tenths grams of VI was dissolved in 80 ml. of ethylene chloride and 20 g. of aluminum chloride was added. The mixture was heated on the steam bath for 2 hr., then decomposed with dilute hydrochloric acid. The aqueous layer was drawn off and the organic layer washed with water, then with dilute sodium hydroxide solution. The alkaline solution was acidified and extracted with ethylene chloride. The ethylene chloride was removed *in vacuo* and the residual oil crystallized from benzene to give 4.1 g. of VII, m.p. 128°.

3-Hydroxyxanthone (VIII) *and 2,2'-dihydroxy-4-methoxybenzophenone* (IX). Pyridine hydrochloride (70 g.) and 21.0 g. of V were gently refluxed for 4 hr., then poured into water, and the precipitate, A, was collected on a filter. The solid, A, was added to 100 ml. of water and made alkaline with 50% sodium hydroxide solution; the solution was filtered and acidified; the precipitated solid amounts to 7.0 g. This crude material was suspended in 25 ml. of warm acetic anhydride and a drop of sulfuric acid added. Heating was continued until solution was complete. After cooling, the precipitate was collected and then recrystallized from benzene to give 7.0 g. of 3-acetoxyxanthone,[6] VIIIa, m.p. 160°. Saponification of 19.0 g. of VIIIa gave 15 g. of 3-hydroxyxanthone, m.p. 242°. 3,6-Diacetoxyxanthone,[7] m.p. 203–204°, from xylene was prepared from I in a manner similar to that just described.

2-Acetoxy-4-methoxyacetophenone (XI). *m*-Dimethoxybenzene (57 g., 0.54 mole) and 60 ml. of acetyl bromide were refluxed for 3 hr. and distilled. A fraction (32 g., 38% yield) was collected, b.p. 155–160°/5 mm., which is essentially XI, n_D^{20} 1.550.

Anal. for $C_{11}H_{12}O_4$. Calcd.: C, 63.3; H, 5.8. Found: C, 63.8; H, 5.8.

The 2,4-dinitrophenylhydrazone of XI was prepared in the usual manner, but in the process, the acetyl group is lost, m.p. 230°, from dioxanebutanol.

2-Hydroxy-4-methoxyacetophenone (XII). 2,4-Dimethoxyacetophenone (18 g.) in 70 ml. of benzene was treated with 29 g. of aluminum chloride. A vigorous reaction ensued. After the reaction had subsided, the mixture was heated on the steam bath for 0.5 hr., then decomposed with iced hydrochloric acid. The benzene layer was extracted with dilute alkali, and the alkaline layer was acidified to give an oil. This, on distillation, gave 8 g. of XII, b.p. 145–147°/5 mm., which solidified, m.p. 46–48°, phenylhydrazone, m.p. 107–108°. Saponification of XI with alcoholic potassium hydroxide also gave XII, as proved by the identity of its phenylhydrazone, m.p. 107–108°, with that prepared above. The 2,4-dinitrophenylhydrazone (m.p. 230°) of XII is identical to that of XI.

Acknowledgment. We are indebted to D. W. Stewart of these Laboratories for the ultraviolet spectra reported.

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(6) St. v. Kostanecki and R. Rutishauer, *Ber.*, **25**, 1648 (1892).

(7) R. Meyer and A. Conzetti, *Ber.*, **32**, 2103 (1899).

[CONTRIBUTION FROM THE EDGAR C. BRITTON RESEARCH LABORATORY OF THE DOW CHEMICAL CO.]

Aromatic Phosphorodichloridites and Phosphorodichloridothioates. I. Aryl Phosphorodichloridites

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Received April 22, 1958

A series of aryl phosphorodichloridites were prepared in yields of 84 to 98% by treating phenols with PCl_3 at a mole ratio of about 1:6 at reflux under atmospheric pressure and then completing this reaction by addition of catalytic amounts of anhydrous magnesium chloride.

