barium chloride. The most active compound was N-(3-isobutyl-3-phenylpropyl)-piperidine hydrochloride which was 69 times as effective as papaverine against barium induced spasms and 9.5% as effective as atropine sulfate as an acetylcholine antagonist.

Acknowledgment.—The author is indebted to Mr. M. E. Auerbach and Mr. K. D. Fleischer and staff for the analytical data.

Experimental

Chloroethylamine Hydrochlorides.—Dimethylaminoethyl chloride and diethylaminoethyl chloride hydrochlorides are commercially available. 2-(N-Pyrrolidyl)-ethyl chloride,[10] and 2-(N-piperidyl)-ethyl chloride[11] hydrochlorides were prepared by published procedures. 2-(N-2-Methylpyrrolidyl)-ethyl chloride hydrochloride was prepared by treating 2-(N-2-methylpyrrolidyl)-ethanol[12] with thionyl chloride in chloroform and recrystallized from isopropyl alcohol-ethyl acetate.

Anal. Calcd. for $C_7H_{14}ClN.HCl$: N, 7.61; Cl, 38.52. Found: N, 7.84; Cl, 38.40.

The base distilled at 60–62° (8 mm.), $n^{25}D$ 1.4622.

Nitriles.—Diphenylacetonitrile is commercially available. Cyclohexylphenylacetonitrile,[13] cyclopentylphenylacetonitrile,[14] n-hexylphenylacetonitrile,[6] isobutylphenylacetonitrile[15] and isobutylidenephenylacetonitrile[16] were prepared by published procedures. β-Methallylphenylacetonitrile was prepared by treating β-methallyl chloride with phenyl-

(10) J. B. Wright, H. G. Kolloff and J. H. Hunter, This Journal, 70, 3098 (1948).

(11) F. F. Blicke and C. E. Maxwell, *ibid.*, 64, 428 (1942).

(12) R. O. Clinton, U. J. Salvador and S. C. Laskowski, *ibid.*, 71, 3366 (1949).

(13) W. E. Bachman, "Organic Syntheses," Vol. 25, John Wiley and Sons, Inc., New York, N. Y., 1945, p. 25.

(14) G. Vasiliu, V. Dumitrascu and H. Vulcan, Soc. Chim. România Sect. române Stiinte, *Bul. chim. pură apl.* (2) **3A**, 54 (1941–1942), *C. A.*, 38, 5493 (1944).

(15) F. Bodroux and F. Taboury, *Bull. soc. chim. France*, [4] 7, 668 (1910).

(16) J. V. Murray and J. B. Cloke, This Journal, 58, 2016 (1936).

acetonitrile in benzene with the aid of sodium amide and distilling the product through a 30-cm. column packed with glass helices. β-Methallylphenylacetonitrile was obtained in 34% yield, b.p. 124–128° (5 mm.), $n^{25}D$ 1.5183.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.29; H, 7.67; N, 8.07.

The reaction also produced a 29% yield of dimethallylphenylacetonitrile, b.p. 146–148° (5 mm.), $n^{25}D$ 1.5228.

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.28; H, 8.49; N, 6.22. Found: C, 85.32; H, 8.48; N, 6.29.

Substituted α-(β-Aminoethyl)-phenylacetonitriles.—Diphenylacetonitrile was alkylated with the appropriate aminoethyl chloride by a published procedure.[3]

The alkyl- and cycloalkylphenylacetonitriles were prepared in the following manner. A mixture of 0.15 mole of aminoethyl chloride hydrochloride, 0.15 mole of alkylphenylacetonitrile and 0.3 mole of sodium amide in 200 ml. of dry benzene was stirred and gradually heated to about 60°. The exothermic reaction was then controlled by occasional cooling with an ice-bath. When the ammonia evolution had diminished the reaction was heated at 65° for about two hours. To the cooled mixture water was added and the benzene layer separated and washed with water. The product was then extracted with diluted hydrochloric acid, converted back to the base, extracted with ether and dried over sodium hydroxide pellets. After removing the solvent the product was distilled under reduced pressure. The yields of basic nitriles were generally good ranging from 68 to 90%. They are described in Table I.

3-Phenylpropylamines.—To a well stirred mixture of about 0.4 mole of sodium amide in 100 ml. of refluxing xylene was added, dropwise, a solution of 0.1 mole of a basic nitrile in 100 ml. of xylene. The reaction was vigorously stirred and refluxed for ten hours. The excess sodium amide was decomposed by the careful addition of water to the stirred mixture. The xylene layer was separated, washed with water and then extracted with diluted hydrochloric acid. The acid layer was made strongly basic with 35% sodium hydroxide, extracted with ether and the ether solution dried over sodium hydroxide pellets. The solvent was removed and the amine distilled under reduced pressure. The substituted 3-phenylpropylamines, obtained in yields of 48 to 95%, are described in Table II.

