sulfur dioxide, and the resulting liquid was distilled *in vacuo*. There was obtained a fuming, water-white liquid, b.p. 107–109° (12 mm.), 83–84° (2 mm.), n^{20}D 1.4688, d^{20}_4 1.1748; MR summation,[18,29] 47.22; MR experimental, 48.13. The yield was 4.8 g. (51.6%). Soborovskii, *et al.*,[5] gave b.p. 85–87° (2 mm.), n^{20}D 1.4728, d^{20}_4 1.1796.

Anal. Calcd. for $C_6H_{13}Cl_2OP$: Cl, 34.92; P, 15.25. Found: Cl, 34.85, 34.78; P, 15.25, 15.20.

Highly Branched Alkylphosphorus Compounds.
II.   Synthesis of 1,1,2-Trimethylpropylphosphonyl Chloride[1]

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The reaction of 2-chloro-2,3-dimethylbutane with phosphorus trichloride and aluminum chloride does not give the expected product, but instead produces *t*-butylphosphonyl chloride as the predominant product. The reaction of Grignard reagents with N,N-diethylphosphoramidic dichloride was extended to include *t*-alkyl Grignard reagents. 1,1,2-Trimethylpropylphosphonyl chloride could not be prepared by the normal procedures, such as condensing the phosphonic acid with phosphorus pentachloride or thionyl chloride. A method was devised for the synthesis of 1,1,2-trimethylpropylphosphonyl chloride and related highly branched alkylphosphonyl chlorides.

The previous paper[4] described the synthesis of 2,3-dimethylbutylphosphonyl chloride, one of the two possible products of the oxidative phosphonation of 2,3-dimethylbutane. This paper is devoted to the synthesis of the other isomer to be expected in this reaction, 1,1,2-trimethylpropylphosphonyl chloride (VI). In the course of this work, there were encountered some unexpected properties of compounds in which phosphorus is attached to a tertiary carbon atom. The large steric requirements of such molecules are believed to be primarily responsible for such properties.

Clay[5] and Kinnear, and Perren[6] have shown that when an alkyl halide is treated with phosphorus trichloride and aluminum chloride, followed by a careful hydrolysis of an intermediate complex, good yields of alkylphosphonyl chlorides can be obtained. Such reactions are quite analogous in many ways to the well-known Friedel–Crafts reaction, with the phosphorus trichloride playing the role of the nucleophilic reagent. Furthermore, in both the Kinnear and Perren reaction and the Friedel–Crafts reaction, the carbon chain of the alkyl halide is often isomerized. For example, Kinnear and Perren have shown that n-propyl, n-butyl, and isobutyl chlorides yield isopropyl-, isobutyl-, and *t*-butylphosphonyl chlorides, respectively. As also might be expected, *t*-butyl chloride produced *t*-butylphosphonyl chloride.

Such data indicated that one should be able to synthesize 1,1,2-trimethylpropylphosphonyl chloride in one step from 2-chloro-2,3-dimethylbutane, phosphorus trichloride, and aluminum chloride. Such expectations not only did not materialize, but the major product from this reaction was *t*-butylphosphonyl chloride, which was recovered in 47.4% yield. In addition, there appeared to be a variety of other higher boiling phosphorus-containing products, no one of which was isolated in a pure condition.

Crofts and Kosolapoff[7] reported the recovery of *t*-butylphosphonyl chloride from the reaction involving *t*-amyl chloride, phosphorus trichloride, and aluminum chloride, an apparently related rearrangement of this type. They made no attempt to explain this, but simply mentioned that a methylene group had been lost. We believe that both of these observations can be rationalized on the basis of a mechanism similar to that proposed by Whitmore[8] for the acid-catalyzed dimerizations of olefins.

In a somewhat related study Friedman and Morritz[9] have shown that *t*-butyl derivatives are produced during the Friedel–Crafts reaction of isoamylene with aromatic hydrocarbons. The mechanism these workers have proposed to explain their results could be used, after slight modification, to explain our results. Essentially the same mechanism could be employed to explain the results of Crofts and Kosolapoff.[7] Molecular models support the idea that the *t*-butyl carbonium ion should react more readily with phosphorus trichloride than the carbonium ion from 2-chloro-2,3-dimethylbutane.

