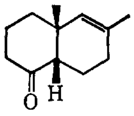
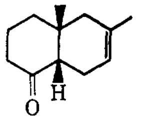


IX



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 ~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).

under the conditions used here. $F_2PPF_2 \cdot BH_3(g)$ is relatively stable but undergoes slow decomposition involving both cleavage of the P–P bond and shift of a fluorine. The equation describing the process is

$$F_2PPF_2 \cdot BH_3 \longrightarrow F_3PBH_3(g) + PF(s)$$

The solid yellow $(PF)_n$ is presumably polymeric. No evidence for decomposition to $P_2F_4(g)$ and $B_2H_6(g)$ was observed. It is also significant that F_2PPF_2, in sharp contrast to the related fluorides of nitrogen,[3] reacts smoothly and nonexplosively with diborane.

A 1.03-mmole sample of B_2H_6 (Callery Chemical Co.) was frozen into a 50-ml bulb on the vacuum line. A 1.04-mmole sample of P_2F_4[1] was frozen into a second evacuated 250-ml bulb, connected to the first bulb through a stopcock. With the stopcock closed between the two, the P_2F_4 and B_2H_6 were allowed to vaporize and warm to room temperature. The vapors were then allowed to mix by opening the stopcock between the units. After 3–4 hr at 25°, the gaseous mixture was passed through traps held at −85, −100, and −196°. The $P_2F_4 \cdot BH_3$ retained in the −100° trap was further purified by opening the −100° trap to a −196° trap for 20–36 hr. The product, a white crystalline solid at −100°, represented a 30% conversion of P_2F_4 to $P_2F_4 \cdot BH_3$. The molecular weight as determined by vapor density was 155 (calculated for $F_4P_2 \cdot BH_3$: 152); H^- (by hydrolysis in acid solution): $3.1 H^-/P_2F_4 \cdot BH_3$. Vapor pressure data were not obtained because of decomposition in the liquid phase to PF_3BH_3 and its decomposition products, but the product is sufficiently volatile to pass through a trap at −85°.

Major mass spectrometer peaks given as mass number (tentative assignment) and relative abundance are: 152 $(P_2F_4 \cdot BH_3^+)$, 1.67; 138 *$(P_2F_4^+)$, 8.15; 119 *$(P_2F_3^+)$, 5.71; 83 $(F_2PBH_3^+)$, 8.05; 82 $(F_2PBH_2^+)$, 11.0; 81 $(F_2P^{10}BH_2^+$ and $F_2P^{11}BH^+)$, 3.43; 80 $(F_2P^{10}BH^+)$, 1.55; 69 *(F_2P^+), 100; 50 *(PF^+), 24.5; and 31 *(P^+), 25.6. Much of the pattern (marked by an asterisk) is identical with that for P_2F_4. The over-all pattern is consistent with the formula assigned. Infrared absorptions are listed as [frequency, cm^{-1} (probable assignment), and intensity]: 2432 (ν_{B-H}), m br; 1102 (δ_{B-H}), w; 1042 (δ_{B-H}), m; 902 $(\nu_{as,\ P-F})$, vvs br; 850 $(\nu_{sym,P-F})$, s; 727 (ρ_{BH_3}) m; 670–680 (?), w, br; 598 $(\nu_{P-B}?)$, w; 442 (δ_{F-PF}), vw, 395 (τ_{B-P}), w; 370 (δ_{F-P-F}), wm. The spectrum of the solid shows resolution of the B–H stretching region near 2400 cm^{-1} into two distinct peaks as expected. (The symbols used above are defined as follows: ν = stretch, δ = deformation, ρ = rocking, τ = torsional.) The ^{11}B nmr taken at −80° on the neat liquid shows a quartet with J_{B-H} = 101 cps and δ (relative to $B(OCH_3)_3$) equal to 60 ppm.

No splitting of the ^{11}B signal by phosphorus is observed, whereas other compounds containing a B–P bond of comparable stability show a definite doublet pattern.[2] Broadening of the ^{11}B signal suggests that rapid exchange of the BH_3 moiety between phosphorus atoms might be occurring. More detailed analysis of the ^1H, ^{19}F, and ^{31}P spectra is currently being carried out.

P_2F_4 appears to be stronger as a Lewis base toward BH_3 than is PF_3; slow decomposition of $P_2F_4 \cdot BH_3$ by fluoride shift and cleavage of the P–P bond gives F_3PBH_3 which then decomposes to give significant concentrations of F_3P and B_2H_6. On the other hand, no P_2F_4 was ever detected in the system during decomposition, and B_2H_6 appeared only after the appearance of F_3PBH_3. These observations suggest that the B–P interaction in the adduct may be enhanced by partial double-bond interaction between phosphorus atoms in the parent P_2F_4. Such interaction would enhance the basicity of one phosphorus atom at the expense of the other and in a manner which contrasts sharply with the basicity toward BH_3 of other bidentate ligands such as hydrazine.

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[3] T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, **78**, 1524 (1956). No reaction of N_2F_4 with B_2H_6 is reported in the literature, but the above reference indicates an explosive reaction of NF_3 and B_2H_6.

Crystalline Catalysts Containing Al–O–Al or Zn–N–Zn Groups for Stereospecific Polymerization of Propylene Oxide

Sir:

Since the pioneering work by Price on the stereospecific polymerization of propylene oxide,[1] a large number of papers dealing with the mechanism of the polymerization as well as with the nature of catalysts have been published.[2] But, unfortunately, the ill-defined nature of catalysts and the rather low stereospecificity of polymerization make the detailed interpretation of the stereoregulating mechanism difficult. We now wish to report two types of crystalline catalyst for stereospecific polymerization of propylene oxide.[3] These catalysts are the organometallic compounds, one containing aluminum and oxygen and another zinc and nitrogen.

Bis(diethylaluminum) oxide ($Et_2AlOAlEt_2$, II) has been mentioned as one of the reaction products of triethylaluminum with carbon dioxide[4] or with water,[5] but has not been isolated in a pure form. It was found, by a new route according to eq 2, that exactly equimolar amounts of lithium diethylaluminate (Et_2AlOLi, I)[6] reacted in toluene at low temperature with diethylaluminum chloride to give bis(diethylaluminum) oxide ($Et_2AlOAlEt_2$, II) accompanied by the precipitation of lithium chloride in a quantitative amount.[7] This oily product disproportionated to

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[7] H. Tani, T. Araki, and T. Aoyagi, presented at the 13th Annual Meeting of the Society of High Polymers, Japan, May 2, 1965, Tokyo.