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PHOSPHORANYLATIONS

PREPARATION OF 5-MEMBERED CYCLIC OXYPHOSPHORANES AND SPIROOXYPHOSPHORANES FROM THE REACTION OF PENTAPHENOXYPHOSPHORANE WITH CATECHOL

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Abstract—One mole of catechol displaced two moles of phenol from *pentaphenoxyphosphorane* ($\delta^{31}P = +85.6$ ppm *vs* H_3PO_4) in CH_2Cl_2 and gave *catecholtriphenoxyphosphorane* ($\delta^{31}P = +60.8$ ppm). Two moles of catechol displaced four moles of phenol from pentaphenoxyphosphorane and gave *spirodicatecholphenoxyphosphorane* ($\delta^{31}P = +29.8$ ppm). The 5-membered cyclic pentaoxyphosphoranes are more stable than the acyclic analogues because the intramolecular crowding present in the trigonal bipyramidal structure of pentavalent phosphorus is minimized when the groups on the phosphorus are held in a ring. The reaction of catechol with PCl_5 was investigated in various solvents at several temperatures, using various mole ratios of the reactants. Previously suggested structures for *trichlorocatecholphosphorane* ($\delta^{31}P = +26.5$ ppm) and for *chlorospirodicatecholphosphorane* ($\delta^{31}P = +9.4$ ppm) were confirmed. However, the structure of a *catechol-bis(spirodicatecholphosphorane)* now in the literature, was shown to be in error. The procedures now in the literature for the synthesis of catecholtriphenoxyphosphorane and of spirodicatecholphenoxyphosphorane did not lead, in fact, to these substances.

The transfer of pentacoordinated phosphorus from one molecule to another, for example, $(RO)_4PX + R'OH \rightarrow (RO)_4POR' + HX$, can be termed *phosphoranylation*, just as the transfer of tetracoordinated phosphorus has been called *phosphorylation*, for example, $(RO)_2P(O)X + R'OH \rightarrow (RO)_2P(O)OR' + HX$. One of the purposes of this investigation was to examine the possibility of using pentaphenoxyphosphorane, **1**, as a phosphoranylating agent.

It was recently shown[1] that the reaction of two moles of phenol with one mole of dichlorotriphenoxyphosphorane, **2**, according to the procedure described by Anschütz *et al.*,[2] did not give pentaphenoxyphosphorane, **1**, as had been claimed. This compound, however, could be prepared in two stages. In the first step, one mole of phosphorus pentachloride was added to five moles of γ-collidine in hexane solution at 0°. In the second step, a benzene solution containing five moles of phenol was added, very slowly, to the cold suspension of the PCl_5–collidine complex. The ^{31}P NMR shift of pentaphenoxyphosphorane, **1**, was very similar to that of PCl_5 in the same solvent. Moreover, the shift of **1** was very similar in various solvents, i.e. $+85.7$ ppm in benzene and $+86.2$ ppm in diethyl ether. The shift of PCl_5 in benzene was $+81.3$ ppm, in CCl_4, $+81.1$ and in CS_2, $+80.9$ ppm, in general agreement[1] with previous data.[3] It is known that *crystalline* PCl_5 gives two ^{31}P NMR signals which have been attributed[3b] to the pair of ions, PCl_4^+ and PCl_6^-.

Hydrogen chloride caused the rapid displacement of two moles of phenol from

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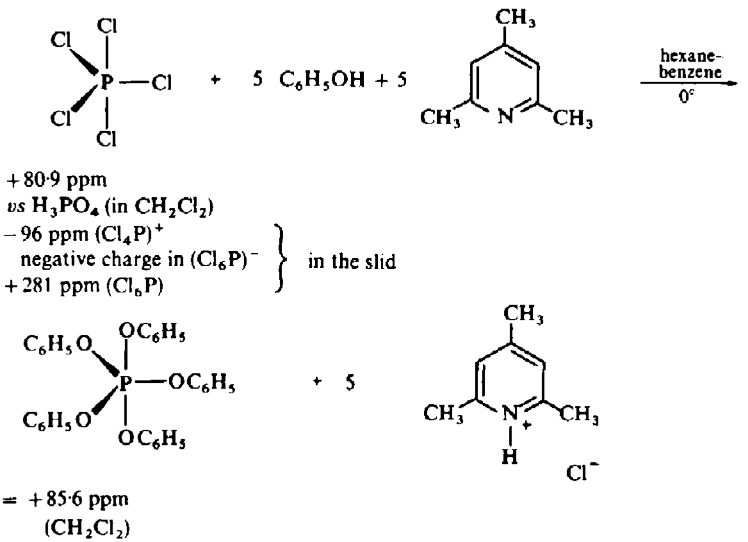


