[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

An Improved Method of Synthesis of Aromatic Dichlorophosphines[1]

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The reactions used previously in the preparation of aryldichlorophosphines have failed to produce a pure product in high yield. These include the reaction of an aromatic hydrocarbon and phosphorus trichloride in a hot tube,[3] a diarylmercury compound and phosphorus trichloride,[4] or an aromatic hydrocarbon and phosphorus trichloride catalyzed by aluminum chloride.[5] The best of these, the Michaelis modification of the Friedel–Crafts reaction, is inadequate owing to the lengthy reaction period, the difficult extraction, and the contamination of product with catalyst. Improvement of the isolation procedure of the Michaelis modification has been made by Dye[6] who employed phosphorus oxychloride as a complexing agent to remove the catalyst.

From the work of Kosolapoff and Huber,[7] who have prepared diethyl benzenephosphonate in 80% yield through the phenyldichlorophosphine intermediate, it was presumed that the Michaelis modification of the Friedel–Crafts reaction was satisfactory in preparing aryldichlorophosphines. The utilization of a complexing agent and the development of satisfactory reaction conditions have led to the isolation of the aryldichlorophosphines in high yields.

Discussion

The conditions for a satisfactory synthetic method were determined from a series of reactions using phosphorus trichloride and toluene as reactants, aluminum chloride as a catalyst, and phosphorus oxychloride as a complexing agent and various reaction temperatures and times. The best results were obtained when the temperature of the liquid phase attained a maximum of 80° in reactions using a 4:1 ratio of phosphorus trichloride to toluene and the reaction time was three hours. As a result of varying the quantities of constituents in several trial reactions, the most favorable ratio was found to be 1.2:0.3:0.4 of phosphorus trichloride, toluene and aluminum chloride, respectively. The yields of reactions in which the complexing agent was used were more than double those of reactions in which it was omitted. The granular phosphorus oxychloride–aluminum chloride complex obtained in reactions using aluminum chloride and toluene in a 4:3 ratio permitted easier extraction of the product.

The most favorable conditions thus determined for tolyldichlorophosphine were successfully applied to the syntheses of ethylphenyl- and isopropylphenyldichlorophosphines. Equally high yields were obtained. When the quantities of reactants and catalyst were trebled, the liquid phase temperature was several degrees lower and the yields were notably diminished. All the syntheses of the higher aryldichlorophosphines, except tolyl-, ethylphenyl- and isopropylphenyldichlorophosphines, were performed with the threefold larger quantities of materials (Table I). A high yield of phenyldichlorophosphine was obtained despite use of the larger quantities and the lower temperature.

Previous work[7,8,9] has shown that the reaction of phosphorus trichloride and toluene leads to a mixture of para- and ortho-tolyldichlorophosphines with the para isomer being the principal product. During the course of the work reported herein, only derivatives (phosphinic and phosphonic acids, phosphonic di-*p*-toluides) of the para isomers of tolyl- and ethylphenyldichlorophosphines were isolated. However, the low yield of the purified para derivatives obtained does not preclude the possibility of considerable ortho substitution. The clear-cut fractions obtained on redistillation of the crude aryldichlorophosphines indicates that negligible isomerization of the alkyl side-chains had occurred.

Experimental[10]

Materials.—Phosphorus trichloride (C.P.) and aluminum chloride (C.P.) were used without further purification. These reagents were exposed to the atmosphere as little as possible. Most of the hydrocarbons, all of high purity, as well as the phosphorus oxychloride (Eastman Kodak Co. practical grade), were distilled once from a Claisen flask. For want of adequate supply, *n*-propylbenzene was used without distillation, but *s*-amylbenzene and *s*-butylbenzene (technical grades) were each twice distilled at 187–190° and 173–174°, respectively. The petroleum ether and the hydrocarbons were stored over anhydrous calcium chloride and decanted through filter paper before use.

