Reaction between Chloromethyltrimethylsilane and Lithium in Inert Solvents.—In a three-necked flask, equipped with a stirrer and a reflux condenser, a mixture of 100 g. of chloromethyltrimethylsilane, 200 ml. of *n*-heptane, and 7 g. of lithium wire was refluxed with vigorous stirring. Under these conditions, the reaction began immediately. After 24 hr. the reaction mixture was hydrolyzed and the organic layer separated and dried. The product solution obtained in this way was pale yellow in color. Tetramethylsilane and the solvent were removed from the mixture by an atmospheric pressure distillation through a column packed with glass helices. After removal of the solvent the residual mixture was cooled and a fractionation was carried out under a pressure of 1 mm. The receiver was maintained at room temperature and a −79° trap was placed between the collecting head of the fractionating column and the pump. The product mixture then was separated into the material collected in the −79° trap, the material which remained in the receiver, and the residue remaining in the reaction (boiling) flask.

The products were identified by matching chromatograms with authentic samples. The material collected in the −79° trap contained 2,2,5,5-tetramethyl-2,5-disilahexane and 2,2,4,4-tetramethyl-2,4-disilahexane, the mixture in the receiver contained isomers VIII and IX of molecular formula $C_{12}H_{32}Si_3$, and the residue in the boiling flask appeared to be a complex mixture of less volatile materials.

Attempted Preparation of 1,1-Dimethyl-1-silacyclopropane. A. 1. Reaction of Chloromethyltrimethylsilane with Lithium.—One hundred grams of chloromethyltrimethylsilane dissolved in 200 ml. of *n*-heptane was refluxed with 6 g. of lithium wire in a three-necked flask fitted with a glass helix packed distilling column equipped with a reflux head. The material boiling below 30° was removed continuously from the top of the column. The material, thus recovered, was introduced into the vacuum apparatus and fractionated in a low temperature vacuum distillation column at −79°. The infrared spectrum of the distillate showed a strong tetramethylsilane spectrum and a weak absorption at 1030 cm.$^{-1}$. Several subsequent distillations through the low temperature column at −79° increased the concentration of the constituent exhibiting the infrared absorption with typical pqr structure at 1030 cm.$^{-1}$, but it proved impossible to obtain this substance in a pure form by this means. Passage of the mixture through a silicone rubber gas chromatography column also failed to effect a separation and apparently destroyed the substance responsible for the peak at 1030 cm.$^{-1}$.

2. Attempted Chemical Separation of the Volatile Product Mixture.—Treatment of 16 mmoles of the distillate, just described, with excess chloroplatinic acid in acetic anhydride in the vacuum apparatus produced a brown precipitate. Fifteen mmoles of volatile material was recovered from the treatment. The recovered material exhibited no infrared absorption at 1030 cm.$^{-1}$. Treatment of the brown precipitate with either potassium iodide in acetone or tributylphosphine failed to regenerate any material exhibiting an infrared absorption at 1030 cm.$^{-1}$.

Treatment of pure tetramethylsilane with chloroplatinic acid in acetic anhydride also produced a brown precipitate similar in appearance to that previously described.

B. Reaction of Chloromethyltrimethylsilane with Sodium.—A reaction between chloromethyltrimethylsilane and sodium, under conditions where the most volatile products could be removed continuously resulted in the removal only of tetramethylsilane.

C. Reaction of Previously Prepared Organometallic Compounds with Chloromethyltrimethylsilane.—In several different experiments, solutions of chloromethyltrimethylsilane in *n*-heptane were treated with various nucleophilic reagents dissolved in or suspended in hexane. The bases studied in this fashion were potassium *t*-butoxide, triphenylmethylsodium, phenylsodium, and lithiomethyltrimethylsilane. All of these reactions were carried out under an atmosphere of dry nitrogen. In most cases the reactions were effected at reflux temperature (about 100°) and the more volatile materials were removed as formed. In some cases the reaction mixture was stirred at room temperature and the volatile products removed by a nitrogen sweep into a −79° trap. Only in the case of reactions involving *n*-butyllithium, carried out at elevated temperature, did the volatile product show an infrared absorption at 1030 cm.$^{-1}$. The fraction in which this absorption was found exhibited six peaks when samples of it were injected into a 20-ft. Apiezon M on Chromosorb gas chromatography column maintained at 60° or a 4-ft. silicone rubber column maintained at 25°. Isolation and examination of the materials corresponding to each of these peaks showed that none of them was the desired 1,1-dimethyl-1-silacyclopropane and none of these materials exhibited the infrared absorption at 1030 cm.$^{-1}$.

