times, and infrared and nmr spectra with those of authentic samples. The over-all conversions were about 40–50% for the runs at high [HBr] and 10–20% for those at low [HBr].

The blank runs showed no reaction except for traces of 2,2-dibromopropane (ionic diadduct) at 8 *M* HBr and higher. No correction for ionic addition was necessary and the reaction products were calculated throughout to be resulting from the free-radical addition of Br· to the terminal or the central carbon of allene.

No isomerization of allene to methylacetylene was observed.

Acknowledgment.—The authors wish to thank Professor G. A. Russell of Iowa State University for helpful discussion.

The Controlled Alkylation of Mono-*n*-alkylphosphines

HUGH R. HAYS

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

Received June 13, 1966

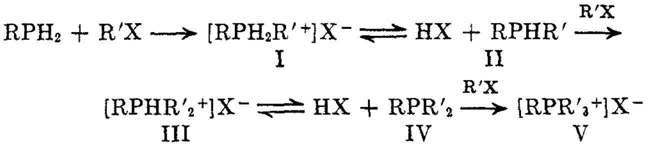
The controlled alkylation of mono-*n*-alkylphosphines by methyl and *n*-alkyl halides under a variety of conditions has been investigated. Trialkylphosphines of the type RPR_2' (R = *n*-alkyl, R′ = methyl or *n*-alkyl) can be obtained simply and in excellent yields (78–94%) from mono-*n*-alkylphosphines and methyl or *n*-alkyl iodides, using the alcohol corresponding to the alkyl iodide as solvent. With more elaborate control of reaction variables, methyl chloride and dodecylphosphine gave 80 ± 10% yields of dimethyldodecylphosphine; small amounts of dodecyltrimethylphosphonium chloride were also produced. Simple dialkylphosphines can be obtained in good yield by moderately heating methyl or *n*-alkyl iodides and primary phosphines without solvent. Factors involved in the controlled alkylation of mono-*n*-alkylphosphines are discussed. A number of trialkylphosphines have been prepared and characterized by conversion to phosphine oxides and phosphonium salts.

A number of methods are potentially available for the synthesis of simple trialkylphosphines of the type RPR_2' (R = *n*-alkyl, R′ = methyl, or *n*-alkyl).[1,2] Many of these methods are long, tedious, and result in poor over-all yields, or require starting materials that are not readily available or are difficult to handle.[3] In considering possible synthetic routes to trialkylphosphines, the direct conversion of mono- to trialkylphosphines by controlled alkylation appeared promising from the standpoint of directness and simplicity.[4,5] The results of the alkylation of mono-*n*-alkylphosphines with methyl and *n*-alkyl halides are summarized in Table I.

Discussion

The preparation of trialkylphosphines by controlled alkylation of monoalkylphosphines is dependent upon close control of a number of variables. These include the alkylating agent, solvent, temperature, time, reactant ratio, the strength of the acid by-product, and the acid concentration. The role of these factors is best understood by considering the complete alkylation sequence, along with our findings concerning the influence of the reaction variables.

The complete alkylation of primary phosphines involves two types of reactions: (1) alkylation or nucleophilic substitution, and (2) dissociation of the hydrogen halide salts formed by the alkylation reaction. The



$$RPH_2 + R'X \longrightarrow \underset{\mathrm{I}}{[RPH_2R'^+]X^-} \rightleftharpoons HX + \underset{\mathrm{II}}{RPHR'} \xrightarrow{R'X}$$
$$\underset{\mathrm{III}}{[RPHR'^+_2]X^-} \rightleftharpoons HX + \underset{\mathrm{IV}}{RPR'_2} \xrightarrow{R'X} \underset{\mathrm{V}}{[RPR'^+_3]X^-}$$

individual alkylation steps proceed faster according to the order of nucleophilicity of alkylphosphines: $R_3P > R_2PH > RPH_2$.[6a] On the other hand, dissociation of the hydrogen halide salts becomes more difficult as substitution of alkyl groups occurs.[6b] The successful synthesis of a trialkylphosphine is then dependent upon preparing its hydrohalide salt (III) under conditions such that further dissociation does not occur. If any dissociation of III does occur, then the free trialkylphosphine will be alkylated to the tetraalkylphosphonium salt under the conditions required for the initial alkylation.

