

Preparation of Some Organophosphorus Compounds¹

BY DASU RAMASWAMI² AND ERNST R. KIRCH

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In a previous publication³ we reported our studies on the effect of substituting the C=O group in phenylurethan by the P=O group. We wish to present the details of the synthesis of compounds.

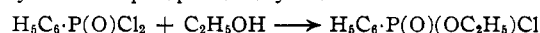
Experimental

Dialkyl anilidophosphates were synthesized according to the following scheme reactions: Dialkyl chlorophosphates, the intermediates were prepared (in yields of 80–90%) from phosphorus trichloride and the respective alkanol according to the procedure of McCombie, *et al.*⁴

Chlorination in the second step was carried out according to the procedure of Atherton, *et al.*,⁵ using sulfuryl chloride.

immersed in ice-water. The mixture was set aside for an hour, extracted with boiling benzene and filtered. The filtrate was evaporated to a sirup which solidified. The mass was crystallized from alcohol twice.

The rest of the chloro- and dichloro-compounds were prepared by a procedure represented by the following example: Ethyl benzene phosphorus oxychloride



Benzene phosphorus oxydichloride (39 g., 0.2 mole) dissolved in 100 ml. of chloroform was kept in a freezing mixture and absolute alcohol (9.5 g., 0.2 mole) added dropwise with stirring keeping the temperature at 0° or below. The mixture was distilled under reduced pressure.

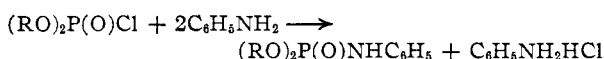
Table I summarizes the physical constants and analytical data of these compounds.

Acknowledgment.—We are indebted to Victor Chemical Works for a gift of some of the starting compounds.

TABLE I

No.	Compound	Carbon, %		Hydrogen, %		M.p. or b.p. °C. cor.	Mm.	n _D ²⁰
		Calcd.	Found	Calcd.	Found			
1	(<i>n</i> -Pr-O) ₂ P(OH)	43.36	43.67	9.09	9.29	93–95	11	1.4140
2	(<i>n</i> -Pr-O) ₂ P(O)Cl	35.93	36.20	7.04	7.30	95–97	2	1.4230
3	(<i>n</i> -Pr-O) ₂ P(O) (NHC ₆ H ₅)	56.02	56.35	7.84	7.91	54.5–55.5		
4	(<i>n</i> -Bu-O) ₂ P(O) (NHC ₆ H ₅)	58.92	58.58	8.48	8.35	191	1	1.4907
5	(<i>n</i> -Am-O) ₂ P(OH)	54.03	53.98	10.43	10.67	138–139	6	1.4300
6	(<i>n</i> -Am-O) ₂ P(O)Cl	46.78	47.09	8.65	8.85	141–142	6	1.4342
7	(<i>n</i> -Am-O) ₂ P(O) (NHC ₆ H ₅)	61.74	62.10	8.41	8.23	201–203	2.5	1.4810
8	(<i>i</i> -Am-O) ₂ P(O) (NHC ₆ H ₅)	61.74	62.01	8.41	8.53	191	2	1.4863
9	(H ₅ C ₂ O) ₂ P(S) (NHC ₆ H ₅)	48.96	48.63	6.58	6.37	140–142	1.5	1.4950
10	(C ₆ H ₅)(H ₅ C ₂ O):P(O)NHC ₆ H ₅	64.36	64.08	6.17	6.20	130–132		
11	(C ₆ H ₅)(H ₅ C ₂ O) P(S)NHC ₆ H ₅	60.61	60.33	5.81	5.90	81–82		
12	(H ₅ C ₆)(H ₅ C ₂ O) P(S)Cl	43.53	43.61	4.57	4.30	115–116	1.5	1.4950
13	H ₅ C ₆ P(O) (OC ₂ H ₅)Cl	46.96	46.50	4.94	5.05	120	2	1.5372

The dialkyl chlorophosphate was then treated with aniline in the molar ratio of 1:2. The end-product in each case was extracted with boiling benzene and separated from the solid aniline hydrochloride by filtration. Purification was effected by distillation under reduced pressure in the case of liquids or by repeated crystallization in the case of solids.



The following detailed procedure is a typical example for the series.—**Di-*n*-propyl Hydrogen Phosphite** (HO)P(O-*n*-propyl)₂: *n*-Propyl alcohol (54 g., 0.9 mole) was dissolved in 54 ml. of carbon tetrachloride in a flask immersed in ice-water. Phosphorus trichloride (41.5 g., 0.3 mole) dissolved in 15 ml. of carbon tetrachloride was added slowly with stirring. The mixture was allowed to stand for one hour and then distilled under reduced pressure in a claisen flask. The residue after removing hydrogen chloride and carbon tetrachloride distilled at 78–80° (15 mm.), yield 85%.

Di-*n*-propyl Chlorophosphate (*n*-propyl-O)₂P(O)Cl.—Di-*n*-propyl hydrogen phosphite from the previous step (43 g., 0.28 mole) was stirred, keeping the flask in ice-water while sulfuryl chloride (37 g., 0.28 mole) was added dropwise maintaining the temperature at 35–40°. The mixture was stirred for a further 90 minutes and distilled under reduced pressure. The residue after removing sulfur dioxide and hydrogen chloride distilled at 87–88° (11 mm.), yield 87%.

Di-*n*-propyl Anilidophosphate (*n*-propyl-O)₂P(O)NHC₆H₅.—Diisopropyl chlorophosphate (10 g., 0.05 mole) was slowly added to aniline (9.3 g., 0.1 mole) the mixture being

DEPARTMENT OF CHEMISTRY
COLLEGE OF PHARMACY
UNIVERSITY OF ILLINOIS
CHICAGO 12, ILLINOIS

Diethyl Vinyl Phosphate, Divinyl Benzenephosphonate and their Polymers

BY R. W. UPSON

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Although unsaturated esters of phosphorus acids, such as allyl, methallyl and crotyl phosphates and phosphonates^{1–4} have been reported, no reference has been made in the literature to vinyl esters of phosphorus acids. It was therefore of interest to prepare vinyl esters of typical phosphorus acids and to investigate their polymerization.

Diethyl vinyl phosphate and divinyl benzenephosphonate have been synthesized by dehydrohalogenation of the corresponding 2-chloroethyl esters.⁵ The 2-chloroethyl esters were prepared by reaction of diethyl chlorophosphate and benzenephosphonyl dichloride with ethylene oxide by the procedure described by Daly and Lowe⁶ for the preparation of tris-(2-chloroethyl) phosphate.

Copolymers of diethyl vinyl phosphate with styrene, methyl methacrylate and acrylonitrile were prepared. Attempts to form homopolymers

(1) Experimental data taken in part from the thesis submitted by Dasu Ramaswami in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Pharmaceutical Chemistry.

(2) D. R. is indebted to the University of Illinois for a fellowship.

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