichlorotriphenoxyphosphorane (**1**) from the reaction of phenol with phosphorus pentachloride had been first described by Autenrieth[3] in 1908. Previously, Anschütz, *et al.*,[4] had made **1** by chlorination of triphenyl phosphite. This reaction was later reinvestigated in detail by Rydon and coworkers.[5]

$$(C_6H_5O)_3P + Cl_2 \longrightarrow \underset{\mathbf{1}}{(C_6H_5O)_3PCl_2}$$

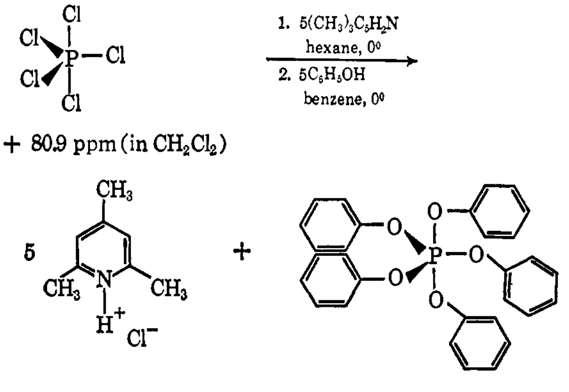
In 1959, Zhmurova and Kirsanov[6] reported the confirmation of Anschütz's[2] preparation of pentaphenoxyphosphorane (**2**). The Russian authors[6] gave the melting point of 80–90°, but furnished no elemental analysis or any other proof of structure. Dichlorotriphenoxyphosphorane (**1**), in this case, was made from the reaction of phosphorus pentachloride with triphenyl phosphite.

$$(C_6H_5O)_3P + PCl_5 \longrightarrow \underset{\mathbf{1}}{Cl_2P(OC_6H_5)_3} + PCl_3$$

This paper shows that the procedures described by Anschütz and his coworkers[2] and by Zhmurova and Kirsanov[6] do not, in fact, lead to pentaphenoxyphosphorane (**2**). An authentic sample of this material can, however, be prepared by a different procedure. This paper describes also a study of the reaction of phosphorus pentachloride with various mole ratios of phenol and of triphenyl phosphite. The main analytical tool employed was high-resolution ^{31}P nmr spectrometry.

Results

Pentaphenoxyphosphorane (2). An authentic sample of this material was obtained by the following two-stage procedure. (1) Phosphorus pentachloride was added to a hexane solution of 5 molar equiv of γ-collidine at 0°. (2) A benzene solution containing 5 molar equiv of phenol was slowly added to this mixture at 0°.



$\delta^{31}P$ + 80.9 ppm (in CH_2Cl_2)

2, $\delta^{31}P$ + 85.6 (in CH_2Cl_2) and + 85.7 ppm (in benzene)

The structure of pentaphenoxyphosphorane (**2**) was based on (1) the elemental analysis and (2) the large positive value[7] of the ^{31}P nmr shift relative to H_3PO_4. The ^1H nmr and the infrared spectra were also consistent with this structure. The molecule is drawn as a trigonal bipyramid with the phosphorus at its center, by analogy with the structure of a related five-membered cyclic pentaoxyphosphorane (**3**) which was determined by X-ray diffraction techniques.[8]

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[2] L. Anschütz, H. Boedeker, W. Broeker, and F. Wenger, *Ann.*, **454**, 71 (1927).

[3] W. Autenrieth and A. Geyer, *Ber.*, **41**, 151 (1908).

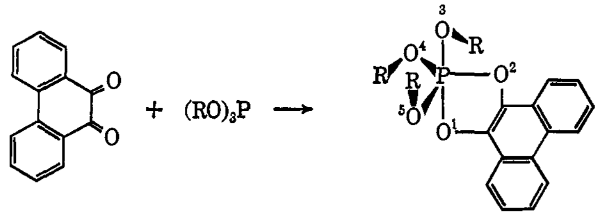
[4] (a) R. Anschütz and W. O. Emery, *Ann.*, **239**, 312 (1887); (b) *ibid.*, **253**, 112 (1889).