δP^{31} = +80·9 ppm
vs H_3PO_4 (in CH_2Cl_2)
δP^{31} = −96 ppm $(Cl_4P)^+$ } in the slid
negative charge in $(Cl_6P)^-$
+281 ppm (Cl_6P)

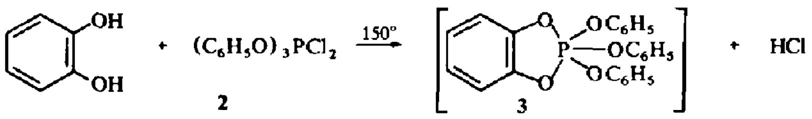
1: δP^{31} = +85·6 ppm (CH_2Cl_2)

pentaphenoxyphosphorane, **1**, in methylene chloride at 25° resulting in the formation of dichlorotriphenoxyphosphorane, **2**. This explains Anschütz's[2] failure to prepare pentaoxyphosphorane, **1**. The substitution of phenoxy groups by Cl atoms stopped at the dichlorotriphenoxy-stage.

$$\underset{\mathbf{1}}{(C_6H_5O)_5P} + \underset{\text{excess}}{HCl} \xrightarrow[25^\circ]{CH_2Cl_2} (C_6H_5O)_3PCl_2 + 2\,C_6H_5OH$$

2, δP^{31} = +22·8 ppm

Anschütz[2] *et al.* had also reported the preparation of a 5-membered cyclic pentaoxyphosphorane, **3**, from the reaction of one mole of catechol with one mole of dichlorotriphenoxphorane, **2**, at 150°.

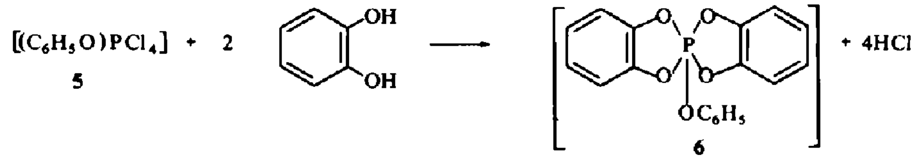


2 **3**

The present investigation was also an attempt to confirm this method of preparation of the oxyphosphorane, **3**. This compound was said to be one of the first four members of the family of "orthophosphates" ever prepared. The second member was pentaphenoxyphosphorane, **1**. The third member was the spirodicatecholphenosyphosphorane, **6**, which Anschütz[2] claimed to have made from the reaction of two moles of catechol with one mole of tetrachlorophenoxyphosphorane, **5**. The latter was obtained by chlorination of phenylphosphorodichloridite., **4**.

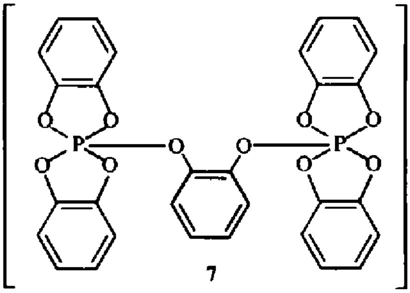
Anschütz[2] reported a m.p. of 192° for this substance **6** but gave no elemental analysis or other proof of structure for it. He purified it by distillation at 245–250° (10 mm) and stated that it was insoluble in benzene. Our experience with other

$$\underset{4}{C_6H_5OPCl_2} + Cl_2 \rightarrow \underset{5}{[C_6H_5OPCl_4]}$$



oxyphosphoranes[4] was inconsistent with these properties for a structure like **6**. Therefore, we re-examined this aspect of the problem also.

The fourth pentaoxyphosphorane described in the literature[2] was the catechol-*bis*(spirodicatecholphosphorane), 7, which was said[2] to result from the rapid addition of "two moles of catechol to one of phosphorus pentachloride" in benzene at 25°, followed by prolonged heating. This material was characterized[2] by elemental analysis and mol wt determination and was said to melt at 200–240°. A structure like 7 would be of interest in connection with the stereochemistry of pentavalent phosphorus;[4] therefore, its synthesis was reinvestigated.



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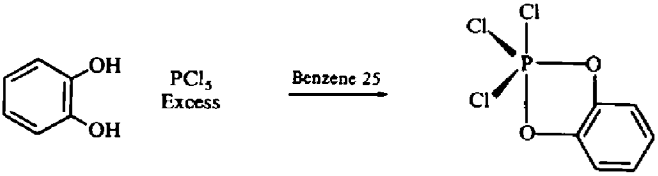
RESULTS AND DISCUSSION

*Reaction of catechol with phosphorus pentachloride** [5–7]

The main product of the addition of catechol to an excess of PCl_5 in benzene solution at 25° was the *trichlorocatecholphosphorane*, **8**. The ^{31}P NMR shift of this compound was positive and did not vary significantly in solvents as different as hexane, acetonitrile and nitrobenzene. For reasons given below, the cyclic structure, **8**, previously proposed[2,5] is supported by these data.



