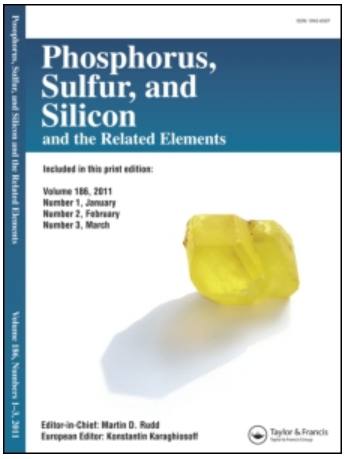

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PREPARATION OF SOME ALKYL CHLORIDES BY DECOMPOSITION OF ALKOXYPHOSPHONIUM CHLORIDES AND BICHLORIDES

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PREPARATION OF SOME ALKYL CHLORIDES BY DECOMPOSITION OF ALKOXYPHOSPHONIUM CHLORIDES AND BICHLORIDES

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A number of alkoxyphosphonium chlorides and bichlorides have been prepared as stable intermediates or transient species. The thermal decompositions of these salts have been studied under a variety of conditions. The salts decompose by S_N2 and S_Ni processes in a fairly predictable manner. There are two decided advantages to using these salts as precursors to alkyl halides. The first is that in systems that are normally prone to rearrangements under substitution conditions, the products of the decompositions of the salts are often formed with less rearrangement than is often found in other systems. The second is that the phosphates and phosphine oxides are excellent leaving groups and thus substitutions can be effected at centers that normally react very slowly.

Various reagents derived from trivalent phosphorus compounds and halogens or carbon tetrachloride or methyl iodide have been used for the preparation of alkyl and aryl halides as well as for a variety of other synthetic conversions.[1] The basic chemistry involves the formation of a phosphonium salt with at least one phosphorus oxygen bond. This salt then decomposes to yield the appropriate phosphoryl compound and usually the product of substitution at the carbon which was originally bonded to oxygen. A popular synthetic procedure involves reaction of triphenylphosphine, **1**, and chlorine, **2**, to give an adduct, **3**, whose structure, i.e. either salt or phosphorane, varies with the nature of the medium.[2] Reaction of **3** with an alcohol forms the salt, **4**, which can decompose to

$$(C_6H_5)_3P + Cl_2 \longrightarrow (C_6H_5)_3\overset{+}{P}—Cl + Cl^- \rightleftharpoons (C_6H_5)_3PCl_2$$
1 **2** **3**

$$(C_6H_5)_3\overset{+}{P}—OR + HCl_2^- \longrightarrow (C_6H_5)_3P{=}O + RCl + HCl$$
4 **5**

alkyl chloride, triphenylphosphine oxide and hydrogen chloride. An intermediate, **6**, similar to **4** can be generated by allowing triphenylphosphine or other trivalent phosphorus compounds to react with alkyl hypochlorites.[3] In this report

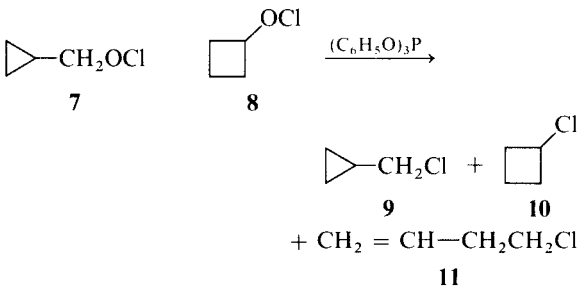
$$(C_6H_5)_3P + ROCl \longrightarrow (C_6H_5)_3\overset{+}{P}—OR + Cl^-$$
1 **6**

results obtained from the decompositions of salts **4** and **6** will be presented.

