TABLE II

ANALYTICAL WAVE LENGTHS USED FOR QUANTITATIVE CALCULATIONS OF PINANE AND ISOBORNYLANE

| | |
|---|---|
| 8.13[a] | 7.78 |
| 8.54 | 8.47 |
| 10.21 | 9.27 |
| 10.50 | 10.69 |
| 11.65 | 12.40[a] |

[a] Major analytical wave lengths.

tained from the hydrogenolysis of nopol and hydronopol were determined according to the procedure described previously.[19] The infrared absorption spectra of these pure hydrocarbons were identical with those reported by the American Petroleum Institute Project 44. The wave lengths used for the quantitative determination of pinane and isobornylane are given in Table II.

The infrared absorption spectra of 2,2-dimethylnorpinane, obtained from the hydrogenolysis of myrtanol is given in Fig. 1.

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[19] V. N. Ipatieff, H. Pines and M. Savoy, THIS JOURNAL, **69**, 1948 (1947).

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[CONTRIBUTION FROM THE ROSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

# The Anhydrides of Di-*n*-propyl- and Di-*n*-butyl-phosphinic Acids

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The preparation of the anhydrides of di-*n*-propyl- and di-*n*-butylphosphinic acids, by means of interaction of the chlorides and the ethyl esters of the respective acids, is reported. The anhydrides, *i.e.*, compounds of the type $R_2P(O)OP(O)R_2$, are reactive substances, as shown by facile interaction with water and with the lower aliphatic alcohols. It was shown that the atomic refraction value for phosphate phosphorus (3.75) is applicable to calculations of molar refractions of tetraalkyl pyrophosphates. The value of atomic refraction of phosphorus in phosphinic structure has been tentatively established at 4.79 units.

Interest in the tetraalkyl pyrophosphates, $(RO)_2P(O)OP(O)(OR)_2$, has been stimulated largely by the discovery of the insecticidal properties of these esters. Since there is no information in the literature concerning the structurally related anhydrides of phosphinic acids, *i.e.*, compounds of type $R_2P(O)OP(O)R_2$, we have prepared and examined the anhydrides of di-*n*-propyl- and di-*n*-butylphosphinic acids.

The preparation of these compounds by thermal treatment of the respective free phosphinic acids was unsuccessful, since heating the acids to 300–320° failed to produce any reaction. This fact is in line with the earlier observation by Collie[1] concerning the thermal stability of diethylphosphinic acid.

The anhydrides were readily prepared, however, by the interaction of the respective phosphinyl chlorides with the ethyl esters of the acids

$$R_2P(O)Cl + (RO)P(O)R_2 = RCl + R_2P(O)OP(O)R_2$$

Reactions of this type have been used in the preparation of the pyrophosphates from trialkyl phosphates and dialkyl chlorophosphates.[2]

The anhydrides proved to be very reactive substances. Their hydrolysis to the corresponding phosphinic acids in water occurs within a few minutes, and they react with alcohols rather rapidly at moderately elevated temperatures, forming a molecule of the free phosphinic acid and the corresponding alkyl ester of the acid. Such behavior indicates the profound effect of the replacement of the OR groups of the pyrophosphates by the radicals R, directly bound to the respective phosphorus atoms. The corresponding pyrophosphates react with water rather sluggishly and require drastic conditions for alcoholysis.

The possible toxicity of the anhydrides may be mentioned at this time. A crude test involving deposition of about 0.1 ml. of the butyl compound on the dorsal side of a large cockroach resulted in convulsion and death of the insect within a few minutes.

## Experimental Part

**Di-*n*-propylphosphinic Anhydride.**—The necessary di-*n*-propylphosphinic acid was prepared by the Grignard reaction, extending the earlier work of Gilman and Vernon,[3] who had found that Grignard reagents readily replace the OR groups in tertiary phosphites by the R groups of the Grignard reagent. We used dialkyl phosphites, *i.e.*, $(RO)_2POH$, in order to secure the attachment of but two radicals to the phosphorus atom; the reaction was realized very readily. The Grignard reagent from 32 g. of magnesium and 110 g. of *n*-propyl chloride (activated with a few drops of the iodide) in 400 ml. of dry ether was treated over one hour with 55.5 g. of diethyl phosphite with vigorous stirring. The reaction mixture separated into two layers near the end of the addition period. The mixture was refluxed with stirring for two hours, cooled and poured into 300 ml. of ice-water, acidified with a little hydrochloric acid. The mixture was warmed by an infrared lamp until the ether layer evaporated, the clear solution was treated with 54 ml. of 85% phosphoric acid and was made alkaline with concentrated ammonium hydroxide for the removal of the magnesium ion. The filtrate from the mixture was concentrated until crystallization of inorganic salts began and, after cooling and filtration, the new filtrate was cautiously treated with 20 ml. of 30% hydrogen peroxide in small portions (3–4 ml.) with stirring. This results in the oxidation of the phosphinous acid, *i.e.*, $R_2POH$, which is expected from the Grignard reaction. Further concentration of the solution led to the separation of an oily layer of the desired phosphinic acid, which was extracted with 100 ml. of ether, which was evaporated to dryness and re-evaporated with a small amount of water to yield 33 g. (55%) of crude di-*n*-propylphosphinic acid in the form of yellowish crystals.

