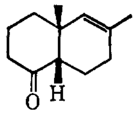
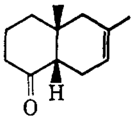


IX



X

base effected partial conversion into the respective *trans* isomers, VIII and VI.

Since there is no stereochemical crossover in the cyclization of the two isomeric acetals, the process is stereospecific and must either be synchronous or involve cationic intermediates that maintain their stereochemical integrity.

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Fluorine Oxidation of Tetravalent Uranium and Neptunium to the Pentavalent State[1]

Sir:

Fluorine oxidation of uranium tetrafluoride in a slurry of anhydrous liquid HF has been found to be a new and useful synthesis for pentavalent uranium compounds. We find that fluorine oxidation of UF_4 dispersed in liquid anhydrous HF proceeds readily to UF_5 but then goes only very slowly to UF_6. When *both* alkali fluoride and UF_4 are present in liquid HF, fluorine oxidation halts at U(V) in the form of the soluble UF_6^- ion. This technique is especially useful in the preparation of pure MUF_6 compounds, avoiding the separate preparation and handling of UF_5.

The pentafluorides of the heavier actinides, neptunium and plutonium, have not been prepared although the tetra- and hexafluorides of both are well known.[2] Therefore, after successfully preparing UF_5 by the method just described, we attempted to extend the technique to neptunium. Although oxidation of Np(IV) to Np(V) was observed in cesium hydrogen fluoride solution, NpF_5 itself could not be isolated.

Fluorine Oxidation of U(IV) to U(V). (a) We prepared UF_5 from UF_4 by stirring a suspension of high-surface-area UF_4 in liquid anhydrous HF at 25° under 10 psig of F_2. (High-surface-area UF_4 was made by dehydrating $UF_4 \cdot 2.5H_2O$ in a stream of gaseous H_2 and HF for 2 hr at 200° followed by 3 hr at 450°.) The oxidation on a 3–5-g scale essentially halted at β-UF_5 in 1–4 hr, and many more hours were required before significant quantities of UF_6 were formed.

(b) A stirred slurry of CsF and UF_4 (1:1 mole ratio) in liquid HF reacted smoothly with F_2 at 10 psig and 25°, yielding a clear blue solution of $CsUF_6$. (A Teflon-coated bar magnet is convenient for stirring.) On evaporation of HF, blue crystals of pure $CsUF_6$ were obtained; with RbF, light yellow $RbUF_6$ crystals were deposited.[3] The UF_4 need not be of high surface area since the reaction proceeds readily to completion, probably because the MUF_6 reaction products are soluble.

To avoid weighing hygroscopic, heavy alkali fluorides, the nonhygroscopic chlorides can be substituted. In this case, HF is condensed onto the alkali chloride–UF_4 mixture and the HCl, which is formed when the mixture is warmed, is vented through a trap. After this step, F_2 is admitted and the suspension is stirred. We use weighable, translucent Kel-F tubes (with a flared end for connection to a Monel line) to observe the course of the reaction. Five-gram quantities of UF_4 are conveniently oxidized to soluble MUF_6 in 30–45 min at 25°. *Caution:* Before admitting fluorine, any *hydrogen* frequently present in the tank of HF *must be removed;* this is done readily by condensing the HF and pumping off gases volatile at liquid nitrogen temperatures.

Preparation of Np(V). At 25°, a slurry of NpF_4 (0.17 g) in HF was not oxidized to NpF_5 by 10 psig of F_2. However, when 10 g of CsF was added and the excess HF pumped off, the green NpF_4 dissolved in the warm $CsF \cdot 2HF$ melt (mp $\sim$50°). Neptunium(IV) was then oxidized by F_2 at 70° to a soluble, magenta-colored Np(V) fluoride complex. The absorption spectrum of Np(V) in this cesium difluoride melt closely resembled that of pure $CsNpF_6$; in addition, $CsNpF_6$ was identified as the pink solid deposited from this solution.[4] When several milliliters of liquid HF was recondensed on this Np(V) material, *disproportionation* took place leaving green NpF_4 behind and yielding orange, volatile NpF_6. This behavior contrasts with that of $CsUF_6$ which is completely stable in anhydrous HF.

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

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The Basic Properties of Tetrafluorodiphosphine. The Synthesis of Tetrafluorodiphosphine Borane

Sir:

In recent papers, reactions of the new compound P_2F_4 with some Brønsted–Lowry acids of general formula HX, to give products of the forms F_2PH[1a] and F_2PX, were mentioned very briefly.[1b] On the basis of present evidence, a transition-state complex of the form $F_2PPF_2 \cdot HX$ could account for the products, or a free-radical mechanism involving $F_2P \cdot$ radicals would be reasonable. A cleavage of the P–P bond to give F_2POPF_2 has also been reported by Lustig, Ruff, and Colburn,[2] but, as in the other cases, the nature of the transition state was not defined.

When a Lewis acid containing only hydridic hydrogen (*i.e.*, BH_3) is used in place of a Brønsted–Lowry acid, the complex $F_2PPF_2 \cdot BH_3$ is formed. The reaction can be described by the equation

$$P_2F_4(g) + 0.5B_2H_6(g) \xrightarrow{25°} P_2F_4 \cdot BH_3(g)$$

No evidence for a double adduct has yet been obtained

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[1] (a) Reaction of F_2PH with HI to give F_2PH HI has also been noted: R. W. Rudolph, Ph.D. Dissertation, University of Michigan, 1966; (b) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

[2] M. Lustig, J. K. Ruff, and C. B. Colburn, *ibid.*, **88**, 3875 (1966).