[5] (a) D. G. Coe, S. R. Landauer, and H. R. Rydon, *J. Chem. Soc.*, 2281 (1954); (b) H. N. Rydon and B. L. Tonge, *ibid.*, 3043 (1956).

[6] I. N. Zhmurova and A. V. Kirsanov, *J. Gen. Chem. USSR*, **29**, 1668 (1959).

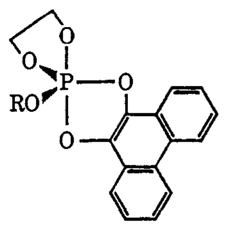
[7] (a) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (b) F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966).

[8] (a) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 2268 (1967); (b) R. D. Spratley, W. C. Hamilton, and S. J. Ladell, *ibid.*, **89**, 2272 (1967).



3, R = *iso*-C_3H_7; $\delta^{31}P$ + 48.6 ppm
4, R = CH_3; $\delta^{31}P$ + 44.7 ppm
5, R = C_6H_5; $\delta^{31}P$ + 58.6 ppm

The cyclic oxyphosphorane **3** was prepared from phenanthrenequinone and triisopropyl phosphite.[9] Note the large positive value of the ^{31}P nmr shift of the various oxyphosphoranes **3**, **4**, and **5**. It is known that the introduction of an additional five-membered ring into the molecule leads to a significant decrease in the positive value of the ^{31}P shift, as in the spiro-oxyphosphoranes[10] **6** and **7**.[9c] Consequently, the value found for the ^{31}P shift of pentaphenoxyphosphorane (**2**) is in complete agreement with previous data.



6, R = CH_3; $\delta^{31}P$ + 23.0 ppm
7, R = C_6H_5; $\delta^{31}P$ + 27.0 ppm

Denney[11] and his coworkers reported the value of +70.7 ppm for the rather unstable pentaethoxyphosphorane, which they obtained by the reaction of diethyl peroxide with triethyl phosphite.

The five-membered cyclic pentaoxyphosphoranes **3**–**5** are considerably more stable than the acyclic analogs. This has been attributed[8a,12] to the intramolecular crowding in the trigonal bipyramidal structure of these compounds. Thus, the apical oxygen of the phospholene ring, O-1 in formula **3**, was very close (2.63 Å) to the carbon attached to the equatorial oxygen, C-4. Likewise, the apical oxygen of the alkoxy group O-3, was very close (2.70 Å) to the carbon attached to the other equatorial oxygen, C-5. Other short distances[8] were: C-3···O-2 = 2.74 Å and C-3···O-4 = 2.86 Å. The effect of this crowding on the relative stabilities of a series of oxyphosphoranes having groups with different steric requirements attached to the phosphorus has already been discussed.[12] These comparisons were made in a series of compounds having the same type and number of elements attached to the phosphorus. It is also known that the stability of the trigonal bipyramid increases with an increasing number of elements of high electronegativity directly attached to the phosphorus atom.[12,13]

Another point of interest concerning the trigonal bipyramidal structure ascribed to pentaphenoxyphosphorane (**2**) is related to positional exchangea mong the groups attached to the phosphorus.[9,14] In all cases so far investigated,[7,9,10,14] this positional exchange in the case of *pentaoxyphosphoranes* of the type **3**–**5** has been found to be relatively rapid in the time scale of the ^1H nmr phenomenon in the temperature range of −60 to +30°. However, in a number of tetraoxyalkyl-, trioxyalkylaryl-, and dioxyalkyldiarylphosphoranes the positional exchange has been "frozen" at various temperatures[15,16] in the range of −60 to +140°. The positional exchange is known to occur by two types of mechanisms depending on the temperature. At lower temperatures, the positional exchange occurs by an intramolecular process or pseudo-rotation first discussed in detail by Berry[17] in 1960. At higher temperatures, positional exchange occurs by the fission and re-formation of a phosphorus–oxygen bond in the trigonal bipyramid.[13,15,16]

