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Registry No. Fe(1,7-CTCl)ClO$_4$, 31122-42-6.

Contribution from the Department of Chemistry,
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Hypophosphite in Methanol. A Rapid, Nonaqueous Route to Germanium(II) Compounds[1]

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A well-known route[2] to the reduction of germanium(IV) compounds involves the reaction of a 4:1 molar excess of hypophosphorous acid (H_3PO_2) with germanium(IV) chloride ($GeCl_4$) in approximately 3 *M* hydrochloric acid. Reaction times are on the order of 3 hr and temperatures are kept near 95°. Work in our laboratory showed that many of the above parameters could be reduced or excluded without altering the basic nature of the reaction. Specifically, (a) reaction 1 goes essentially to completion at 1:1 molar ratios

$$GeCl_4 + H_3PO_2 + H_2O \xrightarrow[HCl]{3\,M} GeCl_2(aq) + H_3PO_3 + 2HCl \qquad (1)$$

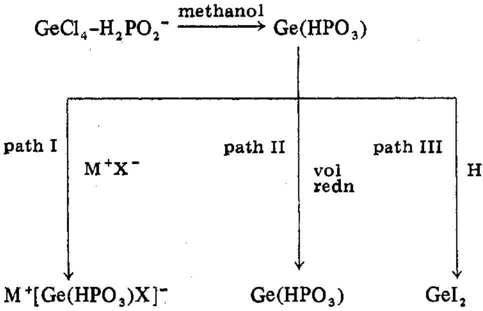
of H_3PO_2:$GeCl_4$, (b) hydrochloric acid is neither essential to the reductive process nor required for the prevention of $GeCl_4$ hydrolysis, and (c) reaction 1 is quite rapid (in the order of several minutes) at temperatures ranging from 65 to 85°.

While investigating the implications of points a-c above, it was discovered that hydrated sodium hypophosphite, $NaH_2PO_2 \cdot H_2O$, in methanol solution effectively and almost instantaneously reduces germanium(IV) chloride. To our knowledge, this is the first example of a successful Ge(IV)-Ge(II) reduction reaction in a nonaqueous solvent.

$$GeCl_4 + NaH_2PO_2 \cdot H_2O \xrightarrow{\text{methanol}} Ge(HPO_3) + \underline{NaCl} + 3HCl \qquad (2)$$

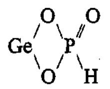
Scheme I summarizes data now known about the hypophosphite-germanium(IV) reduction system in solvent methanol. It is possible to isolate and characterize a chloride salt of $Ge(HPO_3)$ by filtering the initial solid sodium chloride from the reaction mixture and then adding a large cation such as trimethylammonium (path I). A white precipitate of $(CH_3)_3NH^+[Ge(HPO_3)Cl]^-$ immediately forms. It is a high-melting (>250° with decomposition), highly insoluble, hygroscopic salt. Preliminary evidence indicates that the cesium ion will act in like manner.

Scheme I. The Hypophosphite-Germanium(IV) Reduction System[a]



[a] M^+ is a large cation such as trimethylammonium, Cs^+, Rb^+, etc.

Evaporation under vacuum (path II) causes the eventual precipitation of the $Ge(HPO_3)$ species, a compound first claimed by Everest[3] in the reaction of GeO_2 with H_3PO_2 in phosphorous acid solvent. The germanium(II) hydrogen phosphite moiety as obtained herein is either anhydrous or contains one molecule of water. Infrared data (see Experimental Section) seem to indicate the appropriate P–H, P–O, and P=O frequencies consistent with a bidentate structure such as



A proton nmr spectrum taken of the salt dissolved in deuterated methanol showed a sharp, widely spaced doublet (524 Hz) attributable to the P-H linkage and an expectedly large J_{P-H} coupling constant. The J_{P-H} value for $NaH_2PO_2 \cdot H_2O$ in methanol was 500 Hz. No evidence for phosphorous acid (J_{P-H} = 707 Hz)[4] was observed. H_3PO_3 (reaction 1) is formed when germanium tetrachloride is reduced in the aqueous acidic medium. The central germanium(II) atom is no doubt four-coordinated in the solid $Ge(HPO_3)$ structure much like it is in polymeric GeF_2.[5] X-Ray analysis has now been initiated for complete structure elucidation.