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Highly Branched Alkylphosphorus Compounds.
I. Synthesis of 2,3-Dimethylbutylphosphonyl Chloride[1,2]

SIDNEY H. METZGER AND A. F. ISBELL[3]

The Department of Chemistry, Agricultural and Mechanical College of Texas, College Station, Texas

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A number of unequivocal syntheses leading to 2,3-dimethylbutylphosphonyl chloride have been developed. This and related compounds have been characterized carefully. These syntheses have provided the opportunity to make a brief study of the chemical reactivity of alkyl halides, an alcohol derivative, and an ester of an alkylphosphonic acid, all of which contained the 2,3-dimethylbutyl group. As expected, these compounds were found to have low orders of reactivity in SN2 type reactions.

During the study of the reaction of hydrocarbons with phosphorus trichloride and oxygen,[4] the hydrocarbon 2,3-dimethylbutane was employed. From this reaction, one might expect to obtain the two isomeric compounds, 2,3-dimethylbutylphosphonyl chloride (I) and 1,1,2-trimethylpropylphosphonyl chloride (II). In fact, Soborovskii, Zinov'ev, and Englin[5] claimed to have isolated these two products from the reaction in question and reported that the product contained 92 parts of II to 8 parts of I. Since this is a very important reaction in the study of the oxidative phosphonation of hydrocarbons, since Soborovskii and coworkers gave little evidence of the purity or even the identity of the two isomers, and since their analytical procedure seemed to be open to question, we have un-

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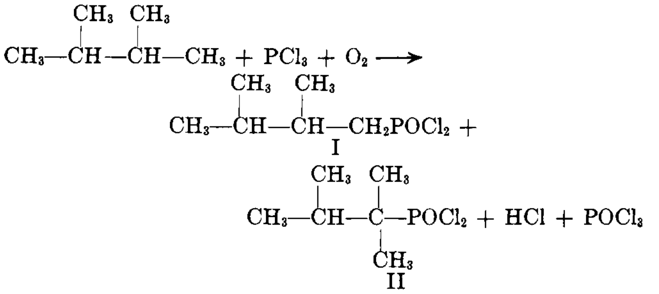
[1] Taken in part from the thesis submitted by S. H. Metzger in partial fulfillment of the requirements for the M. S. degree at the A. & M. College of Texas, August, 1956.

[2] Presented in part at the 134th National Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

[3] To whom all inquiries should be addressed.

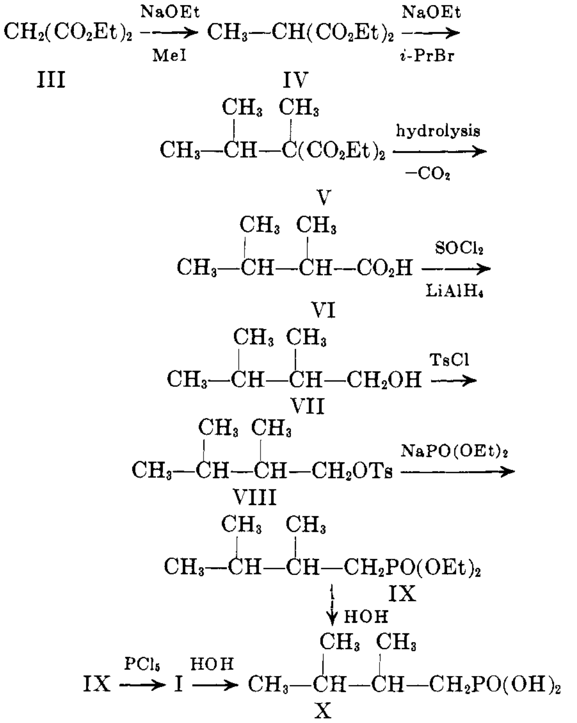
[4] A. F. Isbell and F. T. Wadsworth, *J. Am. Chem. Soc.*, **78**, 6042 (1956).