Methanol was chosen as solvent for the initial methylation studies, because of its polar character (polar solvents facilitate the alkylation steps) and its relatively nonbasic character (basic solvents facilitate the dissociation reactions). Subsequent methylation studies showed that the reaction was considerably slower in ethanol and produced ethylated by-products to the extent of 8%. The latter factor requires that the alcohol corresponding to the alkyl halide be used.

With regard to the alkylating agent, methyl iodide is not only the most reactive alkyl halide but is essentially nonbasic, and leads to salts of hydrogen iodide, the strongest acid in the series HI, HBr, and HCl. These factors contribute to the successful preparation

---

[1] L. Maier, *Prog. Inorg. Chem.*, **5**, 84 (1963).

[2] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp 33–36.

[3] (a) W. J. Bailey, S. A. Buckler, and F. Marktscheffel, *J. Org. Chem.*, **25**, 1996 (1960); (b) H. Hellmann and O. Schumacher, *Angew. Chem.*, **72**, 211 (1960), and unpublished results from these laboratories; (c) M. Grayson, P. T. Keough, and G. A. Johnson, *J. Am. Chem. Soc.*, **81**, 4803 (1959); (d) G. Kamai and L. A. Khismatullina, *Zh. Obshch. Khim.*, **26**, 3426 (1956); *Chem. Abstr.*, **51**, 9512*h* (1957).

[4] (a) A. W. Hofmann, *Chem. Ber.*, **6**, 292 (1873). Dialkyl- and trialkylphosphines were prepared by alkylation of mono- and dialkylphosphines, respectively. Information concerning the yields and specificity of these alkylations appears sketchy and has led to some confusion concerning the worth of this method. Information concerning the direct conversion of mono- to trialkylphosphines was not available. (b) Methods utilizing Grignard reagents and alkylphosphonous dichlorides or dialkylphosphinous chlorides or metal phosphides and alkyl halides offer no advantage for the simple trialkylphosphines, since the phosphorus compounds in both cases are generally obtained from the corresponding phosphines. For further discussion of these methods see ref 1, pp 90, 91 and K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhushanam, "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 18, 19.

[5] Subsequent to this investigation, a simplified synthesis of trialkylphosphine oxides was developed; see T. H. Siddall and M. A. Davis, *J. Chem. Eng. Data*, **10** (3), 303 (1965). This synthesis coupled with trichlorosilane reduction of the phosphine oxide constitutes an excellent route to simple trialkylphosphines; see H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **98**, 171 (1965).

[6] (a) W. A. Henderson, Jr., and S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 5794 (1960); (b) W. A. Henderson, Jr., and C. A. Streuli, *ibid.*, **82**, 5791 (1960).

TABLE I

THE CONTROLLED ALKYLATION OF MONO-*n*-ALKYLPHOSPHINES[a]

R'X	Solvent[b]	Temp, °C	Time, hr	Yield of RPR'_2,[c] %
1. CH_3I	CH_3OH	Reflux	5	85–94
2. CH_3I	CH_3OH	Reflux	5	92
3. C_2H_5I	C_2H_5OH	Reflux	48	81
4. *n*-C_4H_9I	*n*-C_4H_9OH	75–80	64	78
5. CH_3Cl[d]	CH_3OH	125	1.5	75–80[e]
6. CH_3Cl[d]	CH_3OH	100	6	90[e]
7. $(CH_3)_2SO_4$	CH_3OH	Reflux	...[f]	...
8. CH_3I	...	50–55	2.5	<1[g]
9. CH_3I–$AlCl_3$	...	...	16	...[h,i]
10. *n*-$C_{12}H_{25}Br$	CH_3OH	Reflux	16	...[j]
11. *n*-$C_{12}H_{25}Br$–$AlCl_3$[k]	...	90	...	...

