hydrochloric acid. The ether layer was separated and the aqueous layer was extracted three times with ether. The combined ethereal solution was dried with anhydrous magnesium sulfate and filtered. The ether was evaporated and the residue was distilled. The yields and boiling points of products are shown in Table II. Five of the diketones were new compounds; their copper chelates were also prepared. The analyses of the diketones and copper chelates are given in Table II.

Nucleophilicity Comparison between Disodio Salts (Table I).—In expt 1 a solution of 10 g (0.10 mole) of acetylacetone and 12.8 g (0.10 mole) of dipropionylmethane in 30 ml of tetrahydrofuran was added to a stirred suspension of 0.40 mole of sodium amide in 600 ml of liquid ammonia to form a solution[6] of disodio salts **2''** and **3''** (0.1 mole of each). After 30 min, 100 ml of tetrahydrofuran was added; then 12.4 g (0.09 mole) of butyl bromide was added over 10–12 min. After 30 min, 6 g of ammonium chloride was added, and the reaction mixture was worked up as described above. Vpc of the crude product showed peaks for acetylacetone, dipropionylmethane, 2,4-nonanedione, and 6-methyl-3,5-decanedione. The mole ratio of 2,4-nonanedione to 6-methyl-3,5-decanedione was 80:20. The products were identified by comparison of retention times with those of authentic samples. The product ratios were obtained by integration of peak areas. The average was taken of several chromatograms.

Experiments 3–6 and 8 were conducted similarly. In expt 2 only 0.01 mole of butyl bromide was employed. Experiments 7 and 9 were conducted on one-half the scale of expt 1.

Reaction of 5-Chloro-2-hydroxybenzophenone and Phosphorus Pentachloride. Structural Studies[1]

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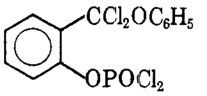
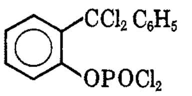
The product from the reaction of 5-chloro-2-hydroxybenzophenone and phosphorus pentachloride has been shown to have the phosphorodichloridate structure VI on the basis of P^{31} nmr and infrared spectra and chemical evidence. 5-Chloro-2-hydroxybenzophenone reacts with phosphorus oxychloride to form the phosphorodichloridate ketone (V). Reaction of V with phosphorus pentachloride converts it into VI, which was obtained from the above reaction, the reaction with V being the normal reaction for conversion of a keto group into a dichloromethylene group. The analogous phosphorodichloridate ester (IV) did not undergo a reaction with phosphorus pentachloride; thus the possibility of an exchange reaction in the phosphorodichloridate group was obviated.

VI reacts with 2 equiv of phenol in the presence of *t*-amine (or sodium phenolate) to form Xa as evidenced by P^{31} nmr, infrared spectra, and basic hydrolysis of the dichloromethylene to a carbonyl group. The dichloromethylene chlorines could not be replaced by phenoxide groups under various conditions attempted. VI was hydrolyzed in homogeneous aqueous dioxane solution to 5-chloro-2-hydroxybenzophenone; the crystalline VI is fairly stable to hydrolysis. VI does not react with sulfur dioxide under various conditions attempted.

The products from the reactions of phenyl salicylate and 2-hydroxybenzophenone with phosphorus pentachloride have been designated as *ortho*-substituted phenyl phosphorodichloridates (I and II, respectively) rather than alternative heterocyclic structures on the basis of P^{31} nmr and chemical studies.[2] Since most of the chemical studies aimed at structure elucidation were with the product from phenyl salicylate, further work on the 2-hydroxybenzophenone product (II) was desirable since the chemical evidence rested mainly on analogy with the results on the phenyl salicylate product. Furthermore, it was of interest to compare the behavior of the phenolic ketone product with that from phenyl salicylate. Since 5-chloro-2-hydroxybenzophenone (III) was readily obtainable commercially,[3] it was selected in place of the less available 2-hydroxybenzophenone.[4]



