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# Structure of Products from Reactions of Phosphorus Pentachloride with Phenyl Salicylate and 2-Hydroxybenzophenone; Related Compounds. p31 N.M.R. and Chemical Studies (1)

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The compounds obtained from the reactions of phenyl salicylate and 2-hydroxybenzophenone with phosphorus pentachloride have been shown to have structures I A and II A, respectively, rather than alternative heterocyclic structures on the basis of the comparison of the  $P^{31}$  chemical shifts with appropriate reference compounds and additional chemical evidence. Compound I reacts with two equivalents of phenol in the presence of two equivalents of triethylamine to form mainly compound VIII (substitution on phosphorus). Structure VIII is confirmed via  $P^{31}$  n.m.r. and IR spectra and the fact that partial hydrolysis forms the same compound (VII) that is obtained from the reaction of compound III with phenol (only phosphorus substitution possible). A mechanism with initial reaction of phosphorus pentachloride (as tetrachlorophosphonium ion) on the phenolic hydroxyl is postulated on the basis of the available evidence. The  $P^{31}$  chemical shifts for compounds XIV A and XV A confirm these structures as heterocyclic in accord with previous chemical evidence. Structure XIV A is of historical importance as one of the first three cyclic structures ever published in the classical paper in which Couper announced his structural theory of organic chemistry.

Heterocyclic structures have been favored over acyclic alternatives for products from the novel reactions of phosphorus pentachloride with phenyl salicylate (I) (4) and 2-hydroxybenzophenone (II) (5) to account for the absence of carbonyl stretching bands in the infrared spectra and on the basis of the experimental evidence on hand. A structure (I C) containing the  $-OPCl_4$  grouping proposed by Michaelis and Kerkhof (6) in 1898 was excluded by the absence of an infrared carbonyl stretching band (4). However, conclusive evidence was not available for a definite decision between the alternative structures. In this paper the  $P^{31}$  n.m.r. spectra of these products are reported and compared with appropriate reference compounds enabling definite assignments of structures which support the chemical evidence presented.

## RESULTS AND DISCUSSION

The values for the  $P^{31}$  n.m.r. chemical shifts are listed in Table I in the order of increasing magnitude of the shift. The chemical shifts for compounds I and II were the same,  $0.0 \pm 1.0$  p.p.m. (7). These values are close to the ones for phosphorodichloridates, III (phenyl phosphorodichloridate) at  $-1.5$  p.p.m. (8, 9) and IV (an *o*-substituted phenyl phosphorodichloridate) at  $-3.7$  p.p.m.

The heterocyclic structures I B, II B, and II C which contain pentavalent and hexavalent phosphorus,

are excluded by the following considerations. Pentavalent phosphorus compounds in general show large positive shifts ranging from +26 for compound V (8) to +53 for compound VI (10) and +80 for  $PCl_5$  (8, 11). The  $PCl_6^-$  anion which incorporates a hexavalent phosphorus, has the extremely large value (8, 12) of +300.

The infrared spectra can be interpreted in terms of the phosphorodichloridate structures for compounds I, II, III and IV, respectively, (wave lengths in  $\mu$ ): P=O stretching (13, 14), 7.70, 7.66, 7.78, 7.68; C-O link of P-O-C (arom.) (13, 14), 8.38, 8.34, 8.39, 8.44; P-O link of  $P^{31}$ -O-C (arom.) (13, 14) (*ca.* center of broad band) 10.50, 10.47, 10.60, 10.59.