Preparation of Tolyldichlorophosphine.—The reactions were performed in an all-glass apparatus consisting of a one-liter three-necked flask equipped with a long-stem thermometer, rubber-sealed mechanical stirrer, and a Friedrich condenser. Phosphorus trichloride, 165 g. (1.2 moles), toluene, 27.6 g. (0.3 mole), and aluminum chloride, 53 g. (0.4 mole) were placed in a flask and heated gently while being continuously stirred. The hydrogen chloride which evolved was absorbed in a trap filled with sodium hydroxide solution. The reaction mixture was protected from moisture by inserting a tube filled with "Drierite" between the condenser and gas trap. After two hours the reaction mixture was refluxed as vigorously as possible. Cold water, approximately 0°, was circulated by means of a water-pump in order to increase the efficiency of the condenser. At the end of the third hour, the evolution of hydrogen chloride had practically ceased. The heat source was removed and, while the mixture was still hot, phosphorus oxychloride, 61.3 g. (0.4 mole) was gradually added from a dropping funnel. After the apparatus was disassembled, six to eight petroleum ether extractions of 100 ml. each were used to remove tolyldichlorophosphine and the unreacted starting materials from the reaction flask. The granular residue was transferred to a Buchner funnel, washed with several small portions of petroleum ether, and the combined extracts and washings were concentrated under vacuum. Crude tolyl-

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[1] The opinions contained herein are the private ones of the writers and are not to be construed as official or reflecting the views of the Navy Department or the naval service. Article not copyrighted.

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(3) Michaelis, *Ber.*, **6**, 601 (1873).

(4) Michaelis, *Ann.*, **181**, 265 (1876).

(5) Michaelis, *Ber.*, **12**, 1009 (1879).

(6) Dye, THIS JOURNAL, **70**, 2595 (1948).

(7) Kosolapoff and Huber, *ibid.*, **69**, 2020 (1947).

(8) Michaelis and Panek, *Ber.*, **13**, 653 (1880).

(9) Michaelis and Panek, *ibid.*, **14**, 405 (1881).

[10] All melting points are corrected.

TABLE I

SOME ARYLDICHLOROPHOSPHINES

Aryldichlorophosphines	Yield, %	Fractn. range, °C.	mm.	Refractive index n^{25}D	Density d^{25}_4	Analyses, %: Phosphorus Calcd.	Phosphorus Found	Chlorine Calcd.	Chlorine Found[h]	M.p. of the phosphonic di-*p*-toluide, °C.
Phenyl-	78	68–70	1.0	1.5962[c]	1.3173[e]	17.32	17.37	39.66	39.20	195–196[i] dec.
Tolyl-	66	107–110	10.0	1.5865	1.2661	16.06	16.00	36.78	36.23	182–183[j,k] dec.
Ethylphenyl-	69	122–125	10.0	1.5776[d]	1.2266[f]	14.97	14.87	34.30	33.62	200–201 dec.
Isopropylphenyl-	64	129–132	10.0	1.5677	1.1917[g]	14.02	14.25	32.13	31.80	187–188[l] dec.
n-Propylphenyl-	47	127–131	5.0	1.5658	1.1905	14.02	14.13	32.13	31.23	146–147
n-Butylphenyl-	39	116–119	1.0	1.5591	1.1611	13.19	13.03	30.21	29.85	164–164.5[m]
s-Butylphenyl-	33[a]	116–120	1.5	1.5644	1.1840	13.19	13.15	30.21	29.07	193.5–194.5
s-Amylphenyl-	22[b]	118–121	1.0	1.5541	1.1437	12.45	12.42	28.51	27.77	Oil
n-Hexylphenyl-	50	146–149	1.5	1.5478	1.1157	11.78	11.87	27.00	26.38	161–162[n]

