potassium hydroxide. Under these conditions, ammonia was evolved and IV was formed in good yield. The dimethoxyethane is required for solvent purposes; in aqueous base alone, hydrolysis did not occur.

ACKNOWLEDGMENT

The author expresses his appreciation to J. B. Holbrook for helping with the experimental work, to H L. Joyce for interpreting the infrared spectra, and to J. B. Strow for interpreting the nuclear magnetic resonance spectra.

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RECEIVED for review March 7, 1968. Accepted August 26, 1968.

Synthesis of Some Bis(Halomethyl) Phosphorylmethyltriphenylphosphonium Halides and a Stable Phosphine Methylene

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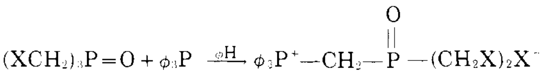
The 1 to 1 triphenylphosphine adducts of tris(chloromethyl)phosphine oxide, tris(bromomethyl)phosphine oxide, and tris(iodomethyl)phosphine oxide were prepared in 80% yield. The chloro derivative was converted to triphenylphosphinebis(chloromethyl)phosphorylmethylene by reaction with aqueous ammonium hydroxide. The phosphine methylene was stable and capable of regenerating the predecessor by reaction with hydrogen chloride. It also reacted with bromine to form bis(chloromethyl)phosphorylmethyltriphenylphosphonium bromide. Infrared and NMR spectra of the subject compounds were recorded.

IN THE SIMPLEST PROCESS for the preparation of phosphonium compounds an alkyl halide and a tertiary phosphine are mixed and heated (*1*). The authors have prepared the 1-to-1 adducts of triphenylphosphine and some halomethylphosphine oxides. The ionic halogens were replaced by a picrate moiety for proof of structure.



$$(XCH_2)_3P{=}O + \phi_3P \xrightarrow{\phi H} \phi_3P^+{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}(CH_2X)_2X^- \quad (1)$$

Schlosser reported that acyl- or benzoylmethylidetriphenylphosphonium halides undergo deuterium exchange without the use of a catalyst (*3*). The authors observed that the phosphoryl group affects the lability of the methylene hydrogens in a like manner, when deuterium oxide was added to a chloroform solution of bis(chloromethyl)phosphorylmethyltriphenylphosphonium chloride (I) during an NMR analysis.

Ramirez synthesized hexaphenylcarbodiphosphorane, which reacted with water to form triphenylphosphinediphenylphosphorylmethylene (*2*). The stability of the latter compound was explained by the effect of the adjacent phosphoryl group on the negative charge. By reaction of I with an aqueous 2% solution of ammonium hydroxide, the authors prepared triphenylphosphinebis(chloromethyl)phosphorylmethylene (IV).

$$\phi_3P{-}CH_2{-}P{-}(CH_2Cl)_2Cl \xrightarrow{NH_4OH} \phi_3P{=}CH{-}P{-}(CH_2Cl)_2 \text{ (IV)} \quad (2)$$

The stability of IV was affected by its slight hygroscopic properties. NMR studies showed that water reacts slowly with IV to produce a phosphonium compound, undoubtedly the phosphonium hydroxide. The reaction of a benzene solution of IV with hydrogen chloride regenerated I. Methylene chloride solutions containing bromine were decolorized by IV. However, the only product obtained was bis (chloromethyl) phosphorylmethyltriphenylphosphonium bromide (V) and not the expected product, a bromomethyltriphenylphosphonium bromide.

The reaction of ammonium hydroxide with dibromomethylphosphorylmethyltriphenylphosphonium bromide (II) produced only a quantitative yield of triphenylphosphine oxide.