Chemical studies were also carried out to obtain further evidence of structure. In attempting to differentiate between structures I A and I B for the phenyl salicylate - phosphorus pentachloride product, the reaction of this product with phenol was studied. It was hoped that a selective replacement of the chlorine atoms might result in stable products in which the phenoxy groups could be located as to whether substitution took place on phosphorus or carbon. It was found that a disubstituted product could be isolated from the reaction in carbon tetrachloride using two equivalents of triethylamine; however, this was an oily material which could not be obtained crystalline or purified by vacuum distillation. The infrared spectrum showed a P=O absorption band at  $7.72 \mu$ , a P-O-C (aromatic) band



CHART II

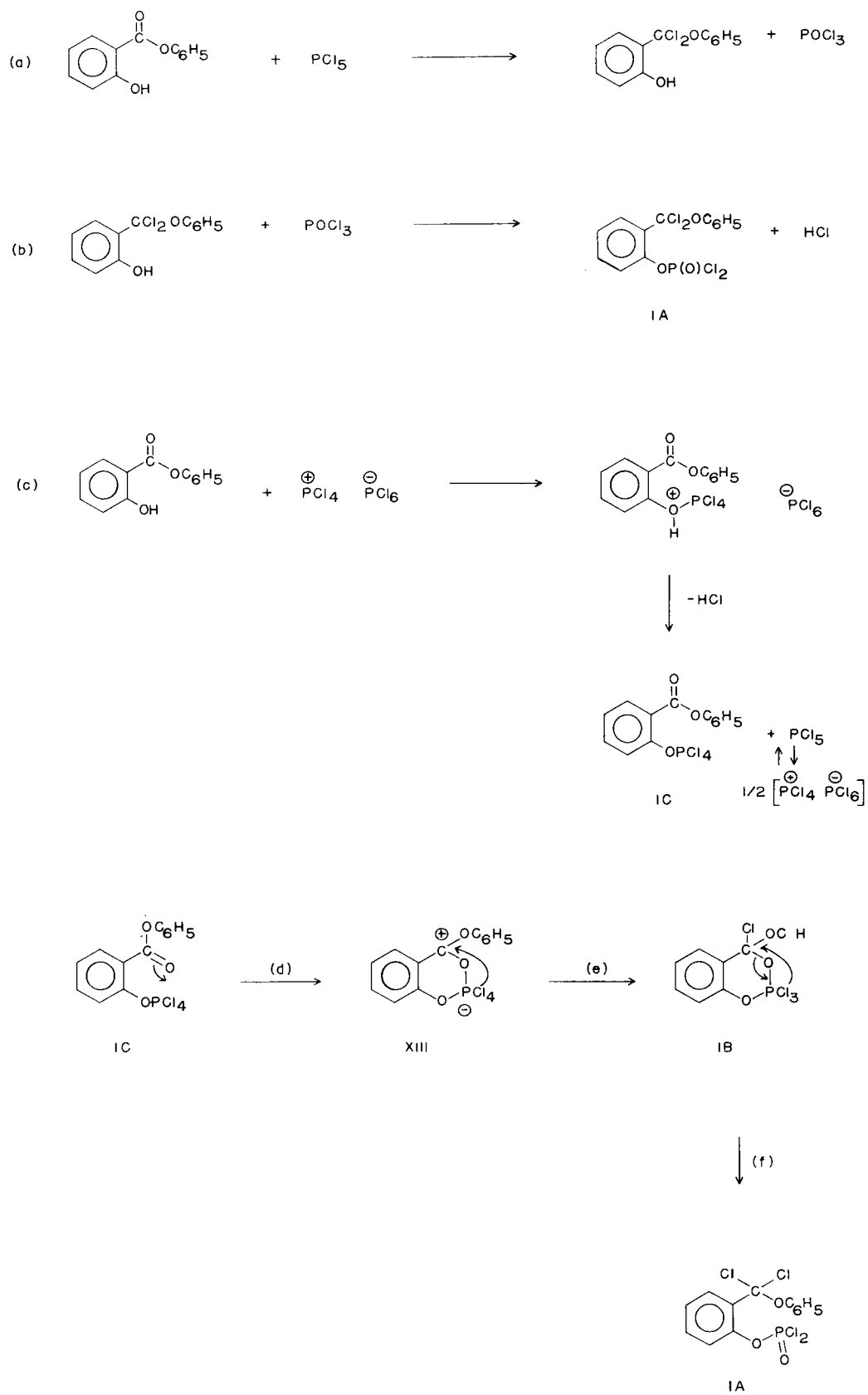


TABLE I

 $P^{31}$  N.M.R. Data on Some Organophosphorus Compounds

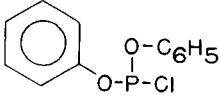
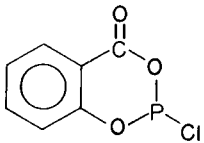
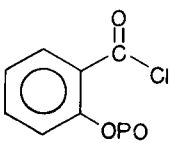
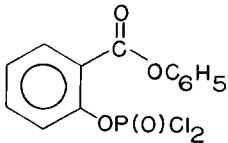
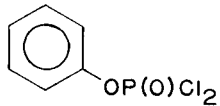
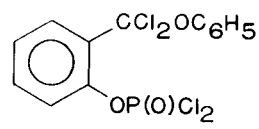
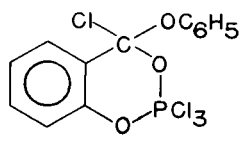
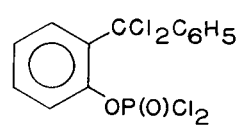
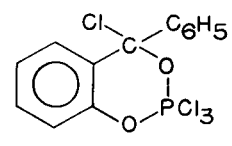
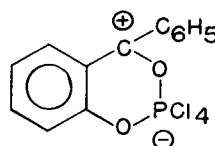
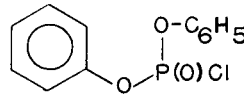
Structures	Solvent or State	Chem. Shift (p.p.m.)
 <p>XVI</p>		-159
 <p>XVa</p>	benzene	-151.2
 <p>XVb</p>		
 <p>III</p>	$CH_2Cl_2$	-3.7
 <p>IV</p>		-1.5
 <p>Ia</p>	benzene	$0.0 \pm 1.0$
 <p>Ib</p>		
 <p>IIa</p>	benzene	$0.0 \pm 1.0$
 <p>IIb</p>		
 <p>IIc</p>		
 <p>XI</p>		+6.2

TABLE I (con't.)

Structures	Solvent or State	Chem. Shift (p. p. m.)
	benzene	+9.5
		+17
	benzene	+18.5
	carbon tetrachloride	+18.9
		+26.0
	benzene	+53
VI		
