Preparation of Some Organophosphorus Compounds[1]

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In a previous publication[3] 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.

Table I

No.	Compound	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	M.p. or b.p. °C. cor.	Mm.	n^{20}D
1	$(n\text{-Pr-O})_2\text{P(OH)}$	43.36	43.67	9.09	9.29	93–95	11	1.4140
2	$(n\text{-Pr-O})_2\text{P(O)Cl}$	35.93	36.20	7.04	7.30	95–97	2	1.4230
3	$(n\text{-Pr-O})_2\text{P(O)}\ (\text{NHC}_6\text{H}_5)$	56.02	56.35	7.84	7.91	54.5–55.5		
4	$(n\text{-Bu-O})_2\text{P(O)}\ (\text{NHC}_6\text{H}_5)$	58.92	58.58	8.48	8.35	191	1	1.4907
5	$(n\text{-Am-O})_2\text{P(OH)}$	54.03	53.98	10.43	10.67	138–139	6	1.4300
6	$(n\text{-Am-O})_2\text{P(O)Cl}$	46.78	47.09	8.65	8.85	141–142	6	1.4342
7	$(n\text{-Am-O})_2\text{P(O)}\ (\text{NHC}_6\text{H}_5)$	61.74	62.10	8.41	8.23	201–203	2.5	1.4810
8	$(i\text{-Am-O})_2\text{P(O)}\ (\text{NHC}_6\text{H}_5)$	61.74	62.01	8.41	8.53	191	2	1.4863
9	$(\text{H}_5\text{C}_2\text{O})_2\text{P(S)}\ (\text{NHC}_6\text{H}_5)$	48.96	48.63	6.58	6.37	140–142	1.5	1.4950
10	$(\text{C}_6\text{H}_5)(\text{H}_5\text{C}_2\text{O})\text{:P(O)NHC}_6\text{H}_5$	64.36	64.08	6.17	6.20	130–132		
11	$(\text{C}_6\text{H}_5)(\text{H}_5\text{C}_2\text{O})\ \text{P(S)NHC}_6\text{H}_5$	60.61	60.33	5.81	5.90	81–82		
12	$(\text{H}_5\text{C}_6)(\text{H}_5\text{C}_2\text{O})\ \text{P(S)Cl}$	43.53	43.61	4.57	4.30	115–116	1.5	1.4950
13	$\text{H}_5\text{C}_6\cdot\text{P(O)}\ (\text{OC}_2\text{H}_5)\text{Cl}$	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.

$$\text{(RO)}_2\text{P(O)Cl} + 2\text{C}_6\text{H}_5\text{NH}_2 \longrightarrow \text{(RO)}_2\text{P(O)NHC}_6\text{H}_5 + \text{C}_6\text{H}_5\text{NH}_2\text{HCl}$$

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-)$_2$P(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)$_2$P(O)NHC$_6$H$_5$.—Diisopropyl chlorophosphate (10 g., 0.05 mole) was slowly added to aniline (9.3 g., 0.1 mole) the mixture being 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

$$\text{H}_5\text{C}_6\cdot\text{P(O)Cl}_2 + \text{C}_2\text{H}_5\text{OH} \longrightarrow \text{H}_5\text{C}_6\cdot\text{P(O)(OC}_2\text{H}_5\text{)Cl}$$

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.

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[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.

[3] D. Ramaswami, E. R. Kirch and E. H. Jenney, *Science*, **116**, 58 (1952).

[4] H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

[5] F. R. Atherton, H. T. Howard and A. R. Todd. *ibid.*, 1106 (1948).

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 Lowe[6] 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

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[1] L. N. Whitehill and R. S. Barker, U. S. Patent 2,394,829 (1946).

[2] A. D. F. Toy, This Journal, **70**, 186 (1948).

[3] A. D. F. Toy, U. S. Patent 2,425,765 (1947).

[4] British Patent 534,826 (1941).

[5] R. W. Upson, U. S. Patent 2,557,805 (1951).

[6] A. J. Daly and W. G. Lowe, U. S. Patent 2,157,164 (1939).

from diethyl vinyl phosphate were unsuccessful. A soft, tacky homopolymer of divinyl benzenephosphonate was obtained. The vinyl ester group in diethyl vinyl phosphate is stable toward water and dilute hydrochloric acid solution.

Experimental

Diethyl Vinyl Phosphate.—Diethyl 2-chloroethyl phosphate used in the preparation of diethyl vinyl phosphate, was prepared by reaction of diethyl chlorophosphate with ethylene oxide by the general procedure of Daly and Lowe.[6] After this work was completed, Saunders, *et al.*,[7] reported the preparation of diethyl 2-chloroethyl phosphate by reaction of diethyl chlorophosphate with ethylene chlorohydrin.

To a stirred solution containing 387 g. (2.24 moles) of diethyl chlorophosphate and 3.9 g. (0.03 mole) of anhydrous aluminum chloride was added 114 g. (2.6 moles) of ethylene oxide over a period of 8 hours at room temperature. Distillation of the reaction mixture under reduced pressure gave 400 g. (82.5%) of diethyl 2-chloroethyl phosphate, b.p. 115–117° (5 mm.), n^{25}D 1.4281.

Anal. Calcd. for $C_6H_{14}O_4ClP$: P, 14.32; Cl, 16.37. Found: P, 14.46; Cl, 16.48.

A solution containing 56.1 g. (1.0 mole) of potassium hydroxide, 1000 ml. of ethanol and 216 g. (1.0 mole) of diethyl 2-chloroethyl phosphate was refluxed for 11 hours. The potassium chloride that separated (59 g.) from the reaction solution during this time was removed by filtration. Distillation of the filtrate gave 93 g. (49%) of diethyl vinyl phosphate, b.p. 67° (2.5 mm.), n^{25}D 1.4040.