RESULTS AND DISCUSSION

Cyclopropylcarbinyl hypochlorite, **7**, and cyclobutyl hypochlorite, **8**, have been prepared and allowed to react with triphenyl phosphite in

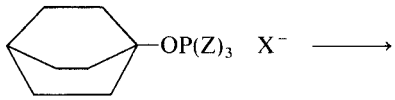
methylene chloride at −78°C. In both cases, cyclopropylcarbinyl chloride, **9**, cyclobutyl chloride, **10**, and allylcarbinyl chloride, **11**, were formed. In the case of the products from **7** the percentages were 90%, **9**, 8.5%, **10**, and



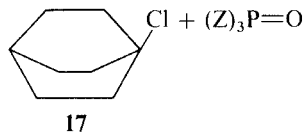
1.5%, **11**. The product ratios from **8** were significantly different from those of **7**. They were 66%, **9**, 29%, **10**, and 5%, **11**. Roberts and Mazur[4] have studied the reactions of cyclopropylcarbinol and cyclobutanol with thionyl chloride. The products percentages were 69%, **9**, 26%, **10**, and 5%, **11**. They concluded that a common intermediate, a carbonium ion, was formed from both starting materials and that it was captured by chloride ion to give the observed products. The percentages of products from the reaction of **8** are so similar to those found by Roberts and Mazur that it seems entirely reasonable to conclude that the same carbonium ion was involved in this reaction sequence. On the other hand, the percentages of products from **7** are quite different from the carbonium ion derived products and it seems reasonable to conclude that another path for product formation must be available. Direct displacement by chloride on the intermediate salt in a S_N2 process is of course such a path. The data of Roberts and Mazur allow one to calculate that the intermediate salt derived from **7** decomposes via S_N2 and S_N1 processes in the ratio 68:32. Reactions of the cyclopropylcarbinyl and cyclobutyl systems have been studied in great detail and extensively reviewed.[5] The results obtained in this study are not unexpected.

A number of alcohols containing bicyclic ring systems were converted into chlorides by the techniques discussed earlier. For example, chlorine, triphenyl phosphine and 1-adamantanol, **12**, were allowed to react at 25°C. After 7.5 minutes the reaction was complete and 1-chloroadamantane and triphenylphosphine oxide were formed. An intermediate salt could be detected by ^1H NMR spectroscopy. In a separate experiment 1-chloroadamantane was isolated in 51% yield.

Bicyclo[2,2,2]octan-1-*ol*, **13**, chlorine and triphenylphosphine, yielded the salt **14**, which decomposed slowly at 60°C, half life ca. 37 hrs, to give **17**



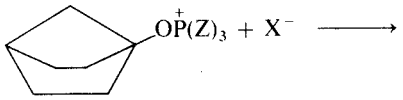
14 Z = C_6H_5 X^- = HCl_2^-
15 Z = C_6H_5 X^- = Cl^-
16 Z = OC_6H_5 X^- = HCl_2^-



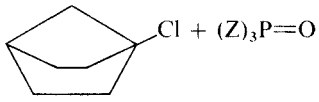
and triphenylphosphophine oxide. The hypochlorite derived from **13** was allowed to react with triphenylphosphine to give the salt, **15**, which also decomposed slowly at 60°C, half life 19 hrs, to give **17**, 75%, and triphenylphosphine oxide. The reaction of **13**, chlorine and triphenyl phosphite was over in a few minutes at 0–5°C. The chloride, **17**, was isolated in 50% yield. Triphenyl phosphate was the other product. Although **16** was undoubtedly an intermediate, no evidence for its formation was obtained. The rapid decomposition of **16** as compared to **14** and **15** is in accord with other observations concerning the relative ease of loss of phosphate as compared to phosphine oxide in S_N1 and S_N2 reactions. In both reactions phosphorus-oxygen double bonds are being formed. There are though considerable differences in the bond energies with that of triphenylphosphine oxide being 128 kcal/mole and a typical phosphate ca. 150 kcal/mole.[6] This difference manifests itself in a lower transition state energy for the formation of phosphate.

Because phosphate is a better leaving group than phosphine oxide one might conclude that the reactants triphenyl phosphite, chlorine and alcohol will constitute the synthetic method of choice in all cases. It should be noted though that a salt such as **16** can exchange with alcohol with the liberation of phenol. If this occurs then the yield of alkyl halide will be reduced.