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



dertaken the unequivocal synthesis of these two compounds. The synthesis of I is reported herein and the synthesis of the related isomer in the succeeding paper.

The following was the first successful route to I.



Although this rigorous synthesis presented a number of problems, all were solved. Alkylation of malonic ester (III) with methyl iodide produced IV, which was separated from unalkylated III by the excellent procedure of Michael.[6] Following the procedure of Wallingford, Thorpe, and Homeyer,[7] IV was alkylated with isopropyl bromide, giving V. The acid (VI) and the alcohol (VII) were produced by relatively conventional procedures as was also the tosyl ester (VIII). The procedure of Myers, Preis, and Jensen[8] was employed for the formation of the phosphonate ester (IX). Although the expected product was obtained, the reaction was quite sluggish. If this reaction proceeds by the S_N2 mechanism, the methyl and isopropyl groups on C-2 would be expected to produce serious strain in the transition state. Of course, this is quite similar to the sluggish behavior of neopentyl halides in S_N2 reactions. The ester (IX) could be converted to the corresponding acid (X) and the desired acid chloride (I). The acid chloride (I) was hydrolyzed rapidly to the acid (X) at room temperature, whereas refluxing the ester (IX) with a mixture of alcohol and hydrochloric acid required a number of days for complete hydrolysis. Our physical constants for I differed from those reported by Soborovskii, *et al.*[5]

Since VI was available, a quantity was converted into the N-methylanilide and an attempt was made to reduce this anilide with lithium aluminum hydride by the method of Weigand and co-workers[9] to 2,3-dimethylbutyraldehyde. It was believed that this aldehyde could be converted into X by a two-step synthesis, but the failure to obtain significant quantities of 2,3-dimethylbutyraldehyde prevented further investigations along this line.

Another synthesis which appeared worthy of investigation involved the anti-Markownikoff addition of HBr to the terminal olefin, 2,3-dimethyl-1-butene (XI), especially since this reaction apparently has never been reported and we wished to determine the reactivity of the highly branched bromide, 1-bromo-2,3-dimethylbutane (XII), with triethyl phosphite.

The dehydration of 2,3-dimethyl-2-butanol (XIII) resulted in a mixture of the two olefins, 2,3-dimethyl-1-butene (XI) and 2,3-dimethyl-2-butene (XIV). Whitmore[10] has shown that a mixture of these two olefins can be isomerized completely to the terminal olefin (XI) by taking advantage of the mobile equilibrium between the two and the lower boiling point of XI. The addition of HBr to XI in a hexane solution in the presence of benzoyl peroxide at −33 to −20° produced only the tertiary bromide, 2-bromo-2,3-dimethylbutane, but a similar reaction at −48° in the presence of the more reactive and more soluble peroxide, ascaridol, gave a 60% yield of pure XII.

The bromide (XII) was converted into the phosphonate ester (IX) by the Arbuzov reaction, but the reaction was surprisingly sluggish.

Since the synthesis of the olefin (XI) by way of the Grignard reaction on methyl isopropyl ketone and the tertiary alcohol (XIII) is a somewhat laborious procedure, some shorter routes from readily available starting materials were investigated. These further reactions provide additional knowledge concerning the nature of certain reactions capable of producing organophosphorus products. The peroxide-catalyzed chlorination of 2,3-dimethylbutane with sulfuryl chloride produced what appeared to be a mixture of the isomeric monochlorides (XV). This crude mixture was dehydrohalogenated to the mixture of olefins (XI and XIV), which was converted completely to the terminal olefin (XI) by isomerization.