For the preparation of the aryl phosphorodichloridites no satisfactory method was known at the outset of this investigation, although the first member of this series of compounds was described in 1883.[1] There were two synthetic methods mentioned in the literature:[1,2]

$$ArOH + PCl_3 \longrightarrow ArOPCl_2 + HCl \qquad (1)$$

$$(ArO)_3P + 2PCl_3 \rightleftharpoons 3ArOPCl_2 \qquad (2)$$

Phenol and its homologs were reported to react readily with phosphorus trichloride in equimolar proportions in the absence of catalysts or hydrochloric acid acceptors, at about 20–60°. However, during the actual course of reaction 1 substantial amounts of bis- and tris-esters were regularly produced.[1,3–5]

The reaction involving *p*-chlorophenol was reported to require a large excess of phosphorus trichloride in order to produce even small yields of *p*-chlorophenyl phosphorodichloridite.[4]

Even recently the yields for aryl phosphorodichloridites were reported to be not better than 25–50% of theory.[6,7]

Reaction 2 was reported to require a reaction temperature of 150° and to give only a 47% yield of phenyl phosphorodichloridite.[2] All previous in-

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(1) E. Noack, *Ann.*, **218**, 87 (1883).

(2) J. B. Conant, V. H. Wallingford, and S. S. Gandheker, *J. Am. Chem. Soc.*, **45**, 764 (1923).

(3) R. Anschutz and W. O. Emery, *Ann.*, **239**, 309 (1887).

(4) W. Strecker and Ch. Grossmann, *Ber.*, **49**, 85 (1916).

(5) W. Broeker, *J. prakt. Chem.* (2) **118**, 287 (1928).

(6) G. R. Cebrian, *Arch. inst. farmacol. exptl.* (*Madrid*), **8**, 61 (1956).

(7) J. C. Bill and B. A. Hunter, U. S. Patent **2,732,365** (1956).

vestigators mentioned that the thermal instability of aryl phosphorodichloridites at temperatures above 150° made it additionally difficult to obtain these compounds in even moderate yields.

Our development work was concentrated on reaction 1 and revealed that this reaction, apparently because of its equilibrium character, required conditions which reduced the hydrochloric acid concentration in the reaction mixture to a minimum. Operation under reduced pressure, causing reduction of reaction temperature, made it more difficult to complete the conversion of less reactive phenols. A final reaction temperature of about 80° and operation under atmospheric pressure were found to be desirable to complete the reactions within a reasonable time.

It was found necessary to use an excess of phosphorus trichloride. A substantially smaller excess gave greatly reduced yields, in agreement with literature and patent examples.[7,8] As substantially larger excess of phosphorus trichloride was not found to increase the yield.

The reaction rate of various phenols in reaction 1 was found to decrease with increaseing dissociation constants of the phenols. With 2,4,5-trichlorophenol this rate was so low that the reaction with 5 moles of phosphorus trichloride at 80° did not go to completion within 24 hr. We found that the presence of anhydrous magnesium chloride, known as a catalyst for this type of reaction,[8] brought the conversion of 2,4,5-trichlorophenol essentially to completion within less than 10 hr. This catalyst was found to affect the reaction rate of other phenols in a similar manner. The presence of catalyst was necessary in all reactions involving orthohalogenated phenols, in order to produce maximum yields in minimum reaction times. The proper timing of catalyst addition was found to be of importance. The presence of catalyst in the reaction mixture during the entire reaction time gave noticeably smaller yields than presence of catalyst during the reaction of the second half of the phenol only.

In the absence of catalyst and in the presence of sufficient excess of PCl_3 halophenols reacted without side reaction according to reaction 1 exclusively but their reaction did not proceed to the point of complete conversion of the phenol. $MgCl_2$ as a catalyst promoted not only reaction 1 but also undesired side reactions involving di- and trisubstitution. Maximum yields were obtained when $MgCl_2$ was added after the noncatalytic part of the reaction of phenols with PCl_3 had come almost to a standstill.