Reaction of Pentaphenoxyphosphorane with Hydrogen Chloride. Pentaphenoxyphosphorane was rapidly converted into dichlorotriphenoxyphosphorane (**1**) and phenol at 25°. *This reaction is responsible for the failure of previous investigators to obtain pentaphenoxyphosphorane* (**2**) *from the reaction of phenol with dichlorotriphenoxyphosphorane* (**1**). It should be noted that

$$\underset{2}{(C_6H_5O)_5P} + 2HCl \longrightarrow \underset{1}{Cl_2P(OC_6H_5)_3} + 2C_6H_5OH$$

only two of the five phenoxy groups attached to the phosphorus in pentaphenoxyphosphorane could be replaced by chlorine atoms. The optimum stability of this combination is undoubtedly the result of an interplay of electronic and of steric factors, as discussed above. The molecular geometry of the chlorophosphorane **1** is not known[17a] and is at present under investigation by X-ray diffraction techniques. Considerable information is available on the molecular geometry of the chlorofluorophosphoranes.[18,19]

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(9c) NOTE ADDED IN PROOF. For an interesting series of spirooxyphosphoranes see M. Sanchez, R. Wolf, R. Burgada, and F. Mathis, *Bull. Soc. Chim. France*, 773 (1968).

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(17a) NOTE ADDED IN PROOF. There are three possible diastereomeric trigonal bipyramids, all *meso* forms. In the general case, P(A1.A2.E1.E2.E3), where all the groups are different but symmetric, there are ten pairs of enantiomers, (a,a′), (b,b′), . . ., (j,j′) of the trigonal bipyramid. They can be derived by pseudo-rotations as follows (the "pivot" is given in parentheses): a ⇄ b (E2); a ⇄ c (E1); a ⇄ d (E3) b ⇄ e (A1); b ⇄ f (A2); c ⇄ g (A1); c ⇄ h (A2); d ⇄ i (A1); d ⇄ j (A2). Five *consecutive* pseudo-rotations using *different* groups as pivots convert a trigonal bipyramid into its enantiomer, for example: a ⇄ b (E2) ⇄ e (A1) ⇄ j′ (E1) ⇄ d′ (A2) ⇄ a′ (E3). See ref 18a and E. L. Muetterties *Inorg. Chem.*, **6**, 635 (1967); R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

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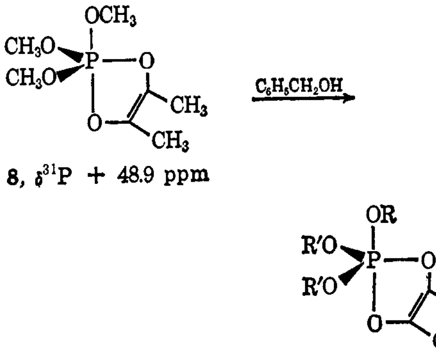
Nucleophilic substitution of the alkoxy groups attached to the phosphorus in five-membered cyclic oxyphosphoranes by reactions with alcohols have been reported recently.[20]



8, $\delta^{31}P$ + 48.9 ppm

9, R = $CH_2C_6H_5$; R′ = CH_3; $\delta^{31}P$ + 49.8 ppm
10, R = CH_3; R′ = $CH_2C_6H_5$; $\delta^{31}P$ + 50.6 ppm
11, R = R′ = $CH_2C_6H_5$; $\delta^{31}P$ + 51.3 ppm

Reinvestigation of Previously Reported Syntheses of Dichlorotriphenoxyphosphorane (1). The addition of chlorine to triphenyl phosphite *in hexane solution*[4,5] yielded a colorless precipitate. We have been unable to purify this material to the point at which its elemental analysis agrees with that of $(C_6H_5O)_3PCl_2$. All that can be said about this substance is that, in CH_2Cl_2 solution, it gives only one signal in the ^{31}P nmr spectrum. The chemical shift does not vary significantly in several solvents. The shift appears to be identical with the shift of the substance made by the action of HCl on pentaphenoxyphosphorane (2) in CH_2Cl_2 solution. The action of chlorine on triphenyl phosphite in various solvents seems to result in complex phenomena now under investigation.