Since the exchange of Cl for I takes place with ease with a primary chloride but essentially not at all with a tertiary chloride, an attempt was made to convert the chlorohexanes (XV) to 1-iodo-2,3-dimethylbutane (XVI). This appeared especially feasible because any tertiary iodide produced should hydrolyze quickly on contact with water. Although such predictions appear to have been realized, pure XVI was not recovered; it seemed to have been contaminated with ketone condensation products. Such products could have originated from the production of some HCl or HI (dehydrohalogenation or hydrolysis of tertiary

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[6] A. Michael, *J. prakt. Chem.*, [2]**72**, 537 (1905).

[7] V. H. Wallingford, M. A. Thorpe, and A. H. Homeyer, *J. Am. Chem. Soc.*, **64**, 580 (1942).

[8] T. C. Myers, S. Preis, and E. V. Jensen, *ibid.*, **76**, 4172 (1954).

[9] F. Weigand, G. Eberhard, H. Linden, F. Schafer, and I. Eigen, *Angew. Chem.*, **65**, 525 (1953).

[10] F. C. Whitmore, *Chem. Eng. News*, **26**, 668 (1948).

halide), which in turn would cause the condensation of the reaction solvent, 2-butanone.

That the crude iodohexane contained at least 32% of 1-iodo-2,3-dimethylbutane was shown by the fact that the crude XVI was converted into IX in a yield of 32%. Even a mixture of primary and tertiary hexyl iodides in the crude XVI was expected to produce IX as the only phosphonate ester because tertiary halides generally fail to take part in the Arbuzov reaction. The assumptions relating to the preparation of IX from XV appear to have been valid because IX was recovered in good state of purity from the Arbuzov reaction and there was no evidence of an isomeric impurity. Although the production of IX from 2,3-dimethylbutane through XVI gave an over-all yield of only about 10%, in a number of respects this is an excellent route because of the use of readily available reagents and because of the simplicity of the reactions.

A further route to the symmetrical olefin (XIV) was indicated by the claim[11] that bromination of 2,3-dimethylbutane produces a quantitative yield of 2,3-dibromo-2,3-dimethylbutane (XVII), and debromination of XVII with zinc produces XIV. The bromination reaction was found to be excellent, but debromination of XVII gave a disappointing yield of XIV. There was evidence that the zinc bromide, produced during the debromination reaction, brought about some extensive isomerization and polymerization reactions, but these by-products were not investigated.

A number of investigators[12] have shown that dialkyl phosphonates and related compounds may be added to certain olefins in the presence of peroxides or free radical-generating catalysts to give the expected anti-Markownikoff products. It seemed desirable to determine the utility of this reaction when a highly branched olefin such as XI is employed. We found this to be one of the best routes to the phosphonate ester (XI).

Experimental[13]

Diethyl Methylisopropylmalonate (V).—The preferred method was that of Wallingford, Thorpe, and Homeyer.[7] A mixture of sodium ethylate (4.2 moles) in 1.2 kg. of ethyl carbonate was prepared. To this slurry 730 g. (4.2 moles) of IV was added and ethanol, as well as some of the ethyl carbonate, was removed by distillation through as 18-in. column at 75–78 mm. To the resulting clear solution, 542 g. (4.41 moles) of isopropyl bromide was added dropwise at 91–99°. When the reaction was complete, the inorganic salt was extracted with water and the product was dried and distilled. There was recovered 621.5 g. (68.5%) of liquid, b.p. 115.5–124° (27 mm.). Careful redistillation gave a product, b.p. 121–124° (27.4 mm.),[14] n^{25}_{D} 1.4226.