The salts, **18**–**20**, were prepared from 1-hydroxy-bicyclo[2,2,1]heptane or the hypochlorite and their decompositions were studied. Both **18** and **19** decomposed at about the same rate, half-lives of 610 and 650 minutes respectively, in *p*-dichlorobenzene at 168–170°C to give 1-chlorobicyclo[2,2,1]heptane, **21**, and triphenylphosphine



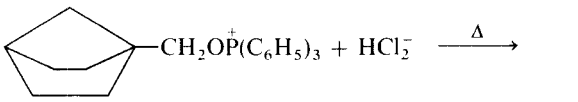
18 Z = C_6H_5 X^- = HCl_2^-
19 Z = C_6H_5 X^- = Cl^-
20 Z = OC_6H_5 X^- = HCl_2^-



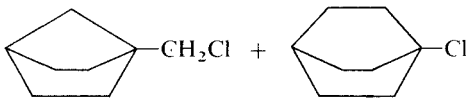
21

oxide. Compound, **20**, decomposed in chlorobenzene at 120.5°C with a half-life of 11 minutes. In tetrachloroethane at 120.5°C the half-life was 30 minutes. In both cases, **21**, and triphenyl phosphate were the products. The rapid decomposition of **20** is illustrative of the ready loss of triphenyl phosphate from these salts. In this particular example the very unstable bridgehead carbonium ion was formed as an intermediate.[7]

1-Hydroxymethylbicyclo[2,2,1]heptane, **22**, chlorine and triphenylphosphine reacted to give the salt, **23**. Pyrolysis of **23** at 92°C or heating a solution of **23** in methylene chloride at 40°C led to its decomposition. In the latter case the half-life was 42 minutes. In both cases the products



23



24 **25**

were **24**, 95%, and **25**, 5%. The total yields were 65%. The high yield of **24** relative to that of **25** is illustrative of the lack of rearrangement that is often found in the decomposition of these salts. Substitutions on systems similar to **23**, i.e. same skeleton but a different leaving group have led to extensive rearrangement.

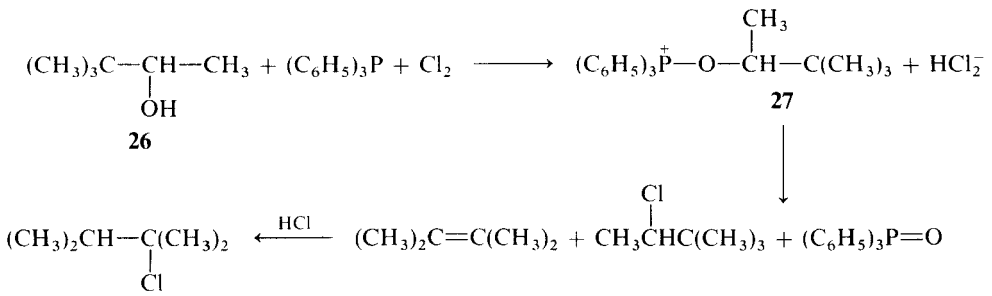
Schaefer and Weiber[8] have studied the reactions of optically active *exo*- and *endo*-norborneols with triphenylphosphine and bromine. In the case of the *endo* isomer optically active *exo*-bromide was formed by a S_N2 displacement reaction. The *exo* isomer yielded 79% optically inactive *exo*-bromide, 9% nortricyclene and 12% optically active *endo*-bromide. The first two products were formed by a S_N1 process and the last by a S_N2 reaction.

Reaction of *exo*-norborneol, triphenylphosphine and chlorine afforded a very unstable salt which decomposed at room temperature in seven minutes to give *exo*-norbornyl chloride, hydrogen chloride and triphenylphosphine oxide.

The *endo*-alcohol, chlorine and triphenylphosphine yielded a relatively stable salt which decomposed at 61.5°C in 1,2-dichloroethane with a half-life of 42 minutes. The products were *exo*-norbornyl chloride and triphenylphosphine oxide. The *endo*- alcohol, triphenyl phosphite and chlorine were allowed to react at 0°C. The intermediate salt was not detected. The products were *exo*-norbornyl chloride and triphenyl phosphate.