The crude acid was directly converted to the phosphinyl chloride by treatment with 41.6 g. of phosphorus pentachloride in 300 ml. of dry benzene, with gentle refluxing for one hour until the hydrogen chloride evolution stopped. Distillation under reduced pressure gave 26.5 g. (78%) of the di-*n*-propylphosphinyl chloride, b.p. 126–128° at 17 mm.; Plets[4] reports b.p. 112–114° at 15 mm.

The chloride (16.5 g.), diluted with dry benzene to 50 ml.,

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[1] Collie, *J. Chem. Soc.*, **127**, 964 (1925).

[2] Hall and Jacobson, *Ind. Eng. Chem.*, **40**, 694 (1948); Kosolapoff, U. S. Patent 2,486,658 (1949); Toy, THIS JOURNAL, **71**, 2268 (1949).

[3] Gilman and Vernon, *ibid.*, **48**, 1063 (1926).

[4] Plets, Dissertation, Kazan, 1938.

was slowly added with stirring and ice cooling to sodium ethoxide, prepared from 2.2 g. of sodium and 40 ml. of dry ethanol, in 200 ml. of dry benzene, after which the mixture was permitted to stand overnight. After filtration of sodium chloride, the solution was distilled under reduced pressure, yielding 14 g. (80%) of ethyl di-*n*-propylphosphinate, a colorless liquid, b.p. 110–112° at 14 mm.; $n^{21}$D 1.4369, $d^{21}_4$ 0.9567; *MR* found 48.6, calcd. 48.8. Calcd. for $Pr_2P(O)OEt$: P, 17.40. Found: P, 17.31.

The ester (10.5 g.) was mixed with an equimolar amount of the corresponding chloride (10 g.) and the mixture was heated on oil-bath in a distillation apparatus connected to a brine-chilled trap, where ethyl chloride began to condense when the mixture attained the temperature of 150°; after one hour at 150–160° the reaction was complete and distillation of the residue yielded 14.5 g. (88%) of di-*n*-propylphosphinic anhydride, a viscous colorless oil, b.p. 138–140° at 1 mm.; $n^{21}$D 1.4629, $d^{21}_4$ 1.0299; *MR* found 75.4, calcd. 75.42. On chilling, the product crystallized slowly to a mass of feathery needles which melted at 28–30°. The material supercools very readily, before solidification. Calcd. for $Pr_2P(O)OP(O)Pr_2$: P, 21.97. Found: P, 21.9.

The anhydride reacts with water very rapidly, resulting in complete hydrolysis in a few minutes at room temperature. Titration of a sample with standard sodium hydroxide, using thymolphthalein indicator, gave the saponification equivalent of 282.6, against the calculated 282.

Evaporation of the hydrolysis solution readily yielded pure di-*n*-propylphosphinic acid, which was dried by repeated evaporation with benzene, followed by drying *in vacuo*. The product forms colorless flat needles, m.p. 56–57°, readily soluble in water. Plets[4] reported this acid as an oil. Found neut. equiv. 150.2, calcd. neut. equiv. 151.

**Di-*n*-butylphosphinic Anhydride.**—The procedure for preparing this substance closely followed the one outlined above. The reaction of the Grignard reagent from 32 g. of magnesium and 190 g. of *n*-butyl bromide in 400 ml. of dry ether, with 55.5 g. of diethyl phosphite gave, after hydrolysis, followed by evaporation of the mixture to remove the ether, an oily layer, presumably of $R_2POH$ (the butyl compound was considerably less soluble in water than the propyl analog and could be separated at this point). The material had a pronounced phosphine odor. This was extracted with 200 ml. of benzene and the extract was evaporated under an infrared lamp, with addition of a small amount of water near the end of evaporation to facilitate the removal of the solvent. Treatment of the residual oil with 30 ml. of 30% hydrogen peroxide (the same precautions as given above) resulted in a delayed vigorous reaction. After treatment of the mixture with a small amount of sodium bisulfite solution for decolorizing, the crude di-*n*-butylphosphinic acid was filtered off. Crystallization from benzene gave 51 g. (72%) of the pure compound, m.p. 71°; previously reported m.p. 70.5–71.0°.[5]

Treatment of the acid (60 g.) with 70 g. of phosphorus pentachloride in 125 ml. of dry benzene, gave 58.5 g. (88.5%) of the di-*n*-butylphosphinyl chloride, b.p. 143–145° at 16 mm.; Plets[4] gives b.p. 132–134° at 15 mm.

