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Synthesis of Some Halomethylphosphine Oxides

LEON H. CHANCE, DONALD J. DAIGLE, and GEORGE L. DRAKE, Jr.
Southern Regional Research Laboratory, New Orleans, La.

Tris(chloromethyl)phosphine was converted to methyl bis(chloromethyl)phosphine oxide through an oxidation and rearrangement by refluxing in ammonium hydroxide. Tetrakis(bromomethyl)phosphonium bromide was prepared in 93% yield by the reaction of tetrakis(hydroxymethyl)phosphonium chloride and phosphorus pentabromide. The bromide was converted to tris(bromomethyl)phosphine by reaction with aqueous sodium bicarbonate, and the phosphine was converted to tris(bromomethyl)phosphine oxide in 71% yield by oxidizing with aqueous hydrogen peroxide in tetrahydrofuran. Methyl bis(iodomethyl)phosphine oxide was prepared in 47% yield by refluxing methyl bis(chloromethyl)phosphine oxide and sodium iodide in acetone. Infrared and NMR spectra of the subject compounds were recorded.

THE PREPARATION of tetrakis (chloromethyl)phosphonium chloride (I) by the reaction of PCl_5 with tetrakis-(hydroxymethyl)phosphonium chloride (II) was first described by Hoffman (*2*). He also reported the conversion of I to tris(chloromethyl)phosphine (III) by treatment with aqueous $NaHCO_3$ and the oxidation of III to the oxide by boiling with nitric acid. The authors carried out the oxidation with 5% aqueous H_2O_2 in tetrahydrofuran.

Kabachnik and Tsvetkov discovered that the reaction of III with sodium ethylate in ethanol yielded methyl bis(ethoxymethyl)phosphine oxide (*3*). The alcoholysis is accompanied by a redox rearrangement which they termed a "pseudoallyl" rearrangement. They also discovered that the rearrangement of III took place in the presence of hydrochloric acid, and that methyl bis-(chloromethyl)phosphine oxide (IV) was formed. The authors refluxed III with ammonium hydroxide in an effort to form tris(aminomethyl)phosphine. However, a compound was obtained having the identical infrared curve, NMR curve, and melting point of IV. This proved that the rearrangement also takes place in the presence of ammonium hydroxide. Obviously, ammonium hydroxide was not a strong enough base to replace the two remaining chlorine atoms.

Anteunis, Verzele, and Dacremont reported the preparation of tris(bromomethyl)phosphine oxide (V) in only 5% yields from phosphorus pentabromide and diazomethane (*1*). The authors prepared V by a method similar to that used by Hoffman to prepare tris(chloromethyl)phosphine oxide, except that hydrogen peroxide was used instead of nitric acid (*2*). Tetrakis(bromomethyl)phosphonium bromide (VI) (a new compound) was prepared by the reaction of II with PBr_5. Tris(bromomethyl)phosphine, obtained by treating VI with aqueous $NaHCO_3$, was oxidized to V with aqueous H_2O_2 in tetrahydrofuran.

Another compound, methyl bis(iodomethyl)phosphine oxide (VII), was prepared by reacting IV with sodium iodide in acetone.

The same coupling constant, 7 c.p.s., was observed from NMR data for each of the compounds IV, V, and VII. Since each of these compounds contains a different halogen, the authors expected that the coupling constants would be different.

EXPERIMENTAL

Rearrangement and Oxidation of Tris(chloromethyl)phosphine (III) in Ammonium Hydroxide. III (5.95 grams, 0.033 mole) was refluxed with 40 ml. of concentrated ammonium hydroxide for 11 hours. During the reflux, ammonia gas was bubbled into the mixture. The resulting solution was evaporated to dryness, and the solid extracted several times with boiling benzene. After evaporation of the benzene a colorless liquid remained which upon cooling crystallized to a white solid, yield 1.5 grams (28%), m.p. 48-50° C. The infrared spectra (KBr) (Perkin-Elmer Model 137B Infracord) exhibited peaks at 3.28 (w), 3.38 (w), 7.05 (w), 7.1 (w), with a shoulder at 7.2 (w), 7.65 (m), 8.03 (m), 8.3 (s), with a shoulder at 8.15 (m), 8.45 (m), 8.79 (w), 8.88 (w), 10.95 (m) with a shoulder at 10.7 (m), 11.6 (m), 11.9 (w), 13.0 (w), 13.2 (w), 13.7 (w), 13.9 (w), 14.5 (w), and 14.8 μ (w).

The NMR (Varian A-60A Spectrometer) of a deuteriochloroform solution of IV showed a doublet centered at δ 1.7 p.p.m., Jp-ch = 14 c.p.s. and a doublet centered at δ 3.92 p.p.m., Jp-ch = 7 c.p.s. in the ratio of 3 to 4, respectively.

Infrared and NMR spectra were identical with those of methyl bis(chloromethyl)phosphine oxide prepared by the method of Kabachnik and Tsvetkov (*3*).

Anal. calcd. for $C_3H_7Cl_2OP$: C, 22.38; H, 4.38; Cl, 44.05; P, 19.24. Found: C, 22.36; H, 4.43; Cl, 44.24; P, 19.32.