$$(C_6H_5O)_3P + Cl_2 \longrightarrow (C_6H_5O)_3PCl_2$$

$\delta^{31}P$ −127.1 ppm

1, $\delta^{31}P$ +22.8 (CH_2Cl_2), +23.5 (acetonitrile), and +23.4 ppm (nitrobenzene)

It is of interest to compare the ^{31}P nmr shift of the material regarded as dichlorotriphenoxyphosphorane (1) with that of PCl_5. We have verified the previously reported[21-25] values of the latter in those solvents in which it appears to exist in a nonionic form: +80.9 (CH_2Cl_2), +81.1 (CCl_4), +81.3 (benzene), and +80.9 (CS_2) ppm. Crystalline PCl_5 is known[21a,b] to give two signals, −96 and +281 ppm, attributed to the ions PCl_4^+ and PCl_6^-, respectively. Related ions with hexacoordinated phosphorus have been detected in solutions by ^{31}P nmr spectrometry.[26] Chlorinated tertiary phosphines are reported to exist as the ions $R_3PCl^+Cl^-$ in certain solvents.[27]

The reaction of 3 mol of phenol with 1 mol of PCl_5 as described[2,3] gave a material whose ^{31}P nmr spectrum in CH_2Cl_2 solution exhibited two signals. One of these was at δ +22.7 ppm corresponding to the dichlorophosphorane 1. The other was at +296.8 ppm and must be due to hexacoordinated phosphorus; probably it is associated with either $(C_6H_5O)P^{-}Cl_5H^{+}$ (12) or $(C_6H_5O)_2P^{-}Cl_4H^{+}$ (13) although $P^{-}Cl_6H^{+}$ is not entirely excluded. These species, 12 and 13, are the products of the addition of HCl to $(C_6H_5O)PCl_4$ (14) and $(C_6H_5O)_2PCl_3$ (15), respectively. It was found that HCl did not change the ^{31}P nmr shift of the assumed $(C_6H_5O)_3PCl_2$ (1); *i.e.*, the species $(C_6H_5O)_3P^{-}Cl_3H^{+}$ was not detected. These assignments are speculative at this time.

The reaction of 5 mol of phenol with 1 mol of PCl_5 at 25°, in the absence of solvent, gave a material whose ^{31}P nmr spectrum varied somewhat with time. When the material was examined in CH_2Cl_2 solution, after 15 min, one signal was observed at +27.7 ppm. If the same material was kept 72 hr at 25°, or 3 hr at 140°, in the absence of solvent, the spectrum gave one signal at +22.8 ppm, as before, in CH_2Cl_2. Possible explanations for these changes are being investigated.

The reaction of equimolar amounts of triphenyl phosphite and PCl_5 as described[6] gave a mixture of the assumed dichlorotriphenoxyphosphorane (1) and PCl_3, according to the ^{31}P nmr spectrum. In addition we noted significant amounts of the species with $\delta^{31}P$ +296.8 ppm.

When an excess of triphenyl phosphite was allowed to react with PCl_5, a very complex reaction mixture was produced. In addition to triphenyl phosphite and the assumed dichlorophosphorane (1), there were two materials whose ^{31}P nmr shifts corresponded to diphenylphosphorochloridite, $(C_6H_5O)_2PCl$, and phenylphosphorodichloridite, $(C_6H_5O)PCl_2$. The mixture had also the material responsible for the shift at +296.5 ppm, but contained no PCl_3. These replacements of phenoxy groups by chlorines could involve intermediates with tetravalent and pentavalent phosphorus, the key step being

$$(C_6H_5O)_3P + [Cl_2\overset{+}{P}(C_6H_5O)_2, (C_6H_5O)_2\overset{-}{P}Cl_4] \longrightarrow (C_6H_5O)_2PCl + [(C_6H_5O)_3\overset{+}{P}Cl, (C_6H_5O)_2\overset{-}{P}Cl_4]$$

Reinvestigations of the Procedures Given by Anschütz, *et al.*,[2] and by Kirsanov, *et al.*,[6] for the Synthesis of Pentaphenoxyphosphorane. The reactions described by these two groups of investigators were repeated in the manner given in the Experimental Section. It was shown conclusively that pentaphenoxyphosphorane was not a constituent of the reaction mixtures which were produced by these methods.

