and opening the vessel, the contents were filtered to remove solid sodium phenoxide and some small pieces of sodium. The liquid products, which weighed 258 g., were then carefully fractionated at 4 mm. The first material collected from this fractionation was shown to be a mixture of phenyldimethylphenoxysilane and dimethyldiphenoxysilane by its infrared spectrum and by vapor phase chromatography. In this case the chief component of the mixture had a retention time identical to that of an authentic sample of phenyldimethylphenoxysilane. Chromatographic analysis of some of the last materials to distil from this reaction mixture indicated that one of the components was 1,3-diphenyltetramethyldisiloxane. Infrared analysis of this sample also confirmed the presence of a phenyl-silicon bond.

Tetraethoxysilane and Sodium.—Tetraethoxysilane (350 g., 1.68 moles) and sodium (42 g., 1.82 g.-atoms) were heated 24 hours at 260°. A slow pressure increase was observed, reaching a maximum of 580 p.s.i. at 259° at the end of the heating period. On opening the pressure vessel a non-condensable gas was recovered whose infrared spectrum showed that it was ethylene. The liquid fractions contained no compounds with an ethyl–silicon bond.

Benzyltriethoxysilane and Sodium.—Benzyltriethoxysilane (214 g., 0.84 mole) was gently refluxed in the presence of 0.5 g. of sodium. The temperature of the refluxing liquid decreased from 240° to 190° during a 10-hour period. The liquid was cooled, the pellet of sodium was removed, and the liquid was acidified by adding trimethylchlorosilane. On distillation the following fractions were recovered: tetraethoxysilane (50.4 g.) boiling at 93° at 30 mm., $n^{25}\mathrm{D}$ 1.3872, d^{25} 0.9298, $R\mathrm{D}$ 0.2532, (calcd. 0.2499); benzyltriethoxysilane, 96.5 g., boiling at 150° at 30 mm., $n^{25}\mathrm{D}$ 1.4621, d^{25} 0.9825, $R\mathrm{D}$ 0.2799 (calcd. 0.2795); $(C_7H_7)_2Si(OEt)_2$, b.p. 176° at 5 mm., $n^{25}\mathrm{D}$ 1.5146, d^{25} 1.024, $R\mathrm{D}$ 0.2939; $(C_7H_7)_2Si(OEt)_2$, b.p. 203° at 5 mm., $n^{25}\mathrm{D}$ 1.5082, d^{25} 1.0437, $R\mathrm{D}$ 0.2864. The calculated $R\mathrm{D}$ value for dibenzyldiethoxysilane is 0.2935. The calculated $R\mathrm{D}$ value for ditolyldiethoxysilane is 0.2862. Vapor phase chromatograms of these two fractions showed two components present. The total yield of these two fractions was 53.3 g.

1,2-Dimethyltetramethoxydisilane with Sodium. At Lower Temperature.—1,2-Dimethyltetramethoxydisilane (105 g., 0.50 mole) was heated to reflux (164°) with about 0.1 g. of sodium. The temperature of the boiling liquid slowly decreased to 146°. The liquid was cooled and placed under a fractionating column. Fractionation of the material resulted in the recovery of 18.2 g. of methyltrimethoxysilane, b.p. 102–103°, $n^{25}\mathrm{D}$ 1.3698, d^{25} 0.9458. The material in the flask was filtered to give 84.8 g. of a clear white liquid whose Si–Si equivalent was 163. The Si–Si analysis shows that both the starting material and the final residue contain 0.52 equivalent of silicon bonded to silicon. The residue therefore must contain materials such as a trisilane or higher polysilane.

At 250°.—A mixture of 1,2-dimethyltetramethoxydisilane (136.6 g., 0.65 mole) and sodium (12 g., 0.53 g.-atom) was heated 16.5 hours at 250°. The pressure within the vessel rose rather sharply during the warming up period and showed a slow rise from 203 to 297 p.s.i. at constant temperature. There were recovered from the products Me_2O (10 g., 0.22 mole) which collected in a Dry Ice trap; Me_3SiOMe, b.p. 57° (5.6 g., 0.05 moles); $Me_2Si(OMe)_2$, b.p. 81–82° (39.1 g., 0.32 mole); and $MeSi(OMe)_3$, b.p. 102–103° (31.8 g., 0.23 mole). There remained a non-volatile residue weighing 62 g. This residue was a gray solid containing some pieces of unreacted sodium.