Study in Terpene Series. XI.[1] The Dehydroxymethylation of Bicyclic Primary Terpenic Alcohols by Hydrogenolysis in the Presence of Nickel Catalysts[2]

By V. N. Ipatieff, G. J. Czajkowski and Herman Pines

The dehydroxymethylation of primary bicyclic alcohols to hydrocarbons containing one carbon atom less than the original alcohols has been studied. The catalysts used were nickel–Kieselguhr, Raney nickel and nickel–alumina. The alcohols investigated were: hydronopol, nopol, myrtanol and 2-methyl-5-hydroxymethylbicyclo[3.2.1]octane. The hydrogenolysis proceeded in most cases in good yields at 160–180° and 65–100 atmospheres of pressure. 2,2-Dimethylnorpinane formed from the hydrogenolysis of myrtanol, yielded isopropylbenzene on the dehydrogenation over platinum–alumina catalyst.

In previous papers[1,3] it was shown that, in the presence of nickel catalysts, primary alcohols yield hydrocarbons having one less carbon atom. The extensive isomerization that occurs during many reactions in the terpene series made it of interest to ascertain if the cleavage of primary bicyclic terpene alcohols is accompanied by isomerization. Nickel–kieselguhr,[4] nickel–alumina[1] (77% NiO–23%

Al_2O_3) and W-6 Raney nickel,[5] containing alumina,[6] were used as catalysts. The following alcohols were investigated: hydronopol,[7] nopol,[7] myrtanol and 2-methyl-5-hydroxymethyl-bicyclo[3.2.1]octane.[8] The latter compound was prepared by hydrogenating the unsaturated aldehyde obtained from the selenium dioxide oxidation of 2,6-dimethyl-2-bicyclo[3.2.1]octene.[9]

(1) For paper X of this series, see V. N. Ipatieff, W. W. Thompson and H. Pines, This Journal, 73, 553 (1951).

(2) This work was made possible through the financial assistance of Universal Oil Products Company, Chicago, Illinois.

(3) V. N. Ipatieff, G. S. Monroe, L. E. Fischer and E. E. Meisinger, *Ind. Eng. Chem.*, 41, 1802 (1949).

(4) V. N. Ipatieff and B. B. Corson, *ibid.*, 30, 1039 (1931).

(5) H. Adkins and H. R. Billica, This Journal, 70, 695 (1948).

(6) V. N. Ipatieff and H. Pines, *ibid.*, 72, 5320 (1950).

(7) J. P. Bain, *ibid.*, 68, 638 (1946).

(8) V. N. Ipatieff, J. E. Germain, W. W. Thompson and H. Pines, unpublished results.

(9) V. N. Ipatieff, H. Pines, V. Dvorkovitz, R. C. Olberg and M. Savoy, *J. Org. Chem.*, 12, 34 (1947).

The cleavage of the above mentioned alcohols occurred readily at 160–180° and under 60–100 atm. of hydrogen pressures in the presence of nickel–Kieselguhr.

Hydronopol.—Infrared spectral analysis showed the product resulting from the hydrogenolysis of hydronopol in the presence of nickel–Kieselguhr at 160–170°, to consist of 90% pinane and 10% isobornylane; the gases were composed of hydrogen and methane.
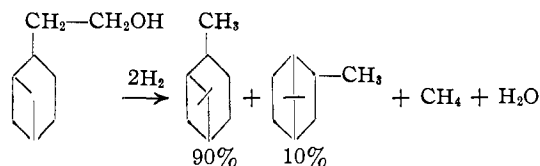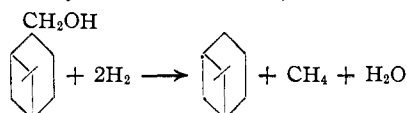

When the reaction temperature was increased to 190–200° (Expt. 2), the concentration of pinane in the product dropped to 40% due to rupture of the four-membered ring; the structure of the monocyclic hydrocarbons obtained was not ascertained.