8: $\delta P^{31} = +26{\cdot}5$ ppm (in CH_2Cl_2)

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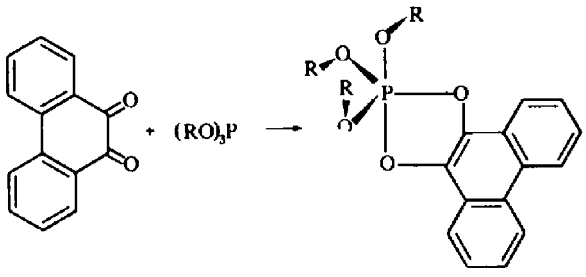
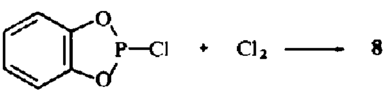
* For recent investigations of the reactions of catechol with PCl_5 see Ref. 5. A recent review on this subject has appeared, cf. Ref. 6. Some related reactions of PCl_5 with salicylic acid and with *o*-hydroxybenzophenone have been reinvestigated recently, see Ref. 7.

We have observed[8] that certain oxyphosphoranes gave widely different ^{31}P NMR shifts in different solvents, and have shown that this situation occurs whenever the oxyphosphoranes, with pentavalent phosphorus, have comparable stability than the corresponding open dipolar ions with tetravalent phosphorus. In those cases, the pentavalent phosphorus had a positive ^{31}P NMR shift and the tetravalent phosphorus had a negative ^{31}P NMR shift. The two forms were in equilibrium with each other. The equilibrium was established rapidly in the time scale of the NMR phenomenon. The position of the equilibrium varied significantly with the nature of the solvent. The absence of this effect in the case of trichlorocatecholphosphorane, **8**, suggests that the structure with pentavalent phosphorus is considerably more stable than the structure with tetravalent phosphorus. The preferred molecular geometry in the crystalline state and in solutions is not known in this compound. However, in a related cyclic pentaoxyphosphorane, **9**, X-ray analysis disclosed that the molecule was a trigonal bipyramid and that the ring was in an apical-equatorial position.[4h] Therefore, a likely configuration for the chloro compound is shown in formula **8**.



9: R = iso-C_3H_7; δP^{31} = +48·6 ppm

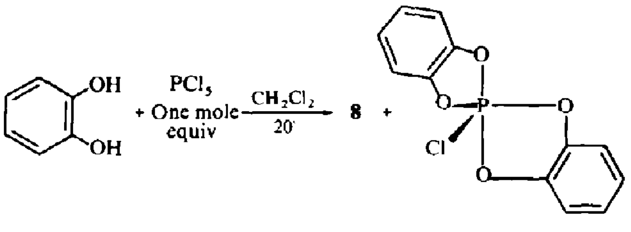
The trichlorocatecholphosphorane, **8**, has received considerable attention from Gross *et al.*[5] A substance with the same structure, **8**, was said to result from the chlorination of the 5-membered cyclic phosphorochloridite, **10**. The latter, in turn, was obtained from the reaction of PCl_3 with catechol.[5] We have repeated these reactions and have verified that the materials made by the two routes, i.e. from PCl_5, and from PCl_3 followed by chlorination, lead to the same ^{31}P NMR spectrum in CH_2Cl_2 solution. This point is of some importance because the results of this investigation, and of a previous one,[1] have shown that the final products derived by these two procedures can be quite different. The reaction of a phenol with PCl_5 or with a related chlorooxyphosphorane, $P(Cl)_{5-n}(OR)_n$, where n = 0 to 4, involves the formation of HCl during the reaction. The reaction of a trivalent phosphorus compound with chlorine involves the formation of intermediates with quadruply- and quintuply-connected phosphorus, which are generated in the presence of the species with trivalent phosphorus. Therefore, the results of these processes can be quite different.[1]



10: δP^{31} = −173·0 ppm

A complex mixture resulted when *equimolar amounts* of PCl_5 and a catechol were combined in CH_2Cl_2 at 0°. The mixture contained both, the monocyclic phosphorane, **8**, and the *chlorospirodicatecholphosphorane*, **11**.[2,5,6] Some unreacted PCl_5 and a fourth, unknown, component were also present. *Evidently, the reaction of catechol with the trichlorophosphorane,* **8**, *and with* PCl_5 *occurred at comparable rates.* Mixtures are always formed.