Concentrated hydriodic acid (HI) appears to be the only strong acid (path III) capable of completely liberating HPO_3 from $Ge(HPO_3)$ to form the corresponding GeX_2 salt. There is no significant reaction when varying quantities of HBr, HCl, HF, H_2SO_4, and HNO_3 are added. It is probable that an equilibrium exists between GeI_2 and the $Ge(HPO_3)$ species in methanol solution

$$Ge(HPO_3) + 2HI \rightleftharpoons GeI_2 + H_3PO_3$$

and that excess HI (about 15:1 molar ratio) is required to effect a significant yield of approximately 60% germanium(II) iodide product. Work is continuing in attempts to maximize yields of GeI_2 and to determine why only HI of all the strong halogen and mineral acids will conveniently precipitate out a GeX_2 salt.

In the course of our studies it was shown that if hexanol and formic acid were used in place of methanol solvent in performing the sodium hypophosphite reduction of germanium tetrachloride, germanium(II) species were indeed produced, but yields were invariably lower and reaction times considerably lengthened. When, however, equimolar quantities of the solid $NaH_2PO_2 \cdot H_2O$ and liquid $GeCl_4$ were mixed neat under an atmosphere of nitrogen, no reaction took place over a period of 5 hr at room temperature. A

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(1) Based in part on the M.S. thesis of C. P. Guengerich, 1972.

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trace of methanol added at this point immediately gave evidence of germanium(II) production.

Sodium hypophosphite in aqueous 3 *M* hydrochloric acid has also been found to be an effective reducing medium for germanium tetrachloride, presumably *via* reaction 1. It has thus been possible to precipitate out, for the first time, a $(Ge^{II}Cl_3)_2$ salt by adding ethylenediammonium chloride to the aqueous $GeCl_2$ species. White crystals of ethylenediammonium bis[trichlorogermanate(II)] appeared upon volume reduction and cooling.

Work is currently under way to generalize new reaction pathways for the facile isolation and preparation of all the GeX_2 salts (X = F, Cl, Br, I) and new divalent germanium species in methanolic hypophosphite. In addition, diverse inorganic and organic systems are currently being treated and tested with $NaH_2PO_2 \cdot H_2O$ in methanol. It has, for instance, recently been found that silver(I) and copper(II) salts are reduced to the elemental metallic state. Mercury(II) chloride is reduced halfway to the mercury(I) chloride salt, Hg_2Cl_2.

Experimental Section

Preparation of $(CH_3)_3NH^+[Ge(HPO_3)Cl]^-$. Sodium hypophosphite monohydrate (J. T. Baker Chemical Co.) was dried at 110° for 1 hr with no significant weight loss. In a typical experiment, 18.4 g (0.086 mmol) of germanium tetrachloride (Eagle-Picher Chemical Co.) in 75 ml of absolute methanol was cooled to 0° and then added to 9.1 g (0.086 mol) of $NaH_2PO_2 \cdot H_2O$ in 100 ml of the same solvent also at 0°. The reductive reaction was essentially over upon mixing of solutions. A white precipitate (4.5 g, 0.077 mol, 90% yield) of NaCl formed during the above mixing process and was filtered off. Addition of trimethylammonium chloride (0.086 mol) to the filtrate immediately precipitated out another white salt (13.42 g, 63% yield) formulated as $(CH_3)_3NH^+[Ge(HPO_3)Cl]^-$. *Anal.* Calcd for $C_3H_{11}NO_3PClGe$: C, 14.52; H, 4.44; N, 5.64. Found: C, 14.63; H, 4.39; N, 5.61. Analyses were performed by M-H-W Laboratories, Garden City, Mich.

The above reaction took place either under atmospheres of nitrogen or ordinary air. Reduction was also observed in solvents *n*-hexanol and formic acid, but reaction times were lengthened to several hours and yields of germanium(II) species were invariably lowered.

Preparation of $Ge(HPO_3)$ or $Ge(HPO_3) \cdot H_2O$. In like manner to the above, germanium tetrachloride was reduced with methanolic sodium hypophosphite, the solid sodium chloride filtered off, and the volume of filtrate solution slowly reduced (under vacuum) until white crystals first appeared. A 72% yield of solid formulated as $Ge(HPO_3) \cdot H_2O$ was obtained. *Anal.* Calcd for H_3O_4PGe: P, 18.16. Found: P, 17.85.