X = - Me, - C <sub>6</sub> H <sub>5</sub>		

Two other components of the reaction mixture were present in approximate amounts of 15% and 5%. The 15% component had a chemical shift of 18.1 p.p.m., the position of which indicated it to be a triphenyl phosphate also, possibly structure IX (Chart I). The chemical shift for the third component (*ca.* 5%) of the mixture was at +7.4. This position would indicate this compound to have possibly the diphenylphosphorochloridate structure X since the shift is close to the value reported (8,9) for diphenylphosphorochloridate (XI) of +6.2.

It is of interest to note the difference between the reactions of the phenyl salicylate - phosphorus pentachloride product (I A) with phenol on the one hand and with water on the other (Chart I). The reaction with phenol occurs primarily at phosphorus whereas water reacts at the dichloromethylene group. The difference may be attributable largely to steric reasons. The chlorine atoms on the dichloromethylene group, being activated by the attached aryl group and the ether oxygen (17) can be considered to be generally more reactive than those on the phosphorodichloridate group (18). This would account for the reaction with water at the dichloromethylene carbon. The phenol molecule, having larger steric requirements than water, would react at this position with relatively more difficulty because of the steric effect of the *ortho*-situated phosphorodichloridate group. However, the phosphorodichloridate group can assume a conformation (I A<sub>a</sub>) (Chart I) in which the phosphorus atom is inclined away from the *ortho*-situated dichlorophenoxymethyl group leaving the former exposed to attack by phenol. The fact that compound VIII also reacts readily with water at the dichloromethylene group is in accord with the preceding postulate.