Tetrakis(bromomethyl)phosphonium Bromide (VI). Bromine (131.0 grams, 0.818 mole) was added dropwise with vigorous stirring to a flask containing 30.0 grams (0.157 mole) of tetrakis(hydroxymethyl)phosphonium chloride and 221.8 grams (0.818 mole) of phosphorus tribromide in 500 ml. of carbon tetrachloride. The bromine was added at a rate such that the temperature did not exceed 50° C. The mixture, which contained a large amount of solid, was then refluxed for 6 hours. During this time the mixture turned from a dark red color to a yellow color. The cooled mixture was filtered, and yielded 71.3 grams (93% yield) of crude VI. Pure white crystals, m.p. 242-3° C., were obtained after two recrystallizations from benzene-methanol. The infrared spectrum (KBr) exhibited peaks at 3.28 (m), 3.35 (m), 7.05 (w), 7.2 (m), 8.23 (w), 8.43 (w), 8.78 (w), 8.95 (w), 9.08 (w), 9.2 (w), 11.7 (s), 11.95 (s), and 12.35 μ (w).

Anal. calcd. for $C_4H_8Br_5P$: C, 9.86; H, 1.64; Br, 82.13; P, 6.40. Found: C, 10.00; H, 1.80; Br, 81.98; P, 6.37.

Tris(bromomethyl)phosphine Oxide (V). VI (71.3 grams, 0.148 mole) was placed in 200 ml. of water, and solid sodium bicarbonate was added with stirring until the solution was alkaline. The oil layer, consisting of crude tris(bromomethyl)phosphine, was separated from the water layer. It had a disagreeable odor resembling that of tris(chloromethyl)phosphine. Tetrahydrofuran was added to the oil and an excess of 3% aqueous hydrogen peroxide was gradually added with stirring. The reaction temperature was not allowed to go above 50° C. After stirring for 2 hours at room temperature, the solution was evaporated to a solid mass. The solid was triturated with hot chloroform. After the chloroform evaporated, 36.8 grams (71% yield) of crude V was obtained. Pure white crystals, m.p. 126.5-127.5° C., were obtained after three recrystallizations from cyclohexane. The infrared spectrum (KBr) exhibited peaks at 3.28 (w), 3.35 (w), 7.2 (w), 8.2 (s) with a shoulder at 8.3 (w), 8.58 (w), 9.15 (w), 9.32 (w), and 12.25 (s) with a shoulder at 12.15 μ (s).

The NMR spectrum of a deuteriochloroform solution of V showed a doublet centered at δ 3.88 p.p.m., Jp-ch = 7 c.p.s.

Anal. calcd. for $C_3H_6Br_3OP$: C, 10.94; H, 1.82; Br, 72.95; P, 9.42. Found: C, 10.97; H, 1.85; Br, 72.72; P, 9.64.

Methyl Bis(iodomethyl)phosphine Oxide (VII). IV (10.0 grams, 0.062 mole) and 20.0 grams (0.133 mole) of sodium iodide were refluxed in 300 ml. of acetone for 35 hours. The hot solution was filtered to remove the sodium chloride. When the filtrate had cooled, 9.9 grams (46.7% yield) of crude VII were obtained. Pure white crystals m.p. 176-77° C., were obtained by recrystallization from 50% aqueous dimethylformamide. The infrared spectrum (KBr) exhibited peaks 3.3 (w), 3.38 (w), 7.2 (w), 7.3 (w), 7.63 (m),, 8.32 (s) with a shoulder at 8.55 (w), 8.75 (w), 8.9 (w), 9.4 (w), 9.53 (w), 11.0 (s), 11.3 (w), 12.3 (m), and 13.1 μ (m).

The NMR spectrum of deuteriochloroform solution of VII showed a doublet centered at δ 1.92 p.p.m., Jp-ch = 13 c.p.s. and a doublet centered at δ 3.41 p.p.m., Jp-ch = 7 c.p.s. in a ratio of 3 to 4, respectively.

Anal. calcd. for $C_3H_7I_2OP$: C, 10.47; H, 2.04; I, 73.82; P, 9.02. Found: C, 10.57; H, 2.09; I, 73.62; P, 9.08.

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Levopimaric Acid as a Ready Source of Abietic Acid

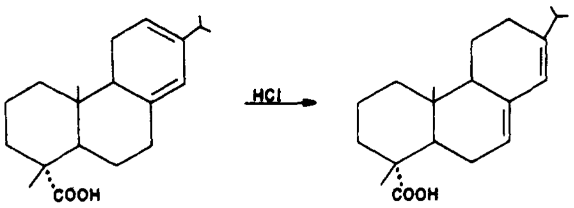
WALTER H. SCHULLER, HIROSHI TAKEDA, and RAY V. LAWRENCE

Naval Stores Laboratory, Olustee, Fla.

A simple process for the preparation of abietic acid from levopimaric acid is described.

ABIETIC ACID (II), a major resin acid of pine gum and of most all types of rosin, is generally prepared for laboratory use by isolation from rosin (*2*). This procedure is relatively laborious. Furthermore, abietic acid is not stable on storage. Small amounts are generally freshly prepared immediately before use.

The availability of pure levopimaric acid (I) from pine gum (*3, 4*) has led the authors to develop a very simple process for its conversion to abietic acid. Levopimaric acid is a stable compound and can be stored for years without decomposition. Thus it provides an ideal source for a ready supply of freshly prepared, pure abietic acid. The procedure involves the acid isomerization of the homocylic diene to the heterocyclic diene in the presence of acid.



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