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Discussion

In 1957, we reported[28] that the phosphorus of trialkyl phosphites had a tendency to attack the carbonyl oxygen of *p*-quinones. The products were the alkyl ethers of *p*-quinol phosphates, which were formed from the unstable dipolar ion intermediates. This procedure was exploited as a new approach to the pentaoxyphosphoranes. The latter resulted when the *o*-quinones, rather than the *p*-quinones, were allowed to react with trialkyl phosphites.[9] In this manner five-membered cyclic oxyphosphoranes like **3–5** were first prepared. The pentacovalency of the phosphorus in the oxyphosphoranes was first deduced[7,9] from the ^{31}P nmr and the infrared spectra and was later confirmed by X-ray analysis.[8] Related oxyphosphoranes were prepared from the reactions of trialkyl phosphites with α-diketones, α-ketoaldehydes, and vicinal triketones.[7,29] Many other 2,2,2-trialkoxy-2,2-dihydro-1,3,2-dioxaphospholenes and 2,2,2-trialkoxy-2,2-dihydro-1,3,2-dioxaphospholanes have been made by this procedure.[29]

Birum and Dever[30] also described the preparation of 2,2,2-trialkoxy-2,2-dihydro-1,3,2-dioxaphospholenes from the reactions of trialkyl phosphites with α-diketones.

Kukhtin[31] and his coworkers have described reactions of trialkyl phosphites with α-diketones. They have proposed a variety of structures for their products, later shown to be incorrect. However, in some of their later papers, they have reformulated some of their structures as cyclic pentaoxyphosphoranes.

The present investigation demonstrates conclusively that the early reports[2,6] of the preparation of pentaphenoxyphosphorane (**2**) were unfounded.

Experimental Section

The analysis were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. The instrumentation was described previously.[32] All ^{31}P nmr shifts are given in parts per million (ppm) from 85% H_3PO_4 as 0; they were measured at 40.5 Mcps.

Pentaphenoxyphosphorane (2). Phosphorus pentachloride (3.38 g, 16.3 mmol) was added in small portions to a solution of γ-collidine (9.86 g, 81.6 mmol) in hexane (45 ml) at 0° over a 2-min period. The off-white suspension was treated very slowly at 0° with a solution of phenol (7.65 g, 81.6 mmol) in benzene (15 ml). The addition was effected over a 2-hr period, and the mixture was kept an additional 3 hr at 0°. The mixture was filtered under N_2 through a sintered-glass funnel. An aliquot of this solution was concentrated at 10 mm, and the solution was analyzed by ^{31}P nmr spectrometry. The main component was pentaphenoxyphosphorane (**2**), δ^{31}P +85.6 ppm. In addition, there was a weak signal at +17.9 ppm which could be due to triphenyl phosphate.

The filtrate was freed from solvent at 25° (25 mm), and the residue was treated with hexane (20 ml) and filtered. The crude pentaphenoxyphosphorane (**2**) (3.5 g, mp 87–88°) was recrystallized from hexane to give material, mp 103–104°; δ^{31}P +85.7 (benzene), +85.4 ($CDCl_3$), and +86.2 ppm (diethyl ether). The ^{1}H nmr had a complex aromatic signal centered at τ 2.98. The infrared spectrum (CH_2Cl_2) had bands at (μ) 6.28, 6.72, 8.15–8.30, 8.60, 9.35, 9.75, 10.5, and 12.6.

Anal. Calcd for $C_{30}H_{25}O_5P$: C, 72.6; H, 5.1; P, 6.2. Found: C, 72.1; H, 5.2; P, 5.8.