Since our first attempts to synthesize 1,1,2-trimethylpropylphosphonyl chloride failed, we turned to an entirely different route (Scheme I).

Kosolapoff[10] has shown that the reaction between a Grignard reagent and N,N-diethylphosphoramidic chloride (I) at 5–15° results in monoalkylation of the phosphorus atom whereas, at higher temperatures and with an excess of the Grignard reagent, dialkylation takes place. When this reaction was attempted with compounds I and II at 5–15°, there was no evidence of reaction. However, at 35° an exothermic reaction took place to produce what turned out to be only the monoalkylated product, even when excess Grignard reagent was employed. Molecular models show that

(1) Taken in part from the thesis submitted by S. H. Metzger in partial fulfillment of the requirements for the M. S. degree at the A. & M. College of Texas, August, 1956. Presented in part at the 131st and 134th National Meetings of the American Chemical Society, Miami, Fla., April, 1957, and Chicago, Ill., September, 1958, respectively.

(2) Post-doctoral fellow.

(3) To whom all inquiries should be addressed.

(4) S. H. Metzger and A. F. Isbell, *J. Org. Chem.*, **29**, 623 (1964).
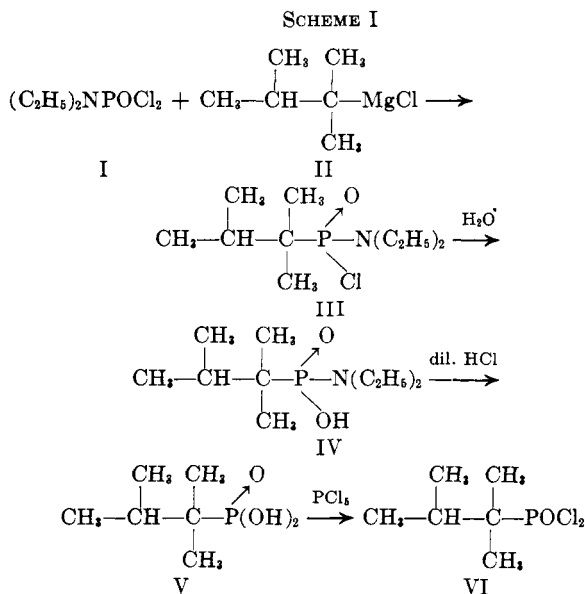
(5) J. P. Clay, *ibid.*, **16**, 892 (1951).

(6) A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(7) P. C. Crofts and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 3379 (1953).

(8) F. C. Whitmore, *Chem. Eng. News*, **26**, 668 (1948).

(9) B. S. Friedman and F. L. Morritz, *J. Am. Chem. Soc.*, **78**, 3430 (1956).

(10) G. M. Kosolapoff, *ibid.*, **71**, 369 (1949); **72**, 5508 (1950).

Scheme I

$$(C_2H_5)_2NPOCl_2 + CH_3\!-\!\overset{\overset{\displaystyle CH_3}{|}}{CH}\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\!-\!MgCl \longrightarrow$$

I　　　　　　　　II

$$CH_3\!-\!\overset{\overset{\displaystyle CH_3}{|}}{CH}\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\!-\!\overset{\nearrow O}{\underset{\searrow Cl}{P}}\!-\!N(C_2H_5)_2 \xrightarrow{H_2O}$$

III

$$CH_3\!-\!\overset{\overset{\displaystyle CH_3}{|}}{CH}\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\!-\!\overset{\nearrow O}{\underset{\searrow OH}{P}}\!-\!N(C_2H_5)_2 \xrightarrow{dil. HCl}$$

IV

$$CH_3\!-\!\overset{\overset{\displaystyle CH_3}{|}}{CH}\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\!-\!\overset{\nearrow O}{P}(OH)_2 \xrightarrow{PCl_5} CH_3\!-\!\overset{\overset{\displaystyle CH_3}{|}}{CH}\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\!-\!POCl_2$$

V　　　　　　　　　　　　　　VI

III could form without the development of serious strain, but the formation of the dialkylated product would be highly improbable, if not impossible.