The formation of *ortho*-substituted phenyl phosphorodichloridate structures (19) from the reactions of the phenolic esters and ketones with phosphorus pentachloride constitutes a remarkable transformation as will be evident from consideration of possible reaction mechanisms. The reaction with phenyl salicylate is perhaps the most surprising in that the carbonyl group of an ester is converted into a dichloromethylene group under very mild conditions (room temperature) in practically quantitative yield, the carbonyl oxygen being transferred to phosphorus (Chart II). Simple esters do not appear to be reported to undergo such a reaction (conversion of the carbonyl to a dichloromethylene group); phenyl benzoate, for example did not react with phosphorus pentachloride under various vigorous conditions attempted (4). An attempt was made in the present study to bring about a reaction between compound III and phosphorus pentachloride under various conditions; very little if any reaction was observed by comparison of infrared spectra.

In a few special cases, however, where there are two carbonyl groups in  $\alpha,\beta$ -positions, as in dialkyl oxalates (20), alkyl or aryl oxamates (21), one of the carbonyl groups reacts with phosphorus pentachloride. The difficulty of reaction at a mono-ester

carbonyl would appear not to favor initial reaction at this position to produce a dichloromethylene group and phosphorus oxychloride (Chart II, equation a) as in a mechanism such as that proposed by Newman and Wood (22) for reactions of ketones with phosphorus pentachloride. The second step of such a reaction would involve phosphorus oxychloride reacting with the phenolic hydroxyl group (Chart II, equation b). However, reactions of phenols with phosphorus oxychloride generally require the presence of tertiary amines, catalysts, or vigorous conditions (23). For these reasons a mechanism in which the first step occurs at the phenolic hydroxyl group (equation c) would be more likely to occur. Thus, it is well-known that phenols react readily with phosphorus pentachloride at room temperature (24).

Further evidence for initial attack at the hydroxyl group was obtained in the present work in a study of the reaction of *p*-hydroxybenzophenone and phosphorus pentachloride. In this reaction the hydroxyl and the carbonyl groups competed for reaction with the one equivalent of phosphorus pentachloride. Although the product could not be isolated in pure form, the infrared spectrum of the reaction mixture showed the disappearance of the O-H stretching band which was present at 3.06  $\mu$  in the spectrum of *p*-hydroxybenzophenone. Also the carbonyl band of *p*-hydroxybenzophenone at 6.02  $\mu$  had shifted to 5.99  $\mu$  in the reaction product. These results indicate reaction at the hydroxyl group. For confirmation of these results, the room temperature reaction of benzophenone and phosphorus pentachloride was studied. The infrared spectrum of the reaction mixture showed a slight shift of the carbonyl frequency from 6.05  $\mu$  in benzophenone to 6.07  $\mu$  in the reaction product. This shift to longer wavelengths is indicative of association at the carbonyl oxygen. Thus, Cook (25) showed that the carbonyl stretching band at 6.10  $\mu$  ( $1639\text{ cm}^{-1}$ ) in the infrared spectrum of 2,6-dimethylpyrone (XII) moved to lower frequencies (longer wavelengths) in complexes with Lewis acids.

Possible reaction mechanisms for initial reaction at the hydroxyl group can now be considered. The first step at the hydroxyl group would be followed by a ring closure reaction involving the carbonyl oxygen to form structure XIII (Chart II, equation d). A shift of chloride ion from phosphorus to carbon (equation e) would form the heterocyclic structure I B as an intermediate. A subsequent shift of another chlorine ion from phosphorus to carbon and breaking of the carbon-oxygen bond (equation f) would then form the final product I A. A similar mechanism can be written for the reaction of 2-hydroxybenzophenone and phosphorus pentachloride. In the absence of definitive kinetic data (26), no statements can be made as to the relative rates of the various steps or whether stepwise or simultaneous bond making and breaking occur at different stages. It would seem that a conclusive answer to the question as to whether initial reaction takes place at the carbonyl or the hydroxyl group could be obtained

by means of an experiment in which labeled phosphorus oxychloride (having radioactive phosphorus or isotopic oxygen) would be introduced into the reaction to see whether or not it would be incorporated into the product.