I



II

Results and Discussion

The reaction of phosphorus pentachloride with 5-chloro-2-hydroxybenzophenone (III) was entirely analogous to the reaction with 2-hydroxybenzophenone. The colorless crystals obtained gave the correct elemental analysis and molecular weight for the expected product. Active chlorine (nonaromatic) as determined by basic hydrolysis followed by potentiometric titration of an acidified solution with silver nitrate showed that the expected 4 equiv of chloride ion were present. Although the crystals were stable to water, 5-chloro-2-hydroxybenzophenone was obtained by hydrolysis of an aqueous dioxane solution, showing that the basic carbon skeleton of the compound was unchanged from that of the starting compound. The infrared spectrum of the product showed no absorption bands in the carbonyl or hydroxyl stretching regions. The pertinent infrared absorption bands were close to those observed previously for the corresponding product (II) from 2-hydroxybenzophenone[2]: P=O stretching at 7.70 μ; P–O–C (aromatic) (C–O portion) at 8.38 μ; P^{+5}–O–C (aromatic) (P—O portion) at 10.50 μ. The value for the P^{31} nmr chemical shift was the same as that found previously[2] for the analogous product (II) from 2-hydroxybenzophenone, a value of 0.0 ppm.

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(1) Based on M.S. Thesis of L. Y. C. M., Baylor University, 1964.

(2) A. G. Pinkus, P. G. Waldrep, and S. Y. Ma, *J. Heterocyclic Chem.*, **2**, 357 (1965).

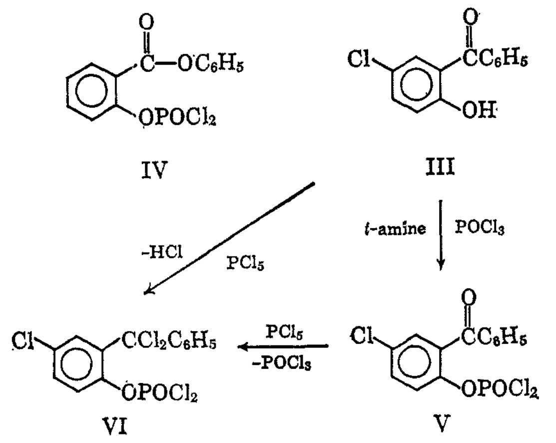
(3) The authors express appreciation to the Dow Chemical Co. for gifts of generous samples.

(4) 2-Hydroxybenzophenone is obtained in low yield from the Fries rearrangement of phenyl benzoate[5] or by the Friedel-Crafts benzoylation of phenol.

(5) N. M. Cullinane, N. M. E. Morgan, and C. A. J. Plummer, *Rec. Trav. Chim.*, **56**, 627 (1937).

This is close to the value reported[6,7] for phenyl phosphorodichloridate of −1.5 ppm and values for other phosphorodichloridates,[2,8] thus indicating the structure to be a phosphorodichloridate.

Phenyl salicylate was found[2] to react with phosphorus oxychloride in the presence of 1 equiv of pyridine to form the *ester* phosphorodichloridate (IV). Similarly, the hydroxybenzophenone would be expected to form the analogous *keto* phosphorodichloridate (V).

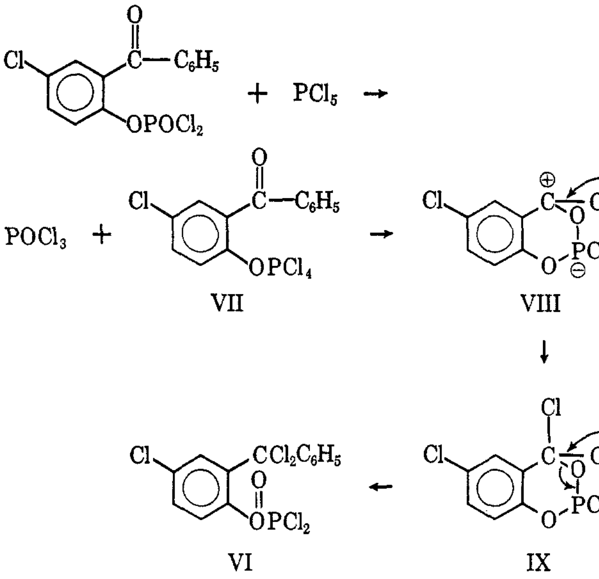


This compound (V), being a diaryl ketone, might be expected to react with phosphorus pentachloride as does benzophenone[9] to form compound VI which should be the same compound obtained from the reaction of 5-chloro-2-hydroxybenzophenone and phosphorus pentachloride; this reaction would constitute a chemical proof of structure for the 5-chloro-2-hydroxybenzophenone–phosphorus pentachloride product.