No attempt was made to isolate III. Its hydrolysis, however, turned out to be difficult. After III was heated in a mixture of concentrated hydrochloric acid and alcohol for 23 hr., followed by the addition of excess caustic, steam distillation removed diethylamine plus a small quantity of heavy oil. This oil solidified after standing for more than 1 yr. It proved to be the monobasic acid (IV). This compound is a weak acid, and its solubility properties are very much like those of a hydrocarbon. Since molecular models show that the polar groups are surrounded completely by the hydrocarbon fragments of the molecule, such properties are not surprising.

From the hydrolysate, a 58% yield of V was recovered, plus an additional quantity of viscous oil. It now appears that this oil may have consisted largely of the partially hydrolyzed product (IV).
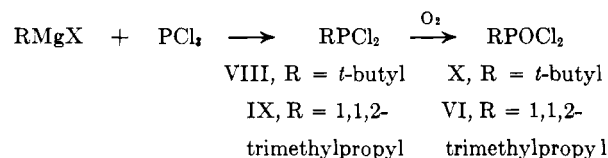
All attempts to convert the acid (V) to the acid chloride (VI) failed. Both phosphorus pentachloride and thionyl chloride, even when present in considerable excess, produced only materials which gave evidence of being polymeric phosphonic anhydrides. From one of the reactions between V and thionyl chloride, a crystalline product was isolated, which gave evidence of being a cyclic anhydride with structure VII.

$$V \xrightarrow{SOCl_2} \begin{array}{c} \\ C_6H_{13}\!-\!P \quad\quad P\!-\!C_6H_{13} \\ \\ P \\ \\ C_6H_{13} \end{array}$$

VII
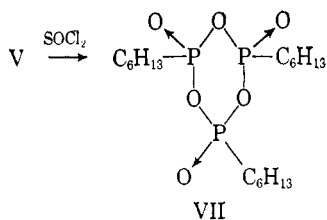
The failure to convert the acid (V) to the corresponding acid chloride (VI) also is believed to be governed by steric factors. Molecular models show that V and VI are both compact molecules, but there appeared to be no obvious reason why VI should be incapable of existence. However, a model of the cyclic anhydride (VII) showed it to be a compact structure with its

P–O–P linkages buried beneath the highly branched alkyl chains. The anhydride linkages are almost equally obscured in the linear polymeric anhydrides. We believe that anhydrides are intermediates in the conversion of phosphonic acids to the corresponding acid halides when such reagents as phosphorus pentachloride and thionyl chloride are employed. Therefore, when the halogenating reagents are prevented from approaching the anhydride linkages, further reaction is prevented. For these reasons, it appears quite unlikely that highly branched alkyl phosphonic acids can be converted to the corresponding acid halides.

In order to prepare 1,1,2-trimethylpropylphosphonyl chloride (VI), it appeared essential that a synthesis be devised which would allow either the PCl_2 or the $POCl_2$ group to be introduced directly into the molecule. A Grignard reaction with phosphorus trichloride or phosphorus oxychloride seemed to satisfy this requirement. However, some of our unpublished work indicated that, when Grignard reagents react with phosphorus oxychloride, the alkylphosphonyl chlorides which are generated form unusually stable complexes with the by-product, magnesium chloride. We have been unable to break such complexes without hydrolyzing the phosphonyl chloride. For these reasons, phosphorus oxychloride did not appear to be the reagent of choice. Since tertiary Grignard reagents react with phosphorus oxychloride under mild conditions to bring about almost exclusive monoalkylation of the phosphorus atom,[7] it seemed reasonable to suspect that tertiary Grignard reagents might behave similarly when treated with phosphorus trichloride. This hypothesis was explored first by the reaction of t-butylmagnesium chloride with phosphorus trichloride. A good yield of the new compound, t-butylphosphonous chloride (VII), resulted. Compound VIII was readily oxidized to t-butylphosphonyl chloride (X) in a carbon tetrachloride solution by the action of elemental oxygen. The analogous reaction of 1,1,2-trimethylpropylmagnesium chloride with phosphorus trichloride produced the corresponding phosphonous chloride (IX), which was in turn oxidized to the desired product (VI). It should be pointed out that certain physical properties of 1,1,2-trimethylpropylphosphonyl chloride failed to correspond closely with those reported for this compound by Soborovskii, Zinov'ev, and Englin.[11]