In earlier work[1,9] it was shown that various neopentyloxyphosphonium salts react with a number of nucleophiles with little or no rearrangement. Tetraneopentloxyphosphonium *p*-toluenesulfonate is an exception. Its decomposition leads to rearranged olefins. Triphenyl-2,2,2-triphenylethoxyphosphonium bichloride decomposed with complete rearrangement to triphenylethylene.[9]

Triphenylphosphine, chlorine and pinacolyl alcohol, **26**, were allowed to react to give the salt, **27**. The decomposition of **27** was followed by ^1H NMR spectroscopy. The spectra showed that 2,3-dimethyl-2-butene was being formed and that it



was reacting with hydrogen chloride to give 2-chloro-2,3-dimethylbutane. Pinacolyl chloride was isolated from the reaction mixture. The ratio of rearranged to unrearranged chlorides was 75:25. The formation of pinacolyl chloride is unusual. Generally speaking only rearranged products are found in this system. When the bichloride ion of **27** was exchanged for *p*-toluenesulfonate by treatment with silver *p*-toluenesulfonate, the major products of decomposition were tetramethylethylene, triphenylphosphine oxide and *p*-toluenesulfonic acid.

EXPERIMENTAL SECTION

Infrared spectra were recorded with a Perkin-Elmer Model 137 infrared spectrometer. ^{1}H NMR spectra were recorded with a Varian A-60. The purities of the intermediate salts were determined by the procedure of D. B. Denney and S. T. Ross, Anal. Chem., 1960, **32**, 1896.

Reaction of triphenyl phosphite with cyclopropylcarbinyl hypochlorite, **7**. Cyclopropylcarbinyl hypochlorite, **7**, was prepared by adding 6.7 g (0.093 mole) of cyclopropylcarbinol, 40 ml of methylene chloride, and 6.7 ml of acetic acid to a mixture of 100 ml of 0.76 M sodium hypochlorite and 20 g of ice. The mixture was stirred for two hours at 0°C. The methylene chloride layer containing **7** was separated, washed with ice water, and dried for 15 minutes with anhydrous magnesium sulfate.

To a mixture of 29.2 g (0.093 mole) of triphenyl phosphite in 300 ml of methylene chloride cooled to −78°C was added the solution of **7**. After the addition of the hypochlorite, the methylene chloride was removed by fractionation. The liquid residue was treated with 300 ml of pentane and cooled to −78°C. The insoluble triphenyl phosphate was removed by filtration and the pentane was removed by fractionation. GC analysis on a 10 ft. 6 M Carbowax column at 70°C was used to identify the reaction products. Authentic samples were prepared and retention times were compared.

Reaction of triphenyl phosphite with cyclobutyl hypochlorite, **8**. A solution of **8** was prepared in exactly the same manner as that of **7** and it was allowed to react with triphenyl phosphite and the reaction mixture was processed as was the reaction products of **7**.

Preparation of 1-chloroadamantane. A solution of 1-adamantanol, 0.89 g (0.006 mole), triphenylphosphine, 1.54 g (0.006 mole) in 10 ml of methylene chloride at −78°C was treated with 5 ml of 1.2 M chlorine in carbon tetrachloride. An additional 25 ml of methylene chloride was added and the reaction mixture was stirred for 1 hour. The reaction mixture was evaporated to dryness and then treated with 100 ml of pentane. A white solid was isolated, 1.05 g (68%) which was shown to be triphenylphosphine oxide by its melting point and infrared spectrum. Evaporation of the pentane and sublimation at 55°C (15 mm) yielded 0.51 g (51%) of crude 1-adamantyl chloride. Recrystallization from methanol gave material mp 167–168°C (lit[11] 165°C). The infrared spectrum was identical to that of an authentic sample.