The reaction of 5-chloro-2-hydroxybenzophenone (III) and phosphorus oxychloride took place in the presence of 1 equiv of either pyridine or triethylamine. The infrared spectrum of the product showed the disappearance of the hydroxyl stretching band of 5-chloro-2-hydroxybenzophenone at 3.19 μ indicating substitution at this position. The spectrum was in accord with structure V: carbonyl stretching[10a] at 5.97 μ; P=O stretching[10b] at 7.54 μ; C–O link of P–O–C (aromatic)[11] at 8.30 μ; P–O link of P^{+5}–O–C (aromatic)[11] at 10.36 μ. V was heated at 110–120° with excess phosphorus pentachloride, the unreacted phosphorus pentachloride being separated from the product by virtue of its insolubility in carbon tetrachloride. The infrared spectrum of the carbon tetrachloride solution showed that the product was the same as that from the reaction of 5-chloro-2-hydroxybenzophenone and phosphorus pentachloride, compound VI. The pure compound was isolated and recrystallized, mp 70.5–70.8° (mixture melting point with authentic material undepressed). Analysis of the crude product using the base-line infrared technique showed a yield of 90 ± 5% of VI.

In order to validate more completely the above chemical proof of structure, it was necessary to obviate the possibility that there might have been an exchange reaction between phosphorus pentachloride and the phosphorodichloridate group which could also lead to the formation of VI. The exchange could conceivably take place in one of two ways: (1) the exchange of the phosphoryl oxygen by two chlorines from phosphorus pentachloride to form VII and phosphorus oxychloride; (2) the exchange of the dichlorophosphoryl group by a tetrachlorophosphonium group also to form VII. VII is a postulated intermediate in the mechanism proposed[2] for the reaction of 5-chloro-2-hydroxybenzophenone and phosphorus pentachloride; according to the proposed mechanism (Scheme I). VII would cyclize in a series of steps to form VI as the final product.

Scheme I



Experimental evidence against the possible occurrence of any exchange was obtained as follows. If such an exchange actually occurred with V, then the same sort of exchange should occur with the ester phosphorodichloridate IV under the same conditions to form an intermediate analogous to VII which would be expected to undergo an analogous series of reactions to form I. However, no reaction could be observed under varying conditions attempted. Thus, the reaction of V with phosphorus pentachloride converts it into VI by the well-established procedure of converting a keto carbonyl group into a dichloromethylene group. This establishes the structure of VI, a compound also obtained from the reaction of 5-chloro-2-hydroxybenzophenone and phosphorus pentachloride.

Further supporting evidence of structure was obtained in a study of the reaction of VI with phenol. In the best of several experiments, a disubstituted product was obtained (80% yield of recrystallized material) in the reaction of 1 equiv of VI with 2 equiv each of phenol and pyridine. Assuming structure VI for the 5-chloro-2-hydroxybenzophenone–phosphorus pentachloride product, three possible diphenoxy-substituted products were considered, Xa–c (Scheme II).

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[6] E. Schwarzmann and J. R. Van Wazer, *J. Am. Chem. Soc.*, **81**, 6366 (1959).

[7] R. A. Y. Jones and A. R. Katritzky, *Angew Chem. Intern Ed. Eng.*, **1**, 32 (1962).

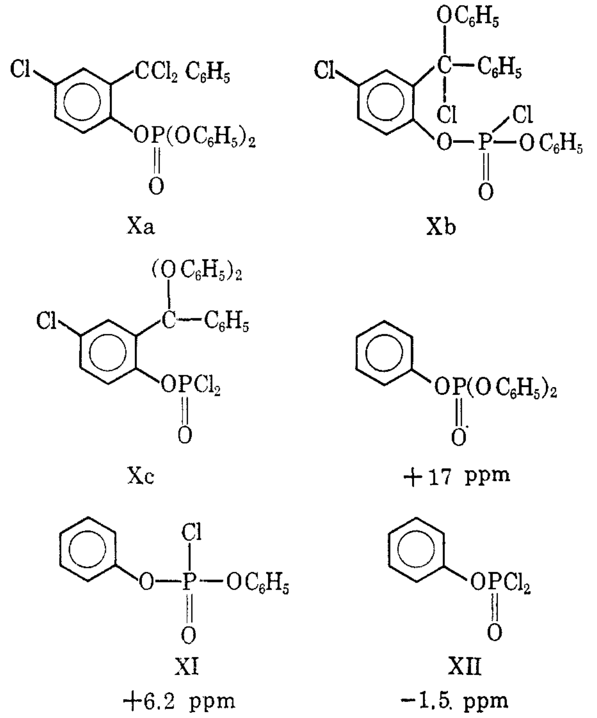
[8] A. G. Pinkus and P. G. Waldrep, *J. Org. Chem.*, **31**, 575 (1966).