2,3-Dimethylbutyric Acid (VI).—The saponification procedure involved some modifications of previously reported methods.[15] A mixture of 714 g. of diethyl methylisopropylmalonate and a solution of 1384 g. of potassium hydroxide in 8 l. of 95% ethanol was boiled under reflux for 29 hr. Water was added and all the alcohol was removed by distillation *in vacuo*. The ice-cold water solution was acidified with concentrated sulfuric acid, the potassium sulfate was removed by filtration, and the methylisopropylmalonic acid was extracted from the water with ether. After removing the ether, the crude acid was dried by an azeotropic distillation with benzene. The malonic acid was decarboxylated by heating for 2 hr. at 144–176°. Initial distillation gave 267.3 g. of product, b.p. 104–107° (27–28 mm.). Careful redistillation produced 224 g. (58.5%) of 2,3-dimethylbutyric acid, b.p. 104.8–107.9° (27–28 mm.), n^{25}_{D} 1.4129; lit.[16] b.p. 90° (16 mm.), n^{20}_{D} 1.4146.

2,3-Dimethylbutyryl Chloride.—This was prepared according to the method of Kent and McElvain.[17] From 224 g. (1.93 moles) of VI and 264 g. (2.22 moles) of thionyl chloride, there was produced a 90% yield of 2,3-dimethylbutyryl chloride, b.p. 133–136°, n^{20}_{D} 1.4248, d^{20}_{4} 0.9760; MR summation,[18] 34.79; MR experimental, 35.25; lit.[16] b.p. 136–137° (751 mm.), d^{20}_{5} 0.9795.

The corresponding amide was prepared and had m.p. 130°, lit.[14] m.p. 129°.

N-Methyl-2,3-dimethylbutyranilide.—To 183 g. (1.81 moles) of triethylamine, 196 g. (1.83 moles) of N-methylaniline, and 500 ml. of dry benzene was added at 8–16° 222 g. (1.65 moles) of 2,3-dimethylbutyryl chloride. Triethylamine hydrochloride was removed by filtration; the filtrate was washed with water, dried, and distilled. The desired product had a boiling point of 109–111° (2 mm.), n^{20}_{D} 1.5102, yield 319.2 g. (94.5%).

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.92, 75.86; H, 9.12, 9.05; N, 6.91, 6.99.

Reduction of N-Methyl Anilides with Lithium Aluminum Hydride.—Repeated attempts to prepare the corresponding aldehydes from N-methyl-2,3-dimethylbutyranilide, N-methylbutyranilide and N-methylisovaleranilide by the reverse addition of lithium aluminum hydride, according to the method of Weigand, *et al.*,[9] failed. Both ether and tetrahydrofuran and combinations of the two were used. All reactions were run in a dry nitrogen atmosphere. The ether was dried over calcium hydride and sodium. The tetrahydrofuran was refluxed for 14 days over sodium and sodium hydroxide, distilled, and then redistilled from lithium aluminum hydride. All reactions were conducted at 0° or below. In all attempts, the characteristic odors of the aldehydes could be detected but no significant amounts of these products were isolated.

2,3-Dimethyl-1-butanol (VII).—The reaction between 17.5 g. (0.46 mole) of lithium aluminum hydride and 99 g. (0.735 mole) of 2,3-dimethylbutyryl chloride was carried out following the general procedure of Nystrom and Brown.[19] There was obtained 63.3 g. (84.4%) of VII, b.p. 85.7–85.9° (68.6 mm.), n^{20}_{D} 1.4206, d^{20}_{4} 0.8279; MR summation,[18] 31.43; MR experimental, 31.34. Gorski[20] gave b.p. 144–145° (761 mm.), $n^{20.5}_{D}$ 1.4195, d^{20}_{4} 0.8297.

2,3-Dimethylbutyl *p*-Toluenesulfonate (VIII).—Since the method of Tipson[21] did not prove to be entirely satisfactory, it was modified. To a solution of 20 g. (0.196 mole) of VII in 200 ml. of dry pyridine was added 41.2 g. (0.217 mole) of *p*-toluenesulfonyl chloride at −5° with vigorous stirring. The mixture was stirred for 2 hr. more and then put in a refrigerator at 0° for 19 hr. To the thick slurry, 20 ml. of water was added with vigorous stirring at such a rate that the temperature did not rise above 0°, then 200 ml. more water was added. The solution was extracted with chloroform and the chloroform extract was washed free of pyridine by adding 300 ml. of ice-cold 5 *N* sulfuric acid while the mixture was stirred and cooled in an ice bath. The chloroform layer was separated, washed with sodium bicarbonate solution and water, and distilled *in vacuo* finally at a pressure of 1 mm. and at a maximum temperature of 75° to remove all volatile materials. The residual crude sulfonate ester weighed 42.3 g.

