EXPERIMENTAL

Lucernic triacetate. Preparation of the saponin,[2] sapogenin, and sapogenin acetate,[1] has been previously described. Purification was accomplished by chromatography of II on 37 times its weight of magnesia-silica gel. Elution of the chromatographic column with benzene-alcohol (95:5) and repeated crystallization from aqueous methanol gave platelets, m.p. 297–299° $[\alpha]_D^{26} = +7.7$ (*c*, 4.9),[5] which showed no high terminal adsorption in the U. V. and gave no color with either tetranitromethane in glacial acetic acid or the Liebermann-Burchard reagent.

λ_{max}^{KBr} 1775, 1730, 1250 cm.$^{-1}$ For analysis it was dried *in vacuo* at 130°.

Anal. Calcd. for $C_{36}H_{52}O_{10}$: C, 67.0; H, 8.1; CH_3CO, 20.0, neutral eq. 644. Found: C, 67.0; H, 8.1; CH_3CO, 20.3, neutral eq. 637.

II was quantitatively saponified with 0.1*N* alkali in methanol.

Anal. Calcd. for 5 equivalents per mole (3 acetyls, 1 carboxyl, and 1 lactone) and the consumption of 0.378 meq. of alkali. Found: 0.388 meq. alkali were consumed.

Methyl lucernate triacetate was prepared by treatment of an etheral solution of II with diazomethane. Recrystallization from aqueous methanol afforded rodlike crystals, m.p. 273–275°; $[\alpha]_D^{25} = -5.9°$ (*c*, 0.5).

$\lambda_{max}^{CCl_4}$ 1774, 1745 cm.$^{-1}$ $\lambda_{max}^{CS_2}$ 1235 cm.$^{-1}$ max

Anal. Calcd. for $C_{37}H_{54}O_{10}$. C, 67.5; H, 8.22; CH_3O, 4.71; CH_3CO, 19.6; mol. wt. 658. Found: C, 67.4; H, 8.32; CH_3O, 4.55; CH_3CO, 19.4; mol. wt. (Rast) 646.

Lucernic acid. Refluxing of II with 0.1*N* KOH in methanol, followed by neutralization, gave amorphous sapogenin. I proved to be almost insoluble in most organic solvents and could not be crystallized. $[\alpha]_D^{25} = +12.4°$ (pyridine) (*c*, 0.6).

λ_{max}^{KBr} 3155, 1745, 1704 cm.$^{-1}$

Anal. Calcd. for $C_{30}H_{46}O_7$: C, 69.2; H, 8.88. Found: C, 69.2; H, 8.86.

Methyl lucernate. Treatment of a suspension of I with diazomethane in ether gave crystalline III. Recrystallization from aqueous methanol afforded rodlike crystals, m.p. 347–350° $[\alpha]_D^{25} = +25.5°$ (*c*, 0.4).

λ_{max}^{KBr} 1758, 1724 cm.$^{-1}$

Anal. Calcd. for $C_{31}H_{48}O_7$: C, 69.9; H, 9.02; CH_3O, 5.82. Found: C, 69.9; H, 9.13; CH_3O, 5.71.

Periodic oxidation of methyl lucernate. 50 mg. of III was dissolved in 4 ml. absolute alcohol. To this solution was added 1 ml. of 0.63M H_5IO_6. The solution was left in the dark at room temperature and analyzed periodically by the standard As_2O_3 technique.

Anal. Calcd. for 1 glycol, or consumption of 0.0866×10^{-3} moles periodate. Found: 0.0833×10^{-3} moles of periodate were consumed.

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U. S. DEPARTMENT OF AGRICULTURE
ALBANY 10, CALIF.

(5) All melting points were made on a Kofler block. Unless noted otherwise, rotations were measured in chloroform solution.

Organophosphorus Compounds. V.[1] Dialkyl Phosphorofluoridates

G. A. OLAH AND A. A. OSWALD[2]

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Dialkyl phosphorofluoridates were first prepared in 1932 by Lange and Krueger[3] using silver phosphorofluoridate and alkyl iodide. They also observed the high toxicity of the compounds. Schrader[4,5] later elaborated a synthesis using halogen exchange of the corresponding dialkyl phosphorochloridates. McCombie and Saunders[6,7] also worked out this reaction independently. Chapman and Saunders[8] reacted phosphorus oxydichlorofluoride with alcohols to prepare dialkyl phosphorofluoridates.