Preparation of **14**. A solution of bicyclo[2,2,2]octan-1-ol, 0.765 g (0.006 mole), triphenylphosphine, 1.57 g (0.006 mole) in 75 ml of ethyl ether was allowed to react with 8 ml of a 1.0 M solution of chlorine in carbon tetrachloride. The oil that was formed solidified on stirring overnight. The solid was triturated with 100 ml of ethyl ether to yield 1.5 g (55%) of **14**, 91% pure by titration, mp 88–91°C. The decomposition of **14** in 1,2-dichloroethane at 60°C was followed by ^{1}H NMR spectroscopy.

Preparation and decomposition of **15**. A mixture of 1.5 ml of glacial acetic acid, 42 ml of 0.76 M sodium hypochlorite solution, 75 ml of methylene chloride and 2.08 g (0.0165 mole) of bicyclo[2,2,2]octan-1-ol was stirred for two hours at 0°C. The layers were separated and the aqueous phase was washed with three 10-ml portions of methylene chloride. The combined organic extracts were washed with three 50-ml portions of aqueous sodium bicarbonate. The methylene chloride solution was dried over magnesium sulfate at 0°C in the dark. Iodometric titration indicated a 47% yield of the hypochlorite.

A solution of triphenylphosphine, 2.1 g (0.080 mole) in 25 ml of methylene chloride was added to the hypochlorite solution over 30 minutes. The resulting solution was concentrated to 30 ml and treated with 200 ml of ethyl ether. A solid formed and this was washed with 100 ml of ether to give 2.69 g (82%) of **15** mp 103–105°C. Titration indicated 93% purity. The ^{1}H NMR spectrum in methylene chloride had two multiplets centered at δ 1.80, aliphatic protons, and δ 7.90 aromatic protons. The areas of these absorptions were in the ratio 15.8:13, calcd. 15:13. A solution of 1.43 g (0.003 mole) of **15** in 25 ml of 1,2-dichloroethane was heated at 60°C. After 1140 minutes, one half of the salt had decomposed as determined by titration.

After heating 9 days, the solution was examined by preparative GC, 1-chlorobicyclo[2,2,2]octane, mp 103.5–104.5°C 103.5–104.5°C) was isolated in 75% yield. Treatment of the remaining solution, 5 ml, with 100 ml of ethyl ether precipitated 0.147 g (82%) of triphenylphosphine oxide whose mp and IR spectrum were identical to those of an authentic sample.

Reaction of bicyclo[2,2,2]octan-1-ol, chlorine and triphenyl phosphite. A solution of triphenyl phosphite, 1.86 g (0.006 mole) and bicyclo[2,2,2]octan-1-ol, 0.71 g (0.006 mole) in 8 ml of chloroform at 0°C was treated with 8 ml of a 0.85 M chlorine solution in carbon tetrachloride. After the addition which took 7 minutes, a 2 ml aliquot was chromatographed on alumina with *n*-pentane as the eluting solvent. There was obtained 0.064 g (59%) of crude 1-chlorobicyclo[2,2,2]octane. The material was sublimed to give pure product. A portion, 10 ml, of the reaction mixture was distilled to dryness. The residue, 100%, was identified as triphenylphosphine oxide.

Preparation and decomposition of **18**. A solution of 1-norbornanol, 3.30 g (0.029 mole) and triphenylphosphine, 7.72 g (0.029 mole) in 50 ml of ethyl ether was allowed to react with 35 ml of a 1.0 M solution of chlorine in carbon tetrachloride. A solid, 10.7 g (82%), formed and it was triturated with 100 ml of dry ethyl ether to give 8.66 g of 95% pure, **18**. Recrystallization from hexane-1,2-dichloroethane afforded material mp 155–157°C.

A solution of **18**, 2.14 g (0.005 mole) in 25 ml of dry distilled *p*-dichlorobenzene was heated at 168–170°C; half of the salt decomposed in ca. 11 hours. After 4 days all of the salt had decomposed, the remaining solution was treated with 100 ml of ethyl ether which precipitated triphenylphosphine oxide. The ether filtrate was concentrated to 1 ml and analyzed by GC.

The chromatogram showed that 1-norbornyl chloride was present. The retention time was identical to that of an authentic sample.