The  $P^{31}$  n.m.r. spectra were also examined for two related model compounds for which structures containing phosphorus in 6-membered rings have been preferred over acyclic alternatives on the basis of chemical evidence. The first of these, structure XIV A, is historically important in that this was one of the first three (27) cyclic structures ever published in the classical paper in which Couper announced his structural theory of organic chemistry. Couper obtained this compound in 1858 as a partial hydrolysis product of a compound obtained from the reaction of phosphorus pentachloride and salicylic acid (30). R. Anschütz first proposed (31) an acyclic structure (XIV B) containing a metaphosphate group, later (32) considered also the heterocyclic structure (XIV A) which he proposed independently not being aware of Couper's formulations, and in his final paper (33) favored structure XIV B which is the structure listed in two well-known reference works (34). More recent chemical evidence favors the cyclic structure XIV A (35).

The  $P^{31}$  n.m.r. spectrum of compound XIV showed a chemical shift of +9.5 p.p.m. The closest reference compound for which  $P^{31}$  data is available is diphenyl phosphorochloridate (XI), the  $P^{31}$  shift being reported (8,9) as +6.2 p.p.m. The increase of +3.2 p.p.m. in the shift for compound XIV may be due to the attachment of the acyl group to oxygen in place of the phenyl as in diphenyl phosphorochloridate or may be the result of ring closure (36) or a combination of both effects. The position of the  $P^{31}$  chemical shift thus substantiates the assignment of the heterocyclic structure (XIV A) as correct in accord with the chemical evidence.

The second related cyclic structure is XV A which is formed by the reaction of phosphorus trichloride and salicylic acid. R. Anschütz and Emery (32) favored the heterocyclic structure XV A over the acyclic one XV B although they did not have conclusive experimental evidence. L. Anschütz (the son of R. Anschütz) later (37) on the basis of studies of the reactions with amines concluded that the acyclic metaphosphite structure (XV A) was correct. The later work of Young (38) and Cade and Gerrard (39) furnished chemical evidence for the heterocyclic structure (XV A).

In the present study, the  $P^{31}$  n.m.r. spectrum of compound XV showed a chemical shift of -151.2 p.p.m. which is close to the reported (8,40) value for the reference compound diphenyl phosphorochloridate (XVI) of -159 p.p.m. Low negative values are generally characteristic of trivalent phosphorus compounds (8). The shift toward a more positive value of compound XV as compared with XVI is analogous to the shift noted earlier for the phosphorochloridate XIV. Thus, the  $P^{31}$  data also confirm the heterocyclic structure XV A as correct.

## EXPERIMENTAL (41)

## Compound I.

Phenyl salicylate (42.3 g., 0.197 mole) dissolved in 75 ml. of dry benzene was added dropwise over a 1 hour period to a stirred slurry of phosphorus pentachloride (41.1 g., 0.197 mole) and 50 ml. of benzene in a 3-necked reaction flask protected from moisture. Hydrogen chloride was evolved rapidly during the addition. After 15 minutes further stirring, the benzene was removed *in vacuo* to yield 76.2 g. (quantitative crude yield) of a white solid. All operations were carried out in a dry-box. Compound I after two recrystallizations from dry isopropyl ether (dried by refluxing and distilling from sodium ribbon), had a m.p. of 94.8-96.1° (42). Comparison of the infrared spectrum of the recrystallized sample with that of the crude reaction product showed no extraneous bands in the latter.

## Compound II.

The procedure for compound II was similar to the one preceding using 0.300 moles each of 2-hydroxybenzophenone (43) and phosphorus pentachloride in benzene solution. After recrystallization from dry petroleum ether (b.p. 30-60°), the colorless crystals had m.p. 65.8-67.0° (44) (sealed tube). Comparison of the infrared spectrum of the recrystallized product with that of the crude reaction product showed no extraneous bands in the latter.