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., PLASTICS DIVISION, SPRINGFIELD, MASS.]

Reactions of Phosphorus Halides with Active Metals in Polar Solvents. I. Cleavage of Tetrahydrofuran with Formation of a Phosphorus–Carbon Bond[1]

BY ALBERT Y. GARNER[2] AND ALFRED A. TEDESCHI

RECEIVED JULY 11, 1962

It has been found that phosphorus halides react with active metals in polar solvents. The course and products of the reactions are dependent upon (1) the valence state of the phosphorus, (2) the number of halogen atoms on the phosphorus and (3) the solvent. Diphenylchlorophosphine, magnesium and tetrahydrofuran react to form diphenyl-4-hydroxybutylphosphine (I). The structure of this product was demonstrated, and mechanistic considerations point to a cyclic transition state rather than a radical or anionic intermediate.

It has been discovered that phosphorus halides react with active metals such as magnesium zinc and lithium in polar solvents. The generality of the reaction for phosphorus halides was shown by experiments using phosphorus oxychloride ($POCl_3$), phosphorus trichloride (PCl_3), phenyldichlorophosphine ($C_6H_5PCl_2$), diphenylchlorophosphine [$(C_6H_5)_2PCl$], diphenylphosphinyl chloride [$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}Cl$], phenylphosphonyl dichloride ($C_6H_5\overset{\overset{O}{\uparrow}}{P}Cl_2$), methyldichlorophosphine (CH_3PCl_2), methylphosphonyl dichloride ($CH_3\overset{\overset{O}{\uparrow}}{P}Cl_2$), phenylchloromethylphosphinyl chloride ($C_6H_5\underset{\underset{Cl}{|}}{\overset{\overset{O}{\uparrow}}{P}}CH_2Cl$), and phosphorus pentachloride with magnesium in solvents such as: tetrahydrofuran, acetone, acetonitrile, chloroform and ethyl acetate. In each case, there was no reaction if any of the three components were absent. When all three components were present, there was an immediate, spontaneous reaction in which the metal was consumed, and the solvent was caused to reflux. Solvents such as benzene, carbon tetrachloride, diethyl ether, dioxane, dimethoxyethane and furan gave no reaction.

Although the reaction of these halides with the metals is a general one, the course of the reaction appears to depend upon (a) the number of halogen atoms which are attached to the phosphorus atom, upon (b) the oxidation state of the phosphorus, and upon (c) the solvent. For these reasons, this initial paper is confined to the reaction of diphenylchlorophosphine with lithium or magnesium and tetrahydrofuran.

Results

When lithium or magnesium, diphenylchlorophosphine and tetrahydrofuran are mixed, there is an immediate, spontaneous reaction which sus-

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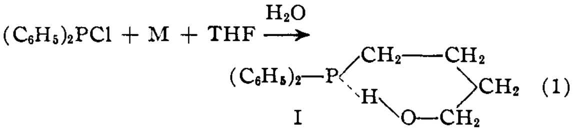
tains itself until all of the metal has been consumed. The reaction appears to be specific for tetrahydrofuran in the ether series, since diethyl ether, furan, 1,4-dioxane, ethylene oxide, dimethoxyethane, tetrahydrothiophene and the dimethyl ether of diethylene glycol do not react appreciably, if at all. In fact, some of these solvents retard the reaction in tetrahydrofuran. The product of the reactions is diphenyl-4-hydroxybutylphosphine (I).