Preparation and decomposition of **19**. A solution of **18**, 4.44g (0.01 mole) in 15ml of dry 1,2-dichloroethane was stirred with 5.0g of calcium oxide for 1 hour. The solution was concentrated and treated with 100ml of ethyl ether. This procedure gave 3.80 g (93%) of **19** mp 195–197°C (lit[3] 193–197°C). Decomposition of **19** was conducted in the same way as that of **18**.

Preparation and decomposition of **20**. A solution of 1-norbornanol, 2.09g (0.018 mole) and triphenyl phosphite, 6.00g (0.019 mole) in 100ml of ethyl ether was treated with a solution of 1.0M (0.02 mole) of chlorine in carbon tetrachloride at 0°C under a nitrogen atmosphere. A solid formed; after drying overnight, the solid was triturated with 100ml of hexane. The product, 4.6g (50%) had a mp of approximately 80°C. Freshly prepared **20**, 5.72g (0.012 mole) was pyrolyzed at 113–140°C in a molecular still to give 0.70g (46%) of 1-norbornyl chloride whose infrared spectrum was very similar to that of the bromide. Triphenyl phosphate was isolated from the pot residue. The decomposition of **20** in solution was followed by titration.

Preparation and decomposition of **23**. A solution of 1-hydroxymethylbicycloheptane, 0.822g (0.006 mole) and triphenylphosphine, 1.572g (0.006 mole) in 40ml of pentane was treated with 6ml of a 1.1M solution of chlorine in carbon tetrachloride over a period of 30 minutes at 0°C. A precipitate formed, 2.3g (90%), which was triturated with ether, mp 78–80°C. The purity was found to be 98%. Pyrolysis in a molecular still at 92–94°C afforded 66% of 1-chloromethylbicycloheptane. The ^{1}H NMR spectrum in CH_2Cl_2 had four absorptions for the bicyclic methylene protons at δ 1.26, 1.40, 1.54 and 1.70. The bridgehead hydrogen was found at δ 2.24 and hydrogens on the methylene group were found at δ 3.70. Integration of the areas gave the expected ratios. GC analysis showed there was 5% of 1-chlorobicyclo[2,2,2]octane present. Triphenylphosphine oxide (97%) was isolated from the pot residue. Decomposition of **23** in solution was conducted as described for the other compounds.

Reaction of exo-norborneol, triphenylphosphine and chlorine. A solution of triphenylphosphine, 8.37g (0.033 mole) in 25ml of methylene chloride was treated with 35ml of a 1M solution of chlorine in carbon tetrachloride. The resulting reaction mixture was allowed to react with 4.0g (0.035 mole) of *exo*-norborneol in 100ml of ethyl ether. A solid formed 7.1g (81%) which was shown to be triphenylphosphine oxide. The filtrate was concentrated and evaporatively distilled to give 1.95g (46%) of *exo*-norbornyl chloride, bp 72–76°C (96 mm). The infrared spectrum was identical to that reported.[13]

Reaction of triphenylphosphine, chlorine and endo-norborneol. A solution of 4.0g (0.04 mole) of 88% *endo*-norborneol, 12% *exo*-norborneol and triphenylphosphine, 9.33g (0.04 mole) in 50ml of methylene chloride at 0°C was treated with 60ml of a 0.81M solution of chlorine in carbon tetrachloride. After stirring one hour, the resulting slurry was concentrated to 30ml and treated with 100ml of pentane. The salt was collected and dried. The yield was 12.3g (90%), mp 98–100°C, purity 97%.

The salt, 2.00g (0.005 mole) in 10ml of 1,2-dichloroethane was heated under reflux for 48 hours. The solvent was removed by distillation. Addition of 25 ml of pentane precipitated 1.00 g (86%) of triphenylphosphine oxide whose mp and IR spectrum was identical to that of authentic material. The pentane was concentrated and the residue was evaporatively distilled, bp 65–71°C (90 mm), to give 0.46g (76%) of *exo*-norboryl chloride whose IR spectrum was identical to that of authentic material.