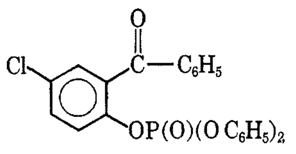
[9] (a) L. J. Andrews and W. W. Kaeding, *J. Am. Chem. Soc.*, **73**, 1007 (1951); (b) M. S. Newman and L. L. Wood, Jr., *ibid.*, **81**, 4300 (1959).

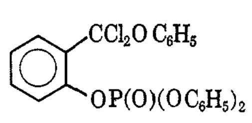
[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958: (a) Chapter 9; (b) Chapter 18.

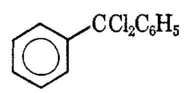
[11] R. A. Nyquist, *Appl. Spectry*, **4**, 161 (1957); L. C. Thomas and R. A. Chittenden, *Chem. Ind.* (London), 1913 (1961); A. C. Chapman and R. Harper, *ibid.*, 985 (1962).

SCHEME II




XIII


XIV


XV

In considering the P^{31} nmr spectrum, three reference compounds were selected considering the substitution about the phosphorus atom: triphenyl phosphate at 17 ppm[7,12] analogous to Xa; diphenyl phosphorochloridate (XI) at 6.2 ppm[6] analogous to Xb; phenyl phosphorodichloridate at −1.5 ppm[6,7] analogous to Xc. The diphenoxy-substituted product showed a P^{31} chemical shift of +19.6 ppm which clearly identifies this product as Xa, a monosubstituted triphenyl phosphate.

In attempting to substantiate structure Xa further by hydrolysis of the dichloromethylene to a keto group, it was found that the compound was surprisingly stable to hydrolysis; no trace of a carbonyl group could be seen in the infrared spectrum when the compound was stirred with water at room temperature or when refluxed with water under basic or acidic conditions. However, in a refluxing homogeneous basic dioxane solution, partial hydrolysis was achieved as evidenced by the appearance of a carbonyl infrared absorption band at 5.97 μ; this is the same wavelength observed above for V and is in the general region for diphenyl ketones.[10a] No hydroxyl stretching band was evident in the infrared curve which eliminated the possibility that the carbonyl might be formed by the hydrolysis of XB since phenol would be expected to form.

The other diphenoxy-substituted structure considered, Xc, is a ketal and would be expected to be stable to basic conditions. Although the compound corresponding to the hydrolysis product XIII could not be isolated in pure form from the hydrolysis mixture, the position of the carbonyl stretching band confirms the evidence from the P^{31} nmr spectrum. The remarkable resistance to hydrolysis is interesting to note in comparison with the facile hydrolysis of the related XIV[2] or of dichlorodiphenylmethane (XV).[9a] In comparing Xa with dichlorodiphenylmethane, the resistance to hydrolysis of Xa would appear to be ascribable to the steric effect of the *ortho*-situated -OP(O)$(OC_6H_5)_2$ group. Since compound XIV has the same *ortho*-situated group as Xa, the facile hydrolysis of the dichloromethylene group may be the result of activation by the attached oxygen; thus, the enhanced hydrolytic activity of the chlorines in α-chloro ethers is well documented.[13]