## Compound III.

## (a) From Reaction of Phenyl Salicylate and Phosphorus Oxychloride.

A solution of dry pyridine (15.8 g., 0.200 mole) and phenyl salicylate (42.8 g., 0.200 mole) in 75 ml. of dry benzene was added dropwise over a 1 hour period to a stirred solution of phosphorus oxychloride (30.7 g., 0.200 mole) dissolved in 25 ml. of benzene in a 3-necked flask protected from moisture. The precipitated pyridine hydrochloride was removed by filtration in a dry-box after standing overnight. A crude yield of 59.2 g. (89.4%) of a white solid was obtained on removal of solvent *in vacuo*. Recrystallization from cyclohexane yielded a product with m.p. 86.8-87.6° (45). In other preparations, better results were obtained by using triethylamine in place of pyridine since pyridine hydrochloride tended to precipitate slowly and to be more hygroscopic as compared with triethylamine hydrochloride, thus causing partial hydrolysis of the product.

## (b) By Hydrolysis of Compound I.

A solution of compound I (3.026 g., 0.007839 mole) in 80 ml. of dry benzene was placed in a 3-necked flask equipped with stirrer and drying tube, and a dropping funnel. Distilled water (0.1410 g., 0.007839 mole) was added and the resulting cloudy mixture was stirred for 11 hours during which time it became clear. The solvent was removed *in vacuo*, yielding 2.8 g. (2.6 g. calcd.) of an oil, the infrared spectrum of which showed that this product was the same as that obtained from the reaction of phenyl salicylate and phosphorus oxychloride.

## Phenyl Phosphorodichloridate (IV).

Phenol (9.0 g., 0.096 mole) dissolved in a minimum amount of dry carbon tetrachloride was added dropwise to a stirred mixture of phosphorus oxychloride (15 g., 0.098 mole) and pyridine (7.5 g., 0.095 mole) in 3-necked flask protected from moisture. The mixture was stirred for 2 hours and allowed to stand overnight. The precipitated pyridine hydrochloride was filtered in a dry-box and carbon tetrachloride removed from the filtrate by distillation. The residue was distilled; b.p. 130-134°, < 1 mm.; yield, 15 g. (75%).

## Compound VII.

Compound III (7.7 g., 0.023 mole) dissolved in 100 ml. of dry benzene was placed in a 3-necked flask equipped with stirrer and dropping funnel. A solution of triethylamine (4.7 g., 0.046 mole) and phenol (4.4 g., 0.047 mole) in 135 ml. of benzene was added dropwise in a 3.5 hour period. The precipitated triethylamine hydrochloride was filtered in a dry-box and the precipitate washed with benzene. An oil (9.4 g., 90% crude yield) which was obtained after removal of solvent *in vacuo* solidified on standing for several days. Crystals of compound VII, m.p. 75.6-76.2°, were obtained on recrystallization from 95% ethanol. Michaelis and Kerkhof (6) reported m.p. 76-77° for the product they obtained from the reaction of compound III with sodium phenolate.

## Reaction of Compound I with Phenol.

A solution of phenol (3.60 g., 0.0382 mole) and triethylamine (4.00 g., 0.0395 mole) of carbon tetrachloride was added to a stirred solution of compound I (7.39 g., 0.0191 mole) in 150 ml. of carbon tetrachloride over a 6 hour period. After standing overnight,

the solution was filtered in a dry-box; the triethylamine hydrochloride precipitate was washed with carbon tetrachloride, dried, and weighed; 4.8 g. (90% based on formation of 2 equivalents of hydrogen chloride). An oily product (9.3 g., 97% crude yield based on replacement of two Cl atoms by phenoxy groups) was obtained after removal of the solvent *in vacuo*. The oil (compound VIII) could not be induced to crystallize (even from several other preparations) and attempted vacuum distillation was unsuccessful. Hydrolysis and subsequent chloride analysis on the crude sample showed a chlorine content of 12.4%; calcd., 14.1% (88% yield based on chlorine content). The infrared and  $P^{31}$  n.m.r. spectra have been discussed earlier.

#### Hydrolysis of Compound VIII.

A sample of compound VIII was spread out on a watch glass and exposed to atmospheric moisture overnight. In this period of time the sample had hydrolyzed and solidified, m.p. 74-75°. The solid was recrystallized from 95% ethanol, m.p. 75.7-76.4°. A mixed melting point with a sample of authentic compound VII obtained above gave no depression; a comparison of the infrared spectra established the identity of the two products.