The chloride (35 g.) was added to sodium ethoxide, from 4.1 g. of sodium and 41 g. of ethanol, in 200 ml. of dry benzene, yielding 28 g. (74%) of ethyl di-*n*-butylphosphinate, b.p. 149–151° at 18 mm.; $n^{22}$D 1.4421, $d^{22}_4$ 0.9349; *MR* found 58.4, calcd. 58.1. Calcd. for $Bu_2P(O)OEt$: sapn. equiv., 206; P, 15.04. Found: sapn. equiv., 205; P, 15.1.

Heating the ester (14 g.) with the chloride (13.5 g.) for 45 minutes at 150–165° gave 22 g. (95.6%) of di-*n*-butylphosphinic anhydride, a colorless, very viscous oil, b.p. 170–172° at 2 mm.; $n^{21}$D 1.4628, $d^{21}_4$ 0.9908; calcd. for $(Bu_2PO)_2O$: P, 18.3; *MR*, 93.9. Found: P, 18.18; *MR*, 93.8.

The anhydride reacted very rapidly with water and a drop placed on the surface rapidly crystallized to the free acid. Titration gave the neutralization equivalent of 338.0, against the theoretical value of 338.4.

The anhydride was kept for eight hours in closed flasks, containing a 25-fold excess of either ethanol, *n*-propanol or isopropyl alcohol, in a thermostatic bath kept at 50°. The following extents of alcoholysis were determined by titration: ethanol 78%, propanol 65% and isopropyl alcohol 43%.

The phosphorus analyses of all the phosphinic derivatives listed above require drastic conditions for decomposition. Of several methods tried, the most consistent and satisfactory results were obtained only with Marie's method of decomposition.[6]

**Molecular Refraction Data.**—Determination of the molecular refractions of the substances under consideration in this paper brought forth some information of interest. The recently evaluated atomic constants for phosphorus[7] give excellent correlation between the calculated and the experimental values of molar refraction in the families of phosphites (tertiary), phosphates and phosphonates, as well as their halogen derivatives. Since Kabachnik did not report on the applicability of the "phosphate" value of *AR* for phosphorus (3.75) to the pyrophosphate esters, we carried out the necessary calculations, which are cited below, using data from published values on pure members of the family. The results show excellent correlation, indicating applicability of the 3.75 value to this family of phosphorus compounds.

TABLE I

| Pyrophosphate | $n^{25}$D | $d^{25}_4$ | *MR*, obsd. | *MR*, calcd. | Ref. |
|---|---|---|---|---|---|
| Tetramethyl | 1.4121 | 1.3608 | 42.8 | 43.0 | 8 |
| Tetraethyl | 1.4170 | 1.1845 | 61.5 | 61.48 | Hall[2] |
| Tetra-*n*-propyl | 1.4248 | 1.1037 | 80.1 | 79.95 | 8 |
| Tetraisopropyl | 1.4170 | 1.0854 | 80.0 | 79.95 | 8 |
| Tetra-*n*-butyl | 1.4296 | 1.0533 | 98.4 | 98.4 | 8 |

Evidently, the incorporation of the phosphate into a pyrophosphate structure does not alter the value of the atomic constant.

However, a difficulty arose with the calculation of the values for our phosphinic compounds, since there is no value for *AR* of phosphorus in the phosphinic structure. When the value of 4.27 was used (this is the value assigned by Kabachnik[7] to the phosphonic phosphorus), the results were discordant: the calculated values were approximately one unit below the experimentally found ones for the anhydrides, while the esters showed a similar deviation of about one-half of a unit. Since the transition from the OR group in a phosphate to the R group in a phosphonate causes a rise of the *AR* by 0.52 unit (Kabachnik,[7] from 3.75 to 4.27), it was reasonable that a similar further increment is called for in going from the phosphonate to the phosphinate, where the type of replacement is similar to the above. This gives the *AR* value of 4.79 for phosphorus in phosphinic linkage. When this value was used in calculations of *MR* in our compounds, excellent correlation was found and it is suggested that this value be used for compounds in this family.

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[5] Kosolapoff, THIS JOURNAL, **71**, 369 (1949).

[6] Marie, *Compt. rend.*, **129**, 766 (1899).

[7] Kabachnik, *Izvestiya Akad. Nauk S. S. S. R., otdel, khim. nauk*, 219 (1948).

[8] Toy, THIS JOURNAL, **70**, 3882 (1948).