$$RMgX + PCl_3 \longrightarrow RPCl_2 \xrightarrow{O_2} RPOCl_2$$

VIII, R = t-butyl　　　X, R = t-butyl

IX, R = 1,1,2-　　　VI, R = 1,1,2-

trimethylpropyl　　　trimethylpropyl

Since the free-radical addition of diethyl phosphonate to 2,3-dimethyl-1-butene was successful for the production of diethyl 2,3-dimethylbutylphosphonate,[4] it was of interest to attempt the corresponding reaction with 2,3-dimethyl-2-butene. Because of steric factors it seemed unlikely that the symmetrical olefin would take part in this reaction. Thus, it was surprising to find that, when 2,3-dimethyl-2-butene was heated with diethyl phosphonate in the presence of benzoyl peroxide, diethyl 1,1,2-trimethylpropylphosphonate was

(11) L. Z. Soborovskii, Yu. M. Zinov'ev, and M. A. Englin, *Dokl. Akad. Nauk SSSR*, **73**, 333 (1950).

recovered in approximately 20% yield. It was not surprising to find that reaction of this ester with phosphorus pentachloride produced none of the corresponding acid chloride (VI).

Experimental[12]

2-Chloro-2,3-dimethylbutane was prepared by the method of Norris and Olmstead[13] by shaking 88.5 g. (0.867 mole) of 2,3-dimethyl-2-butanol[4] with 215 ml. of concentrated hydrochloric acid; the boiling point was 48° (79.1–79.3 mm.), n^{25}D 1.4167, d^{25}_4 0.8736; MR experimental,[14] 34.70; MR summation, 34.78; yield 77.7 g. (74%). Stoll, et al.,[15] gave b.p. 46–48.5° (80 mm.), n^{25}D 1.4172.

An alternative procedure, which gave a better yield, was to bubble dry hydrogen chloride through the vigorously stirred 2,3-dimethyl-2-butanol with ice-bath cooling. After saturation, the mixture was allowed to warm to room temperature, the water was drawn off, and the crude alkyl chloride was dried over calcium chloride. The dissolved hydrogen chloride was removed by refluxing in vacuo with an ice water-cooled condenser, and the product was distilled (82.5% yield).

Reaction of 2-Chloro-2,3-dimethylbutane with Phosphorus Trichloride and Aluminum Chloride.—Method C of Kinnear and Perren[6] was followed, except that the reaction was carried out at −30 to −27°. The reagents were 200 g. (1.5 moles) of anhydrous aluminum chloride (Baker and Adamson), 824 g. (6 moles) of phosphorus trichloride, and 181 g. (1.5 moles) of 2-chloro-2,3-dimethylbutane. After dissolving the complex in 800 ml. of methylene chloride, the solution was poured into 2600 g. of crushed ice and 500 ml. of concentrated hydrochloric acid.[7] The dark purple liquid left, after removing the methylene chloride, weighed 280 g.

A large-bore, ice water-cooled condenser was attached to the distilling flask and 124.3 g. of white solid was sublimed from the reaction mixture at 10–11 mm. and at a maximum pot temperature of 97°. The remaining liquid was distilled carefully through an 18-in. vacuum-jacketed Fenske column. Thirteen fractions were recovered, b.p. 76.5–127° at 4–5 mm. The n^{25}D values of these fractions varied from 1.4712 to 1.4806. None of these fractions gave evidence of being a single substance and no attempt was made to identify them.