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(11) A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, **8**, 438 (1943).

(12) (a) S. Preis, T. C. Myers, and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 6225 (1955); (b) W. E. Hanford and R. M. Joyce, Jr., U. S. Patent 2,478,390 (1949); (c) G. A. Loughran and E. O. Hook, U. S. Patent 2,794,821 (1957); (d) U. S. Rubber Company, British Patent 694,772 (1953); (e) N. V. de Bataafsche Petroleum Maatschappij, Dutch Patent 69,357 (1952); (f) A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **74**, 3282 (1958); (g) **80**, 714 (1958).

(13) Melting points were determined with a Hershberg apparatus and are corrected; boiling points are uncorrected. Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn.

(14) P. van Romburgh [*Rec. trav. chim.*, **5**, 232 (1886)] reported b.p. 221° (752 mm.).

(15) A. W. Crossley and H. R. Le Sueur, *J. Chem. Soc.*, **77**, 83 (1900); J. C. Shivers, B. E. Hudson, and C. P. Hauser, *J. Am. Chem. Soc.*, **66**, 309 (1944).

(16) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., 1953, p. 288.

(17) R. E. Kent and S. M. McElvain, *Org. Syn.*, **25**, 58 (1945).

(18) Molar refraction (MR) "experimental" was obtained by substitution of experimental data into the Lorenz–Lorentz equation; molar refraction "summation" was obtained by appropriate summing of the atomic refractivities and of those for linkages in the molecule.

(19) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

(20) A. Gorksi, *Chem. Zentr.*, **1**, 2022 (1913).

(21) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(84.4%). Attempts to distill this ester, even at low pressures, always resulted in decomposition.

Anal. Calcd. for $C_{13}H_{20}O_3S$: C, 60.90; H, 7.86; S, 12.51. Found: C, 60.98, 61.28; H, 7.80, 7.94; S, 12.53, 12.31.

2,3-Dimethyl-2-butanol (XIII).—This was prepared by condensing the Grignard reagent from 292 g. (2.06 moles) of methyl iodide and 53.5 g. (2.20 g.-atoms) of magnesium turnings with 172 g. (2 moles) of 3-methyl-2-butanone. The product weighed 166.6 g. (81.6%), b.p. 62° (75.5 mm.), $d^{25}{}_4$ 0.8201, $n^{25}{}_D$ 1.4140; MR summation,[18] 31.43; MR experimental, 31.13; lit.[22] b.p. 63–66° (80 mm.), $d^{25}{}_4$ 0.8155, $n^{25}{}_D$ 1.4155.

2,3-Dimethyl-1-butene (XI).—This was similar to procedures which have been described previously.[10,23] From 251 g. (2.46 moles) of 2,3-dimethyl-2-butanol and 288 g. of 30% sulfuric acid there was obtained an 85% yield of 2,3-dimethyl-1-butene, b.p. 56.0–56.5° (752.5 mm.), lit.[24] b.p. 55.6–56.0° (760 mm.).

Addition of Hydrogen Bromide to 2,3-Dimethyl-1-butene.—A mixture of 42 g. (0.5 mole) of XI, 400 ml. of *n*-hexane, and 4.2 g. (0.025 mole) of ascaridol[25] was cooled to −40°. Anhydrous hydrogen bromide was passed into the solution at this temperature to saturation over a period of 2 hr. During this time a flocculent solid and finally a dark brown oil separated. After standing overnight at room temperature, the clear solution was distilled at 20 mm. to remove hexane and excess hydrogen bromide. There remained 72.1 g. of crude brown oil (87.4%). This oil was stirred vigorously with aqueous sodium carbonate for 90 min. at room temperature to hydrolyze any tertiary bromide. After washing with water and drying over calcium chloride, the oil was distilled, yielding 49.5 g. (60.0%) of liquid, b.p. 62.5–63.5° (49 mm.), $n^{25}{}_D$ 1.4497, $d^{25}{}_4$ 1.1829; MR summation,[18] 37.67; MR experimental, 37.48.