EXPERIMENTAL

Bis (chloromethyl) phosphorylmethyltriphenylphosphonium Chloride (I). Tris(chloromethyl)phosphine oxide (3.0 grams, 0.0153 mole) was refluxed with triphenylphosphine (4.19 grams, 0.016 mole) in benzene for 18 hours. The resulting solution was filtered and yielded 5.8 grams (83%) of crude I [m.p. 230-1.5° C. (methanol-benzene)]. The infrared spectrum (KBr) (Perkin-Elmer Model 137B Infracord) exhibited peaks at 3.25(w), 3.35(w), 3.42(w), 3.55(m), 3.70(w), 6.3(w), 6.75(w), 6.95(w), 7.15(w), 7.32(w), 7.48(w), 7.60(w), 8.08(m), and 8.20(m) with a shoulder at 8.30(m), 8.42(m), 8.60(w), 9.0(s), 10.05(w), 11.86(m), 12.14(s), 12.9(s), 13.25(s), 13.62(s), and 14.45 microns(s). The NMR spectrum (Varian A-60A spectrometer) of a deuteriochloroform solution showed a phenyl complex centered at δ7.8 p.p.m., two doublets centered at δ5.6 p.p.m., *J*P—CH = 13 c.p.s., and a complex centered at δ3.95 p.p.m. in a ratio of 15:2:4, respectively. The addition of deuterium oxide eliminated the two doublets centered at δ5.6 p.p.m.

Analysis. Calculated for $C_{21}H_{21}Cl_3OP_2$: C, 55.11; H, 4.63; Cl, 23.24; P, 13.29. Found: C, 55.45; H, 4.86; Cl, 22.72; P, 13.29.

The picrate of I had a melting point of 164.5-66° C. Analysis. Calculated for $C_{27}H_{23}Cl_2N_3O_7P_2$: N, 6.46; Cl, 10.90; P, 9.52. Found: N, 6.40; Cl, 10.63; P, 9.02.

Bis(bromomethyl) phosphorylmethyltriphenylphosphonium Bromide (II). The procedure used for the preparation of I was followed, using tris(bromomethyl)phosphine oxide to produce an 87% yield of crude II. Pure white crystals (m.p. 226–28° C.) were obtained by recrystallization from a methanol-benzene mixture. The infrared spectrum (KBr) exhibited peaks at 3.25(w), 3.30(w), 3.40(w), 3.55(m), 3.65(w), 6.28(w), 6.70(w), 6.95(m), 7.20(w), 7.25(w), 7.32(w), 7.45(w), 7.55(w), and 8.15(s), with a shoulder at 8.15, 8.35(w), 9.02(s), 10.03(w), and 10.20(w), 12.2(s) with a shoulder at 12.45(m), and 13.35(s) with a shoulder at 13.25(s), 13.78(s), and 14.5 microns(s). The NMR spectrum of a deuteriochloroform solution of II showed a phenyl complex centered at $\delta 7.8$ p.p.m., two doublets centered at $\delta 5.55$ p.p.m., JP—CH = 12 c.p.s., and a complex centered at $\delta 3.8$ p.p.m. in a ratio of 15:2:4, respectively. Addition of a small amount of deuterium oxide eliminated the two doublets centered at $\delta 5.55$.

Analysis. Calculated for $C_{21}H_{21}Br_3OP_2$: C, 42.67; H, 3.58; Br, 40.56, P, 10.48. Found: C, 44.11; H, 4.14; Br, 39.45; P, 10.53.

The picrate of II had a melting point of 182–83.5° C. Analysis. Calculated for $C_{27}H_{23}Br_2N_3O_7P_2$: N, 5.68; Br, 21.61; P, 8.38. Found: N, 5.44; Br, 20.32; P, 8.08.

Bis(iodomethyl)phosphorylmethyltriphenylphosphonium Iodide (III). The procedure for the preparation of I was followed, using tris(iodomethyl)phosphine oxide and isobutyl alcohol as the solvent. An 85% yield of a crude white solid was obtained (m.p. 228–29° C.) after recrystallization from water. The infrared spectrum (KBr) exhibited peaks at 3.35(w), 3.40(w), 3.58(m), 3.62(w), 6.30(w), 6.74(w), 6.96(m), 7.38(m), 7.62(w), 8.2(s), 8.39(m), 8.45(m), 8.62(w), 8.92(w), 9.05(s), 9.6(w), 9.8(w), 10.05(w), 10.25(w), 12.30(s), 12.45(s), 13.0(w), and 13.35(s) with a shoulder at 13.15(w), 13.75(m), 13.92(m), and 14.55 microns(m). The NMR spectrum of a trifluoroacetic acid solution of III showed a phenyl complex centered at $\delta 7.9$ p.p.m., two doublets centered at $\delta 4.78$ p.p.m., JP—CH = 12 c.p.s., and a doublet centered at $\delta 3.58$ p.p.m., JP—CH = 6 c.p.s. in a ratio of 15:2:4, respectively.