Nickel–alumina was less active than nickel–Kieselguhr for the hydrogenolysis of hydronopol. Only 50% of the alcohol underwent hydrogenolysis to give pinane of 98% purity; the remainder consisted of bis-hydronopyl ether (20%) and unreacted hydronopol.
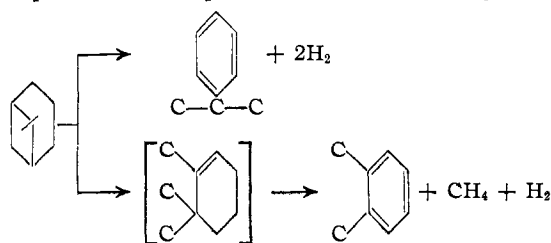
Nopol.—The reaction of nopol with hydrogen under an initial pressure of 100 atmospheres and in the presence of nickel–Kieselguhr or Raney nickel catalyst gives results similar to that of hydronopol.[10] The liquid hydrocarbons formed consisted of 85–90% of pinane, the remainder being isobornylane. It seems that the first step in this reaction is the hydrogenation of nopol to dihydronopol with subsequent hydrogenolysis of the latter.

Myrtanol when treated with hydrogen at 160° and at an initial pressure of 63 atmospheres gave an 80% yield of 2,2-dimethylnorpinane

The latter was identical, according to infrared spectra, with 2,2-dimethylnorpinane obtained synthetically through the ozonolysis of β-pinene followed by the Wolff–Kishner reduction of the resulting ketone.

2,2-Dimethylnorpinane, on dehydrogenation in the presence of a platinum–alumina catalyst[11] at

332°, formed aromatic hydrocarbons consisting of 95% isopropylbenzene and 5% o-xylene. The reaction is similar to the dehydrogenation of pinane and probably proceeds as diagrammed.

2-Methyl-5-hydroxymethylbicyclo[3.2.1]octane gave on hydrogenolysis 2-methylbicyclo[3.2.1]octane. The structure of the latter was proved by comparison of physical constants and infrared absorption spectra with a known sample. The reaction proceeded according to the equation
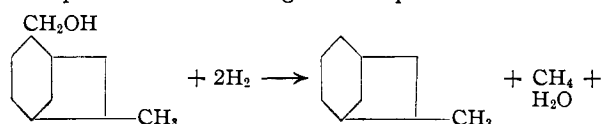
The above described experiments and those reported previously, indicate that hydrogenolysis of primary alcohols to hydrocarbons containing one carbon atom less than the original alcohol can proceed in good yields and without isomerization. This method can be utilized for the synthesis of hydrocarbons that are otherwise difficult to prepare or for the proof of structures by means of selective degradation.

Experimental Part

A. Synthesis of Alcohols: Nopol[12] distilled at 118–118.5° (10 mm.), n^{20}D 1.4940.

Hydronopol was prepared by hydrogenating nopol in solution with an equivalent volume of pentane. The reaction was carried out at 80–90° under 100 atmospheres of hydrogen pressure and in the presence of 10% by weight nickel–Kieselguhr[4] catalyst. The hydronopol, which was produced in an almost theoretical yield, distilled at 128–129° (12 mm.), n^{20}D 1.4890.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.50; H, 11.90. Found: C, 78.11; H, 12.22.

Myrtanol[13]: a. Myrtenal was prepared by oxidation of freshly redistilled α-pinene (b.p. 156–158°) with selenium dioxide according to the general procedure described by Stallcup and Hawkins.[14] Two hundred seventy-two grams (2 moles) of α-pinene, dissolved in 400 ml. of absolute ethanol, was refluxed and stirred while 234 g. (2.1 moles) of selenium dioxide, which had previously been dissolved in 400 ml. of ethanol by heating, was slowly dropped in. The time of addition was one hour. The mixture was then refluxed for an additional five hours, cooled to room temperature and 119 g. of metallic selenium filtered (yield 75%). The filtrate was steam distilled and the distillate was extracted with ether. The myrtenal formed, 99 g. (yield 33%) distilled at 67° at 4 mm., n^{20}D 1.5040, d^{20}_4 0.986.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.57; H, 9.40.

Semicarbazone[15] after recrystallization from water melted at 205°.

Anal. Calcd. for $C_{11}H_{17}ON_3$: N, 20.29. Found: N, 20.39.

Oxime[15] after recrystallization from alcohol–water, melted at 97–97.5°.

Anal. Calcd. for $C_{10}H_{15}ON$: N, 8.47. Found: N, 8.08.

b. Myrtanol was prepared from the myrtenal by means of hydrogenation. Fifteen grams of the aldehyde dissolved in equal volume of cyclohexane was hydrogenated in a 125-cc. capacity rotating autoclave at 55° and at an initial pressure

(10) J. P. Bain[7] reported that nopol on hydrogenation at 65 to 100 atm. at 180–200° in the presence of 1.6% by weight of Raney nickel yielded 80.5% of hydronopol and small amount of hydrocarbons. The difference in results can be ascribed to the low concentration of catalysts used by Bain as compared with those used by the authors.