[a] Dodecylphosphine was alkylated in all cases except for 2 (decylphosphine) and 11 (phosphine). [b] The alcohol corresponding to the alkyl halide was required in 1–7 because the alcohol and the byproduct HX react with the mono-*n*-alkylphosphine under the alkylation conditions. [c] After removal of the excess alkylating agent, the trialkylphosphine was liberated with sodium hydroxide, distilled, and analyzed by gas chromatography. Except where noted the infrared, proton, and phosphorus nmr spectra confirmed the purity of the phosphines. [d] Experiments 5 and 6 represent the optimum conditions of a series of sealed-tube experiments. In all cases, hydrogen chloride was required to suppress the dissociation of the dodecyldimethylphosphonium chloride and thus obtain good yields of the alkyldimethylphosphine. In spite of the additional hydrogen chloride, small amounts of dodecyltrimethylphosphonium chloride were formed. At sufficiently higher temperatures or longer reaction times the latter product was formed exclusively. [e] Owing to the small amounts these yields were estimated by the volume of the phosphine, which was in turn estimated to be 97–98% pure by gas chromatographic and spectral analyses. The impurity consisted of about 2–3% methanol and sodium hydroxide. [f] Upon heating, hydrogen sulfide was evolved and a mixture of methylation and oxidation products was obtained. See the Experimental Section. [g] Dodecylmethylphosphine was obtained in 65–77% yields. [h] Dodecylphosphine was complexed with aluminum chloride, then alkylated by refluxing with excess methyl iodide. After hydrolysis a 93% yield of dodecylmethylphosphine contaminated with 3% dodecyl- and dimethyldodecylphosphines was obtained. [i] In another experiment excess methyl iodide was added to the 1:1 complex at 90°. After hydrolysis and distillation, an 80% yield of a mixture of dodecylphosphine (10%), dodecylmethylphosphine (79%), and dimethyldodecylphosphine (11%) was obtained. Apparently the more rigorous conditions resulted in a greater amount of exchange between the complex, RPH_2–$AlCl_3$, and the product, $[RPH_2CH_3]^+ [AlCl_3I]^-$. The fact that the monoalkylphosphonium trichloroiodoaluminate was not alkylated at 90° attests to the stability of this phosphonium salt. [j] A mixture of the three phosphines was obtained along with several unidentified by-products. Owing to the properties of these phosphines, separation by distillation was very difficult. Consequently, didodecylphosphine and tridodecylphosphine were prepared in excellent yields by the free-radical addition of dodecylphosphine to 1-dodecene using different reactant ratios. [k] Contrary to the report,[7] the reaction of *n*-dodecyl bromide with the 1:1 phosphine–aluminum chloride complex under the conditions described does not produce *n*-dodecylphosphine to any appreciable extent. Instead, a mixture of primary phosphines believed to be structural isomers of *n*-dodecylphosphine was obtained. It seems reasonable that this reaction proceeds by a carbonium ion mechanism analogously to other Friedel-Crafts reactions and is thus unsuitable for the preparation of *n*-alkylphosphines.

of relatively stable hydriodide salts of dialkylphosphines in the absence of solvents, and of trialkylphosphines in methanol, under relatively mild conditions.

Higher alkyl iodides require six- to tenfold greater reaction times than methyl iodide at comparable temperatures because of the lesser reactivity of the *n*-alkyl iodides and the lower polarity of the ethanol and higher alcohols used as solvents. Up to butyl iodide, at least, this is not serious as excellent yields of diethyldodecylphosphine and dibutyldodecylphosphine were obtained.

Alkyl chlorides, on the other hand, are much less reactive than the iodides and lead to salts of hydrogen chloride, a much weaker acid. Even with methyl chloride, complete methylation to dodecyltrimethylphosphonium chloride predominated under conditions where the initial methylation of dodecylphosphine was incomplete (>24 hr at 70°).

When methyl chloride is used, the addition of excess hydrogen chloride to suppress the dissociation of III is essential to the successful preparation of alkyldimethylphosphines. Without added hydrogen chloride all other attempts to stop at III by controlling the temperature, time, and reactant ratio were unsuccessful. Even with added hydrogen chloride and close control of these variables, some dodecyltrimethylphosphonium chloride was formed. Both higher reaction temperatures and longer reaction times led to complete methylation to V.

The strength of the by-product acid, *i.e.*, the stability of the phosphine hydrohalide, is probably one of the most important factors in controlled alkylation. For example, dodecylmethylphosphonium trichloroiodoaluminate apparently does not dissociate to the secondary phosphine to any appreciable extent at 80°. The same is true for dodecylmethylphosphonium iodide in methyl iodide solvent at 50–55°. In alcohol, the hydriodide of the secondary phosphine *does* dissociate, whereas dissociation of the trialklphosphonium iodide does *not* occur. Under comparable conditions the hydrochloride salt readily dissociates and the trialkylphosphine is converted to the tetraalkylphosphonium salt.

