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of Organic Compounds

Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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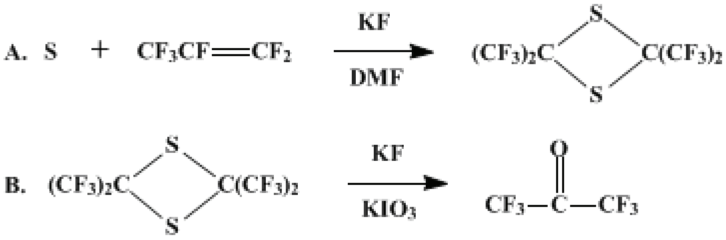
HEXAFLUOROACETONE

[2-Propanone, 1,1,1,3,3,3-hexafluoro-]



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Checked by Evan D. Laganis and Bruce E. Smart.

1. Procedure

Caution! Hexafluoroacetone and its precursor are toxic. Both procedures should be conducted in an efficient hood.

A. *2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane*. A 500-mL, three-necked flask is fitted with a good magnetic stirring bar, thermometer, water-cooled condenser, and a fritted gas inlet tube (Note 1). The outlet of the condenser is attached to a tared −78°C cold trap and the inlet tube is connected via flexible tubing to a graduated −78°C cold trap into which 60 mL (96 g, 0.64 mol) of hexafluoropropene has been condensed under nitrogen. The flask is charged with 3 g of potassium fluoride and is flamed gently under vacuum. The apparatus is cooled while purging with nitrogen. Sulfur (23 g, 0.72 mol) and 200 mL of dry dimethylformamide are then added (Note 2). The reaction mixture is heated to 40–45°C with stirring. The heat source is removed, the stopcock on the trap containing the hexafluoropropene is opened, and the trap is gently thawed. The rate of hexafluoropropene bubbling into the reaction mixture is adjusted to about 0.6 mL (1 g) / min by cooling or warming the trap containing the hexafluoropropene (Note 3),(Note 4),(Note 5). When all the hexafluoropropene has been added, the reaction mixture is cooled to −20°C to −30°C and quickly filtered under suction (Note 6). The filtercake is transferred to an Erlenmeyer flask and is allowed to melt. Water (50 mL) is added, and the mixture is filtered. The lower liquid phase is separated, washed with 50 mL of water, and distilled through a 20-cm Vigreux column at atmospheric pressure to give 93.0–99.4 g (80–85%) of product, bp 106–108°C (Note 7).

B. *Hexafluoroacetone*. A 1-L, three-necked flask is fitted with a sealed mechanical stirrer, thermometer, and condenser. A −78°C glass trap is attached to the condenser via flexible tubing. While the system is purged with nitrogen, 3 g of potassium fluoride is added and the flask and potassium fluoride are flame-dried (Note 8). After the flask has cooled, 300 mL of dry dimethylformamide, 80 g (0.374 mol) of powdered potassium iodate, and 60 g (0.165 mol) of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane are added (Note 9). The stirrer and water condenser are started and the reaction mixture is heated over a 45-min period to 149°C and is kept at 149°C for an additional 15 min. The heat source is then removed, and a slow stream of nitrogen is used to flush any remaining product gas into the cold trap (Note 8). The condensate is transferred under vacuum to a tared, evacuated-gas cylinder (Note 10). The cylinder contains 37.0–39.9 g (68–73%) of material (Note 11). This material is distilled to give 35.0–37.6 g (64–69%) of pure product, bp −28°C [lit.[2] bp −27°C] (Note 12).

2. Notes

1. The checkers dried the glassware overnight at 150°C in an oven and assembled it hot under a nitrogen purge.
2. The checkers obtained potassium fluoride, potassium iodate, dimethylformamide (reagent grades), and sulfur (sublimed) from Fisher Scientific Co. The submitters purchased hexafluoropropene from PCR Research Chemicals, Inc.; the checkers used hexafluoropropene from E. I. du Pont de Nemours &

Company, Inc. The potassium fluoride was predried overnight in a vacuum oven at 110°C. The sulfur was dried in a vacuum desiccator and the dimethylformamide was distilled from P_2O_5 prior to use.

3. The mixture of dimethylformamide, sulfur, and potassium fluoride turns brown prior to the addition of hexafluoropropene, which quickly brings the color back to bright yellow. The submitters report that the reaction mixture will turn blue or green prior to the addition of hexafluoropropene, if the dimethylformamide is dry (less than ca. 0.05% water).

4. The reaction is moderately exothermic. The temperature rises to about 55°C and remains there as the reaction proceeds.