(11) H. Pines, R. C. Olberg and V. N. Ipatieff, THIS JOURNAL, **70**, 533 (1948).

(12) The nopol was kindly supplied by Dr. J. P. Bain, The Glidden Company Naval Stores Division, Jacksonville, Florida.

(13) The data for the preparation of myrtenal and myrtanol and their derivatives were taken from the Ph.D. Dissertation by W. W. Thompson. Northwestern University, June, 1948.

(14) W. D. Stallcup and J. E. Hawkins, THIS JOURNAL, **63**, 3339 (1941).

(15) G. Dupont and W. Zacharewicz, *Bull. Soc. Chim.*, [5] **2**, 533 (1935), reported melting points for the inactive myrtanol: semicarbazone, m.p. 200.5°; oxime. m.p. 101°.

TABLE I

HYDROGENOLYSIS OF PRIMARY BICYCLIC ALCOHOLS UNDER PRESSURE

The reaction was made in a 450-cc. capacity stainless steel rotating autoclave; in each experiment 10% of catalyst was used based on the weight of the alcohol charged. The duration of each experiment was 4–5 hours.

Experiment	Alcohol Kind	G.	Catalyst	Temperature, °C.	Hydrogen pressure, atm. Initial	Hydrogen pressure, atm. Final	Alcohol reacted, %	Yield, ^{c} %	Hydrocarbons from hydrogenolysis Composition, %	
1	Hydronopol	43	Ni-K^a	160–170	61	42^b	95	81^d	Pinane	90
									Isobornylane	10
2	Hydronopol	43	Ni-K	190–200	60	31	95	51^e		
3	Hydronopol	43	Ni-Al$_2$O$_3$	200	62	51	55	23^f	Pinane	98
4	Nopol	80	Ni-K^a	180	102	59	100	45^g	Pinane	85
									Isobornylane	15
5	Nopol	40	Raney Ni	180	100	77^h	100	58^g	Pinane	100
6	Myrtanol	30	Ni-K^a	160	63	50	95	80^i	2,2-Dimethylnorpinane	100
7	2-Methyl-5-hydroxy-methylbicyclo[3.2.1] octane	30	Ni-K	160	63	50	90	70^k	2-Methylbicyclo[3.2.1] octane	100

^{a} Nickel–Kieselguhr catalyst. ^{b} 17.6 liters of gas was recovered consisting of 68.4 mole per cent. of hydrogen and 31.0 of methane. ^{c} The yield is expressed in mole per cent. of the alcohol charged. ^{d} B.p. 163–164°, n^{20}D 1.46214. ^{e} B.p. 158–161°, n^{20}D 1.4488. *Anal.* Calcd. for C$_{10}$H$_{20}$: C, 85.63; H, 14.37. C$_{10}$H$_{18}$: C, 86.87; H, 13.13. Found: C, 86.20; H, 14.07. Corresponds to a mixture of mono- and bicyclic hydrocarbons. The remainder of the product distilled as follows: 120–132°, 14% by weight, n^{20}D 1.4302; 132–152°, 21%, 1.4338; 152–158°, 8%, 1.4425; >161°, 6%. ^{f} About 22% of a product corresponding to bis-hydronopyl ether, based on the alcohol charged, was produced; b.p. 200–205° at 4 mm., n^{20}D 1.4942; d^{20}_4 0.9545. *Anal.* Calcd. for C$_{22}$H$_{38}$O: C, 83.02; H, 11.95; *MR*D, 96.64. Found: C, 82.80; H, 12.23; *MR*D, 97.02. ^{g} The remainder of the product was hydronopol. ^{h} About 30 liters of gas was recovered, which was composed of 92.1% hydrogen and 7.5% methane. ^{i} B.p. 151–152°, n^{20}D 1.4618, d^{20}_4 0.8610. Infrared absorption spectrum was identical with synthetically prepared 2,2-dimethylnorpinane. *Anal.* Calcd. for C$_9$H$_{16}$: C, 87.10; H, 12.90; *MR*D, 39.36. Found: C, 87.22; H, 12.94; *MR*D, 39.58. ^{k} B.p. 148–149°, n^{20}D 1.4592; identical according to physical constants and infrared spectra with synthetically prepared 2-methylbicyclo[3.2.1]octane.^{8} *Anal.* Calcd. for C$_9$H$_{16}$: C, 87.10; H, 12.90. Found: C, 87.35; H, 12.85.

of 65 atmospheres in the presence of 2 grams of nickel-Kieselguhr catalyst. The myrtanol distilled at 92° at 5 mm., n^{20}D 1.4910.

