80% of which was removed by filtration. The balance did not interfere since <0.001% SiO_2 was found in the product. All filtrations were carried out in fritted-glass funnels, since any filter paper shreds in the final product caused reduction of AgCl during single crystal growth. Scrap silver salts, washed free of oil and grease with petroleum ether, reagent grade silver salts and silver metal were used as starting materials.

Experimental

The silver salts[2] were reduced with granular zinc (20 mesh, low in As, Fe and Pb) in (1:10) HCl, and the resulting metal was washed thoroughly, first by decantation, and then by filtration. The metallic silver was dissolved in a minimum amount of dilute (1:1) HNO_3. The resulting solution was diluted and tin, antimony, and the insoluble chlorides allowed to settle out. After filtration, the solution was heated, made ammoniacal, and filtered, removing Fe, Al, most of the Tl and some of the SiO_2. The filtrate was made just acid with HNO_3 and evaporated to a small volume, cooled, filtered and the resulting $AgNO_3$ was dissolved in water and filtered. AgCl was precipitated from the filtrate with concentrated HCl in slight excess.[3] After filtration, AgCl was dissolved in a minimum amount of NH_4OH and any residue filtered off. The solution was gently heated with continuous stirring until crystallization began. Removed from the heat, the solution was placed in the dark. Vigorous stirring was continued to prevent formation of a crust and to allow NH_3 to escape. After a sufficient crop of crystals had formed, they were washed, first with water, then with HCl and finally with water. The solution was reheated and a second and third crop of crystals gathered in the same manner. Proper care was taken throughout to recover silver from filtrates and residues.

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[2] Silver metal was dissolved in a minimum amount of HNO_3; AgCl was precipitated and washed free of nitrates, then treated as above.

[3] When thallium was present in excess of 0.50%, repetition of the preceding steps was necessary; and when copper was present in large quantities, repetition was deemed advisable.

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NEW COMPOUNDS

Preparation of N-Acetylphenyl-2-thienylamine[1,2]

Ten grams (0.075 mole) of acetanilide, 20 g. (0.123 mole) of 2-bromothiophene, 5 g. (0.037 mole) of anhydrous potassium carbonate, about 0.1 g. of a mixture of powdered potassium iodide and powdered copper, a crystal of iodine and 50 ml. of nitrobenzene[3] were stirred in a three-necked 250-ml. flask in a nitrogen atmosphere for 25 hours at 160–170°. The dark mixture was neutralized, steam distilled and the residue cooled. The oil layer was extracted with ether, the ether solution dried with calcium chloride, and the ether removed by vacuum distillation at 100°. The solid, which weighed 14 g., was washed with 50 ml. of Skellysolve A, then dissolved in 25 ml. of hot absolute ethanol, treated with Norite A and filtered. The crystals which separated on cooling were collected on a filter and dissolved in 400 ml. of boiling water by addition of the minimum amount of ethyl alcohol. The precipitate which separated on cooling was collected on a filter and dried in vacuum over sulfuric acid, yielding 2.2 g. (14%) of white crystals melting at 100–101°.

Anal. Calcd. for $C_{12}H_{11}ONS$: N, 6.44; S, 14.74. Found: N, 6.33; S, 14.76.

Experimental conditions sufficiently vigorous to cause hydrolysis of N-acetylphenyl-2-thienylamine invariably resulted in formation of tars.

When 2-iodothiophene was substituted for 2-bromothiophene in the above procedure, a yield of 2.5 g. (31%) of crude N-acetyl phenyl 2-thienylamine was obtained. When 2-chlorothiophene was used, no product was obtained. Use of the method with N-acetyl-2-aminothiophene and iodobenzene gave less than a gram of crude N-acetyl phenyl 2-thienylamine. From N-acetyl-2-aminothiophene and 2-bromothiophene no acetyl-di-2-thienylamine could be obtained.

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Preparation of Ethyl Pyrazinoylacetate

A mixture of 13.8 g. of methyl pyrazinoate and 14.8 g. of ethyl acetate was added slowly with stirring to 10.7 g. of alcohol-free sodium ethoxide. After standing at room temperature for one hour, the mixture was refluxed for five hours. The reaction mixture was then cooled, dissolved in 125 ml. of water and extracted with ether to remove the unreacted esters. The solution was neutralized to a *p*H of 7 with hydrochloric acid and exhaustively extracted with ether. The ether extract was dried over sodium sulfate and evaporated to a small volume to give 13 g. (67%) of ethyl pyrazinoylacetate (yellow crystals), which melted at 66–67° when recrystallized from petroleum ether.

Anal. Calcd. for $C_9H_{10}O_3N_2$: C, 55.6; H, 5.15; N, 14.4. Found: C, 55.7; H, 5.28; N, 14.4.

The following derivatives of ethyl pyrazinoylacetate were prepared: 2,4-dinitrophenylhydrazone, yellow crystals which melted at 187–189° when recrystallized from ethanol.

Anal. Calcd. for $C_{15}H_{16}O_6N_6$: N, 22.5. Found: N (Dumas), 22.8.

Phenylhydrazone, yellow crystals which melted at 131–132° when recrystallized from ethanol.

Anal. Calcd. for $C_{15}H_{16}N_4O_2$: N, 19.7. Found: N (Dumas), 19.5.

3-(2-Pyrazyl)-pyrazolone-5 light tan crystals which melted with decomposition at 245–246° when recrystallized from methanol.

Anal. Calcd. for $C_7H_6N_4O$: N, 34.6. Found: N (Dumas), 34.6.

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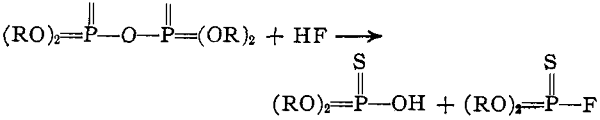
Diethylthionomonofluorophosphate

The preparation of dialkylmonofluorophosphoric esters, $(RO)_2POF$, by the interaction of anhydrous hydrogen fluoride with symmetrical pyrophosphoric acid diesters has been previously described.[1] A similar procedure has now been found satisfactory for obtaining analogous thioesters. The general reaction is



$$(RO)_2{=}\overset{\overset{\Large S}{\|}}{P}{-}O{-}\overset{\overset{\Large S}{\|}}{P}{=}(OR)_2 + HF \longrightarrow (RO)_2{=}\overset{\overset{\Large S}{\|}}{P}{-}OH + (RO)_2{=}\overset{\overset{\Large S}{\|}}{P}{-}F$$

The higher volatility of the fluoro-ester permits its separation by fractional distillation from the acid ester.

To 7.8 g. of anhydrous hydrogen fluoride in a platinum bottle cooled in ice 101.2 g. of tetraethyldithionopyrophosphate[2] was slowly added. In spite of some vaporization

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[1] From the M.S. thesis of Peter Panzera, June, 1949.

[2] This work was supported in part by a Research Corporation Grant-in-aid.

[3] I. Goldberg, *Ber.*, **40**, 4541 (1907).

[1] A. Hood and W. Lange, THIS JOURNAL, **72**, 4956 (1950).

[2] The tetraethyldithionopyrophosphate was kindly supplied by the Victor Chemical Works. For description of this and related compounds, see A. D. F. Toy, *ibid.*, **73**, 4670 (1951).