The difficulty of substitution at the dichloromethylene carbon was further exemplified by attempts to react Xa with phenol or the 5-chloro-2-hydroxybenzophenone–phosphorus pentachloride product (VI) with 4 equiv of phenol. Only the diphenoxy-substituted product (Xa) was obtained in experiments in which VI was reacted with 4 equiv of phenol using 4 equiv of pyridine or triethylamine in benzene or dioxane solution. The reaction of VI with 4 equiv of phenol in the absence of solvent or amines took place spontaneously at room temperature to form a dark red material. The product appeared to be a complex mixture judging from broad bands in the infrared spectrum which included a broad hydroxyl stretching band indicating unreacted phenol. A similar result was obtained when pyridine was used in the absence of solvent. In an additional attempt using 4 equiv of sodium phenoxide, the aqueous washings were collected and titrated for chloride ion; 3.5 equiv of chloride was indicated; however, no definite product could be isolated. A complex mixture was also obtained in a reaction of VI with 2 equiv of sodium phenoxide. The reaction of VI with absolute ethanol was also studied. Complex mixtures were obtained from reactions carried out under the following conditions: use of an excess of ethanol under reflux; the additional use of pyridine or triethylamine; the use of sodium ethoxide. A liquid mixture which could not be purified was obtained in all cases; decomposition occurred during attempted vacuum distillation. Similar results were also obtained with methanol.

In the previous studies[2] with the phenyl salicylate–phosphorus pentachloride product (I), it was observed that a partial hydrolysis of the compound could be carried out to obtain the phosphorodichloridate ester (IV), the dichloromethylene group being selectively hydrolyzed. In the present work, no such difference in the reactivity of the dichloromethylene and phosphorodichloridate groups of VI was observed. When partial hydrolysis was attempted under various conditions using 1 equiv of water, mixtures indicating hydrolysis at both positions were obtained. Also experiments designed to differentiate between the reactivity of the chlorines by hydrolysis or titrations

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(12) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).

(13) L. Summer, *Chem. Rev.*, **55**, 301 (1955).

under various conditions showed a comparable reactivity of the chlorines in the two groups.

Further evidence against cyclic structures such as VIII and IX was obtained by attempted reactions with sulfur dioxide. The conversion of phosphorus polyhalides into phosphonyl halides by reaction with sulfur dioxide is a well-known[14] reaction and can be used as a test for the presence of such groupings.

$$RPX_4 + SO_2 \longrightarrow RP(O)X_2 + SOX_2$$

$$R_2PX_3 + SO_2 \longrightarrow R_2P(O)X + SOX_2$$

In attempting reactions of the 5-chloro-2-hydroxybenzophenone–phosphorus pentachloride product (VI) under conditions ranging from bubbling sulfur dioxide into (1) a benzene solution at room temperature to (2) a melt of the compound at 110–120° for several hours, no reaction could be detected from the infrared spectrum of the compound before and after.

Experimental Section[15]

Reaction of Phosphorus Pentachloride and 5-Chloro-2-hydroxybenzophenone.—A solution of 5-chloro-2-hydroxybenzophenone (11.63 g, 0.05000 mole) in 26 ml of dry benzene was added dropwise over a period of 1 hr to a stirred slurry of phosphorus pentachloride (10.41 g, 0.05000 mole) in 20 ml of dry benzene in a three-necked flask protected by means of a drying tube. The yellow color of the 5-chloro-2-hydroxybenzophenone solution disappeared immediately as the drops reacted with the phosphorus pentachloride mixture; hydrogen chloride was evolved. After removing the solvent *in vacuo*, 20.0 g (99% crude yield) was obtained of a colorless viscous liquid which crystallized on cooling (mp 65.0–66.5°). On recrystallization from dry cyclohexane, colorless crystals of VI were obtained, mp 70.5–70.8°.

Anal. Calcd for $C_{13}H_8Cl_5O_2P$: C, 38.59; H, 1.97; Cl, 43.75; hydrolyzable chlorine, 35.02; mol wt, 405. Found[16]: C, 38.45; H, 1.99; Cl, 43.64; hydrolyzable Cl,[17] 34.91; mol wt,[18] 407.