Recrystallization of the solid fraction several times from petroleum ether gave white, easily sublimed plates, which had m.p. 117.5–119.5° and resembled camphor in both odor and appearance. The melting point of t-butylphosphonyl dichloride has been reported[7] as 122–123.5°. The yield was 47.4%, assuming a theoretical production of 1 mole of t-butylphosphonyl chloride from each mole of alkyl chloride.

Anal. Calcd. for $C_4H_9Cl_2OP$: Cl, 40.52. Calcd. for $C_6H_{13}Cl_2OP$: Cl, 34.92. Found: Cl, 39.90, 39.56.

The acid chloride was hydrolyzed by boiling under reflux for 26 hr. with excess hydrochloric acid and alcohol. Recrystallizations of the resulting solid from benzene gave white needles, m.p. 190.3–190.8°. Crofts and Kosolapoff[7] gave m.p. 190–191° for t-butylphosphonic acid.

Anal. Calcd. for $C_4H_{11}O_3P$: P, 22.43; neut. equiv., 138.1. Found: P, 22.43; neut. equiv., 138.7.

A dianilide, prepared from the acid chloride, melted at 254–255°. Kinnear and Perren[6] gave m.p. 256–257° for the dianilide of t-butylphosphonic acid.

N,N-Diethylphosphoramidic Chloride (I).—This compound was prepared (83.4% yield) by the method of Michaelis[16] from 1.4 moles of diethylamine and 4.57 moles of phosphorus oxychloride; the boiling point was 117.8–119° (28.5–29.2 mm.), n^{20}D 1.4639. Michaelis[16] gave b.p. 100° (15 mm.).

1,1,2-Trimethylpropylphosphonic Acid (V).—The method of Whitmore and Badertscher[17] was followed for the production of 1,1,2-trimethylpropylmagnesium chloride (75% yield) from 241 g. (2 moles) of 2-chloro-2,3-dimethylbutane and 48.6 g. (2 g.-atoms) of magnesium turnings (Merck).

To the Grignard reagent was added with stirring 174 g. (0.916 mole) of I, diluted with an equal volume of dry ether. Whereas there was no reaction at 4°, raising the temperature to 35° caused an exothermic reaction, which was controlled by the rate of addition of I. After the mixture stood overnight, excess Grignard reagent was destroyed by adding cracked ice and ammonium chloride solution, plus a small amount of hydrochloric acid to dissolve the basic magnesium salts. The ether layer was separated and the water solution was extracted twice with ether. To the combined ether extracts was added 500 ml. of concentrated hydrochloric acid and the ether was removed by distillation. After the residue was boiled under reflux for 24 hr., 250 ml. more concentrated hydrochloric acid was added, and boiling was continued for several additional hours. The resulting mixture consisted of a clear water layer and an upper layer of orange-colored oil (202 g.).

The water layer was evaporated to dryness in vacuo, and the residue was dissolved in an excess of strong sodium hydroxide solution. Steam distillation of the strongly alkaline solution produced 27.6 g. of diethylamine (determined by titration) and a small amount of heavy, water-insoluble oil with an odor resembling camphor. The remaining alkaline solution was filtered to remove some white solid. The filtrate was extracted twice with benzene and then made strongly acid with hydrochloric acid. The acidic solution was evaporated to dryness in vacuo and the residue was extracted with hot benzene. Concentration of the benzene solution to a small volume, followed by chilling, produced 4.1 g. of white solid, m.p. 147–152°. Further concentration of the filtrate produced only a viscous oil.

To the water-insoluble oil layer (202 g.) was added 1 l. of concentrated hydrochloric acid and 675 ml. of alcohol; the solution was boiled under reflux for 23 hr. Removal of the alcohol by distillation left an aqueous solution containing a small amount of heavy oil. This solution was concentrated to dryness in vacuo and the products were recovered as described above. From the steam distillation, 15.5 g. of additional heavy oil was recovered along with 25.7 g. of additional diethylamine (total recovery of amine was 53.3 g., 80.1%). The additional crude phosphonic acid weighed 84.6 g., giving a total yield of 88.7 g. (58.3%). Two recrystallizations of the phosphonic acid from benzene and one recrystallization from water produced small cubes, m.p. 163.5–164°. A potentiometric titration of this acid gave a sharp break at approximately pH 6.0 and a very faint break at approximately pH 9.5.

