Arrhenius plots of ln k against $1/T$ gave the following activation energies: (i) at 72.3% acid, 23400 cal. mole^{-1}; (ii) at 50.6% acid, 23800 cal. mole^{-1}. (These figures are subject to an estimated uncertainty of 300 cal. mole^{-1}.) (Note: The range of temperature in which the rate of reaction can be investigated in solutions of low acidity is limited at the upper end by the vapor pressure of the solution and at the lower end by the slowest rate which can be measured conveniently using the thermostat arrangement described. The rate at temperatures below 100° may, however, be measured with the aid of a suitable thermostat which can be left unattended for longer periods).

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Heterocyclic Organophosphorus Compounds. I. Pentamethylenephosphinic Acid

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Cyclic compounds in which an atom of phosphorus forms a part of the ring are of obvious interest in studies of physico-chemical properties of substances in which the hetero-atom is varied. Although several compounds have been reported in the literature, in the past forty years, in which phosphorus is a part of the ring, most of these substances have been truly cyclic amides or esters, with nitrogen or oxygen being integral parts of the ring along with phosphorus. A few carbocyclic phosphorus compounds have been reported as well, but all of these have been either phosphines or phosphonium compounds. It was of considerable interest to prepare a phosphorus-containing acid in which the phosphorus atom is a part of an otherwise carbocyclic ring. Obviously, a true carbon analog of such a substance is impossible for it would demand a carboxylic acid group being a part of a ring structure. Phenphosphazinic acid[1] is the only acid of the type described above that has been reported to date; however, in this compound a nitrogen atom is also present in the carbon–phosphorus ring.

Examination of the possible routes to such a substance indicated that the most probable synthesis could be developed by either or both of the schemes

$$(CH_2)_x(MgX)_2 + (RO)_2P(O)H \longrightarrow (CH_2)_xP(O)MgX \xrightarrow{HOH} (CH_2)_xP(O)H \xrightarrow{(O)} (CH_2)_xP(O)OH \quad (I)$$

$$(CH_2)_x(MgX)_2 + R_2NP(O)Cl_2 \longrightarrow (CH_2)_xP(O)NR_2 \longrightarrow (CH_2)_xP(O)OH \quad (II)$$

Obviously, both of these routes could be expected to produce many other substances. Thus, in route I the intermediate compound with PMgX link could be expected to react with any, as yet unreacted, dialkyl phosphite, thus forming a phosphine oxide. At the same time the reaction of the bifunctional Grignard reagent could be expected to involve not one but two phosphorus-bearing molecules, thus leading to formation of a polymeric substance based on the unit

$$-P(O)H-(CH_2)_xP(O)H-(CH_2)_x-$$

which, in turn, could react further with the intermediate mentioned above. In route II the most serious obstacle is the reaction of the latter type, *i.e.*, reaction of the bifunctional Grignard reagent not only with one molecule of the phosphorus dihalide, but with two of these, thus forming a polymeric substance of the phosphinic amide type

$$-(CH_2)_xP(O)(NR_2)-(CH_2)_xP(O)(NR_2)-$$

Both routes were explored with pentamethylene-bis-magnesium bromide which was selected as a desirable starting material in order to prepare a cyclic compound with a six-membered ring. A shorter chain of the Grignard reagent, such as that with tetramethylene radical, could not be expected to give high yields of the desired cyclic product; this was observed previously in the synthesis of five- and six-member ring cyclic phosphines.[2]

Route I failed to yield any detectable amounts of the desired acid, the products being polymeric substances with and without acidic properties. Route II, however, yielded some 10% of the desired cyclic product, pentamethylenephosphinic acid, along with considerable amounts of acidic polymeric material. This yield of the product was attained by a form of "infinite dilution" technique, since conventional addition of one reagent to the other gave only the polymeric materials, as could be expected from consideration of the nature of the probable reactions.

The procedure used in the isolation of the product may be expected to be useful for the removal of magnesium from Grignard reactions with organophosphorus compounds, and for separation of some phosphinic acids from mixtures. Details are given in the Experimental part.

Experimental

Pentamethylene bromide was prepared conventionally from tetrahydropyran, but the product was steam distilled from the mixture, instead of the recommended mechanical separation[3]; the modification improved the yield by some 10%, to 91–93%.