3,5-Dinitrobenzoate melted at 75°, after recrystallization from methanol.

Anal. Calcd. for C$_{17}$H$_{20}$N$_2$O$_6$: C, 58.61; H, 5.79; N, 8.04. Found: C, 58.44; H, 5.58; N, 7.86.

2-Methyl-5-hydroxymethylbicyclo[3.2.1]octane.—The synthesis of this alcohol will be described in a separate paper.^{8}

tion. The nopinone obtained distilled at 100–105° at 23 mm., n^{20}D 1.4780; yield 40%.

b. **2,2-Dimethylnorpinane.**—The Wolff–Kishner reduction of nopinone to 2,2-dimethylnorpinane was carried out as described by Huang-Minlon.[17] Four grams of the ketone, 5.2 g. of 85% hydrazine hydrate, 4 g. of potassium hydroxide and 28 ml. of diethylene glycol was used in the reaction. The 2,2-dimethylnorpinane formed, amounting to 2.8 g., distilled at 149–150°, n^{20}D 1.4593.

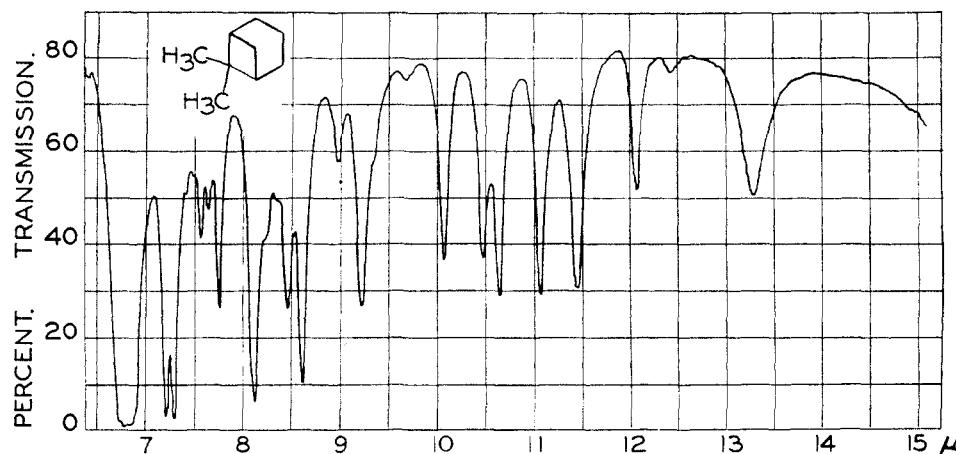

Fig. 1.—Infrared spectra of 2,2-dimethylnorpinane: prism, sodium chloride; cell thickness, 0.1 mm.

B. Synthesis of 2,2-Dimethylnorpinane[16]: a. Nopinone.
—β-Pinene, 10.2 g. dissolved in 100 ml. of carbon tetrachloride was ozonized at 0°. After the reaction was completed the product was allowed to stand overnight in a cold room, and then decomposed by adding it in small portions to a solution of 40 ml. consisting of equal volumes of 30% hydrogen peroxide and 10% sodium carbonate. The mixture was stirred vigorously for 0.5 hour, then warmed to 65° and stirred for an additional 3 hours.

The product was steam distilled, and nopinone was separated from the carbon tetrachloride by fractional distilla-

The 2,2-dimethylnorpinane obtained by this method showed two minor intensity bands (impurity bands) not present in the 2,2-dimethylnorpinane produced by hydrogenolysis of myrtanol (Experiment 6).

C. Hydrogenolysis of Alcohols.—The summary of the experimental conditions and results obtained are given in Table I.

D. Infrared Spectral Analysis.[18]—The percentages of pinane and isobornylane present in the hydrocarbons ob-

(16) Synthesized by W. D. Huntsman of our laboratories.

(17) Huang-Minlon, THIS JOURNAL, 68, 2487 (1946).

(18) E. Baclawski, Research Laboratories, Universal Oil Products Company.

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.

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

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

BY GENNADY M. KOSOLAPOFF AND RICHARD M. WATSON

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, $(RO)_2$-$P(O)OP(O)(OR)_2$, 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., $(RO)_2$-POH, 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.,

(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.