Reaction of 5-Chloro-2-hydroxybenzophenone and Phosphorus Oxychloride.—A solution of 5-chloro-2-hydroxybenzophenone (4.7 g, 0.020 mole) in 50 ml of dry carbon tetrachloride was added over a period of 5 hr to a stirred solution of redistilled phosphorus oxychloride (3.1 g, 0.020 mole) and dry redistilled pyridine (1.6 g, 0.020 mole) in 50 ml of carbon tetrachloride in a three-necked flask protected with drying tubes. During the addition the yellow color of the 5-chloro-2-hydroxybenzophenone solution disappeared and a precipitate of pyridine hydrochloride formed. Several filtrations were necessary to remove the precipitated pyridine hydrochloride which tended to precipitate in the filtrate. After removal of solvent *in vacuo*, a light yellow viscous oil (compound V) was obtained in 85% crude yield. The infrared spectrum showed the disappearance of the hydroxyl band of 5-chloro-2-hydroxybenzophenone at 3.19 μ, the presence of a carbonyl band at 5.97 μ, a P=O stretching band at 7.54 μ, a P–O–C (aromatic) absorption band (C–O–portion) at 8.30 μ, and a P^{+5}–O–C (aromatic) absorption band (P–O–portion) at 10.36 μ. The compound could not be crystallized and carbonized on attempted vacuum distillation. A sample of the compound was used directly in the experiment described below.

Reaction of 2-Benzoyl-4-chlorophenylphosphorodichloridate (V) with Phosphorus Pentachloride.—2-Benzoyl-4-chlorophenylphosphorodichloridate (V) (4.60 g, 0.0130 mole) and an excess of phosphorus pentachloride (8.32 g, 0.0400 mole) were mixed in a flask equipped with a condenser protected with a drying tube and heated to 110–120° by means of an oil bath. After 6 hr of heating, more phosphorus pentachloride was added to replace the material that had sublimed on the sides of the flask and the mixture was heated for 6 additional hr. After cooling, 100 ml of carbon tetrachloride was added to the mixture and the excess insoluble phosphorus pentachloride was separated by filtration. An infrared curve on the filtrate showed that the product was VI obtained previously from the reaction of 5-chloro-2-hydroxybenzophenone and phosphorus pentachloride. Using the baseline technique,[19] the yield of VI was estimated as 90 ± 5%. After the solvent was removed *in vacuo*, 4.62 g (87% crude yield) of a colorless viscous oil was obtained which crystallized when seeded with an authentic crystal of VI. On recrystallization from cyclohexane, the sample had mp 70.5–70.8° and was shown to be identical with the 5-chloro-2-hydroxybenzophenone–phosphorus pentachloride product (VI) by mixture melting point and comparison of infrared spectra.

Reaction of 5-Chloro-2-hydroxybenzophenone–Phosphorus Pentachloride Product (VI) with 2 Equiv of Phenol.—A solution of VI (8.08 g, 0.0200 mole) and pyridine (1.66 g, 0.0210 mole) in 50 ml of carbon tetrachloride was added over a period of 1 hr to a stirred solution of phenol (3.76 g, 0.0400 mole) in 100 ml of carbon tetrachloride in a three-necked flask protected from moisture. A precipitate of pyridine hydrochloride formed as the solutions came in contact. After the completion of the addition, the mixture was stirred for 2 more hr. The precipitate was separated by filtration and the solvent was removed *in vacuo* from the filtrate. The residue was a viscous liquid (9.5 g, 95% crude yield) which crystallized on standing when seeded with crystals obtained from a previous preparation (see below). A yield of 8.2 g (80%) of crystals of Xa, mp 74.8–75.6°, was obtained after one recrystallization from cyclohexane.

The reaction was first carried out by the reaction of sodium phenolate (prepared from 2.00 g, 0.0200 mole, of phenol in 100 ml of benzene and excess sodium) and the 5-chloro-2-hydroxybenzophenone–phosphorus pentachloride product (VI) (4.00 g, 0.0100 mole) in 50 ml of benzene, the latter being added to the former over a 2-hr period. After filtration and removal of solvent *in vacuo* from the filtrate, a red-orange, sticky residue (4.91 g) was obtained. White crystals, mp 75.6–76.0°, were obtained after three recrystallizations from cyclohexane.

Anal. Calcd for $C_{25}H_{18}Cl_3O_4P$: C, 57.76; H, 3.49; Cl, 20.47; P, 5.96. Found:[20] C, 58.17; H, 3.65; Cl, 20.02; P, 5.61.