Reaction of endo-norborneol with triphenyl phosphite and chlorine. A solution of *endo*-norborneol, 4.3g (0.039 mole) and triphenyl phosphite, 12.3g (0.039 mole) in 100ml of ethyl ether was treated with stirring at 0°C with a solution of 1.0M chlorine, 40ml (0.04 mole) in carbon tetrachloride. The solvents were removed and the residue was distilled to give 2.3g (63%) of *exo*-norbornyl chloride. The residue yielded, 10.0g (80%) of triphenyl phosphate which was recrystallized from *n*-hexane to give material whose mp and IR spectrum was identical to that of authentic material.

Preparation and decomposition of **27**. A solution of pinacolyl alcohol, 10.2g (0.100 mole) and triphenylphosphine, 26.2g (0.100 mole) in 450 ml of hexane was treated with 100ml of chlorine, 1.35M, in carbon tetrachloride dropwise over a period of 45 minutes. The reaction mixture was stirred for 19 hours and then it was diluted with 200ml of ethyl ether. Filtration and washing of the precipitate afforded after drying, 38.6g, mp 111–117°C, purity 96% of **27**. The ^{1}H NMR spectrum in methylene chloride has aromatic hydrogen absorptions, δ 7.70–8.14. The methine proton is found as a pair of overlapping quartets at δ 4.37 (J_{POCH} = 7 Hz; J_{HCCH} = 7 Hz). The hydrogens of the α-methyl group are found as a doublet centered at δ 1.37 (J_{HCCH} = 7Hz) and the hydrogens of the methyl groups of the t-butyl group absorb at δ 0.98.

The ^{1}H NMR spectrum of **27** in methylene chloride was recorded as a function of time. An absorption at δ 1.64 increased and then disappeared. Authentic 2,3-dimethyl-2-butene also absorbs at δ 1.64.

A solution of **27**, 35.7g (0.0895 mole) in 130 ml of methylene chloride was allowed to stand for 6 days. It was then stirred with calcium oxide to remove hydrogen chloride. The reaction mixture was filtered and the volatiles were removed at room temperature *in vacuo* and condensed in a trap cooled by liquid nitrogen. The residue, 24.3g, was shown to be essentially pure triphenylphosphine oxide.

The volatiles were fractionated to give 9.8g of product whose ^{1}H NMR spectrum indicated it consisted of 82% of 2-chloro-2,3-dimethylbutane and 18% of pinacolyl chloride. Selective solvolysis of the tertiary chloride was accomplished by stirring the residue with 5.0 ml of acetone, 50 ml of distilled water and 5.60g of sodium bicarbonate for 66 hours at room temperature. The reaction mixture was extracted with ether, after drying, the solvent was removed by distillation through a Vigreux column. The residue was molecularly distilled and a fraction was collected at a block temperature between 92–102°C. Preparative GC allowed the collection of pinacolyl chloride whose IR spectrum was identical to that reported.[14] The ^{1}H NMR spectrum in carbon tetrachloride has a quartet at δ 3.83 (J_{HCCH} = 7 Hz) for the absorption of the methine proton, a doublet at δ 1.45 (J_{HCCH} = 7 Hz) for the absorption of the hydrogens of the α-methyl group and a singlet at α 1.03 for the absorption of the hydrogens of the methyl groups of the t-butyl group. Integration gave relative areas of 0.9:2.9:9.0.

Decomposition of triphenylpinacolylphosphonium tosylate. Triphenylpinacolyphosphonium bichloride, 15.0g (0.0376 mole) was dissolved in 150 ml of 1,2-dichloroethane and the reaction mixture was cooled to −24°C. The cooled reaction mixture was

stirred with 25.0g (0.0896 mole) of silver tosylate and 7.0g (0.066 mole) of sodium bicarbonate at −22°C for 4.5 hours. After filtration and allowing the mixture to stand for four days, the ^{1}H NMR spectrum of the reaction mixture showed that triphenylphosphine oxide, 2,3-dimethyl-2-butene and *p*-toluenesulfonic acid were present.

ACKNOWLEDGEMENT

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REFERENCES AND NOTES

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