Anal. Calcd. for $C_6H_{15}O_3P$: P, 18.64; neut. equiv., 166.2. Found: P, 18.81, 18.68; neut. equiv., 167.0.

To a concentrated solution of the monosodium salt of 1,1,2-trimethylpropylphosphonic acid was added a slight excess of an aqueous solution of benzylisothiouronium chloride. Two recrystallizations of the resulting solid from water gave white needles with a decomposition point of 209.5°.

Anal. Calcd. for $C_{14}H_{25}N_2O_3PS$: P, 9.32; S, 9.65. Found: P, 9.24, 9.25; S, 9.85, 9.74.

A portion of the heavy oil which steam distilled along with diethylamine during the recovery of 1,1,2-trimethylpropylphosphonic acid was saved. After standing at room temperature for slightly more than 1 yr., this oil partially solidified to white flakes. This oily solid had very unusual solubilities. It was insoluble in water, but excessively soluble in organic solvents such as n-hexane, benzene, carbon tetrachloride, ethyl ether, methanol, and ethanol. Attempts to recrystallize the solid from water–alcohol mixtures failed, as did attempts to sublime and to chromatograph the solid. The solid was finally purified by dissolving each gram of the crude material in approximately 2 ml. of n-hexane. This solution was chilled to −50° and the liquid was decanted rapidly from the solid. This process was repeated five times. Although appreciable losses occurred during each recrystallization, a small amount of purified solid was recovered with m.p. 61.0–62.5°.

Anal. Calcd. for $C_{10}H_{24}NO_2P$: C, 54.28; H, 10.93; N, 6.33; P, 14.00. Found: C, 54.22, 54.31; H, 11.46, 11.21; N, 6.15, 6.22; P, 13.73, 13.80.

(12) All melting points are corrected and were determined in a Hershberg apparatus, boiling points are uncorrected, and analyses were determined by Galbraith Laboratories, Knoxville, Tenn.

(13) J. S. Norris and A. W. Olmstead, "Organic Synthesis," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 138.

(14) Molar refraction (MR) "experimental" was obtained by insertion of experimental data into the Lorenz–Lorentz equation; molar refraction "summation" was obtained by summing the atomic and linkage refractivities.

(15) A. Stoll, T. Petrzilka, and V. R. Ruschmann, *Helv. Chim. Acta*, **35**, 1249 (1952).

(16) A. Michaelis, *Ann.*, **326**, 129 (1903).

(17) F. C. Whitmore and D. E. Badertscher, *J. Am. Chem. Soc.*, **55**, 1559 (1933).

The analysis strongly suggested that this compound was N,N-diethyl-1,1,2-trimethylpropylphosphonamidic acid (IV). Although this seemed unlikely because of the fact that this material had steamed distilled from a strongly alkaline solution, the fact that this was an acid was confirmed by a potentiometric titration. A sharp break was obtained at pH 9.2, which corresponded to the neut. equiv. 219.5. The calculated neutralization equivalent for IV is 221.3. A molecular model of this substance showed that the polar groups in the molecule would be surrounded completely by the hydrocarbon groups and, although this is a rather unusual structure, it is believed that such a molecule would exhibit all the properties described.

Further confirmation of the structure of this compound was provided by the observation that heating a portion for 8 days in equal parts of acetic acid and concentrated hydrochloric acid produced diethylamine and the acid (V).

Reaction of 1,1,2-Trimethylpropylphosphonic Acid with Phosphorus Pentachloride and Thionyl Chloride.—To 20 g. (0.12 mole) of 1,1,2-trimethylpropylphosphonic acid (V) was added 50 g. (0.24 mole) of phosphorus pentachloride. After the initial spontaneous reaction, the semiliquid mixture was heated under reflux for 2 hr. Removal of phosphorus oxychloride in vacuo left only a viscous, nonvolatile oil.