We found considerable difficulty in the preparation of phosphorus oxydichlorofluoride as the main product, using the Swarts reaction.[9] Therefore, we investigated the use of the more readily available phosphorus oxyfluoride.

Phosphorus oxyfluoride was prepared by the Swarts reaction from phosphorus oxychloride without using antimony pentachloride catalyst with 94% yield (and 5% phosphorus oxydichlorofluoride).

$$POCl_3 + SbF_3 \longrightarrow POF_3 + SbCl_3$$

Similarly phosphorus oxyfluoride can be prepared from phosphorus oxybromide, according to Booth and Seegmiller.[10]

$$POBr_3 + SbF_3 \longrightarrow POF_3 + SbBr_3$$

During the course of our investigation we prepared dimethyl, diethyl, and diisopropyl phosphorofluoridate (DFP) from phosphorus oxyfluoride and the corresponding alcohols.

$$POF_3 + 2\ ROH \longrightarrow (RO)_2\ POF + 2\ HF$$

The HF was removed from the DFP before distillation by neutralization with dry ammonia or was bonded with pyridine.

There have been described the preparation of dialkyl phosphorochloridate under acid free conditions through the chlorination of dialkyl phosphite with *N*-chlorosuccinimide.[11] Previously,[12] we obtained dialkyl phosphorochloridates as acid

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(2) Present address: Research Department, Imperial Oil Limited, Sarnia, Ontario, Canada.

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free products from the reaction of sodium alcoholate and phosphorus oxychloride in toluene. Using a similar method dialkyl phosphorofluoridates were also now prepared from phosphorus oxyfluoride and sodium alcoholates.

An advantage of the method described herein is the complete absence of any chlorine containing compounds. Since phosphorus oxyfluoride can be prepared with excellent yield the described method seems to be generally applicable for the preparation of any dialkyl phosphorofluoridates.

EXPERIMENTAL

Phosphorus oxyfluoride. Phosphorus oxychloride, 230 g. (1.5 mole) was placed in a four neck round bottom flask equipped with an efficient sealed mechanical stirrer, a feeder for antimony trifluoride powder, a thermometer, and a distillation column. The flask was then heated to 50°. The column was connected to a water cooled descending condenser and three traps cooled with ice water, dry ice–acetone, and liquid air. Antimony trifluoride 178.7 g. (1 mole) was added during 3 hr. to the reaction mixture while the temperature was maintained at 50–70°. The stirring mixture was then heated for an additional 2 hr. The reaction products distilled into the condenser system.

On redistilling the condensed products 20.5 g. phosphorus oxydichlorofluoride (5% based on SbF_3), b.p. 53° and 98 g. phosphorus oxyfluoride (94% based on SbF_3), b.p. −40° and a trace of phosphorus oxychlorodifluoride, b.p. +3° were obtained.

An analogous reaction, using phosphorus oxybromide was carried out in a similar manner, except that the further 2 hr. heating was carried out at 100°. Phosphorus oxyfluoride, b.p. −40° was again the main product. Phosphorus oxybromodifluoride (b.p. 30°) and phosphorus oxydibromofluoride (b.p. 110°) were also formed as low-yield products.

Dialkyl phosphorofluoridate from phosphorus oxyfluoride with alcohols. Diisopropyl phosphorofluoridate. (a) Absolute ether (250 ml.) was placed in a 500 ml. four neck round bottom flask equipped with a sealed mechanical stirrer, dropping funnel, thermometer, and feeding neck closed with a calcium chloride tube. The flask was cooled in a dry ice–acetone mixture. To the cooled ether solution 26 g. (0.25 mole) of phosphorus oxyfluoride, and then, with continuous stirring and cooling 30 g. (0.5 mole) of isopropyl alcohol were added. After the addition of the isopropyl alcohol was complete, the temperature of the solution was allowed to reach 20° and dry ammonia gas was introduced until the reaction mixture was neutral to litmus. The ammonium fluoride which separated was removed by filtration. The ether was stripped from the system and the product distilled to give 30.8 g. (67%) diisopropyl phosphorofluoridate, b.p. 60–61°/10 mm.