$$(C_6H_5)_2PCl + M + THF \xrightarrow{H_2O} \quad (1)$$

I

The structure of the product was shown by (a) its infrared spectrum which shows an intra molecularly bonded hydroxyl group, phosphorus–phenyl absorption and two kinds of carbon–hydrogen absorption; (b) correspondence of its elemental analysis with the calculated values; (c) its oxidation with hydrogen peroxide to diphenyl-4-hydroxybutylphosphine oxide (II), which is obtained also from the reaction of diphenylphosphinyl chloride (III) with magnesium and tetrahydrofuran and whose infrared spectrum and elemental analysis are consistent with the oxide structure; (d) its oxidation with aqueous potassium permanganate to diphenyl-3-carboxypropylphosphine oxide (IV), neutral equivalent 294.0, calculated 288.0, and whose infrared spectrum shows carbonyl, phosphonyl and phenylphosphorus absorption.

$$I + H_2O_2\ aq. \xrightarrow{acetone} (C_6H_5)_3\overset{\overset{O}{\uparrow}}{P}CH_2CH_2CH_2CH_2OH\ (II) \quad (2)$$

$$\underset{III}{(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}Cl} + Mg \xrightarrow[2,\ H_2O]{1,\ THF,\ N_2} II \quad (3)$$

$$(C_6H_5)_2PCH_2CH_2CH_2CH_2OH \xrightarrow[aq.]{KMnO_4} (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}OH\ (IV) \quad (4)$$

Mechanistic considerations are based on the following experimental facts: (a) Tetraphenylbiphosphine (V), which is formed reportedly from active metals and diphenylchlorophosphine,[3] fails to give I in tetrahydrofuran.

$$2(C_6H_5)_2PCl + 2Na \xrightarrow[N_2]{} (C_6H_5)_2P\text{-}P(C_2H_5)_2\ (V) + 2NaCl$$

$$V + THF \not\rightarrow I \quad (5)$$

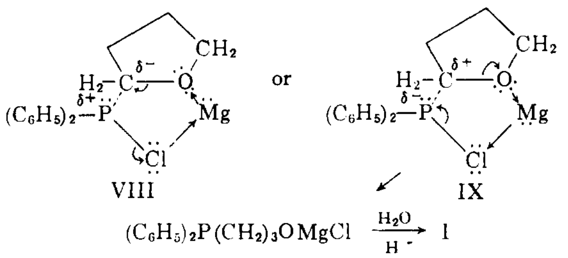
(b) Sodium and lithium diphenylphosphide (VI) also fail to react with tetrahydrofuran to give I, thus eliminating any free anion as an intermediate.

$$(C_6H_5)_2PH + Li \xrightarrow{liq.\ NH_3} \underset{VI}{(C_6H_5)_2PLi} \xrightarrow[N_2]{1,\ THF \\ 2,\ H_2O} (C_6H_5)_2PH + (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}OH \quad (6)$$

(c) The failure of diphenylphosphinomagnesium chloride (VII) to give I in tetrahydrofuran eliminates it as an intermediate.

$$C_5H_{11}MgCl + (C_6H_5)_2PH \xrightarrow[N_2]{THF} (C_6H_5)_2PMgCl + C_5H_{12} \xrightarrow{H_2O} (C_6H_5)_2PH \quad (7)$$

(d) The failure of active monomers such as styrene, acrylonitrile and ethyl acrylate to polymerize in this system eliminates any active free radical as an intermediate. These facts lead to the conclusion that a mechanism involving a cyclic activated complex as depicted below is operative here.



VIII IX

$$(C_6H_5)_2P(CH_2)_3OMgCl \xrightarrow[H^-]{H_2O} I$$

Discussion

The cleavage of tetrahydrofuran and similar compounds by organometallic compounds to form a carbon–carbon or a carbon–metal bond is certainly not a new reaction as shown by the examples

(a)[4] $(C_6H_5)_3CNa + (C_6H_5)_3B \xrightarrow{THF} [complex] \xrightarrow{H_2O} (C_6H_5)_3C(CH_2)_3CH_2OH\ \ X$

$$(C_6H_5)_3CNa \xrightarrow[prolonged\ heating]{THF\ 100°} X$$

(b)[5] $RMgX + \overline{CH_2CH_2CH_2O} \longrightarrow R(CH_2)_2CH_2OH$

(c)[6] $RMgX + THF \xrightarrow{200°} R(CH_2)_3CH_2OH$

(d)[7] $(C_6H_5)_3GeLi + \overline{CH_2CH_2CH_2\text{-}O} \longrightarrow (C_6H_5)_3Ge(CH_2)_2CH_2OH$