Anal. Calcd. for $C_6H_{13}Br$: Br, 48.41. Found: Br, 48.39, 48.30.

2,3-Dibromo-2,3-dimethylbutane (XVII).—An essentially quantitative yield of XVII resulted when bromine was added to an excess of 2,3-dimethylbutane.[11] No attempt was made to purify water-sensitive XVII.

The best procedure for the debromination of XVII involved the slow addition of zinc granules (40 mesh) to a 95% ethanol solution of XVII with cooling at 20° and with good stirring. When there was no further exothermic reaction, the mixture was distilled until a vapor temperature of 75° was attained. The distillate was washed well with water to remove ethanol, dried over calcium chloride, and redistilled. The combined crude product from a number of such preparations gave only a 13.2% yield of XIV, b.p. 73°, lit.[24] b.p. 72.9–73.2° (760 mm.). In addition to this fraction, considerable quantities of lower and higher boiling products were recovered.

Chlorination of 2,3-Dimethylbutane.—A mixture containing 268 g. (3.21 moles) of 2,3-dimethylbutane, 135 g. (1.0 mole) of redistilled sulfuryl chloride, and 2.42 g. (0.01 mole) of benzoyl peroxide was treated by the general procedure of Kharasch and Brown.[26] The first distillation of the product resulted in an 81% yield of crude monochlorides, b.p. 47–56° (80 mm.). This was redistilled at atmospheric pressure in the hope of being able to separate the two isomers. However, pure products were not recovered. The fraction boiling at 112–119.5° (756 mm.) appeared to contain 61.5% of 2-chloro-2,3-dimethylbutane by the analytical method of Walling, Kharasch, and Mayo,[27] and the fraction boiling at 119.5–124° (756 mm.) indicated an 11.6% content of the tertiary chloride. Assuming the remaining material to be 1-chloro-2,3-dimethylbutane, the chlorination reaction produced the two isomers in the ratio of 48 parts of the tertiary chloride to 52 parts of the primary chloride.

This mixture of crude chlorides was dehydrohalogenated with alcoholic potassium hydroxide to an approximate 50% yield of the mixture of olefins XI and XIV.

1-Iodo-2,3-dimethylbutane (XVI).—An 82.4-g. portion of the crude monochloride, b.p. 119.5–124°, from the previous preparation was treated with 133 g. of sodium iodide and 990 ml. of 2-butanone.[28] After removing most of the solvent, the crude product was washed with water, dilute sodium bisulfite, dilute sodium bicarbonate, and water. It was dried first over anhydrous magnesium sulfate and then over Drierite. Careful distillation of the product produced a number of fractions, b.p. 59–65.5° (20–22 mm.), wt. 111 g. The $d^{25}{}_4$ values of these fractions were less than 1.20. Since the densities of hexyl iodides are of the order of 1.44, these fractions were obviously impure. Furthermore, they all possessed the characteristic odor of ketone condensation products.

Diethyl 2,3-Dimethylbutylphosphonate (IX).—A solution of 0.144 mole of diethyl sodiophosphonate in dry tetrahydrofuran was added to 32.2 g. (0.126 mole) of VIII, also dissolved in dry tetrahydrofuran, following the procedure of Myers, Preis, and Jensen.[8] However, after standing overnight at room temperature, no solid had separated. Refluxing the solution for 26 hr. caused the slow separation of a white solid. The removal of this sodium *p*-toluenesulfonate by filtration was difficult because of its finely divided state. Therefore, 200 ml. of petroleum ether (b.p. 30–60°) was added and the solution was filtered until a clear filtrate resulted. The solid was washed well with tetrahydrofuran. Distillation of the filtrate produced 12.7 g. (50%) of IX, b.p. 108–109° (5.5 mm.), $n^{20}{}_D$ 1.4303, $d^{20}{}_4$ 0.9705; MR summation, 59.24[18,29]; MR experimental, 59.20.