Experimental Section

Where possible, all reactions, including oxidations and quaternizations, were carried out under argon in a well-ventilated hood.

***n*-Alkylphosphines.**—Dodecylphosphine[8] and decylphosphine[9] were prepared by reduction of the diethyl alkylphosphonates according to the procedure of Pass and Schindlbauer.[8] The purity of the *n*-alkylphosphines was confirmed by gas chromatographic analysis using a column of 20% Apiezon L on Chromosorb W. The infrared spectrum[10] showed two characteristic bands at 4.37 (PH, intense) and at 9.2 μ (medium). The phosphorus nmr spectrum[11] showed a triplet at +139 ppm (J = 190 cps). The proton nmr spectrum[12] showed a triplet at τ 5.93 (J_{CHPH} = 7 cps) characteristic of one-half of the PH_2 spectrum. The remaining triplet (PH_2) upfield 190 cps was not discernible from the methyl triplet at 9.20 ($J_{CH_2CH_3}$ = 4 cps) and the methylene singlet at 8.82.

Mixture of Dodecylphosphines.—The procedure of Pass, Steininger, and Zorn[13] was used to prepare 0.2 mole of the phosphine–aluminum chloride complex. To this complex, 12 g of *n*-dodecyl bromide (0.05 mole) was added at 80°. Basic hydrolysis and distillation gave a 77% yield of liquid, bp 60–75° (0.1 mm), $n^{20}D$ 1.4599. The infrared spectrum was nearly identical with that of *n*-dodecylphosphine; however, gas chromatographic analysis showed at least seven components. One of the four minor peaks had the same retention time as *n*-dodecylphosphine (estimated yield 0.2% or less). Another of the minor peaks had the same retention time as a mixture of unresolved dodecenes.

---

(7) F. Pass, E. Steininger, and H. Zorn, *Monatsh. Chem.*, **93**, 230 (1962).

(8) F. Pass and H. Schindlbauer, *ibid.*, **90**, 148 (1959).

(9) H. Schindlbauer and E. Steininger, *ibid.*, **92**, 868 (1961).

(10) Recorded on a Perkin-Elmer Infracord spectrophotometer.

(11) Recorded on a Varian HR-60 at 24.3 Mc (reference 85% H_3PO_4).

(12) Recorded on a Varian A-60 at 60 Mc (reference tetramethylsilane).

(13) See Table I, footnote *k*.

The three major peaks were about equal in area and comprised roughly 90% of the total area. The phosphorus nmr spectrum showed triplets centered at +87.8, 95.0, 103.8, and 123.6 ppm. The shifts downfield in the phosphorus nmr spectra and the retention times are believed consistent with structural isomers of *n*-dodecylphosphine.

Dodecylmethylphosphine. A.—Dodecylphosphine (20 g, 0.1 mole) and 42.6 g of methyl iodide (0.3 mole) were heated at a bath temperature of 50–55° for 2.5 hr. (The optimum time was ascertained by gas chromatographic analysis of samples that were freed of methyl iodide, then neutralized.) After the excess methyl iodide was removed under reduced pressure, 8 g of powdered sodium hydroxide (0.2 mole) and 25 ml of methanol were added. Separation and distillation gave dodecylmethylphosphine, bp 93–95° (0.5 mm), in 65–77% yields. Gas chromatographic analysis indicated 99–100% purity with less than 1% of dimethyldodecylphosphine. The infrared spectrum showed two characteristic bands at 4.37 (PH, intense) and 10.06 μ (medium). The PCH_3 absorption at 7.7 μ was barely observable in the spectra of the methylphosphines prepared in this study. The phosphorus nmr spectrum showed a doublet centered at 85.3 ppm (J_{PH} = 194 cps).

B.—Dodecylphosphine (22 g, 0.109 mole) and 14.4 g of aluminum chloride (0.109 mole) were mixed and heated to 110°, then added dropwise to 71 g of refluxing methyl iodide (0.5 mole) over a period of about 30 min. Reaction was incomplete after several hours so the mixture was stirred overnight in a 90° oil bath. After removing the excess methyl iodide under reduced pressure, 250 ml of 30% sodium hydroxide was added with cooling. After separation and extraction with ether, distillation gave a 93% yield of dodecylmethylphosphine (97% pure). About 3% of dodecyl- and dimethyldodecylphosphines was observed.