The Grignard reagent was prepared from 98 g. of pentamethylene bromide and 20.8 g. of magnesium in 400 ml. of dry diethyl ether. Traces of unreacted magnesium were separated by decantation and filtration. One pound of dry diethyl ether was brought to reflux and the Grignard reagent and a solution of 81.0 g. of N,N-diethylamidophosphoryl dichloride in 100 ml. of dry diethyl ether were slowly and simultaneously dropped into the stirred refluxing ether over a period of seven hours. Our previous experience indicated that reflux temperature is necessary to complete the reaction of an amido dichloride with a Grignard reagent. The addition was made in such a manner that the dichloride solution was kept slightly "ahead" of the Grignard reagent. The mixture in the reaction flask separated into two layers during the reaction, the bottom layer being a yellowish, relatively viscous liquid. After addition the mixture was stirred with refluxing for a further period of three hours and was then allowed to stand overnight. The bottom layer had set by this time to a semi-solid mass. The mixture was added gradually to 300 g. of ice-water and was treated with 150 ml. of concentrated hydrochloric acid to yield two clear phases. The ether layer was evaporated,

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(1) P. G. Sergeev and D. G. Kudryashov, *J. Gen. Chem. USSR*, **8**, 266 (1938).

(2) G. Grüttner and E. Krause, *Ber.*, **49**, 438 (1916); G. Grüttner and M. Wiernik, *ibid.*, **48**, 1473 (1915).

(3) "Organic Syntheses," Coll. Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 692.

at slightly above room temperature, under an infrared lamp (in experiments in which the two phases were separated at this time and worked up individually, no improvement in yield was observed). The solution was then treated with 400 ml. of concentrated hydrochloric acid and concentrated under an infrared lamp over 24 hours to a volume of about 300 ml. in order to hydrolyze the amides, formed in the reaction, cooled, diluted with water to 1500 ml., and separated from a small amount of insoluble brown gum (this was base-insoluble and presumably consisted of products of tertiary substitution). Magnesium and diethylamine were removed by means of ion exchange. A column was prepared from 700 g. of Dowex 50-X8 resin (100–200 mesh; the weight was that of resin containing 50% moisture), the resin bed being 4.5 cm. in diameter and 53 cm. high. The reaction solution was passed through the resin in three batches of 450, 450 and 600 ml., respectively; each portion, after passage, was combined with 600 ml. of water with which the resin bed was downwashed. The resin bed was regenerated after each such treatment by passage of 1 liter of 1:1 hydrochloric acid, followed by wash water (usually about 1.5 liters) until the effluent was essentially neutral to Alkacid indicator paper.

The reaction mixture and the afterwashes combined with it were free of magnesium and contained only traces of diethylamine. Evaporation was effected by means of an infrared lamp to a volume of 300 ml. The resulting solution was brought to *p*H 10 by addition, with stirring, of a solution of barium hydroxide, making a total volume of 600 ml. The precipitated barium salts of the polymeric phosphinic acids were separated and washed with 300 ml. of hot water and 500 ml. of cold water. The combined filtrates were again evaporated by means of an infrared lamp to a volume of 400 ml., thereby expelling the residual traces of diethylamine. The barium ions in the solution were carefully precipitated by addition of 1:1 sulfuric acid; the precipitate, washed with 200 ml. of water, was discarded. The combined filtrates were evaporated to constant weight under an infrared lamp, yielding 20 g. of brownish viscous liquid, which was then dried by means of benzene azeotrope for 18 hr., 5 ml. of an aqueous phase being separated during that time. The benzene solution was then treated with 31 g. of phosphorus pentachloride, added gradually, and the mixture was refluxed for 2 hours until the evolution of hydrogen chloride ceased. The dark-brown solution was freed of benzene and phosphorus oxychloride by distillation on a water-bath at 30 mm. vacuum and the viscous residue was added slowly to an ice-cooled solution of 4.6 g. of sodium in 150 ml. of dry butanol. After stirring for three hours the mixture was filtered from sodium chloride and distilled, yielding 9 g. of crude butyl pentamethylenephosphinate, a viscous liquid, b.p. 85° (1.5 mm.).

Anal. Calcd. for $C_9H_{19}O_2P$: P, 16.3. Found: P, 15.0, 14.9.

The ester was hydrolyzed by refluxing overnight with 50 ml. of concentrated hydrochloric acid and the solution was evaporated to dryness. The residue was taken up in 50 ml. of water, decolorized with charcoal, and again evaporated to dryness. The residue was taken up in 20 ml. of benzene and part of the solvent was boiled off in order to remove the traces of moisture. The benzene solution was then cooled, diluted with hexane, and chilled in order to precipitate the bulk of pentamethylenephosphonic acid. The acid was removed by filtration and a second crop was obtained by evaporating the filtrate and adding more hexane to the residue. The product was recrystallized for a 1:6 mixture of benzene–hexane, yielding 5.8 g. of the acid, in the form of short stubby needles, m.p. 128–129°. The acid gave a titration curve with a single inflection at *p*H 7.5.