Reactions of 5-Chloro-2-hydroxybenzophenone–Phosphorus Pentachloride Product (VI) with 4 Equiv of Phenol.—A powdered sample of the 5-chloro-2-hydroxybenzophenone–phosphorus pentachloride product (VI) (1.671 g, 0.004000 mole) and solid phenol (1.504 g, 0.01600 mole) were mixed together. An exothermic reaction took place at room temperature with the melting of the mixture and formation of a dark red color. The mixture was then heated for 1 hr by means of an oil bath at 80–90° and then allowed to cool to room temperature. The product was dissolved in 40 ml of benzene; an infrared spectrum was taken of this solution. The spectrum showed broad bands including an –OH stretching band at *ca.* 2.78 μ and a carbonyl band at *ca.* 5.94 μ. No pure products could be isolated from the mixture.

In another experiment pyridine was used in addition to the two reactants with the reaction being carried out under a nitrogen atmosphere to prevent air oxidation of the phenol. The mixture turned to a red color during a heating period. When the mixture was dissolved in benzene, the expected pyridine hydrochloride did not precipitate. The solution was extracted with three portions of water and dried. An infrared spectrum of the solution showed broad bands indicating a complex mixture. Decomposition occurred on attempted vacuum distillation.

The reaction with 4 equiv of sodium phenoxide under a nitrogen atmosphere was also studied. The mixture turned a dark

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(14) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 62; E. L. Gefter, *J. Gen. Chem. USSR*, **31**, 876 (1961); G. K. Fedorova and A. V. Kirsanov, *ibid.*, 546; K. N. Anisimov, G. M. Kunitskaya, and N. A. Slovokhotova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 55 (1961).

(15) Melting points were taken with total immersion thermometers in a Thiele melting point apparatus and are corrected by means of a calibration curve constructed from pure standard reference compounds. Boiling points are uncorrected. Melting points of moisture-sensitive compounds were obtained by using sealed capillaries [A. G. Pinkus and P. G. Waldrep, *Mikrochim. Acta*, 772 (1959)]. Moisture-sensitive operations were carried out in a drybox whenever necessary.

(16) Analyses were by Clark Microanalytical Laboratory, Urbana, Ill.

(17) By potentiometric titration; sample hydrolyzed with aqueous 10% sodium hydroxide, acidified with nitric acid, and titrated with standard silver nitrate solution.

(18) Cryoscopic in benzene.

(19) The calculations were based on the absorption at three wavelengths: 6.76, 7.70, and 8.38 μ, taking the average of these calculations.

(20) Analyses were by Geller Laboratories, Bardonia, N. Y.

red color on heating; after 2 hr of heating, the mixture was cooled and benzene was added. No residue of the expected sodium chloride was observed. The solution was washed with water and the washings were collected and combined. Titration of the washings with standard silver nitrate solution showed the presence of 3.5 equiv of chloride ion (based on 4 equiv of nonaromatic-bound chlorine in VI). An infrared spectrum on the dried benzene solution showed broad bands indicating a mixture of products; this spectrum differed from the previous ones. No pure compounds could be isolated from the mixture. Attempted chromatography on alumina and silica gel columns was unsuccessful.

Reaction of Compound Xa with Phenol.—The diphenoxy-substituted product (Xa) (0.1700 g, 0.003300 mole) was mixed with sodium phenoxide (0.0714 g, 0.00670 mole) and heated by means of an oil bath at 135–140° for 7 hr. The mixture gradually became dark red. After cooling, 10 ml of carbon tetrachloride was added and the mixture was filtered; the filtrate was washed with three portions of water and dried with sodium sulfate. An orange-red oil which remained on removal of the solvent *in vacuo* did not crystallize on cooling or standing. An infrared spectrum of the oil in carbon tetrachloride showed the presence of a carbonyl stretching band at 6.1 μ and a broad hydroxyl stretching band at 2.9 μ and other generally broad bands indicating a mixture.

Attempted Partial Hydrolysis of VI.—The 5-chloro-2-hydroxybenzophenone–phosphorus pentachloride product (VI) (4.211 g, 0.1050 mole) was dissolved in 20 ml of dry 1,4-dioxane and the solution added to a solution of *ca.* 1 equiv of water (0.1890 g, 0.1030 mole) in 20 ml of 1,4-dioxane. The solution was stirred for 2 days and the solvent removed *in vacuo*. An infrared spectrum on a sample of the residue dissolved in benzene showed broad bands in the hydroxyl and carbonyl stretching regions as well as in the remainder of the spectrum indicating a complex mixture of products.