(e)[7] $(C_6H_5)_3SiLi + THF \xrightarrow[reflux]{2.7\ days} (C_6H_5)_3Si(CH_2)_3CH_2OH\ \ (18\%)$

$$(C_6H_5)_3SiLi + THF \xrightarrow[125°\ sealed\ tube]{3\ hours} XI\ (71\%)$$

It should be noted, however, that the cited reactions require prolonged heating of the reactants, elevated temperatures or both. The reaction presented here, by contrast, requires the mere mixing of the phosphorus halide, the metal and tetrahydrofuran to produce a vigorous reaction which produces product in good yield in a relatively short time. Furthermore, the corresponding metal phosphide does not react with tetrahydrofuran under these mild conditions.

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[3] W. Kucheo and H. Buchwald, *Angew. Chem.*, **69**, 307 (1957).

[4] G. Wittig and A. Rueckert, *Ann.*, **566**, 104 (1950).

[5] S. Searles, *J. Am. Chem. Soc.*, **73**, 124 (1951).

[6] H. Normant, *Compt. rend.*, **239**, 1510 (1954).

[7] Notes on unpublished work in paper by D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 2677 (1955).

Experimental

All infrared spectra were run on a Perkin–Elmer model 137 infracord. All elemental analyses were by Galbraith Laboratories, Knoxville, Tenn.

The tetrahydrofuran used was treated with potassium hydroxide and refluxed several days over sodium before distillation. This material was kept over sodium. The reactions were run under nitrogen. These conditions prevailed, although experiments run in unpurified tetrahydrofuran and without nitrogen showed no significant differences. The diphenylchlorophosphine was prepared essentially by the method of Senear, Valient and Wirth,[8] and Brown and Silver.[9]

Diphenylchlorophosphine and Lithium in Tetrahydrofuran.—One-half mole (3.5 g.) of lithium ribbon was added in small pieces to a solution of 55.0 g. (0.25 mole) of freshly prepared diphenylchlorophosphine in purified tetrahydrofuran in a 3-necked, round-bottomed, 500-ml. flask to which was attached a dropping funnel, a thermometer and a reflux condenser. The mixture was blanketed with nitrogen and was stirred. The solution turned red. After 24 hours, all of the lithium had disappeared, and the reaction mixture had turned brown. The addition of water gave two layers. The organic layer was separated and dried over anhydrous magnesium sulfate. Removal of the solvent left a thick, pasty oil. Attempts at crystallization failed.

The oil was distilled from a small, Hickman-type molecular still over a 5-day period. The collection of five fractions at 120–135° (3–4 μ) afforded a 44% yield of material with a range of refractive indices using the sodium D line at 25° of 1.6096–1.6104. All fractions showed hydrogen bonded (OH), ($P-C_6H_5$), ($P\rightarrow O$) and C_6H_5- absorption in their infrared spectra when run neat. The fractions were combined and upon standing crystallized as long needles, m.p. 40°. The material is insoluble in 10% sodium hydroxide, reacts with aqueous, 2% potassium permanganate and with bromine in carbon tetrachloride, and a sodium fusion shows no chlorine.

Anal. Found: C, 73.97; H, 7.16; P, 12.10. Calcd. for $C_{16}H_{19}PO$: C, 74.20; H, 7.35; P, 12.00.

Diphenylchlorophosphine, Magnesium and Tetrahydrofuran.—A tetrahydrofuran solution of 29.8 g. (0.135 mole) of diphenylchlorophosphine was added dropwise under nitrogen with stirring to a slurry of 100 ml. of purified tetrahydrofuran and 3.3 g. (0.135 mole) of magnesium shavings. Reaction occurred immediately. The temperature rose to 68°, and the solvent refluxed. After 4 hours, all of the magnesium had reacted. When the mixture had cooled, water was added. There was a slight temperature rise, and two layers formed. The organic layer was separated and dried over anhydrous magnesium sulfate. Removal of the solvent left a thick oil which was vacuum distilled through a 6" Vigreux column yielding 29.0 g. (83.0%) of material at 170° (0.16 mm.), n^{25}D 1.6103. The infrared spectrum of this product corresponded exactly to that of the product from the reaction of lithium, diphenylchlorophosphine and tetrahydrofuran. Attempts to make a phenylurethan from this product gave a black tar.