A similar reaction was carried out, except that heating was stopped as soon as all the PCl₅ was dissolved. After the removal of phosphorus oxychloride, only an undistillable oil remained.

In a third attempt to produce the acid chloride (VI), a 3:1 molar ratio of PCl₅ to phosphonic acid was used. After all the PCl₅ had been dissolved by heating to 75°, excess PCl₅ was destroyed by reaction with SO₂. The results were the same as in the previous attempts.

A mixture of 43 g. (0.36 mole) of thionyl chloride and 10 g. (0.06 mole) of V was heated under reflux for 5 hr. Removal of excess thionyl chloride in vacuo left a viscous residue. The addition of petroleum ether to this residue dissolved the greater portion of it, but a fraction separated as a sticky white solid. Recrystallization of this solid from petroleum ether gave 2.58 g. of solid, m.p. 108-110°, and a second crop of 0.34 g., m.p. 103-105°. Further recrystallization gave white cubes, m.p. 111.7-112.8°. This product contained no chlorine and no sulfur.

Anal. Calcd. for C₁₈H₃₉O₆P₃ (cyclic trimer anhydride): C, 48.65; H, 8.85; P, 20.91; mol. wt., 444.14. Found: C, 48.14, 48.41; H, 8.56, 8.71; P, 20.79, 20.92; mol. wt., 467.5 (cryoscopic in benzene).

This data strongly indicates that the solid had a structure corresponding to VII. The product of greater solubility in hexane is believed to be a mixture of linear polymeric anhydrides.

t-**Butylphosphinous Chloride (VIII).**—The filtered *t*-butyl-magnesium chloride[17] solution (0.80 mole) was added dropwise to a solution of 237 g. (2.0 moles) of phosphorus trichloride in 400 ml. of ether in a nitrogen atmosphere and at a temperature of −48°. The addition required 2 hr. with vigorous stirring. The mixture was warmed to room temperature; the solid MgCl₂ was removed by filtration under nitrogen and was washed with dry ether. The filtrate was distilled, first at atmospheric pressure and finally at reduced pressure, until the excess PCl₃ was removed. At room temperature a crystalline residue remained. This was sublimed twice at 25 mm. in an atmosphere of nitrogen. This partially purified solid weighed 79.8 g. (62.8%), m.p. 51.5-52.5°.

Anal. Calcd. for C₄H₉Cl₂P: C, 30.21; H, 5.71; Cl, 44.60; P, 19.49. Found: C, 28.79, 28.48; H, 6.14, 6.24; Cl, 43.82, 44.11; P, 18.21, 18.49.

This material seemed to be easily oxidized and gave evidence of being somewhat unstable. These are believed to be the reasons for its unsatisfactory analysis. However, its further reactions are assumed to be adequate evidence for its identity.

t-**Butylphosphonyl Chloride (X).**—A 38.2-g. quantity of VIII was dissolved in 30 ml. of carbon tetrachloride (dried over CaH₂). Oxygen was introduced into this solution, contained in a small, special apparatus which has been described previously.[18] The exothermic reaction was moderated by cooling in an ice bath. The resulting solution was concentrated in vacuo and the solid

residue was sublimed at 25 mm. There was recovered 28.9 g. (68.8%) of solid with a very pleasant camphor-like odor, m.p. 116°. A mixture of this with *t*-butylphosphonyl chloride from the Kinnear and Perren reaction melted at 116-117°.

A sample of this acid chloride, when hydrolyzed with a mixture of concentrated hydrochloric acid and alcohol for 24 hr., gave *t*-butylphosphonic acid, m.p. 190°. When this was mixed with *t*-butylphosphonic acid from the Kinnear and Perren reaction, the m.p. was 190-191°.

1,1,2-Trimethylpropylphosphonous Chloride (IX).—When 0.665 mole of 1,1,2-trimethylpropylmagnesium chloride and 2 moles of PCl₃ were treated by the method employed for preparing VIII, there resulted 53.5 g. (43%) of a fuming liquid, b.p. 50-52° (4-5 mm.), n^{25}D 1.4978.