In another experiment, addition of excess methyl iodide to the complex at 90° resulted in a distilled yield of 80% of a mixture of dodecylmethylphosphine (79%), dodecylphosphine (10%), and dimethyldodecylphosphine (11%).

Dimethyldodecylphosphine. A.—To 101 g of dodecylphosphine (0.5 mole) and 200 ml of methanol was added 145 g of methyl iodide (1.02 mole). The mixture was refluxed with stirring for 5 hr. (The optimum time was ascertained by gas chromatographic analyses of methyl iodide free samples that were treated with sodium hydroxide.) The excess methyl iodide was removed under reduced pressure without heat. After cooling the methanol solution in an ice bath, 44 g of powdered sodium hydroxide (1.1 mole) was added in portions. Upon warming to room temperature, the methanol layer, nearly saturated with sodium iodide, was removed. The remaining layer was estimated to be 97–98% dimethyldodecylphosphine containing about 2–3% methanol. Distillation gave 100% pure dimethyldodecylphosphine, bp 80–83° (0.03 mm), in 85–94% yields. Infrared and phosphorus nmr spectra of the small amount of residual sodium iodide and the sodium iodide from the methanol phase showed no evidence of dodecyltrimethylphosphonium iodide. The infrared spectrum of dimethyldodecylphosphine showed a medium intensity band at 10.68 μ in addition to the usual CH absorptions. The phosphorus nmr spectrum showed a singlet at +52.5 ppm. The proton nmr spectrum showed a PCH_3 doublet at τ 9.18 and 9.22 (J_{PCH} = 3 cps) along with the usual methylene singlet at 8.81 and the $CH_2\mathit{CH_3}$ triplet at 9.20.

B.—Saturated methanolic hydrogen chloride solutions were prepared at about 20°, standardized, and a given volume (0.1 mole of hydrogen chloride) was transferred to a 125-ml glass ampoule containing methanol (0.625 mole total) and packed in Dry Ice. Liquid methyl chloride (0.1 mole) was added *via* a Dry Ice cooled buret. Dodecylphosphine (0.05 mole) was added *via* syringe and the ampoule was sealed with a torch. The ampoules were then heated in an autoclave equipped with a tight fitting coil through which steam, cold water, or mixtures could be circulated. This allowed rapid heating and cooling of the reactants. Temperatures were measured by a thermocouple between the coil and the ampoule. After reaction, the ampoule was removed, cooled in Dry Ice, and opened under argon. After sufficient powdered sodium hydroxide had been added and the mixture allowed to warm slowly to room temperature, the dimethyldodecylphosphine separated cleanly in those cases where the yield of dodecyltrimethylphosphonium chloride was less than 20–30%. At higher concentrations a gelatinous mixture was obtained. Owing to the small amounts involved, yields were estimated by volume and by gas chromatography. The yield of dimethyldodecylphosphine was 75–80% after 1.5 hr at 125°, 90% after 2 hr at 115°, and 90% after 6 hr at 100°. The remainder of the product was dodecyltrimethylphosphonium chloride, identified by its infrared and phosphorus nmr spectra. Several series of sealed tube reactions were run at each temperature to determine the optimum time. At shorter reaction times mixtures of dodecylphosphine, dodecylmethylphosphine, and dimethyldodecylphosphine were obtained. In general, increasing the reaction time threefold led to the dodecyltrimethylphosphonium chloride exclusively. Attempts to control the methylation in the absence of added hydrogen chloride by varying the temperature from 70 to 150°, the time from 30 min to 24 hr, and using a 2:1 reactant ratio, were unsuccessful. Below 70° the rate of methylation of dodecylphosphine was too slow to be of interest (30% methylated after 24 hr at 50°).

Dimethyldecylphosphine.—The preceding procedure A was used. Distillation gave a 92% yield of dimethyldecylphosphine, bp 85° (0.4–0.5 mm). The proton and phosphorus nmr and the infrared spectra of dimethyldecylphosphine were essentially identical with those of dimethyldodecylphosphine.