Reaction 1 could be expected to be complete after evolution of one mole of hydrochloric acid per mole of phenol used. Owing to contamination of hydrochloric acid with some phosphorus trichloride, the accurate determination of the point at which exactly one mole of hydrochloric acid was formed was rather difficult. A more practical way to find the necessary reaction time was to continue the reaction until the reaction mixture contained only traces of unreacted phenol, as determined by infrared analysis. The method developed did not work well with 2,6-disubstituted phenols owing to steric hindrance.

The aryl phosphorodichloridites prepared were vacuum-fractionated twice for purification. The pure compounds were isolated as heavy, colorless, water-clear liquids. They were found to be soluble without decomposition in those organic solvents which did not contain carbonyl groups or reactive hydrogen. The results obtained were as shown in Table I.

We investigated the hydrolysis of aryl phosphorodichloridites briefly. The reaction with liquid water at room temperature was found to be rather violent with all phosphorodichloridites prepared. Reaction with moist air at room temperature was found to involve at least two different steps:

$$ArOPCl_2 + 2H_2O \longrightarrow ArOP(OH)_2 + 2HCl \qquad (3)$$

and

$$ArOP(OH)_2 + H_2O \longrightarrow ArOH + H_3PO_3 \qquad (4)$$

The two types of hydrolysis product formed, aryl phosphite and free phenol, were identified by the infrared-absorption bands of phosphite-hydroxyl and phenolic hydroxyl, located at 3.8 ± 0.3μ and 2.9 ± 0.1μ, respectively. Hydrolysis of phenyl phosphorodichloridite ($C_6H_5OPCl_2$) and *m*-ethylphenyl phosphorodichloridite (*m*-C_2H_5-$C_6H_4OPCl_2$) was found to proceed according to reaction 3 while hydrolysis of chloroaryl phosphorodichloridites involved reaction 4 also. The rate of reaction 4 apparently was the higher the greater the dissociation constant of the phenol involved.

EXPERIMENTAL

Equipment. A 3-neck, round-bottom flask fitted with a thermometer and glass stirrer was used. Attached to the flask was a dropping funnel for addition of those phenols which were liquid at room temperature. (Solid phenols were added in small, crushed portions.) The flask was connected with a reflux condenser which in turn was connected with a saddle-packed water-scrubber. This permitted estimation of hydrogen chloride as formed in the reaction.

Quality of starting products. Phosphorus trichloride was freshly redistilled from a commercial product. The phenols employed were purified products, as indicated in Table II.

Procedure. The flask was charged with phosphorus trichloride. Then the phenol was added portion-wise with agitation at mole ratios as given in Table I over a period of about 3 hr. at temperatures below +20° in the case of liquid phenols and 25–30° in the case of solid phenols. After a clear solution was obtained the mixture was slowly warmed to reflux at atmospheric pressure. Alkylated phenols were more reactive than halogenated phenols and gave best yields when at least half of the phenol was converted at a reaction temperature of less than 30° before the temperature was raised to mild reflux (about 80° in the mixture). Re-

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(8) C. L. Moyle, U. S. Patents 2,170,833 (1939), 2,220,113 and 2,220,845 (1940).