Anal. Calcd. for $C_6H_{13}O_4P$: P, 17.20. Found: P, 16.80.

Diethyl vinyl phosphate was recovered unchanged after being refluxed in water and in 1% aqueous hydrochloric acid solution for 3–6 hours. There was no evidence that acetaldehyde or ethanol were liberated by these treatments.

Copolymers of Diethyl Vinyl Phosphate.—These were prepared as follows. A solution containing 1.8 g. of diethyl vinyl phosphate, 1.04 g. of styrene and 0.14 g. of benzoyl peroxide was heated under nitrogen at atmospheric pressure for 42 hours at 80°. A colorless, viscous liquid was formed from which 1.2 g. of a white, solid copolymer was obtained by precipitation of the polymerization product with 50 ml. of methanol. The diethyl vinyl phosphate/styrene copolymer softened at 68° and contained 2.52% phosphorus.

Diethyl vinyl phosphate/methyl methacrylate and diethyl vinyl phosphate/acrylonitrile copolymers containing 1.42% phosphorus and 0.91% phosphorus, respectively, were prepared by substitution of equivalent amounts of methyl methacrylate and acrylonitrile for the styrene in the above procedure. The copolymer with methyl methacrylate softened at 110° and the copolymer with acrylonitrile softened at 210–220°. Diethyl vinyl phosphate did not form a copolymer with vinyl acetate under these conditions.

Diethyl vinyl phosphate did not polymerize when heated for 42–70 hours at 80° in the presence of 2–5% α,α'-azodiisobutyronitrile or benzoyl peroxide, at 125° in the presence of di-(*t*-butyl) peroxide, or at −30° in the presence of 2–4% sodium in liquid ammonia. In each case the monomer was recovered almost quantitatively by distillation of the product.

Divinyl Benzenephosphonate.—Bis-(2-chloroethyl) benzenephosphonate was prepared in 77% yield by reaction of 195 g. (1.0 mole) of benzenephosphonyl dichloride with 132 g. (3.0 moles) of ethylene oxide in the presence of 1.95 g. of anhydrous aluminum chloride. The product was a colorless liquid, b.p. 160° (0.8 mm.), n^{25}D 1.5235.

Anal. Calcd. for $C_{10}H_{13}O_3Cl_2P$: P, 10.94; Cl, 25.05. Found: P, 11.05; Cl, 25.63.

A mixture containing 87.3 g. (0.31 mole) of bis-(2-chloroethyl) benzenephosphonate and 65.6 g. (0.62 mole) of anhydrous sodium carbonate was heated for 1.5 hours at 105°, 2 hours at 155° and then for 3 hours at 200°. The sodium chloride that separated from the reaction solution was removed by filtration. Distillation of the filtrate gave 40 g. (61.5%) of divinyl benzenephosphonate, b.p. 174° (3.0 mm.), n^{25}D 1.5258.

Anal. Calcd. for $C_{10}H_{11}O_3P$: P, 14.74. Found: P, 14.96.

The non-volatile residue from the distillation was a viscous liquid polymer of divinyl benzenephosphonate and amounted to 15 g. (23.1%).

Anal. Calcd. for $C_{10}H_{11}O_3P$: P, 14.74. Found: P, 14.90.

Homopolymers.—These ranged from viscous liquids to soft, tacky solids and were obtained by heating divinyl benzenephosphonate at 80° in the presence of 1–3% benzoyl peroxide.

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[7] B. C. Saunders, G. J. Stacey, F. Wild and I. G. E. Wilding, *J. Chem. Soc.*, 699 (1948).

Studies on the Chemistry of Heterocyclics. XXII. Investigations on the Mechanism of Reactions of 2-Thienyl Halides with Sodium Amide and Sodium Acetylide in Liquid Ammonia

BY ALEXANDER VAITIEKUNAS AND F. F. NORD

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In view of the growing importance of the reactions of sodium amide as well as sodium acetylide in liquid ammonia for the syntheses and elucidation of the structure of natural products[1,2,3] it appeared worthwhile to investigate this reaction in the heterocyclic series. It is known that sodium amide in liquid ammonia gave the corresponding acetylenic carbinols[2d] with furan and tetrahydrofuran derivatives and thiophene-2-aldehyde, 3-methyl-thiophene-2-aldehyde as well as β-2-thienylacrolein readily gave the corresponding acetylenic alcohols with sodium acetylide in liquid ammonia.[4] However, the alkylations carried out by this method are unsuccessful when applied to halides in the benzene series.[5] In view of the greater reactivity of the thiophene nucleus it appeared desirable to investigate the reaction of 2-thienyl halides with sodium acetylide in liquid ammonia to attempt the direct synthesis of 2-thienylacetylene.

Preliminary experiments have indicated that 2-chlorothiophene did not react and the starting material was recovered quantitatively while 2-bromothiophene did react vigorously.[5a] However, the main reaction product obtained was not the expected 2-thienylacetylene, but tetrabromothiophene, the monohalide being converted into a tetrahalo derivative. Subsequent investigations with 2-bromothiophene and 2-iodothiophene confirmed the results of the preliminary experiments and we obtained, in the case of 2-bromothiophene, tetrabromothiophene in a yield of 35 to 50%. In the case of 2-iodothiophene the tetraiodo derivative was obtained in a yield of 50% together with a small amount of di- and triiodothiophene.

It appears that in all the above reactions some electrophilic reagent such as NH_2Br or $CH{\equiv}CBr$

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[1] J. Heilbron, *J. Chem. Soc.*, 386 (1948).

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