Dimethyldodecylphosphine Oxide.—Dimethyldodecylphosphine (23 g, 0.1 mole) was added to a slight excess of 3% hydrogen peroxide and stirred until a clear solution was obtained. The dimethyldodecylphosphine oxide was extracted with chloroform and recrystallized from hexane in 74% yield, mp 84–85°. The melting point, and infrared, proton, and phosphorus nmr spectra were identical with those reported by Laughlin.[14]

Dodecyltrimethylphosphonium Halides. Iodide.—Dodecyltrimethylphosphonium iodide, mp 87–88°, was prepared in quantitative yield and analytical purity by addition of 21.3 g of freshly distilled methyl iodide (0.15 mole) to 24.8 g of dimethyldodecylphosphine (0.108 mole) in 100 ml of methanol, followed by refluxing for 30 min and removal of the methanol under reduced pressure. The infrared spectrum showed a sharp $^+PCH_3$ absorption at 7.75 (medium) and medium-strong absorptions at 10.2 and 10.4 μ. The phosphorus nmr spectrum showed a singlet at −26.3 ppm. The proton nmr spectrum showed a $^+PCH_3$ doublet centered at τ 8.07 (J_{PCH} = 14.5 cps) along with the methylene singlet at τ 8.68 and the $CH_2\mathit{CH_3}$ triplet at 9.13.

Anal. Calcd for $C_{15}H_{34}IP$: C, 48.4; H, 8.9. Found: C, 48.3; H, 9.1.

Chloride.—Deoxygenated methyl chloride was passed through refluxing methanol (200 ml) and 69.6 g of dimethyldodecylphosphine (0.3 mole) for 6 hr. After removal of the solvent, a 99% yield of dodecyltrimethylphosphonium chloride remained. The solid phosphonium chloride discolored upon heating to 210–212°. The infrared, proton, and phosphorus nmr spectra agreed with those of the iodide and the bromide.

Anal. Calcd for $C_{15}H_{34}ClP$: C, 64.20; H, 12.2. Found: C, 63.9; H, 12.1.

Bromide.—Dodecyltrimethylphosphonium bromide was prepared in 94% yield using the same procedure as for the chloride. The bromide also discolored at about 210° upon heating in the atmosphere.

Anal. Calcd for $C_{15}H_{34}BrP$: C, 55.4; H, 10.4. Found: C, 55.2; H, 10.5.

Products from the Reaction of Dodecylphosphine and Methyl Sulfate.—Dodecylphosphine (22 g, 0.11 mole) and 26.2 g of methyl sulfate (0.21 mole) were stirred in 40 ml of methanol for 1 hr without apparent reaction. Upon refluxing for 4 hr, hydrogen sulfide (identified as lead sulfide) was evolved. A phosphorus nmr spectrum of the strongly acidic solution showed five peaks at −35, −50, −60, −71, and −76 ppm. Treatment with base and extraction gave very minute traces of dodecylmethylphosphine and dimethyldodecylphosphine (detected by gas chromatographic analysis). The major product isolated in small amounts was dodecylmethylphosphinic acid, identical in melting point (69–70°) and infrared spectrum with a sample prepared by oxidation of dodecylmethylphosphine. The phosphorus nmr spectrum showed a singlet at −51 ppm.

Anal. Calcd for $C_{13}H_{29}O_2P$: C, 62.9; H, 11.8. Found: C, 62.3; H, 11.4.

Also, traces of dodecylmethylphosphine oxide, mp 68–69°, were obtained. The phosphorus nmr spectrum showed a doublet centered at −33.9 ppm (J = 18.6 cps).

Anal. Calcd for $C_{13}H_{20}OP$: C, 67.3; H, 12.6. Found: C, 67.1; H, 12.4.

Diethyldodecylphosphine.—Dodecylphosphine (20 g, 0.1 mole), 34 g of ethyl iodide (0.22 mole), and 40 ml of ethanol were

---

[14] R. G. Laughlin, *J. Org., Chem.*, **30**, 1322 (1965).

refluxed for 24 hr. Reaction was incomplete at this point. Additional ethyl iodide (0.08 mole) was added and refluxing was continued for 24 hr. After the excess ethyl iodide was removed under reduced pressure, 8 g of finely powdered sodium hydroxide was added with cooling. The mixture was warmed to reflux, cooled, and separated. Distillation gave an 80% yield of diethyldodecylphosphine, bp 117–135° (0.6 mm). The infrared spectrum showed a weak absorption at 9.5 μ. The phosphorus nmr spectrum showed a singlet at +25 ppm. The proton nmr spectrum showed chiefly the methylene singlet at τ 8.76 and the $CH_2\mathit{CH}_3$ triplet at 9.15.