Analysis. Calculated for $C_{21}H_{21}I_3OP_2$: C, 34.45; H, 2.89; I, 52.00; P, 8.46. Found: C, 34.98; H, 3.12; I, 52.13; P, 8.26. The picrate of III had a melting point of 167–68° C. Analysis. Calculated for $C_{27}H_{23}I_2N_3O_7P_2$: N, 5.04; I, 30.46; P, 7.43. Found: N, 4.85; I, 30.16; P, 7.13.

Triphenylphosphinebis (chloromethyl) phosphorylmethylene (IV). I (2.5 grams, 0.00546 mole) was dissolved in 75 ml. of water. Upon the addition of 75 ml. of a 2% aqueous ammonium hydroxide solution, a thick oily substance separated, which with shaking eventually turned into a white solid. The yield of crude IV was 1.42 grams (62%). White crystals (m.p. 129–30° C.) were obtained by recrystallization from benzene-hexane. Upon evaporation of the filtrate 0.46 gram of triphenylphosphine oxide was obtained, which accounted for 28% of the triphenylphosphine in I. When hydrogen chloride was bubbled into a benzene solution of IV (1.0 gram, 0.00238 mole), 0.87 gram (80%) of a white precipitate was obtained. The infrared curve and melting point were identical with those of I. The infrared spectrum of IV (KBr) exhibited peaks at 3.25(w), 3.40(w), 6.3(w), 6.75(m), 6.97(m), 7.2(m), 7.5(w), 7.15(w), 7.87(w), 8.22(s), 8.32(s), 8.45(s), 8.55(s), 8.65(m), 9.03(s), 9.35(w), 9.72(w), 9.95(w), 10.05(w), 10.17(m), 10.29(s), 11.65(w), 11.75(w), 11.95(m), 12.28(m), 13.15(m), 13.35(m), 13.65(w), 13.95(s), 14.39(s), and 14.55 microns(m). The NMR spectrum of a deuteriochloroform solution of IV showed a phenyl complex centered at $\delta 7.3$ p.p.m., a multiplet with 8 lines centered at $\delta 3.4$ p.p.m., and a singlet at $\delta 1.45$ p.p.m. in a ratio of 15:4:1, respectively. The addition of deuterium oxide eliminated the singlet at $\delta 1.45$ p.p.m.

Analysis. Calculated for $C_{21}H_{20}Cl_2OP_2$: C, 59.71; H, 4.73; Cl, 16.82; P, 14.69. Found: C, 59.30; H, 4.66; Cl, 16.28; P, 14.59.

Bis (chloromethyl) phosphorylmethyltriphenylphosphonium Bromide (V). IV (0.5 gram, 0.00119 mole) was dissolved in 50 ml. of methylene chloride and a (methylene chloride) solution of bromine was added until a slight orange color persisted. Evaporation of the solvent gave a semisolid which was dissolved in either methanol or methylene chloride and benzene was added until the solution became cloudy. A white compound weighing 0.42 gram (70%) was obtained (m.p. 225–27° C.). The infrared spectrum (KBr) of V was identical to that of I except that the peak at 9.0 microns was split into two peaks at 8.95(s) and 9.05 microns (s) for the bromide.

Analysis. Calculated for $C_{21}H_{21}BrCl_2OP_2$: C, 50.20; H, 4.18; Br, 15.94; P, 12.35. Found: C, 50.36; H, 4.25; (Br, 16.65) (P, 12.28).

Reaction of Bis(bromomethyl)phosphorylmethyltriphenylphosphonium Bromide (II) with Ammonium Hydroxide. II (1.0 gram, 0.002 mole) was dissolved in 50 ml. of water. Upon the addition of 50 ml. of a 2% ammonium hydroxide solution, a thick oily precipitate was obtained which, upon continuous shaking, turned into a white solid. A yield of 0.45 gram (0.00171 mole) of triphenylphosphine oxide was obtained by recrystallization of the solid from methanol-water. It was identified by melting point and infrared spectrum.

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RECEIVED for review March 8, 1968. Accepted May 31, 1968. One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.