The ^{31}P NMR shift of the chlorospirophosphorane, **11**, was in agreement with the structure. In particular, the decrease in the positive value which we have observed when an additional 5-membered ring is introduced into a 5-membered cyclic oxyphosphorane was also observed in this case.[9]



11: δP^{31} = +9·4 ppm

Anschütz[2] had reported the isolation of chlorospirophosphorane, **11**, in a "monomeric" and a "dimeric" form. We were unable to find evidence for the dimer in our experiments.

The best procedure for the preparation of the chlorospirophosphorane, **11**, involved the addition of two moles of catechol to one of phosphorus pentachloride in boiling benzene. Anschütz[2] had carried out this reaction under identical conditions but he reported the formation of a material melting in the range of 200–240° which he formulated as the catechol-*bis*(spirodicatecholphosphorane), **7**. We were unable to confirm this report.

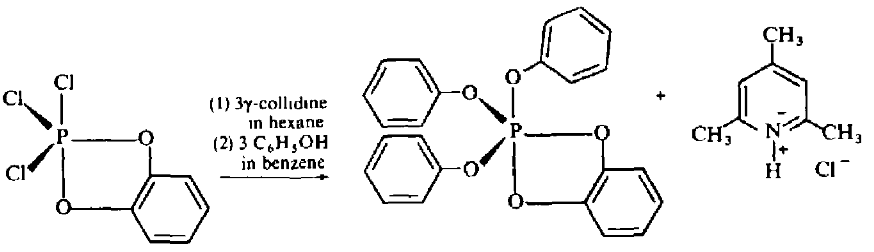
The addition of 2·5 moles of catechol to one mole of phosphorus pentachloride in benzene at 25° gave a sparingly soluble material, m.p. 250–255°. We were unable to characterize further this material, but its physical properties are not consistent with those to be expected of the complex *bis*spirooxyphosphorane, **7**. When the solid was heated with dimethylformamide, partial solution was observed. This solution contained a ^{31}P nucleus at a rather high magnetic field, δP^{31} = ca. + 85 ppm. This nucleus can not correspond to the *bis*spirooxyphosphorane structure **7** for reasons given below; however, its origin is unknown.

Reaction of trichlorocatecholphosphorane, **8**, *with phenol in the presence of amines.* A clear solution was obtained when trichlorocatecholphosphorane, **8**, was added to three equivalents of γ-collidine in hexane at 0°. When this solution was treated at 0°, and very slowly, with a benzene solution containing three mole equivalents of phenol, the *catecholtriphenoxyphosphorane*, **3**, was obtained in 55% yield.

The tetrachloro-derivative of **3**, namely, **12**, was made from the reaction of *o*-chloranil with triphenyl phosphite, following the procedure described by Ramirez, *et al.*[4,10]

Anschütz[2] did not investigate the reaction of the trichlorocatecholphosphorane, **8**, with phenol.

Catecholtriphenoxyphosphorane, **3**, was destroyed rapidly by hydrogen chloride

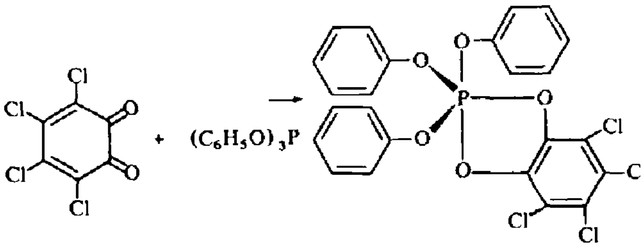


8

3: $\delta P^{31} = +60{\cdot}8$ ppm

in CH_2Cl_2 solution. A number of substances were produced in this reaction, but their structures were not investigated further.

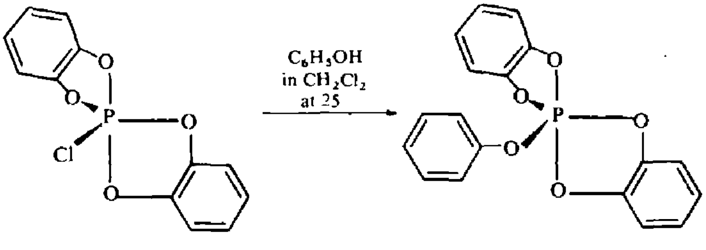
Reaction of chlorospirodicatecholphosphorane, **11**, *with phenol.* When equimolar amounts of the two substances were mixed at 25° in CH_2Cl_2, the *spirodicatecholphenoxyphosphorane*, **6**, was formed in 95% yield. It was shown, independently, that the spirocompound, **6**, was not affected by hydrogen chloride, in contrast to the behavior of the monocyclic and the acyclic pentaoxyphosphoranes, **3** and **1**, respectively.