Diethyldodecylphosphine Oxide.—Diethyldodecylphosphine (12.4 g, 0.05 mole) and 113 g of 3% hydrogen peroxide were mixed and heated for 1 hr on the steam bath. After two extractions with chloroform, distillation gave an 87% yield of diethyldodecylphosphine oxide, bp 135–140° (0.06 mm), mp 48–48.5°. The infrared, proton, and phosphorus nmr spectra were identical with those of a sample prepared by a Grignard reaction.[14]

Dodecyltriethylphosphonium Chloride.—A 150-ml, sealed glass tube containing 10 g of diethyldodecylphosphine (0.038 mole) and 32 g of ethyl chloride (0.5 mole) was heated in an autoclave at 100° for 3 hr. After cooling to 0°, the tube was opened and the excess ethyl chloride was evaporated. Dodecyltriethylphosphonium chloride, mp 106–109°, was obtained in nearly quantitative yield. The infrared spectrum showed weak absorptions at 9.45, 12.25, and 12.7 μ. The phosphorus nmr spectrum showed a singlet at −37 ppm. The proton nmr spectrum showed a $^+P\mathit{CH}_2CH_3$ multiplet centered at τ 7.75 with the methylene singlet at 8.69, and the $(CH_2)_n\text{-}\mathit{CH}_3$ peak at 9.11, superimposed on the $^+PCH_2\mathit{CH}_3$ and the $^+PCH_2R$ multiplets.

Anal. Calcd for $C_{18}H_{40}ClP$: C, 67.0; H, 12.4. Found: C, 66.8; H, 12.5.

Dibutyldodecylphosphine.—Dodecylphosphine (40 g, 0.2 mole) and 75 g of butyl iodide (0.41 mole) were heated at 70–75° in 80 ml of *n*-butyl alcohol for 24 hr. Reaction was incomplete so heating was continued for a total of 64 hr. After the excess butyl iodide was removed, 32 g of 50% aqueous sodium hydroxide was added with cooling. Separation and distillation gave a 78% yield of dibutyldodecylphosphine, bp 135–145° (0.5 mm). The infrared spectrum showed no PH band at 4.3 μ. Gas chromatographic analysis indicated 99.9% purity. The phosphorus nmr spectrum showed a singlet at +32.4 ppm. The proton nmr spectrum showed peaks at τ 8.75, 8.79, and 9.19.

Tridodecylphosphine. A.—Dodecylphosphine (9.9 g, 0.049 mole) and 13 g of dodecyl bromide (0.052 mole) were heated overnight in 10 ml of methanol at a bath temperature of 130–135°. After work-up, distillation gave dodecylphosphine, didodecylphosphine, and tridodecylphosphine (identified by their retention times), and several unidentified products. Owing to the complexity of the mixtures and the properties of the phosphines, further purification was not attempted.

B.—Dodecylphosphine (5 g, 0.025 mole), 33.6 g of 1-dodecene (0.2 mole), and 0.12 g of α,α-azobisisobutyronitrile (ABN) were heated overnight at 85°. Distillation gave an 87% yield of tridodecylphosphine, bp 255–275° (0.05 mm). Gas chromatographic analysis of the tridodecylphosphine was made on an Apiezon L column at 350°. Under these conditions the column was eventually destroyed. The infrared and proton nmr spectra were consistent with the proposed tridodecylphosphine structure. The phosphorus nmr spectrum showed a singlet at +36 ppm.

Tridodecylphosphine Oxide.—Tridodecylphosphine (10.8 g, 0.02 mole) was stirred with 40 g of 3% hydrogen peroxide for 30 min, then heated for 30 min on the steam bath. After extraction with chloroform and recrystallization from acetone, a 64% yield of tridodecylphosphine oxide, mp 59–59.5°, was obtained. The infrared spectrum showed an intense phosphoryl absorption at 8.67 μ. The proton and phosphorus nmr spectra (−53 ppm) were consistent with the tridodecylphosphine oxide structure.

Anal. Calcd for $C_{36}H_{75}OP$: C, 77.9; H, 13.6. Found: C 77.0; H, 13.6.