#### Reaction of Phosphorus Pentachloride and *p*-Hydroxybenzophenone.

A solution of *p*-hydroxybenzophenone (46) (1.895 g., 0.00956 mole) in 50 ml. of dioxane (47) was added dropwise with stirring to phosphorus pentachloride (1.992 g., 0.00956 mole) in a 3-necked flask protected with a drying tube. No evolution of hydrogen chloride was observed during the addition, probably due to the solubility of hydrogen chloride in dioxane. After stirring for 5 hours, the solvent was removed *in vacuo*, leaving a viscous liquid which could not be crystallized. The infrared spectrum of the product in dioxane indicated that the hydroxyl band of *p*-hydroxybenzophenone was not present; a carbonyl band was present at 5.99  $\mu$  compared to the corresponding band at 6.02  $\mu$  for *p*-hydroxybenzophenone.

#### Room Temperature Reaction of Phosphorus Pentachloride and Benzophenone.

A solution of benzophenone (48) (2.265 g., 0.0124 mole) in 20 ml. of dioxane was added dropwise to a slurry of phosphorus pentachloride (2.589 g., 0.0124 mole) and 20 ml. of dioxane. The phosphorus pentachloride dissolved during a 3 hour period of stirring, indicating a reaction with benzophenone. An infrared curve on the solution showed a carbonyl absorption band at 6.07  $\mu$  compared with 6.05  $\mu$  for benzophenone in dioxane.

#### $P^{31}$ N.M.R. and Infrared Spectra.

The  $P^{31}$  spectra were determined on the solutions sealed in glass tubes. Referencing was by means of a duplicate sealed tube containing a small sealed capillary of 85% aqueous phosphoric acid. The chemical shifts are in parts per million from the 85% phosphoric acid reference.

The infrared spectra were obtained on a KM-1 Baird-Atomic instrument. Matched 0.1 mm. sodium chloride cells were used for the solution spectra. The following solvents were used: carbon tetrachloride for compounds I, II, and IV; methylene chloride for III and VIII; and cyclohexane for VII. The preparation of the solutions and filling of the cells for moisture-sensitive compounds were done in a dry-box. The spectra were calibrated against the nearest polystyrene bands run on the same chart as the sample.

#### Acknowledgments.

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- (41) Melting points were taken with total immersion thermometers.



Melting points of moisture-sensitive compounds were obtained by sealing the sample according to a previously described procedure: A. G. Pinkus and P. G. Waldrep, *Mikrochim. Acta*, 772 (1959). Boiling points are uncorrected. Moisture-sensitive operations were carried out in a dry-box whenever necessary.

(42) The m.p. of 44° reported by Michaelis and Kerkhof (6) appears to be in error or possibly the result of hydrolytic impurities since no precautions against moisture were taken in their work. In repeating the exact procedure of Michaelis and Kerkhof of heating the two solids together (except for taking precautions against moisture), the same product was obtained as with benzene solvent.

(43) M.p. 37.8-38.4° prepared by methods of N. M. Cullinane, N. M. E. Morgan, and C. A. J. Plummer, *Rec. trav. chim.*, 56, 627 (1937) or by Friedel-Crafts reaction of phenol and benzoyl chloride in 1,1,2,2-tetrachloroethane.

(44) This m.p. is slightly higher than that reported previously (5), 65.4-66.2°.

(45) Michaelis and Kerkhof (6) report m.p. 70-71°; this lower m.p. again is most likely attributable to hydrolytic impurities as it was noted in the present work that this compound is fairly sensitive to atmospheric moisture.

(46) M.p. 134-135°, recrystallized from aqueous ethanol.

(47) Dried over potassium hydroxide pellets, refluxed with sodium and distilled. Dioxane was used in preference to other solvents tried because of solubility advantages. Although it is generally a poor solvent for infrared studies because of extensive absorption bands, it was suitable for the present case since the regions of interest (hydroxyl and carbonyl stretching) were open.

(48) M.p. 47.8-48.6° recrystallized from 95% ethanol.

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