12: $\delta P^{31} = +60{\cdot}0$ ppm

Anschütz[2] did not investigate the reaction of the chlorospirodicatecholphosphorane with phenol.

The authentic spirophenoxy-compound, **6**, had m.p. 110–112°; hence, the material of m.p. 192°, made by Anschütz following the procedure described below, could not have been **6**, as claimed.

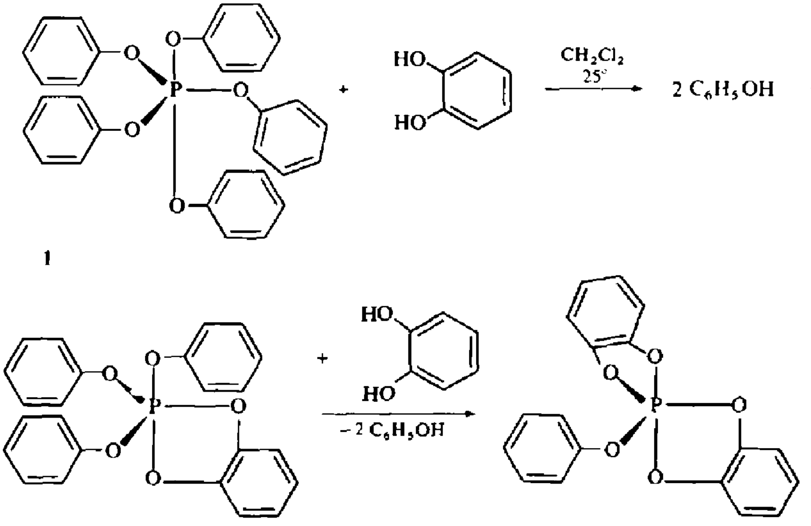


11

6: $\delta P^{31} = +30{\cdot}2$ ppm

The availability of authentic samples of the oxyphosphoranes, **3** and **6**, made it possible to elucidate the nature of the rather complex mixture of products which is formed when trichlorocatecholphosphorane, **8**, is allowed to react with phenol *in the absence* of a tertiary amine. When this reaction was carried out in the absence of solvent, the products were the phosphoranes 3 and 6 *and dichlorotriphenoxyphosphorane*, 2, plus smaller amounts of two unidentified by-products. Evidently, drastic group exchanges can occur in these reactions in the presence of the hydrogen chloride produced.

The phosphoranylation of catechol by pentaphenoxyphosphorane 1. The displacement of two moles and of four moles of phenol from pentaphenoxyphosphorane, 1 by one mole and by two moles of catechol, respectively, could be carried out in a stepwise manner. The products were catecholtriphenoxyphosphorane, 3 and spirodicatecholphenoxyphosphorane, 6. These exchanges occurred rapidly in CH_2Cl_2 solution at 25° and illustrate an important principle of oxyphosphorane chemistry: *oxyphosphoranes with two five-membered rings are more stable than the analogues with one ring, which are, in turn, more stable than the corresponding acyclic oxyphosphoranes.*[1,11] The probable reason for this was discussed in the Introduction. It should also be noted that it was possible to effect a nucleophilic substitution at pentavalent phosphorus under rather mild conditions.* [12-14]



1

3

6

A reinvestigation of the procedures described by Anschütz et al.,[2] *for the syntheses of the pentaoxyphosphoranes,* 3 *and* 6. The procedures described were repeated as shown in the Experimental. When equimolar amounts of dichlorotriphenoxyphos-

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* As before, the configuration of these oxyphosphoranes is based on the results of X-ray diffraction analysis of a related compound, cf. Ref. 4*h*. For discussions of the stereochemistry of the oxyphosphoranes see Refs 12 and 13. The stereochemistry of the halophosphoranes has received a great deal of attention, see Ref. 14. In general, a trigonal bipyramid, P (A1 . A2 . E1 . E2 . E3), in which the five groups on P are different and symmetric, can exist as ten pairs of enantiomers. The ten diastereomers can be designated as: (a, a'); (b, b')... (j, j'). The groups on phosphorus can undergo positional exchange by bon-bendings ("pseudorotation"; cf. Ref. 14*a*, *h*). The pseudorotation of **a** to **b**, using group E2 as "pivot", can be denoted as: a ⇄ b (E2). The remaining eight diastereomers are derived as: a ⇄ c (E1); a ⇄ d (E3); b ⇄ e (A1); b ⇄ f (A2); c ⇄ g (A1); c ⇄ h (A2); d ⇄ i (A1); d ⇄ j (A2). A bipyramid is converted into its enantiomer by five *consecutive* pseudorotations using *different* groups as pivots, for example: a ⇄ b (E2) ⇄ e (A1) ⇄ j' (E1) ⇄ d' (A2) ⇄ a' (E3). In cyclic phosphoranes, the number of diastereomers depends on the ability of the ring(s) to accommodate angles of 90°, 120° and 180° at P. Structure 6 (a *racemate*) is one of two possible diastereomers; the other (*meso*) has one ring in a diequatorial plane.