Methyltridodecylphosphonium Bromide.—A 150-ml sealed glass tube containing 15 g of tridodecylphosphine (0.028 mole) and 50 g of methyl bromide (0.53 mole) was heated in an autoclave for 3 hr at 100°. After cooling to 0°, the tube was opened and the methyl bromide was evaporated to give a nearly quantitative yield of methyltridodecylphosphonium bromide. The infrared spectrum showed a weak $^+PCH_3$ absorption at 7.69 and medium bands at 10.55 and 10.9 μ. The phosphorus nmr spectrum showed a singlet at −32 ppm. The proton nmr spectrum showed a $^+PCH_3$ doublet at τ 8.03 (J_{PCH} = 13.5 cps) along with the methyl and methylene peaks.

Anal. Calcd for $C_{37}H_{78}BrP$: C, 70.1; H, 12.4. Found: C, 70.0; H, 12.8.

Didodecylphosphine.—Dodecylphosphine (50 g, 0.25 mole), 8.4 g of 1-dodecene (0.05 mole), and 0.12 g of ABN were heated overnight at 85°. Distillation gave a 69% yield of didodecylphosphine, bp 170–185° (0.05 mm), mp 55–60°. The infrared spectrum showed a medium PH absorption at 4.37 along with medium to weak bands at 8.45, 8.6, 9.32, 9.7, 10.12, 10.62, 11.2, 11.82, 12.97, and 12.28 μ. The phosphorus nmr spectrum showed a doublet at +71 ppm (J = 193 cps). The proton nmr spectrum showed one-half of the PH spectrum at τ 5.47 along with the usual methylene and methyl peaks.

Didodecylmethylphosphine.—A mixture of 21 g of dodecylmethylphosphine (0.1 mole), 100 g of 1-dodecene (0.6 mole), and 1 g of ABN was heated overnight at 65°. Distillation gave a 91% yield of didodecylmethylphosphine, bp 188–195° (0.022 mm). The infrared spectrum showed two very weak bands at 7.8 and 11.4 μ. The phosphorus nmr spectrum showed a singlet at +34 ppm. The proton nmr spectrum showed a PCH_3 doublet at τ 9.17 (J_{PCH} = 3 cps) along with the methylene peak at 8.77 and the methyl peak at 9.18.

Didodecylmethylphosphine Oxide.—Dilute hydrogen peroxide (60 g of 3%) was added to 9 g of didodecylmethylphosphine (0.023 mole) and stirred for 20 min, then heated for 30 min on a steam bath. Owing to a loss during the extraction with chloroform, only 1 g of crude product was obtained. After two recrystallizations from acetone the didodecylmethylphosphine oxide melted at 72.5–73.5°. The infrared spectrum showed a strong phosphoryl band at 8.64, a weak PCH_3 absorption at 7.77, and medium intensity bands at 11.18, 13.4, and 13.8 μ. The phosphorus nmr spectrum showed a singlet at −53 ppm. The proton nmr spectrum showed $O \leftarrow PCH_3$ doublet at τ 8.40 (J_{PCH} = 13 cps) along with the usual methylene and methyl peaks.

Anal. Calcd for $C_{25}H_{53}OP$: C, 75.0; H, 13.25. Found: C, 74.6; H, 14.3.

Didodecyldimethylphosphonium Iodide.—Didodecylmethylphosphine (30 g, 0.078 mole) was added dropwise to 15 g of methyl iodide (0.1 mole) in 25 ml of methanol with cooling. After most of the methanol was removed, the product was recrystallized from peroxide-free ether, filtered, and washed with hexane under argon. A 61% yield of didodecyldimethylphosphonium iodide, mp 49–50°, was obtained. The infrared spectrum showed a weak $^+PCH_3$ doublet at 7.6 and 7.8 and medium intensity bands at 10.32, 10.51, and 13.8 μ. The phosphorus nmr spectrum showed a singlet at −29.5 ppm. The proton nmr spectrum showed a $^+PCH_3$ doublet at τ 8.06 (J_{PCH} = 13 cps), the (CH_2) singlet at 8.77, and the methyl triplet at 9.18.

Acknowledgments.—The author wishes to thank Dr. R. G. Laughlin and Dr. T. J. Logan for their helpful discussions and Dr. T. J. Flautt for the proton and phosphorus nmr measurements.