Reaction of Pentaphenoxyphosphorane (2) with Hydrogen Chloride. A solution of pentaphenoxyphosphorane (**2**) (1.2 g) in methylene chloride (5 ml) was treated at 0° with an excess of hydrogen chloride gas. The solution contained only one ^{31}P nucleus with δ^{31}P +22.6 ppm, which corresponds to $(C_6H_5O)_3PCl_2$ (**1**); *vide infra.* Removal of the solvent left a mixture of the dichlorophosphorane **1** and phenol.

Reaction of 3 Mol of Phenol with 1 Mol of Phosphorus Pentachloride. Procedure of Autenrieth[3] and Anschütz.[2] Phosphorus pentachloride (9.8 g, 47 mmol) was added in five portions to phenol (13.3 g, 141 mmol) at 25° over 0.5 hr. The mixture was kept 3 hr at 140° under a stream of N_2 until no more hydrogen chloride was evolved. An aliquot of this mixture contained two kinds of phosphorus nuclei in the approximate ratio of 1.5:1 with δ^{31}P +22.7 and +296.8 ppm, respectively (in CH_2Cl_2).

The mixture became solid, but attempts at recrystallization from benzene, or benzene–hexane, failed. The crude material was analyzed, as had been done by previous investigators. Our results follow: *Anal.* Calcd for $(C_6H_5O)_3PCl_2$: C, 56.9; H, 4.0; Cl, 18.6. Calcd for $(C_6H_5O)_4PCl$: C, 65.7; H, 4.6; Cl, 8.1. Found: C, 59.4; H, 4.4; Cl, 13.5.

Autenrieth[3] had reported that his analogous preparation had Cl, 18.1%.

Attempts to Prepare Pentaphenoxyphosphorane by the Method of Anschütz.[4] Phenol (4.32 g, 46 mmol) was added at once to the material made from 3 mol of phenol and 1 mol of PCl_5 as described above (6.45 g, 23 mmol; addition temperature 25°). The liquid mixture was kept 5 hr at 25° under a stream of N_2 until no more HCl was evolved. An aliquot was dissolved in CH_2Cl_2, and the solution was found to contain one ^{31}P nucleus, δ +22.6 ppm.

The reaction mixture was only semisolid at 30°. It was analyzed as had been done by Anschütz, *et al.*[2] Our results were C, 69.1; H, 5.2; Cl, 5.3. The previous investigators[2] regarded this material as pentaphenoxyphosphorane and reported for it the melting point of 46–52° and the correct elemental analysis and molecular weight for $C_{20}H_{25}O_5P$.

Reaction of 5 Mol of Phenol with 1 Mol of Phosphorus Pentachloride. a. Phosphorus pentachloride (2.72 g, 13.1 mmol) was added to phenol (6.15 g, 65.5 mmol) at 25° over 5 min. Evolution of HCl was noted; a clear liquid resulted in 10 min. This material was kept 72 hr at 25°; an aliquot was dissolved in CH_2Cl_2, and the solution was found to contain one type of ^{31}P nucleus at +22.7 ppm. The original material was kept 3 hr at 140°, under a stream of N_2. The resulting material again had the same ^{31}P nmr signal at +22.8 ppm in CH_2Cl_2 solution.

b. Phenol (5 mol) and PCl_5 (1 mol) were mixed at 25° as before; however, the resulting liquid was analyzed by ^{31}P nmr spectrometry, in CH_2Cl_2 solution, *after 10 min.* This fresh solution had one type of ^{31}P nucleus at +27.7 ppm. When the same material was kept 3 hr at 140° under a stream of N_2, the same signal at +22.8 ppm (in CH_2Cl_2), observed in previous preparations, was observed.

c. Phosphorus pentachloride (1.10 g, 0.53 mmol) was added to a solution of phenol (2.49 g, 2.65 mmol) in CH_2Cl_2 (20 ml). The phenol solution contained also 1 mol equiv of γ-collidine (0.65 g, 0.53 mmol) to determine the effect of trapping some of the HCl being formed. The reagents were mixed at 0° and were kept 0.5 hr at 0°. The solution was allowed to reach 25°; it contained one type of ^{31}P nucleus at +22.6 ppm.