[a] A lower boiling aryldichlorophosphine (7%), b.p. 81–90° (2–3 mm.), n^{23}D 1.5830, d_{23} 1.309 was also isolated. [b] Phenyldichlorophosphine (8%), b.p. 68–70° (1.0 mm.), n^{25}D 1.5912, d_{25} 1.327 was also isolated. [c] Zecchini, *Gazz. chim. ital.*, **24**, 34 (1894), reported n^7D 1.6053. [d] Jones, Davies and Dyke, *J. Phys. Chem.*, **37**, 583 (1933), reported n^{25}D 1.5775. [e] Michaelis *Ann.*, **181**, 265 (1876), reported d_{20} 1.319. [f] Michaelis, *ibid.*, **293**, 193 (1896), reported d_{17} 1.227. [g] Michaelis, *ibid.*, **294**, 1 (1897), reported d_{12} 1.190. [h] Low chlorine analyses were due to the ease with which the aryldichlorophosphines hydrolyzed in air. [i] Michaelis, *Ann.*, **407**, 290 (1915), reported m.p. as 220°. [j] Michaelis, *Ann.*, **293**, 193 (1896), reported m.p. as 237°. [k] Calcd.: P, 8.85. Found: P, 8.70. [l] Calcd.: P, 8.19. Found: P, 8.00. [m] Calcd.: P, 7.90. Found: P, 7.83. [n] Calcd.: P, 7.37. Found: P, 7.25.

dichlorophosphine was recovered by vacuum distilling to dryness and purified by fractionating through a 20-cm. column packed with glass helices.

Preparation of Some Aryldichlorophosphines.—The method of synthesis of tolyldichlorophosphine was used to prepare a number of aryldichlorophosphines from the corresponding alkyl-substituted benzene. Yields, physical data, analyses and derivatives are given in Table I.

Boiling Points at Reduced Pressure.—By means of a fractionating column, the boiling points of the aryldichlorophosphines were taken at several reduced pressures. A purified sample (25 ml.) was placed in a 50-ml. still-pot and heated under total reflux. The boiling point of the sample was taken as the vapor temperature in the still-head at a constant pressure. The boiling points obtained below 10 mm. were not reliable because of difficulties of the method (*e.g.*, superheating, rate of reflux), but those obtained at higher pressures were satisfactory, as indicated by the graph of log *p vs.* 1/*T* (Fig. 1).

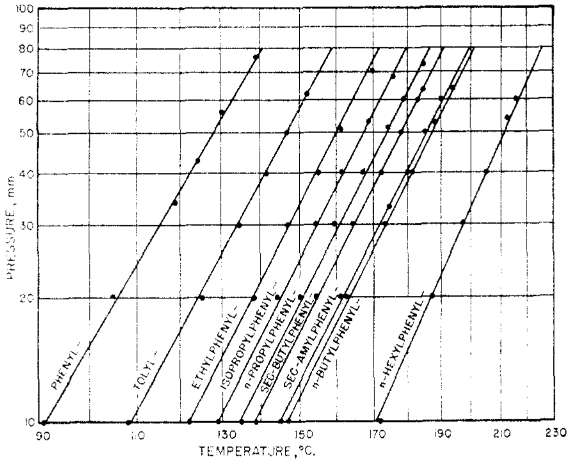

Fig. 1.—Boiling points of the aryldichlorophosphines.

Preparation of the Arylphosphonic Di-*p*-toluides.—A carbon tetrachloride solution of the aryldichlorophosphine was treated with dry chlorine to form the aryltetrachlorophosphine which was treated *in situ* with sulfur dioxide and converted to the aryl oxydichlorophosphine. About 2 g. (0.01 mole) of the crude aryl oxydichlorophosphine and 4.3 g. (0.04 mole) of *p*-toluidine in benzene solution were refluxed for 30 minutes. The mixture was cooled, filtered, and the residue of *p*-toluidine hydrochloride washed with cold benzene. The crude arylphosphonic di-*p*-toluide obtained from evaporation of the filtrate and washings was recrystallized from boiling aqueous ethanol until a constant melting point was obtained.

Summary

1. An improved method of synthesis of aryldichlorophosphines is reported.

2. A series of aryldichlorophosphines has been prepared and characterized by physical properties and derivatives.

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