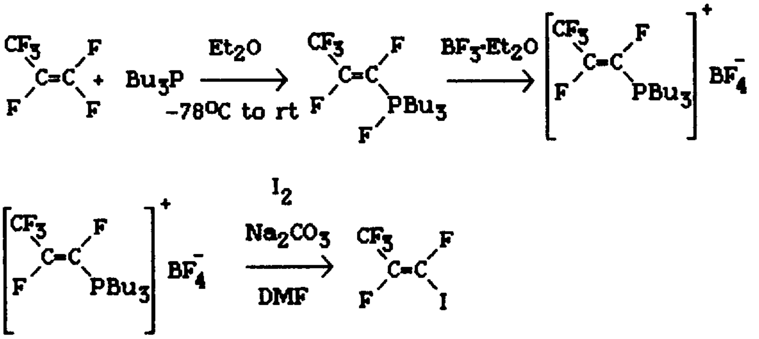
Journal of Fluorine Chemistry, 38 (1988) 131–134

Received: January 20, 1987; accepted: March 28, 1987

FLUORINE CHEMISTRY SYNTHESIS

PREPARATION OF Z-1-IODOPENTAFLUOROPROPENE



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A two liter three-necked roundbottomed flask was equipped with a magnetic stirbar, Dry Ice condenser, rubber septum and pressure-equalizing constant addition funnel. The apparatus was dried with a Bunsen burner under a stream of nitrogen. The flask was charged with 200 ml dry ether[1] and cooled to -78°C (Dry Ice/isopropyl alcohol (ipa)). Hexafluoropropene (62 ml, 620 mmole) was condensed in through the Dry Ice/ipa filled condenser.[2] Tri-*n*-butylphosphine[3] (149 ml, 600 mmole) was added dropwise *via* syringe to the magnetically stirred solution at -78°C over 15-20 minutes. The mixture was stirred after the addition of the tri-*n*-butylphosphine was completed and slowly allowed to warm to room temperature over three hours.

The reaction flask was cooled to 0°C with an ice-water bath and boron trifluoride-etherate (74 ml, 600 mmole) was added dropwise through the constant addition funnel. Solid formed, so vigorous stirring was maintained. When the addition was complete, as much ether as possible was removed with a pipette fitted with a suction bulb.[4] Fresh,

0022-1139/88/$3.50

dry ether (200 ml) was added to the flask and the reaction mixture was stirred for 10 minutes at 0°C. The ether was removed as before (by pipette fitted with a suction bulb) and the reaction flask was evacuated at full vacuum for 90 minutes. (If solid was not present initially, it should appear as the remaining ether is evaporated.[5])

The flask was re-pressurized with nitrogen and equipped with a glass nitrogen tee to maintain an inert atmosphere. The solid was dissolved in 500 ml dry DMF[6] and iodine (400 g, 1.6 mole) was added. The flask was cooled to 0°C with an ice-water bath and 160 g sodium carbonate (1.5 mole) was added *slowly* from a solid addition tube.[7] The mixture was allowed to stir at room temperature for eight hours after the addition of the sodium carbonate was completed.

The reaction flask was then equipped with a flash distillation head with a 250 ml flask for a receiver. The receiver was cooled with Dry Ice/ipa and the flask was evacuated slowly to <1 mm Hg. The reaction flask was then heated to 60°C with an oil bath. Approximately 150 mls of distillate were collected. The distillate was poured into a 1 liter beaker which contained ~500 ml ice-water. The organic layer was washed with cold water (3X 200 ml) and then dried over P_2O_5. The product was simply distilled through a short (3") vigreaux column at 52°C to give 95.1g $\underline{Z}$-$CF_3CF{=}CFI$ (61% yield).[8] The ^{19}F nmr spectrum (CCl_4, *vs.* $CFCl_3$) shows: CF_3 at -68.1 ppm (dd); =$C\underline{F}I$ at -109.3 ppm (dq), JCF_3-$\underline{F}I$ = 20.9 Hz; and $CF_3C\underline{F}$= at -150.3 ppm (dq), JCF_3-$\underline{F}$= 11.7 Hz; JF-F= 148.6 Hz.

Notes

1 Dried over Na wire.

2 The hexafluoropropene (HFP) was measured by condensing it off a Dry Ice/isopropanol-cooled cold finger condenser into a graduated tube cooled in Dry Ice/isopropanol (See Figure A). A rough approximation is one milliliter of HFP is ten millimoles. After the required volume was collected in the tube, the tube was connected to the condenser on the reaction flask *via* a vacuum take-off and Tygon or Nalgene tubing (See Figure B). The tube was then slowly removed from the Dry Ice/isopropanol bath to allow **slow** transfer of the gas. Care must be taken to **not** warm the tube rapidly, because rapid volatilization of the gas will pop off the hose or the ground glass connections.

3 Distilled from sodium under vacuum.

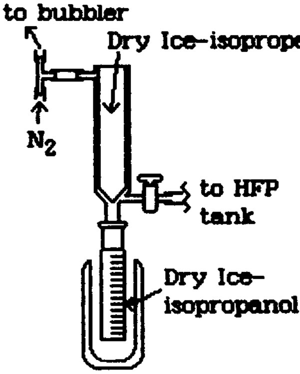
4 If solid does not form, two layers will be present. The upper layer is ether, which should be carefully removed by a pipette fitted with a suction bulb. The lower layer or solid is phosphonium salt. The presence or absence of solid at this point makes no difference in the success of the reaction.

5 It is important to remove all of the ether at this point because it would be difficult to remove from the final product.

6 Distilled from CaH_2 under vacuum.

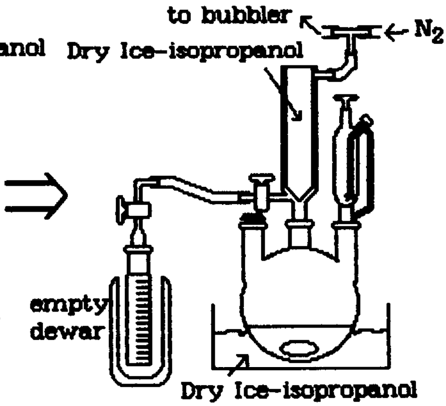
7 Caution must be exercised during the carbonate addition because CO_2 forms. Add only small portions and wait between additions. Rapid evolution of large amounts of CO_2 could cause the reaction mixture to bubble out of the flask.

8 Other difluoromethylene olefins can be converted stereospecifically to vinyl iodides by this method: perfluoro-1-heptene, for example [1]. Hydrolysis of the Z-vinyl phosphorane described above also provides a stereospecific synthesis of E-1-hydropentafluoropropene [2].



Condensation of HFP Into Graduated Tube

Figure A.



Condensation of HFP Into Flask

Figure B.

1 Ph.D. Thesis, S. Shin-Ya, University of Iowa.

2 D.J. Burton, S. Shin-Ya and R.D. Howells, Journal of Fluorine Chemistry 15 (1980) 543.

This preparation has been checked via the described procedure by Dr. William B. Farnham (Central Research Department, E.I. du Pont de Nemours & Co) and satisfactory results were obtained.
Dr. Farnham suggests that a mechanical stirrer in the Na_2CO_3/I_2 reaction would provide better agitation than the magnetic stirrer.
Checker's full address is:

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