Reaction of Phosphorus Pentachloride with Triphenyl Phosphite Following the Procedure of Zhmurova and Kirsanov.[6] Phosphorus pentachloride (23.4 g, 112 mmol) was added to triphenyl phosphite (34.7 g, 112 mmol) at 25° within 5 min. The exothermic reaction raised the temperature to 70°; the clear solution was kept 12 hr at 25°. An aliquot was dissolved in methylene chloride; it had three ^{31}P nuclei in the approximate proportions, 1.5:1.3:1.0 at δ^{31}P +22.6 [$(C_6H_5O)_3PCl_2$], −217.6 [PCl_3], and +296.6 ppm [probably $(C_6H_5OPCl_5)^-H^-$]. The reaction mixture was kept 1 hr at 100° (10 mm) and 3 hr at 150° (10 mm), as had been done by previous investigators. This treatment removed the PCl_3 but left the other two phosphorus-containing compounds.

The main portion of the reaction mixture became a solid at +30°. It was submitted to elemental analysis (Found: C, 49.1; H, 3.4;

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[28] (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957); (b) F. Ramirez and S. Dershowitz, *ibid.*, **22**, 1282 (1957); (c) F. Ramirez and S. Dershowitz, *ibid.*, **23**, 778 (1958); (d) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, 81, 587 (1959).

[29] (a) F. Ramirez, N. B. Desai, and N. Ramanathan, *Tetrahedron Letters*, 323 (1963); (b) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, 30, 2575 (1965); (c) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, and C. P. Smith, *ibid.*, **32**, 2194 (1967); (d) F. Ramirez and C. P. Smith, *Chem. Commun.*, 662 (1967); (e) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, E. H. Chen, and C. P. Smith, *J. Org. Chem.*, **32**, 20 (1967).

[30] G. H. Birum and G. L. Dever, Abstracts, 135th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958, p 101P.

[31] (a) V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **121**, 466 (1958); (b) K. M. Kirillova and V. A. Kukhtin, *Zh. Obshch. Khim.*, **35**, 544 (1965).

[32] (a) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **30**, 2575 (1965); (b) *ibid.*, **31**, 474 (1966); (c) *ibid.*, **31**, 3159 (1966).

Cl, 25.3) which corresponds to $(C_6H_5O)_3PCl_2$ contaminated with some unknown material. Zhmurova and Kirsanov[6] regarded this material as pure dichlorotriphenoxyphosphorane (1) and reported for it a melting point of 76–78° but gave no elemental analysis or any other physical properties.

Reaction of 2 Mol of Phenol with the Product of the Reaction of Phosphorus Pentachloride with Triphenyl Phosphite. Procedure of Zhmurova and Kirsanov.[6] Phenol (4.5 g, 48.5 mmol) was added at once to the product made from triphenyl phosphite and phosphorus pentachloride as described above (Kirsanov procedure[6]) (6.82 g, 24.2 mmol). The mixture was kept 2 hr at 150° and then was kept 1 hr at 100° (10 mm) and 3 hr at 150° (10 mm). An aliquot was dissolved in methylene chloride; this solution had two ^{31}P nuclei in the proportion of 3.4:1 at $\delta^{31}P$ +22.8 [$(C_6H_5O)_3PCl_2$] and +17.5 ppm (probably triphenyl phosphate). The main portion of the reaction mixture became a solid at 30° and was submitted to elemental analysis (Found: C, 67.6; H, 4.9; Cl, 5.2) which corresponds to a mixture of dichlorotriphenoxyphosphorane and phenol. Zhmurova and Kirsanov[6] assumed that this material was pentaphenoxyphosphorane (2); they gave its melting point as 80–90°, but provided no elemental analysis or other physical properties.

