

## Conversion of Primary Fluoroalcohols to Bromides

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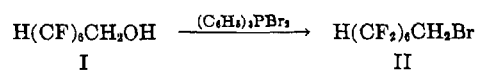
**1,1,7-Trihydrododecafluoroheptanol was converted to 1,1,7-trihydrododecafluoroheptyl bromide in 68% yield by treating with triphenylphosphine and bromine. The reaction is probably general for primary fluorinated alcohols.**

**DIRECT REPLACEMENT** of the hydroxyl group of fluoroalcohols by the usual halogenating agents is usually not possible. Treatment of these alcohols with the common phosphorus or sulfur-containing halogenating agents— e.g.,  $\text{PBr}_3$ ,  $\text{SOCl}_2$  yields the corresponding esters rather than the halides (6). However, conversion of  $\alpha, \alpha$ -bis (trifluoromethyl)-*p*-hydroxybenzyl alcohol to the chloride with thionyl chloride has been reported (6). In this case, resonance contribution of the *p*-OH group to a benzylic carbonium ion in the transition state is apparently sufficient to overcome the destabilizing effect of the trifluoromethyl groups.

The only general method reported to date for conversion of 1, 1-dihydroperfluoroalcohols and  $\alpha, \alpha, \omega$ -trihydroperfluoroalcohols to halides is a two-step reaction which involves preparation and isolation of the tosyl esters, and displacement of the tosylate group with sodium iodide, lithium bromide, or lithium chloride in refluxing di-, tri-, or tetra-glycol solvents (4, 7). Several phenylperfluoroalkylcarbinols were converted to the bromides by heating with phosphorus pentabromide in a sealed tube (8).

Recently, the utility of tertiary phosphine dihalides of the type  $\text{R}_3\text{PX}_2$  in converting alcohols to halides was described (8). The authors have found that the in situ preparation of triphenylphosphine dibromide in an acetonitrile solution of 1, 1, 7-trihydrododecafluoroheptanol (I) afforded a convenient one-step conversion to 1, 1, 7-trihydrododecafluoroheptyl bromide, (II) in good yield. Presumably the method is general for 1, 1-dihydro-fluorinated alcohols. The  $\alpha, \alpha, \omega$ -trifluoro-

alcohols of the general type  $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{OH}$  are readily available from telomerization of methanol and tetrafluoroethylene (E. I. DuPont de Nemours and Co.).



Attempts to convert the secondary fluorinated alcohol, hexafluoroisopropyl alcohol, and the tertiary fluorinated alcohol,  $\alpha, \alpha$ -bis (trifluoromethyl) benzyl alcohol to the respective bromides were not successful.

### EXPERIMENTAL

A sample of 1, 1, 7-trihydrododecafluoroheptanol (Dupont) was fractionated through an 18-inch by 6-mm. I.D. spinning band column. The fraction that distilled at 167–169° C. at 760 mm. was used (lit. (3, 1) b.p. 171–172° C. and 170° C.). Acetonitrile was distilled from  $\text{P}_2\text{O}_5$  after refluxing for 3 hours.

1, 1, 7-Trihydrododecafluoroheptyl bromide was prepared by the following method. To a warm (50–60° C.) stirred solution of 23.30 grams (0.0703 mole) of 1,1,7-trihydrododecafluoroheptanol I, 18.4 grams (0.0703 mole) of triphenylphosphine (M and T Chemicals, Inc.) and 100 ml. of acetonitrile in a 250-ml. 3-necked flask, fitted with a sealed stirrer, a reflux condenser, a drying tube, and an equilibrating dropping funnel, was added dropwise 11.2 grams (0.0703 mole) of bromine over a period of 1 hour. The material, after removal

of the acetonitrile, was fractionated through a spinning band column (18-inch by 6-mm. I.D.), and a cut of 17 grams (61% yield) was taken at 151° C. ( $n_D^{20}$  1.3340) (lit. (4) b.p. 157–159° C.,  $n_D^{20}$  1.3350). This cut gave a single sharp peak on gas-liquid chromatography (25% LAC on Chromosorb W, 6 feet by 1/4 inch, 85° C., 37.2 ml. per min. of helium, retention time 19.0 minute). An additional fraction (2.2 grams) was found to be 90% pure (total yield of product 68%). I.R.  $\lambda_{\text{max}}^{\text{film}}$  strong  $\text{CF}_2$  absorption between 8 and 9  $\mu$ , no OH absorption.