phorane, 2, and catechol were kept 2 hr at 140°, three materials were formed in the approximate proportion of 3·3:1:1·3. These were the spirooxyphosphorane, 6, the original material, 2, and a third compound which was not identified, but which could be triphenyl phosphate formed by hydrolysis. *No catecholtriphenoxyphosphorane, 3 was present, for reasons which are clear from the preceeding discussion.*

The chlorination of phenyl phosphorodichloridite, 4, was carried out as described.[2] The product was treated with two moles of catechol and the resulting product was heated to 250° at 10 mm as suggested by Anschütz.[2] No spirodicatecholphosphorane, 6, could be obtained. It was shown that this purification procedure simply destroyed the phosphorane, 6, since the crude reaction product did have a component which gave a ^{31}P NMR shift of +29·8 ppm, corresponding to that of authentic 6.

The nature of the species which results from the chlorination of the phenyl phosphorodichloridite may depend on the nature of the medium in which the chlorination is carried out. This problem is under further investigation and the results will be reported in a separate communication.* [15]

EXPERIMENTAL

The analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Reaction of one mole catechol with 1·25 moles phosphorus pentachloride in benzene (Anschütz's Procedure[2])

Catechol (30 g, 0·273 moles) was added to a soln of PCl_5 (71 g, 0·340 moles) in benzene (550 ml) at 25° over a 3 hr period. The mixture was kept 10 hr at 25° and the solvent was removed at 50° and 100 mm. The residue was submitted to distillation in vacuum; the first fraction was PCl_5 and the second fraction was 8, (35 g, 58%); b.p. 95° (0·5 mm). The material became a solid, m.p. 57–58°, which gave only one signal in the ^{31}P NMR spectrum in CH_2Cl_2 soln. Two recrystallizations from hexane gave material of m.p. 61–62°. (Found: C, 29·9; H, 1·8. $C_6H_4O_2Cl_3P$ requires: C, 29·4; H, 1·6%); δP^{31} = +25·7 (in hexane), +26·4 (in benzene), +26·2 (in CH_2Cl_2), +26·1 (in diethyl ether), and +26·9 ppm (in CH_3CN).

Reaction of equimolar amounts of catechol and phosphorus pentachloride

(*a*) *In methylene chloride.* Catechol (5 mmoles) was added to a soln of PCl_5 (5 mmoles) in 10 ml CH_2Cl_2 at 0°. The mixture was kept 1 hr at 0°, was allowed to reach 25°, and was evaporated at 25° and 100 mm. The resulting crystalline material was placed in CH_2Cl_2 soln and analyzed by ^{31}P NMR spectrometry. The mixture contained PCl_5 (14%, δP^{31} = +80·9 ppm), 8 (47%, δP^{31} = +26·2 ppm), and 11 (34%, δP^{31} = +9·4 ppm), and a fourth component (ca. 5%) which was not characterized.

(*b*) *In hexane.* Catechol (5 mmoles) was added to a mixture of PCl_5 (5 mmoles) and hexane (10 ml) at 0° over a 1 hr period. The mixture was evaporated at 15° and 10 mm and the residue was dissolved in CH_2Cl_2 and analyzed by ^{31}P NMR spectrometry. There was no PCl_5 left; there was 8 (73%), 11 (18%), and a third unknown component (9%).

(*c*) *In benzene.* Solid PCl_5 (50 mmoles) was added at once to a soln of catechol (50 mmoles) in benzene (125 ml) at 25°. The ^{31}P NMR spectrum showed the presence of three nuclei in the proportion of 4:1:4, with δP^{31} = +9·5 (11), +30·4 (8) and +81·2 ppm (PCl_5).

(*d*) *In boiling benzene–ether (Anschütz's procedure[2]).* Anschütz[3] reported that the addition of one mole of catechol in ether *all at once* to one mole PCl_5 in boiling benzene gave the *monomeric* form of 11, m.p. 166–168° (from benzene–ether). This material had the correct elemental analysis and mol wt. Anschütz also reported that the addition *over a 3 hr period* of one mole PCl_5 to one mole catechol dissolved in benzene at 25° gave a crystalline material m.p. 180–210°, which he regarded as the "*dimer*" of 11. We did not encounter a well characterized structure corresponding to this description.