Reaction of Phosphorus Pentachloride with an Excess of Triphenyl Phosphite at 25°. Phosphorus pentachloride was added to an excess of triphenyl phosphite at 25°. The ^{31}P nmr spectrum of this mixture contained four ^{31}P nuclei in addition to that of triphenyl phosphite ($\delta^{31}P$ −127.5 ppm) in the following proportions: 3.0:4.0:2.0:1.0 at $\delta^{31}P$ +23.0, −176.2, −157.5, and +296.5 ppm. There was no PCl_3 in this mixture.

Chlorination of Triphenyl Phosphite. Chlorine was bubbled through a solution of triphenyl phosphite in hexane. A colorless precipitate was formed. This was filtered in the absence of moisture and was dissolved in several solvents for measurement of the ^{31}P nmr shifts. The values are given in the Results section. No suitable crystallization solvent was found for this material. The closest analytical values for $(C_6H_5O)_3PCl_2$ which could be obtained in this type of preparation were: C, 60.8; H, 4.4.

When this material was treated with 2 molar equiv of phenol, no change in the ^{31}P nmr shift was noted.

New Heteroaromatic Compounds. XXX.[1] A Derivative of 10,9-Borathiarophenanthrene[2,3]

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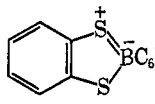
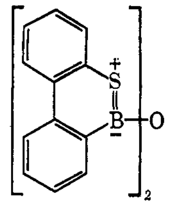
Abstract: Bis(10,9-borathiarophenanthryl) ether has been prepared, this being the first heteroaromatic[5] boron compound containing boron and sulfur in a six-membered aromatic ring. Comparison of its properties with those[4] of the corresponding nitrogen[6] and oxygen[7] compounds shows that the sulfur-containing system is by far the least aromatic.

Previous papers of this series[5–7] have described a novel series of heteroaromatic compounds, isoconjugate with "normal" aromatic systems and derived from them by replacing a pair of adjacent carbon atoms by boron and nitrogen, or boron and oxygen.

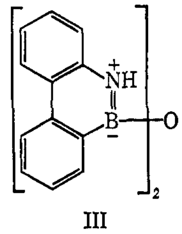
In part II,[8] a compound (I) was described in which two carbon atoms of a typical aromatic system, *i.e.*, thianaphthalene, were likewise replaced by boron and sulfur; as yet, however, no compounds have yet been reported in which boron and sulfur form part of a six-membered aromatic ring. We have now prepared a compound of this type, bis(10,9-borathiaro-10-phenanthryl) ether (II) and examined its properties, with a view to establishing its aromaticity relative to that of the isoconjugate nitrogen[6] (III) and oxygen[7] (IV) derivatives.



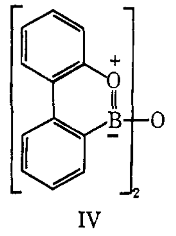
I



II



III



IV

The synthesis of II followed the same general procedure used[6,7] in the preparation of III or IV. 2-Mercaptobiphenyl[9] (V) reacted with an excess of boron trichloride to give, presumably, the dichloride VI. This on treatment with aluminum chloride, followed by moist ether, yielded an oil which solidified when washed with petroleum ether (bp 30–60°). Sublimation of the solid gave a white powder, mp 170–171°, identified as II. Attempts to isolate the intermediate chloride VII failed since it was extremely sensitive to hydrolysis.

The petroleum ether used to wash II contained two other compounds, identified as dibenzothiophene (VIII) and tris(2′-mercapto-2-biphenyl)boroxine (IX). The structures of II and IX were established by ele-

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(1) Part XXIX: M. J. S. Dewar, R. Jones, and R. H. Logan, Jr., *J. Am. Chem. Soc.*, in press.

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(3) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(4) Robert A. Welch Postdoctoral Fellow.

(5) See M. J. S. Dewar, *Progr. Boron Chem.*, **1**, 235 (1964); and R. F. Gould, Ed., Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 227.

(6) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

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