Anal. Calcd. for $C_5H_{11}O_2P$: P, 23.15; equiv. wt., 134. Found: P, 23.1, 23.05; equiv. wt., 133.2.

The distillation residue, after the removal of the above-described ester, was a dark, viscous undistillable material, which showed signs of decomposition on strong heating *in vacuo*. Presumably it consisted of the esters of polymeric phosphinic acids; these were apparently carried through the barium salt step by virtue of some solubility of these salts in water.

The isolation procedure described above appears to be the most satisfactory one, yielding 10.2% of the desired product. Direct distillation of the amides gave a very poor yield of crude material, b.p. 85–105° (1 mm.) from the ether-soluble phase of the reaction mixture. Distillation of the phosphinyl chloride (after treatment with phosphorus pentachloride as described above) gave 6 g. of yellowish product, b.p. 150–152° (30 mm.), which was hydrolyzed to the above-described acid; however, the yield of the chloride was but 6 g. and the distillation was attended by much decomposition.

The insoluble barium salt precipitate was slurried in water, dissolved by addition of hydrochloric acid, and was freed of barium with sulfuric acid. Evaporation of the filtrate yielded the mixed polymeric products in the form of yellowish viscous semi-solid mass, a sample of which was titrated. The titration curve of this specimen indicated the presence of between five and six secondary acidic hydrogens per two primary acidic hydrogens. The curve was not sharply defined and a more accurate estimation was not justified.

A portion of the pure pentamethylenephosphinic acid was converted to the *n*-butyl ester, by conventional conversion to the acid chloride (b.p. 151–152° (30 mm.)) with phosphorus pentachloride, followed by treatment with sodium butoxide in dry butanol. The pure butyl pentamethylenephosphinate was a colorless liquid, b.p. 80° (1 mm.); $n^{30}{}_D$ 1.4405; $d^{30}{}_4$ 0.9771 (*MR* calcd. 51.31; *MR* found 51.30).

Anal. Calcd. for $C_9H_{19}O_2P$: P, 16.3. Found: P, 16.1, 16.2.

Reaction of Pentamethylene-bis-magnesium Bromide with Dibutyl Phosphite.—The reaction was run essentially as described above with 98 g. of pentamethylene bromide, 20.8 g. of magnesium and 55 g. of dibutyl phosphite. The reaction mixture gradually set to a nearly solid mass after the mixing of the components. The hydrolyzed mixture, after the removal of ether, was oxidized by the addition of bromine water to convert the P–H groups to P–OH groups, and the mixture was worked up essentially as described above. No detectable monomeric material could be isolated. The reaction products consisted of base-soluble and base-insoluble waxy semi-solids. The former were similar to the polymeric material isolated from the reaction described above. The base-insoluble material appeared to be the product of trisubstitution. These were not examined further.

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Catalysis of the Dehydration of 1,1,1-Trichloro-2-methyl-2-propanol *via* Thionyl Chloride. Intermediate Chlorosulfinic Ester Formation[1]

BY DONALD G. KUNDIGER, HUEY PLEDGER[2] AND LOUIS E. OTT[2]

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The reaction between thionyl chloride and hydroxy compounds is catalyzed by tertiary amines and amine hydrochlorides.[3] In Gerrard and French's work typical alcohols gave high yields (about 95%) of the corresponding chlorides upon catalysis by tertiary amines.

The dehydration of 1,1,1-trichloro-2-methyl-2-propanol to 3,3,3-trichloro-2-methyl-1-propene is found to be similarly catalyzed by a variety of ten amines, tetramethylammonium chloride and aniline hydrochloride. In each case a small amount (0.007 to 0.06 mole) of the amine or amine salt markedly accelerates the reaction as shown by an immediate evolution of hydrogen chloride.

[1] A preliminary report of part of this work appeared in the Abstracts of Papers, American Chemical Society, Omaha, Nebraska, November, 1954.

[2] This paper is abstracted in part from the Ph.D. Thesis of Huey Pledger, Jr., and the M.S. Thesis of Louis E. Ott, submitted as partial fulfillment for these degrees at Kansas State College.

[3] W. Gerrard and K. H. V. French, *Nature*, **159**, 263 (1947).