Anal. Calcd. for $C_{10}H_{23}O_3P$: P, 13.94. Found: P, 14.07, 13.81.

2,3-Dimethylbutylphosphonic acid (X) was prepared by hydrolyzing the ester (IX) with excess hydrochloric acid. Several recrystallizations of the solid product from petroleum ether gave a white waxy solid, m.p. 95–96°. A potentiometric titration of this acid produced a sharp break at about pH 5.8 and a very weak break at about pH 10.

Anal. Calcd. for $C_6H_{15}O_3P$: P, 18.64; neut. equiv., 166.16. Found: P, 19.09, 19.02; neut. equiv., 167.3.

A solution of the monosodium salt of this acid was prepared by a titration with sodium hydroxide to pH 5.80. An excess of an aqueous solution of benzylisothiuronium chloride was added with stirring, and the mixture was chilled. Several recrystallizations of the resulting solid from water gave white needles, m.p. 182.3° (dec.).

Anal. Calcd. for $C_{14}H_{25}N_2O_3PS$: P, 9.32; S, 9.65. Found: P, 9.32, 9.15; S, 9.73, 9.45.

A mixture containing 25.2 g. (0.3 mole) of XI, 153.5 g. (1.11 moles) of diethyl phosphonate, and 3 g. of benzoyl peroxide was treated by a previously described procedure.[12a] Two distillations of the product gave a 76.6% yield of IX, b.p. 88.5–91.5° (3 mm.), $d^{25}{}_D$ 0.9692, $n^{25}{}_D$ 1.4302. Hydrolysis of a portion of this ester resulted in the recovery of the acid (X), m.p. 95–96°.

Crude XVI (88.1 g.) was heated under reflux for 2.5 hr. with 166 g. of triethyl phosphite. Distillation gave 29.5 g. (32% yield from the crude halide) of IX, b.p. 89–91° (2 mm.), $n^{25}{}_D$ 1.4307. Hydrolysis of this ester also yielded the corresponding acid (X), m.p. 93.5–95.0°.

IX also was prepared in a 27% yield by heating 45.2 g. (0.274 mole) of XII with 91 g. (0.49 mole) of triethyl phosphite under reflux for 6 hr. The product had b.p. 85–87° (2 mm.), $n^{30}{}_D$ 1.4292. XII appeared to react in a very sluggish fashion. The hydrolysis of IX yielded the same acid (X).

It was noted in all instances that ester IX hydrolyzed very slowly. For instance, refluxing the ester with a 50:50 mixture by volume of concentrated hydrochloric acid and 95% ethanol for a period of 48 hr. caused no more than one-third of the ester to be converted to the acid. A much longer hydrolysis eventually resulted in an essentially quantitative yield of the acid.

2,3-Dimethylbutylphosphonyl Chloride (I).—In a 100-ml. flask, protected from moisture, 25.4 g. (0.122 mole) of phosphorus pentachloride was added slowly to 10.17 g. (0.0458 mole) of IX. At room temperature there appeared to be no reaction, but on heating to 60–70° a rather vigorous reaction occurred. The reaction was completed by heating under reflux for 1 hr. The excess phosphorus pentachloride was destroyed by reaction with

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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.), $n^{20}{}_{\text{D}}$ 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.), $n^{20}{}_{\text{D}}$ 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.

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

SIDNEY H. METZGER, OTTOKAR H. BASEDOW,[2] AND A. F. ISBELL[3]

Agricultural and Mechanical College of Texas, College Station, Texas

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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

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[2] Post-doctoral fellow.

[3] To whom all inquiries should be addressed.

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