Because of the discrepancy between the reported boiling point (4) and that found in this work, and because of the difficulties encountered in obtaining reproducible elemental analyses, the NMR and mass spectra are reported.

NMR ( $\tau$ ) (in  $\text{CDCl}_3$  on a Varian HR60 spectrometer). 6.24 (2 protons, triplet,  $J_{\text{HF}}$  15 cps,  $\text{CH}_2\text{Br}$ ), 3.96 (1 proton, 3 triplets,  $J_{\text{HF}}$  gem. 51.9 cps,  $J_{\text{HF}}$  vic. 5.00 cps,  $\text{CHF}_2$ ). Mass spectrum (on a CEC 21-103C). Calcd. for  $\text{C}_7\text{H}_3\text{F}_{12}\text{Br}$ : parent mass 394; parent + 1, 7.61% of parent; parent + 2, 98.0% of parent. Found: parent mass 394; parent + 1, 7.36% of parent; parent + 2, 96.5% of parent. Principal peaks at mass 143 ( $\text{CF}_2\text{CH}_2^{79}\text{Br}^+$ ), 145 ( $\text{CF}_2\text{CH}_2^{81}\text{Br}^+$ ), 93 ( $\text{CH}_2^{79}\text{Br}^+$ ), 95 ( $\text{CH}_2^{81}\text{Br}^+$ ), 51 ( $\text{CHF}_2^+$ ).

Anal. Calcd. for  $\text{C}_7\text{H}_3\text{F}_{12}\text{Br}$ : C, 21.30; H, 0.77; F 57.75; Br, 20.21. Found: C, 21.0 (average of 4 analyses); H, 1.16 (average of 4 analyses); Br, 20.56.

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# Thermal Denitration of Uranyl Nitrate Hexahydrate

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**The thermal decomposition of uranyl nitrate hexahydrate was studied in the temperature range of 250° to 400° C. at atmospheric and at <0.1-mm. pressure. The intermediate and final products of the decomposition were determined. The denitration follows a zero-order reaction until less than half of the uranyl nitrate remains. The specific reaction rate constants were measured for denitration, and from these data the heats and entropies of activation were calculated.**

**T**HE THERMAL DECOMPOSITION of uranyl nitrate hexahydrate (UNH) is an important process in the nuclear energy industry. This material, isolated as an intermediate from spent reactor fuel, is thermally decomposed to uranium trioxide. The trioxide is reduced by hydrogen to the dioxide, which is subsequently hydrofluorinated. Although uranyl nitrate hexahydrate has been processed for years in this manner, the over-all operation has presented various difficulties. One of the problems is the wide range of reactivity toward hydrofluorination of different batches of uranium trioxide.

Lack of information about the decomposition of uranyl nitrate hexahydrate gave rise to a number of uncertainties about process performance. Therefore, a program was initiated to elucidate the mechanism of the decomposition, identify the intermediate products, and determine the kinetics of denitration at temperatures up to 400° C.

Early in the century, uranyl nitrate prepared by the dehydration of the hexahydrate was reported to contain the di- and trihydrate (11, 15). These findings were later verified by several methods including phase relationships (12) and vapor pressure measurements (8). The presence of anhydrous uranyl nitrate has been reported in thermolysis measurements of uranyl nitrate hexahydrate (16) and in the thermal decomposition of uranyl nitrate dihydrate (13). Methods of preparation for the hexa-, tri-, and dihydrates (10) as well as anhydrous uranyl nitrate (5) are readily available.

Five crystalline polymorphs of  $\text{UO}_3$  ( $\alpha$ - $\epsilon$ ) and one amorphous form are known and have been prepared (7). There are also four monohydrates ( $\alpha$ - $\delta$ ), two dihydrates ( $\alpha$ - $\beta$ ), and a hemihydrate (9). All of these would not be expected to be final products in the thermal decomposition of UNH, because of their thermal instability (3). Industrially,  $\gamma$ - $\text{UO}_3$  is the usual product of the