Hydrogen Peroxide Oxidation of Diphenyl-4-hydroxybutylphosphine.—A 3.63-g. (0.014 mole) sample of the product from the reaction of magnesium, diphenylchlorophosphine and tetrahydrofuran was dissolved in C.P. acetone, and an acetone solution of 30% hydrogen peroxide was added slowly. The reaction was vigorous, and the temperature rose rapidly to 65°. More peroxide was added each time the temperature dropped until no further temperature rise occurred. The resulting solution was concentrated on a steam-bath. Distillation of the thick, oily residue from a small Hickman-type molecular still at 140–164° (10–20 μ) gave five fractions with a range of refractive indices using the sodium D line at 25° of 1.5922–1.5962 for a yield of 89.8%. The infrared spectra of all fractions were identical and showed ($P-C_6H_5$), (O–H) and ($P\rightarrow O$) absorption.

Anal. Found (middle cut): C, 70.72; H, 6.58; P, 10.53. Calcd. for $C_{16}H_{19}PO_2$: C, 70.01; H, 6.90; P, 11.30.

Oxidation of Diphenyl-4-hydroxybutylphosphine with Potassium Permanganate.—A 29.0-g. sample (0.112 mole) of product from the reaction of magnesium, diphenylchlorophosphine and tetrahydrofuran was mixed with 35.6 g. (0.224 mole) of potassium permanganate in aqueous solution. Reaction began immediately. After 24 hours at room temperature, the copious precipitate of manganese dioxide was removed by filtration. The resulting, purple solution was heated on a steam-bath to ensure complete reaction. Formalin was added until the purple color was dispelled. Filtration through Celite afforded a colorless solution. Acidification with concentrated HCl gave a heavy, white precipitate, wt. 19.6 g. after air drying (yield 60.6%). Two recrystallizations from hot water and thorough drying under high vacuum at 60° for an hour yielded material melting sharply at 162.5–163.0°; neut. equiv. 294, calcd. for $C_{16}H_{17}PO_3$ 288.

Lithium Diphenylphosphide with Tetrahydrofuran.—Eight and two-tenths grams (0.044 mole) of diphenylphosphine was added dropwise in a nitrogen atmosphere to a solution of 0.304 g. (0.044 mole) of lithium in liquid ammonia. The blue color slowly faded and was replaced by the typical bright red-orange color of the diphenylphosphide anion. The ammonia was distilled and 100 ml. of fresh tetrahydrofuran was added. The mixture was stirred for half an hour at 60°. The color appeared to become redder. The addition of water dispelled the color and precipitated an oil. Ether was added to dissolve the oil. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed, and vacuum distillation of the residual oil through a 6" Vigreux column yielded 3.0 g. (0.016 mole) of diphenylphosphine and a residue of 3.2 g. (0.015 mole) of diphenylphosphinic acid in the pot. Identifications were made through the comparison of the infrared spectra of these products with those of authentic samples. No hydroxylic materials were found.

Tetraphenylbiphosphine with Tetrahydrofuran.—A mixture of 3.0 g. (0.016 mole) of diphenylphosphine and 3.55 g. (0.016 mole) of diphenylchlorophosphine was heated for 3 hours under nitrogen. The resulting product solidified when the mixture was cooled to room temperature. An excess of tetrahydrofuran was added, and the mixture was stirred until the white solid had dissolved completely. The solution was refluxed for 16 hours. The addition of water to the cooled solution precipitated an oil which was taken up in ether. The ether solution was dried over anhydrous magnesium sulfate. Removal of the solvent followed by vacuum distillation gave 1.12 g. (0.006 mole) of diphenylphosphine. The pot contained solid diphenylphosphine oxide. No hydroxyl-containing products could be found. Identifications were made through comparisons with the infrared spectra of authentic materials.