Reaction of two moles catechol with one of phosphorus pentachloride in benzene

(*a*) *Present investigation (optimum conditions for the formation of the chlorospirodicatecholphosphorane,*

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* The problem of the *configuration*, in solution and in the crystalline state, of halooxyphosphoranes remains unsolved. In fact, not much is known about the *structure* of the compounds. The situation seems to be quite complex as can be seen from the work reported and summarized in Ref. 15.

11). Catechol (23·5 g, 0·214 moles) was added all at once to a mixture of PCl_5 (22·3 g, 0·107 moles) in benzene (65 ml) at 25°. The mixture was kept 1 hr at 70° and was then filtered. The solid was washed with ether (20 ml) and dried. Compound **11**, (22 g, 70%) had m.p. 168–160°. It was recrystallized from benzene–hexane 1:1, 100 ml to give material of m.p. 174–175°. (Found: C, 51·2; H, 3·0. $C_{12}H_8O_4ClP$ requires: C, 50·8; H, 2·8%); δP^{31} = +9·4 (CH_2Cl_2).

(*b*) *Anschütz's work*[2]. Anschütz reported that the addition of two moles of catechol, *at once*, to a soln of one mole PCl_5 in benzene at 25° followed by reflux led to a material, m.p. 200–240°, which he formulated as **7**, from elemental analysis and mol. wt. We were unable to verify the formation of this type of material by the same procedure.

Reaction of 2·5 moles catechol with one mole phosphorus pentachloride

Catechol (14 g, 0·125 moles) was added *at once* to PCl_5 (10 g, 0·05 moles) in benzene (30 ml) at 25°. The mixture was refluxed for 15 min and was then filtered to give a sparingly soluble material (8·5 g) m.p. ca. 250–255°. The material could not be fully characterized; it was insoluble in most solvents. The soln obtained from it in boiling dimethylformamide had one ^{31}P NMR signal at +83·1 ppm. This value rules out the structure of **7**. It is not certain that the material in the crystal is the same as the material after boiling with dimethylformamide. The large positive value of the shift suggests a polymeric open-chain pentacatecholphosphorane.

Reaction of equimolar amounts catechol and phosphorus trichloride, followed by chlorination

The procedure described by Anschütz[16] and by Gross and Gloede[5] was followed giving the catecholphosphorochloridite, b.p. 95–96° (25 mm) in 60% yield, δP^{31} = −173 ppm (benzene).

The chloridite was allowed to react with chlorine in CCl_4 at 0° as described. The product had δP^{31} = +26·5 ppm which corresponds to that of **8**.

Reaction of three moles phenol with one mole trichlorocatecholphosphorane, **8**, *in the presence of a tertiary amine*

Compound **8** (4·62 g, 18·8 mmoles) was added at once to a soln containing γ-collidine (6·94 g, 57·5 mmoles) in hexane (25 ml) at 0°. To this clear soln was added slowly over a 1 hr period a soln of phenol (5·40 g, 57·5 mmoles) in benzene (25 ml) at 0°. The mixture was kept 10 hr at 25° and was filtered under N_2. The filtrate was evaporated at 25° (25 mm). An aliquot of the residue was dissolved in CH_2Cl_2; this soln had one ^{31}P nucleus, δP^{31} = +60·8 ppm due to **3**. The main portion of the reaction product was kept for some time at 0° until crystallization occurred. This material was recrystallized from hexane yielding **3** (4·2 g, 53%) m.p. 86–87°. (Found: C, 68·5; H, 4·9; P, 6·6. $C_{24}H_{19}O_5P$ requires: C, 68·9; H, 4·6; P, 7·4%); δP^{31} = +60·8 ppm. The IR spectra (CH_2Cl_2) had bands at (μ): 6·28, 6·72, 7·40, 7·80, 8·12, 8·30, 8·60, 9·10, 9·32, 9·75, 9·90, 10·40, and 10·68.

Anschütz[2] did not report the addition of phenol to **8** under any conditions. He reported the addition of MeOH, of aniline, and of oxalic acid to the trichlorocatecholphosphorane; these reactions were not re-investigated in the present study.

Reaction of phenol with the trichlorocatecholphosphorane, **8**, *in the absence of an amine*

When phenol (60 mmoles) was added at once to **8** (20 mmoles) at 25° and the mixture was kept 2 hr at 140° under a N_2 current, a mixture containing at least 5 phosphorus nuclei was obtained in the approximate proportions of 1:2·5:5·0:5·0:5·0, at δP^{31} = +15·8 (probably a catecholphosphate), +17·4 (probably triphenyl phosphate made by hydrolysis), +23·0 (**2**), +30·6 (**6**), +60·8 ppm (**3**).