5. With good stirring, the reaction proceeds as fast as the hexafluoropropene is added. The dry ice trap attached to the condenser should be checked periodically, however. When the required amount of hexafluoropropene is added, little or no undissolved sulfur remains.

6. 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane melts at 24°C. Thus, this operation must be done quickly to minimize product loss.

7. The product is more than 99% pure by GLPC (6 ft × 1/8 in. 20% FS-1265 on 60/80 Gaschrome R, 50–200°C) and by ^{19}F NMR ($CDCl_3$) φ: −73.3 (s). The submitters report that they obtained 78–90 g of 98% pure product, bp 110°C.

8. The nitrogen initially should come from the cold trap, itself cooled under a nitrogen flush. At the end of the reaction, the flow of nitrogen should be reversed. This can be done by replacing the thermometer with a gas inlet tube.

9. The submitters report that a ratio of KIO_3 to 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane of 2.26 is near the optimum since a ratio of 2.5 did not increase the yield, whereas a ratio of 2.0 gave 5–10% lower yields.

10. This transfer is best done on a vacuum manifold system equipped with a manometer. The trap and a stainless-steel cylinder of 100–300-mL capacity are attached via vacuum tubing to the manifold system, cooled in liquid nitrogen baths, and evacuated to 0.5–1 mm. The system is closed and the trap is removed from its cold bath and is slowly thawed. The volatile material in the trap is transferred to and condensed in the cylinder at such a rate that no positive pressure builds up in the closed system.

11. The submitters report collecting 45–50 g of product (98% pure or better by GLPC on a 10-ft × 1/8-in. Porapak P column) in the cold trap attached to reaction vessel. The checkers found that the trap contained relatively nonvolatile material, principally dimethylformamide, in addition to the desired product.

12. The checkers used a 30-cm jacketed, low-temperature spinning band column for this distillation. The IR spectrum of the distilled product is identical to that of an authentic sample; IR (vapor) cm^{-1}: 1806 (C=O).

3. Discussion

Earlier methods of preparing 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (hexafluorothioacetone dimer, HFTA dimer) include the reaction of hexafluoropropene (HFP) and sulfur over a carbon bed at 425°C[3] and the reaction of HFP and sulfur in tetramethylene sulfone at 120°C in the presence of potassium fluoride (autoclave).[4] Dimethylformamide appears to be a far superior solvent for this reaction, permitting the use of atmospheric pressure and modest temperatures, as well as affording a cleaner product.

The generation of hexafluoroacetone (HFA) from HFTA dimer has been accomplished by the hot-tube oxidation with nitric oxide at 650°C (high temperature converts dimer into monomer).[5] The present method uses the more convenient interconversion of dimer to monomer effected by potassium fluoride in dimethylformamide. This permits many reactions to be conducted on the very reactive monomer without actually isolating it.

For occasional laboratory synthesis of HFA, the present method offers distinct advantages of convenience (cost, workup, standard equipment) over other known methods. These include the epoxidation of HFP followed by isomerization of the epoxide to HFA,[6] [7] the high-temperature halogen exchange of hexachloroacetone with Cr^{3+} /HF,[8] and permanganate oxidation of the extraordinarily toxic perfluoroisobutylene.[9]

Hexafluoroacetone is a reactive electrophile. It reacts with activated aromatic compounds (e.g., phenol), and can be condensed with olefins, dienes, ketenes, and acetylenes. It forms adducts with many compounds containing active hydrogen (e.g., H_2O or HCN). Reduction of HFA with $NaBH_4$ or $LiAlH_4$ affords the useful solvent hexafluoroisopropyl alcohol. The industrial importance of HFA arises largely from its use in polymers and as an intermediate in monomer synthesis.[10]

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

P_2O_5

KIO_3

2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (hexafluorothioacetone dimer, HFTA dimer)

Cr^{3+} /HF

hydrogen (1333-74-0)

phenol (108-95-2)

nitrogen (7727-37-9)

sulfur (7704-34-9)

carbon (7782-42-5)

nitric oxide

potassium fluoride (7789-23-3)

$LiAlH_4$ (16853-85-3)

dimethylformamide (68-12-2)

$NaBH_4$ (16940-66-2)

tetramethylene sulfone (126-33-0)

perfluoroisobutylene (382-21-8)

hexachloroacetone (116-16-5)

Hexafluoroacetone,
2-Propanone, 1,1,1,3,3,3-hexafluoro- (684-16-2)

potassium iodate (7758-05-6)

hexafluoropropene (116-15-4)

2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane (791-50-4)

hexafluoroisopropyl alcohol (920-66-1)