Anal. Calcd. for C₆H₁₃Cl₂P: C, 38.52; H, 7.01; P, 16.56. Found: C, 38.43, 38.34; H, 7.13, 7.18; P, 16.31, 16.37.

1,1,2-Trimethylpropylphosphonyl Chloride (VI).—IX (45.3 g.) was dissolved in 50 ml. of carbon tetrachloride and oxidized as previously described. In this instance, an unusual quantity of phosgene was produced also during the reaction. Distillation gave 16.2 g. (33%) of red-brown liquid, b.p. 74-75° (1.6 mm.), in addition to 11.9 g. of dark viscous residue. A careful redistillation through a short column gave a colorless liquid, b.p. 77° (2.0 mm.), n^{20}D 1.4855, d^{20}_4 1.2138; MR summation, 47.79[19]; MR experimental, 47.99. Soborovskii[11] gave b.p. 81.5-84° (2 mm.), n^{20}D 1.4728, d^{20}_4 1.1882.

Anal. Calcd. for C₆H₁₃Cl₂OP: C, 35.49; H, 6.45; Cl, 34.92; P, 15.26. Found: C, 35.14, 35.19; H, 6.44, 6.39; Cl, 34.78, 34.82; P, 15.36, 15.37.

A portion of the acid chloride was hydrolyzed by refluxing with concentrated hydrochloric acid and alcohol for 24 hr. Evaporation of the solution to dryness and recrystallization of the residue once from water produced white crystals, m.p. 162°; this melting point was not depressed when this product was mixed with V produced from I and II.

Reaction of 2,3-Dimethyl-2-butene with Diethyl Phosphonate.—A mixture of 414 g. (3.0 moles) of diethyl phosphonate, 84 g. (1.0 mole) of 2,3-dimethyl-2-butene (b.p. 73.5-74.0°), and 5 g. of benzoyl peroxide was heated under reflux for 3 hr. An additional 2 g. of benzoyl peroxide was added, the heating was continued, and two additional 2-g. portions of benzoyl peroxide were added at 3-hr. intervals. A total of 11 g. of benzoyl peroxide was added over a 9-hr. heating period during which time the reaction temperature increased from 93° to 110°. Distillation of the product produced 46.2 g. (20.8%) of a liquid boiling at 64-70° (1.3 mm.). The major portion of this fraction boiled at 67-68° (1.3 mm.), n^{25}D 1.4335, d^{25}_4 0.9774; MR summation, 59.76; MR experimental, 59.16.

Anal. Calcd. for C₁₀H₂₃O₃P: C, 54.03; H, 10.43; P, 13.94. Found: C, 54.06, 54.11; H, 10.65, 10.74; P, 13.68, 13.42.

Although the analysis indicated that this compound was slightly impure, it was identified further as diethyl 1,1,2-trimethylpropylphosphonate by hydrolyzing a portion with equal volumes of acetic acid and concentrated hydrochloric acid. The resulting solid melted at 162° and the same melting behavior resulted when this material was mixed with 1,1,2-trimethylpropylphosphonic acid prepared from I and II or from VI.

Reaction of Diethyl 1,1,2-Trimethylpropylphosphonate with Phosphorus Pentachloride.—A 22.2-g. portion (0.1 mole) of diethyl 1,1,2-trimethylpropylphosphonate and 43.6 g. (0.21 mole) of phosphorus pentachloride was heated on a steam bath for 2 days. Excess PCl₅ was destroyed with SO₂ and an attempt was made to distil the crude product. The major product was a viscous, undistillable residue and no VI was recovered. Hydrolysis of this viscous residue resulted in the recovery of V, m.p. 163-164°.

(18) A. F. Isbell and F. T. Wadsworth, *J. Am. Chem. Soc.*, **78**, 6043 (1956).

(19) The value 4.27 was used for phosphonate P [M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 219 (1948)].