A complete hydrolysis was carried out by using approximately the same amounts of solvent and compound as above with an excess (40 ml) of water. After stirring for 12 hr, the solvent was partially removed *in vacuo* and the residue was extracted with benzene and dried with anhydrous sodium sulfate. An infrared spectrum on the benzene solution showed the presence of nearly pure 5-chloro-2-hydroxybenzophenone. On removal of solvent *in vacuo*, the residue melted at 89–90°. On recrystallization from methanol, the compound had the mp 94–95°[21]; mixture melting point with 5-chloro-2-hydroxybenzophenone, 93.5–95.0°.

Titrimetric Hydrolytic Studies on the 5-Chloro-2-hydroxybenzophenone–Phosphorus Pentachloride Product (VI).—A summary of the results of two typical experiments is given. (1) Potentiometric titration of a solution of VI in aqueous dioxane (*ca.* 85% water) with standard silver nitrate showed 4.1 equiv of chloride (4.0 theoretical). (2) VI was dissolved in aqueous dioxane (*ca.* 75% water) and the solution divided into 10 equal parts each of which was extracted with benzene after standing for a certain period of time. The benzene solvent would be expected to extract any unhydrolyzed VI or other benzene-soluble organic products. The aqueous portion was then titrated with standard silver nitrate. The results showed that *ca.* 4 equiv of chloride ion were present in each sample even from the shortest time of hydrolysis of *ca.* 7 min. This experiment demonstrates a fairly rapid complete hydrolysis under these conditions.

Attempted Reaction of VI and Sulfur Dioxide.—Sulfur dioxide was bubbled slowly through a solution of VI (1.325 g, 0.003300 mole) in 20 ml of benzene at room temperature for 16–18 hr. An infrared spectrum of the solution showed that no reaction had taken place.

A sample of VI (5.00 g, 0.0124 mole) was fused by being heated to 110–120° and sulfur dioxide was slowly bubbled through for 12 hr. After cooling, an infrared spectrum on a benzene solution showed that no reaction had occurred.

P^{31} Nmr 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 as an external standard. The solvents used for VI and Xa were benzene and carbon tetrachloride, respectively.

The infrared spectra were obtained on a KM-1 Baird-Atomic instrument. Matched 0.1-mm sodium chloride cells were used for solution spectra with concentrations in the range 3–5% (w/v). Carbon tetrachloride was the solvent for all infrared spectra except those for which another solvent is specifically mentioned. The preparation of the solutions and filling of the cells and nmr tubes for moisture-sensitive compounds were done in a drybox. The infrared spectra were calibrated against the nearest polystyrene bands which were run on the same chart as the sample.

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A Synthetic Entry to the Hydroazulenes. 4,5-Trimethylenetropone

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The synthesis and structure proof of 4,5-trimethylenetropone are discussed. A Robinson–Schöpf condensation of cyclopentane-1,2-dicarboxaldehyde with acetonedicarboxylic acid and methylamine yields 11-methyl-11-azatricyclo$[5.3.1.0^{2,6}]$undecan-9-one. Quaternization followed by Hofmann degradation yields three isomers of 6-oxohexahydroazulene. Catalytic dehydrogenation gives 4,5-trimethylenetropone. The 4,5-trimethylenetropone thus obtained differs from the material previously assigned this structure by Watanabe.

In the course of our study of troponoid compounds we have developed a potentially general synthesis of hydroazulene derivatives which is illustrated by the synthesis of 4,5-trimethylenetropone. This synthesis, which is unequivocal, takes on added interest since the properties previously ascribed to 4,5-trimethylenetropone[2] are grossly at variance with the properties of our product.

The synthetic approach was suggested by the conversion of tropinone to tropone by Meinwald, Emerman, Yang, and Büchi.[3] Bicyclo[3.2.0]hept-6-ene (I), readily accessible by photoisomerization of 1,3-cycloheptadiene,[4,5] provides a convenient source of *cis*-cyclopentane-1,2-dicarboxaldehyde (II). A Robinson–

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