Anal. Calcd. for $C_6H_{14}FO_3P$: F, 10.32. Found: F, 11.0.

(b) A mixture of 60 g. (1 mole) of isopropyl alcohol and 250 ml. of ether was placed in a four-necked round-bottomed flask equipped with a sealed mechanical stirrer, gas inlet tube, dropping funnel, and thermometer. The solution was cooled with a dry ice–acetone mixture and then 52 g. (0.5 mole) of phosphorus oxyfluoride was added with stirring and cooling. The phosphorus oxyfluoride dissolved instantly. Anhydrous pyridine, 79 g. (1 mole) was added to the solution at about −40°. After the addition of the pyridine was complete, the mixture was allowed to reach room temperature about 20° while stirring was continued. When the stirring was stopped, the reaction mixture separated in two phases. The lower pyridine layer was discarded and the upper ethereal layer was distilled. After removing the ether, diisopropyl phosphorofluoridate (84.5 g., 93%) b.p. 60–61°/10 mm. was obtained.

Anal. Found: F, 10.6.

Diethyl phosphorofluoridate was similarly prepared according to method (b). The yield was 89%, b.p. 48–49°/10 mm.

Anal. Calcd. for $C_4H_{10}FO_3P$: F, 12.18. Found F, 12.4.

Dimethyl phosphorofluoridate was also obtained with method (b) in a similar way. Yield 91%, b.p. 58–59°/20 mm.

Anal. Calcd. for $C_2H_6FO_3P$: F, 14.85. Found: F, 14.65.

Dialkyl phosphorofluoridate from phosphorus oxyfluoride with sodium alcoholates. Diisopropyl phosphorofluoridate. In a four neck round bottom flask, equipped as described previously 50 ml. of toluene was added. The flask was cooled in CO_2-acetone and then 26 g. (0.25 mole) phosphorus oxyfluoride was condensed into the cold toluene. To this mixture a sodium isopropylate suspension, prepared by using 11.5 g. (0.5 mole) sodium and 30 g. (0.5 mole) isopropyl alcohol in 200 ml. toluene, was added with efficient stirring and Dry Ice–acetone cooling. Thereafter, the mixture was allowed to reach room temperature with continuous stirring. The separated sodium fluoride was removed by filtration and the filtrate was distilled yielding 27 g. (58%) of diisopropyl phosphorofluoridate, b.p. 82–85°/20 mm.

Anal. Calcd. for $C_6H_{7}FO_3P$: F, 10.32. Found: F, 10.45.

Dimethyl phosphorofluoridate was similarly prepared by the adding the equimolar quantity of sodium methylate as a methanolic solution to the phosphorus oxyfluoride solution. The yield was 77%, b.p. 58–60° at 20 mm.

Anal. Calcd. for $C_2H_6FO_3P$: F, 14.84. Found: 14.6.

Diethyl phosphorofluoride was prepared according to the preparation of dimethyl phosphorofluoridate. In a manner described in the previous example 0.2 mole of sodium ethylate in alcoholic solution was added to 10.4 g. (0.1 mole) phosphorus oxyfluoride also in alcohol with dry ice–acetone cooling. On working up the reaction mixture 12.5 g. (80%) diethyl phosphorofluoridate, b.p. 47–49°/10 mm., was obtained.

Anal. Calcd. for $C_4H_{10}FO_3P$: F, 12.18. Found: F, 12.0.

CONTRIBUTION NO. 9
EXPLORATORY RESEARCH LABORATORY
DOW CHEMICAL OF CANADA, LIMITED
SARNIA, ONT., CANADA

Preparation of Pyridinedicarboxylic Acid *N*-Oxides

DONALD L. HEYWOOD AND JESSE T. DUNN

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Although the pyridinecarboxylic acid *N*-oxides and several substituted pyridinecarboxylic acid *N*-oxides are known[1–7] and were prepared, in most cases, by the usual peracid oxidation of the pyridinecarboxylic acid, none of the corresponding pyridinedicarboxylic acid *N*-oxides are reported.

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