Infrared data (cm^{-1}, Nujol mulls and KBr pellets): 3300 m, br (O–H stretch); 2475 w (P–H stretch); 1650 m, br (O–H bend); 1187 s (P=O stretch); 1055 vs, br (P–O stretch); 848 s and 600 m, br (Ge^{II}–O stretch).

Nmr spectra were recorded in pure methanol or deuterated methanol (Stohler Isotope Chemicals) on a Varian Associates T-60 instrument.

The white crystals melt with decomposition at about 255° (lit.[3] mp 230°). They are readily hydrolyzed, producing the characteristic yellow, yellow-orange color of hydrated germanium(II) hydroxide.

Preparation of $(H_3N^+CH_2CH_2NH_3^+)(GeCl_3^-)_2$. Ethylenediammonium bis[trichlorogermanate(II)] was prepared by mixing equimolar quantities of $GeCl_4$ and $NaH_2PO_2 \cdot H_2O$ in 3 *M* HCl, adding ethylenediammonium chloride, removing solvent under vacuum until white solid first appeared, and then cooling to grow crystals. A 48% yield was thus obtained. *Anal.* Calcd for $C_2H_{10}N_2Cl_6Ge_2$: C, 5.72; H, 2.38; N, 6.66. Found: C, 5.79; H, 2.32; N, 6.89. Analysis was performed by the Analytical Services Division of Northwestern University. The salt is high melting (>300° dec) and is readily hydrolyzed to germanium(II) hydroxide species.

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Registry No. $(CH_3)_3NH^+[Ge(HPO_3)Cl]^-$, 42579-16-8; $Ge(HPO_3)$, 29850-62-2; $(H_3N^+CH_2CH_2NH_3^+)(GeCl_3^-)_2$, 42579-17-9; $NaH_2PO_2 \cdot H_2O$, 10039-56-2; $GeCl_4$, 10038-98-9.

Contribution from Departamento de Quimica Organica, Facultad de Ciencias Exactas and Instituto de Investigaciones Fisicoquimicas Teoricas y Aplicadas, La Plata, Argentina

Preparation of Two New Haloalkyl Fluorosulfates: Dichloromethyl Fluorosulfate ($CHCl_2OSO_2F$) and 1,1,2-Trichlorofluoroethyl Fluorosulfate ($CHClFCCl_2OSO_2F$)

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Studies have been made of the reactivity of several fluoroxy compounds such as fluoroxytrifluoromethane[1] (CF_3OF), 2-fluoroxyperfluoropropane ($(CF_3)_2CFOF$), 2-fluoroxy-2-trifluoromethylperfluoropropane ($(CF_3)_3COF$), and bis(fluoroxy)difluoromethane ($CF_2(OF)_2$) as electrophilic fluorinating agents of organic substrates.[2]

Williamson, *et al.*,[3-5] reported the addition of fluoroxysulfur pentafluoride (SF_5OF) to various simple halogenated olefins. Fluorine fluorosulfate (FSO_2OF) also adds to fully halogenated alkenes.[6,7]

In this work we study, under controlled conditions, the reactivity of fluorine fluorosulfate on hydrogenated haloalkanes and -alkenes, such as chloroform and trichloroethylene.

We report a simple and efficient method to obtain the following two new compounds: dichloromethyl fluorosulfate (I) and 1,1,2-trichlorofluoroethyl fluorosulfate (II). The method is based upon the reactions

$$CHCl_3 + F_2SO_3 \xrightarrow{-78^\circ} \underset{\text{I}}{CHCl_2OSO_2F} + ClF \qquad (1)$$

$$CHCl{=}CCl_2 + F_2SO_3 \xrightarrow{-78^\circ} \underset{\text{II}}{CHClFCCl_2OSO_2F} \qquad (2)$$

Chlorine monofluoride was not detected as a product of reaction 1. Instead, a heavy attack at the glass reactor exit was observed. A small amount of trichlorofluoromethane was obtained as a by-product. So far, we cannot conclude whether the trichlorofluoromethane formed came as a result of the direct fluorination of chloroform either by fluorine fluorosulfate or by chlorine monofluoride. Nevertheless, (1) represents a new type of reaction for fluorine fluorosulfate.

Experimental Section

Materials. Chemicals were reagent grade. Chloroform was freed from ethanol by repeated washing with water, dried over potassium carbonate, and finally distilled. Pure fluorine fluorosulfate obtained photochemically was employed.[8]

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