TABLE I

Aryl—$OPCl_2$

Aryl	Mole Ratio Aryl OH: PCl_3	Reaction Time, Hr.	Yield (% Theory)	P-Analysis, % Theor.	P-Analysis, % Found	d_4^{20}	n_D^{20}	B.P. °/C. at 10 Mm.
C_6H_5—	1:6	10	84	15.89	15.87	1.3539	1.5588	90
m-C_2H_5—C_6H_4—	1:5	11	93.4	13.89	13.93	1.2590	1.5474	115
2-Cl-4-*t*-C_4H_9—C_6H_3—	1:5	10	93.5	10.85	10.91	1.2870	1.5510	154
2-Br-4-*t*-C_4H_9—C_6H_3—	1:5	12	91.1	9.39	9.47	1.4669	1.5676	165
o-Cl—C_6H_4—	1:5	10	98	13.50	13.45	1.4686	1.5736	111–112
p-Cl—C_6H_4—	1:5	9	85		13.48	1.4714	1.5749	113–113.5
2,4-Cl_2—C_6H_3—	1:6	12	88		11.7	1.5651	1.5860	134
2,5-Cl_2—C_6H_3—	1:6	12	86	11.74	11.67	1.5672	1.5869	138
3,4-Cl_2—C_6H_3—	1:5 to 1:20	10 to 20	83 to 87		11.65	1.5736	1.5894	136
2,4,5-Cl_3—C_6H_2—	1:5 to 1:7	10 to 20	90.3 to 90.7	10.38	10.35	1.6556	1.6007	154–155
2,4,6-Cl_3—C_6H_2—	1:6	280[a]	11.0		10.39	1.6563	1.6012	156

[a] Reaction still incomplete.

TABLE II

Phenol	Physical Properties
C_6H_5OH[9]	F.p., +40.8°
m-C_2H_5—C_6H_4OH[9]	B.p., 75–77°/10 mm.
2-Cl-4-C_4H_9—C_6H_3OH[10]	F.p., +12.4°
2-Br-4-C_4H_9—C_6H_3OH[10]	F.p., +7.8°
o-Cl—C_6H_4OH[9]	F.p., +9.4°
p-Cl—C_6H_4OH[9]	M.p., 42–43°
2,4-Cl_2—C_6H_3OH[9]	M.p., 44–45°
2,5-Cl_2—C_6H_3OH[11]	M.p., 56.5–57.5°
3,4-Cl_2—C_6H_3OH[12]	M.p., 64–66°
2,4,5-Cl_3—C_6H_2OH[9]	M.p., 64–65°
2,4,6-Cl_3—C_6H_2OH[9]	M.p., 69–70°

action mixtures containing orthohalogenated phenols were less reactive and directly heated to reflux. The course of the reaction was followed by titration of hydrogen chloride dissolved in the scrubber water. The reaction was not considered complete until the scrubber water showed almost neutral *p*H.

In order to obtain high yields it was found necessary to complete all reactions involving halogenated phenols in the presence of anhydrous magnesium chloride (0.01 mole per mole of phenol used). Originally, this catalyst was added to the clear phenol–phosphorus trichloride solution before warm-up. Better yields were obtained by addition of magnesium chloride after about one-third of the theoretical amount of hydrochloric acid was found in the scrubber water.

The total amount of hydrogen chloride evolved was found to be 124–143% of theory, depending upon the temperature of cooling water going into the condenser. The excess amount of hydrochloric acid found was produced by some phosphorus trichloride being evaporated along with the hydrogen chloride.

To find the point of complete phenol conversion, samples of reaction mixture were taken after the scrubber water had turned almost neutral. When infrared analysis showed the presence of less than 1% of free phenol in the reaction mixture, after removal of excess phosphorus trichloride at low temperature under vacuum, the reaction was considered to be complete.

Main product isolation. The reaction mixture was transferred without filtration to a glass still equipped with thermometer and glass stirrer. Unreacted phosphorus trichloride was taken off by distillation with agitation under atmospheric pressure until the temperature of the reaction mixture had risen to 140–145°. The crude concentrate obtained, remaining liquid at room temperature in all runs undertaken, was then distilled under a pressure of less than 15 mm.

Purification. The main products obtained were fractionally redistilled twice at a pressure of 10 mm. through a fractionation column of 15 cm. length and 3 cm. diameter, packed with Berl saddles. The results obtained were those given in Table I.

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(9) Purified commercial product.

(10) L. E. Mills and C. M. Galloway, U. S. Patents 2,221,807 and 2,221,808 (1940).

(11) E. Noelting and E. Kopp, *Ber.*, **38**, 3510 (1905).

(12) Badische Anilin and Soda-Fabrik; German Patent **156,333** (1903).