Diphenylphosphinomagnesium Chloride with Tetrahydrofuran.—Twenty-six and four-tenths grams (0.142 mole) of freshly prepared diphenylphosphine was added dropwise under nitrogen to a tetrahydrofuran solution of *n*-amylmagnesium chloride which had been prepared from a slight excess of *n*-amyl chloride and 3.45 g. (0.142 mole) of magnesium shavings in tetrahydrofuran. A vigorous reaction ensued. The temperature rose to 80° with the evolution of a low boiling material, presumably, *n*-pentane. The temperature dropped to 68°, and the mixture refluxed. When the mixture which was now brown, had reached room temperature again, deoxygenated water was added. Another vigorous reaction occurred accompanied by a rise in temperature to 58°C. Two layers formed. The bottom layer was milky. The organic layer was separated and was dried over anhydrous magnesium sulfate. Removal of the solvent and fractionation of the residue yielded 10.0 g. of diphenylphosphine, 4.0 g. of a mixture of diphenylphosphine and diphenylphosphine oxide and 7.1 g. of diphenylphosphine oxide. These products were identified by their infrared spectra. No hydroxylic products were found.

Diphenylphosphinyl Chloride Magnesium and Tetrahydrofuran.—Thirty-seven and five-tenths grams (0.158 mole) of diphenylphosphinyl chloride in tetrahydrofuran was added dropwise with stirring to a mixture of 3.48 g. (0.158 mole) of magnesium shavings and 50 ml. of tetrahydrofuran. A nitrogen blanket was used throughout the reaction. The temperature rose to 68°, and the solution turned milky but became yellow toward the end of the reaction. The mixture was heated at reflux for 2 hours after the complete addition of the chloride. The solution turned dark red.

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(8) A. E. Senear, W. Valient and J. Wirth, *J. Org. Chem.*, **25**, 2001 (1960).

(9) M. P. Brown and H. B. Silver, *Chemistry & Industry*, 24 (1961).

The addition of water, followed by dilute hydrochloric acid, dispelled the red color immediately. A solid precipitated but redissolved upon the addition of the acid. The two layers which formed were separated. The organic phase was dried over anhydrous magnesium sulfate. Removal of the solvent left a viscous sirup. Distillation from a molecular still gave 5.56 g. of a material, b.p. 138–148° (0.01 mm.), $n^{25}D$ 1.6092, whose infrared spectrum indicated a mixture of (P–H)-containing compound and an (O–H)-containing compound. Redistillation through a microstill gave 2.58 g. of a material which still contained (P–H) and (O–H) absorption in its infrared spectrum and 2.98 g. of a thick, oily residue in the pot whose infrared spectrum checks exactly that of diphenyl-4-hydroxybutylphosphine oxide.

Diphenylchlorophosphine, Magnesium and Tetrahydrofuran in the Presence of Active Monomers.—Test-tube experiments of the reaction between diphenylchlorophosphine, magnesium and tetrahydrofuran in the presence of acrylonitrile and of ethyl acrylate gave no polymer. A further quantitative test was run with styrene.

Twenty-nine and nine-tenths grams (0.135 mole) of diphenylchlorophosphine was added dropwise, under nitrogen, into a mixture of 3.28 g. (0.135 mole) of magnesium, 100 ml. of tetrahydrofuran and 22.7 g. (0.21 mole) of distilled styrene. Reaction began after a short period, and the temperature rose to 55°. The magnesium became coated, and the temperature began to drop. External heat was used to maintain the temperature at 70° for 3 hours. At the end of this heating period, the reaction mixture did not give a precipitate of polystyrene when a portion of it was added to a large excess of methanol.

The remaining portion of the reaction mixture was heated for 24 hours at 70°. When the mixture was poured into excess methanol, 30.3 g. of a white solid precipitated. Extraction of a small portion of this material with benzene gave mostly an insoluble residue and a colorless solution. A hard, brittle film was cast on rock salt from this solution. The infrared spectrum of this film resembled polystyrene but contained a strong band at 7.0 μ which is generally associated with ($P–C_6H_5$) absorption.