Reaction of catecholtriphenoxyphosphorane, **3**, *with hydrogen chloride*

(*a*) *At* 25°. A soln of **3** in CH_2Cl_2 was treated with HCl at 25° for 5 min. The soln was analyzed by ^{31}P NMR spectroscopy and it was verified that the signal corresponding to the starting material, **3**, had completely vanished as a result of this relatively mild treatment. The product of the reaction was not scrutinized further.

Reaction of pentaphenoxyphosphorane, **1**, *with one mole equivalent of catechol*

Catechol (5·48 mmoles) was added to a soln of **1**[1] (5·48 mmoles) in CH_2Cl_2 (10 ml), at 25°. The mixture was kept 0·5 hr at 25° and was then evaporated at 25 mm giving a residue which was shown to be **3**, by ^{31}P NMR spectroscopy.

Reaction of pentaphenoxyphosphorane, **1**, *with two mole equivalents of catechol*

Catechol (3 mmoles) was added to a soln of **1** (1·5 mmoles) in CH_2Cl_2 (5 ml) at 25°. After 1 hr at 25°, the mixture was evaporated at 25 mm. The residue consisted of **6**[7] as shown by ^{31}P NMR spectroscopy.

Catechol converted **3**, into **6**, in CH_2Cl_2 at 25°, as demonstrated by the ^{31}P NMR spectrum of the soln.

An excess of phenol had no effect on the **6**, even after 0·5 hr at 140° in the absence of solvents.

HCl had no effect on **6**, in CH_2Cl_2, at 25°.

Reaction of the chlorospirodicatecholphosphorane, **11**, *with one mole equivalent of phenol*

A mixture of phenol (1·41 g, 15 mmoles) and **11** (4·25 g, 15 mmoles) was kept 1 hr at 140°. The mixture was cooled, washed with pentane and submitted to analysis without further purification. Compound **6** (4·8 g, 93%) had m.p. 110–112°. (Found: C, 63·5; H, 3·9; P, 8·9. $C_{18}H_{13}O_5P$ requires: C, 63·5; H, 3·8; P, 9·1%); $\delta P^{31} = +29·8$ ppm (CH_2Cl_2).

Anschütz[2] had given the m.p. of 192° for a material regarded as **11** made by a different procedure.

Reaction of dichlorotriphenoxyphosphorane, **2**, *with one mole equivalent of catechol* (*Anschütz's Procedure*[2])

Catechol (0·57 g, 5·2 mmoles) was added to **2** (1·98 g, 5·2 mmoles), and the mixture was kept 2 hr at 150°. The product was dissolved in CH_2Cl_2 and the soln was examined; it contained three types of ^{31}P nuclei in the proportion of 1·3:1·0:3·3, with shifts at +18·1 ppm (probably triphenyl phosphate formed by hydrolysis), +22·8 ppm (unreacted **2**) and +29·9 ppm (**6**).

According to Anschütz[2] this reaction gave **3** with m.p. 95–101°; he reported only a P elemental analysis.

Reaction of the phenylphosphorodichloridite-chlorine adduct, **5**, *with two mole equivalents of catechol* (*Anschütz's Procedure*[2])

Compound **4** ($\delta P^{31} = -177·1$ ppm) was made from PCl_3 and phenol as described.[17] A soln of this material in hexane was treated with Cl_2 at 0°. The material that precipitated was dissolved in benzene. This soln was treated, at its b.p., with an ether soln containing two mole equivs at catechol. The resulting clear soln was evaporated at 25° and 20 mm. The residue had a m.p. of about 105–112°; its ^{31}P NMR spectrum in CH_2Cl_2 had a signal that corresponded to **6**. However, when this material was submitted to the purification procedure suggested by Anschütz,[2] namely, distillation at 250° at 10 mm, complete decomposition occurred. We could not isolate from among the decomposition products the material of m.p. 192° mentioned by Anschütz.[2]

Reaction of o-*chloranil with triphenyl phosphite*

A soln of *o*-chloranil (11·5 mmoles) in CH_2Cl_2 (5 ml) was added to a soln of triphenyl phosphite (11·5 mmoles) in CH_2Cl_2 (5 ml) at 25°. The mixture was kept 1 hr at 40° and was evaporated to give **12** m.p. 85–87° (cyclohexane), $\delta P^{31} = +60·0$ ppm (in CH_2Cl_2). The phosphorane **12** was isolated in 75% yield.

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