Preparation of Diphenylphosphinyl Chloride.—A large excess of thionyl chloride was added slowly to 109.0 g. (0.50 mole) of diphenylphosphinic acid. The solid dissolved slowly with no apparent heat of reaction. When solution was complete, the reaction mixture was refluxed for 8 hours. Vacuum distillation of the mixture yielded 100.9 g. (yield 85.0%) of product, b. 131° (0.1 mm.), $n^{25}D$ 1.6098, whose infrared spectrum shows ($P–C_6H_5$) and ($P \rightarrow O$) absorption and corresponds to that shown by Daasch and Smith.[10]

Acknowledgments.—Especial thanks are given to Professor Earl C. Chapin and Professor Wilbert H. Urry for their helpful discussions during the course of this work.

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[10] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, N. J.]

Reactions of *t*-Alkyl Hypochlorites with Trisubstituted Phosphines and Phosphites[1,2]

BY DONALD B. DENNEY AND ROLAND R. DILEONE

RECEIVED JUNE 11, 1962

The reactions of *t*-alkyl hypochlorites with trisubstituted phosphines and phosphites have been studied. The reactions yield as major products *t*-alkyl chlorides, olefins and the appropriate phosphine oxide or phosphate. Optically active tetrahydrolinalyl hypochlorite reacted with triphenyl phosphite to give optically active tetrahydrolinalyl chloride of inverted configuration. The bridgehead hypochlorite bicyclo[2,2,1]-1-heptyl hypochlorite reacted with triphenylphosphine to give bicyclo[2,2,1]-1-heptyloxytriphenylphosphonium chloride. Several reactions of this material were studied. The mechanisms of the hypochlorite reactions are discussed.

Petrov and Sokol'skii[3] have studied the reaction of ethyl hypochlorite with several trisubstituted phosphites. They observed the formation of phosphates. It was suggested that an intermediate, $(RO)_3\overset{+}{P}–O–C_2H_5Cl^-$, was formed which decomposed to the phosphate and an alkyl chloride. Goldstein[4] has shown that a violent reaction occurs between *t*-butyl hypochlorite and triphenylphosphine at room temperature with the formation of triphenylphosphine oxide. Other products were not isolated.

It was the purpose of this research to study in detail the reactions of *t*-alkyl hypochlorites with trisubstituted phosphines and triphenyl phosphite.

Results

Both tetrahydrolinalyl hypochlorite (I) and methylethylisobutylcarbinyl hypochlorite react rapidly with triphenyl phosphite at *ca.* −78° to give triphenyl phosphate, the appropriate *t*-alkyl chloride, olefins, recovered parent alcohol and minor amounts of other products.[5] Having demonstrated the nature of the reaction, emphasis was placed on studying the reactions of I and conditions for maximum conversion of I to tetrahydrolinalyl chloride (II). At −50° reaction of I with tributylphosphine yielded 5% II, with triphenylphosphine 10% II and with triphenyl phosphite 15% II. Compound I reacted with triphenyl phosphite at −60° to give 30% II and at −75°, 39% II. The best conditions found for the production of II were −75° with triphenyl phosphite as the co-reactant and pentane as solvent. These conditions gave II in yields of 40–50%.

Optically active tetrahydrolinaloöl (III) was converted to optically active I[6] and thence by reaction with triphenyl phosphite to optically active II. Gas–liquid chromatography of II showed that it contained trace amounts of impurities. Because of the small rotation involved, *ca.* −0.5°, it was felt that the impurities could be responsible for the optical activity. This supposition was buttressed by the finding that chromatography of II

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[1] Research supported by The National Science Foundation.

[2] Presented at the symposium on "Mechanisms of Reactions of Organophosphorus Compounds," American Chemical Society, Chicago, Ill., September, 1961.

[3] K. A. Petrov and G. A. Sokol'skii, *Zhur. Obshchei Khim.*, **26**, 3377 (1956); *C.A.*, **51**, 8028 (1957).

[4] B. Goldstein, Ph.D. Thesis, Rutgers University, 1957.

[5] W. J. Hanifin, Jr., has extended this reaction to several other hypochlorites with similar results.

[6] The sign and magnitude of the rotation were not observed. There seems to be little doubt that optically active I should be formed from the alcohol and hypochlorous acid with complete retention of configuration.