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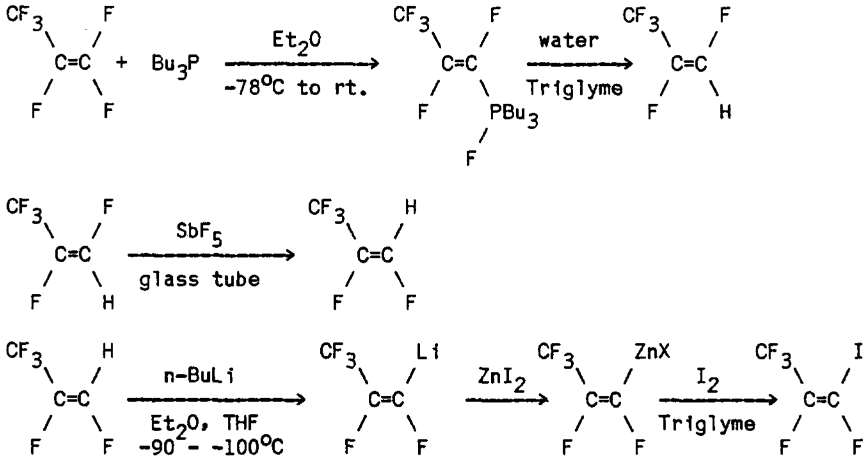
FLUORINE CHEMISTRY SYNTHESIS

PREPARATION OF E-1,2,3,3,3-PENTAFLUOROPROPENE, Z-1,2,3,3,3-PENTAFLUOROPROPENE AND E-1-IODOPENTAFLUOROPROPENE



SCHEME

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PREPARATION OF E-1,2,3,3,3-PENTAFLUOROPROPENE [1]

A two-liter three-necked round bottomed flask was equipped with a magnetic stirbar, dry ice condenser, rubber septum and glass stopper (Fig. B). The apparatus was dried with a Bunsen burner under a stream of nitrogen. The flask was charged with 110 ml dry ether[1] and cooled to -78°C [Dry Ice, isopropyl alcohol]. Hexafluoropropene (32 ml, 320 mmol), previously measured by condensation into a graduated tube (Fig. A), was added via the dry ice/isopropyl alcohol filled condenser.[2] Tri-n-butylphosphine[3] (76 ml, 305 mmol) was added dropwise via syringe to the

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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 3 hours, making sure to keep the condenser cold.

The condenser was rapidly replaced with a flash distillation apparatus that was fitted with a 250 ml receiver cooled in liquid nitrogen (Fig. C). The apparatus was slowly evacuated to prevent bumping of the ether solution. Full vacuum (<0.1 mm Hg) was maintained for 1 hour to ensure that all of the ether was removed. The system was repressurized with dry nitrogen. The flash distillation apparatus was replaced with a vacuum take-off connected with vacuum tubing to a glass trap, with vacuum stopcocks at both the inlet and exit, which was in turn connected to both a Rotaflo tube[4] and vacuum line via a tee (Fig. D). The entire system was then evacuated, and the trap was cooled in liquid nitrogen. Triglyme (80 ml) was added via syringe to the reaction flask.

The hydrolysis was conducted by addition of small portions of water to the flask with a 1 ml syringe. (It is important that the increments be kept small, and that there is enough time between increments, to ensure that a violent gas evolution does not result.) The following water addition schedule has proven effective: 5 x 0.1 ml, 14 x 0.2 ml, and 17 x 1 ml, waiting until all bubbling has stopped before addition of the next aliquot. The solution was stirred for an additional 10 minutes following the last addition. The stopcock at the inlet to the trap was closed, and the Rotaflo tube was cooled in liquid nitrogen. With the system still under full vacuum, the stopcock on the vacuum line was closed to prevent the product from being pumped away in the transfer to the Rotaflo tube. The liquid nitrogen was removed from around the trap to allow the product to slowly transfer to the Rotaflo tube.[5]

The product was purified by simply passing it through a trap cooled to -78°C (Dry Ice/isopropyl alcohol) into a tared Rotaflo tube cooled in liquid nitrogen (Fig. E). (This transfer was conducted most smoothly if both Rotaflo tubes were cooled in liquid nitrogen initially, and the entire system was evacuated.) The stopcock on the vacuum line was then closed, and the tube containing the product was allowed to warm slowly to room temperature. When the transfer was completed, the tap on the tube which contained the product was closed, and the rest of the system was repressurized. The tube containing the product was allowed to warm to room temperature in a safe area[6] before weighing. 33.8 g (88% yield) of E-1,2,3,3,3-pentafluoropropene resulted. ^{19}F NMR (DMF solvent, $CFCl_3$ reference): $CF^a{}_3CF^c=CF^bH$ -68.9 ppm (a, dd), -164.0 ppm (b, ddq), -181.6 ppm (c, dqd), J(ab)=20 Hz, J(ac)=10 Hz, J(bc)=134 Hz, J(bH)=71 Hz J(cH)=4 Hz.

PREPARATION OF Z-1,2,3,3,3-PENTAFLUOROPROPENE

Approximately 3-4 ml of SbF_5 was placed in a dry Rotaflo tube through a funnel under a flow of dry nitrogen (Fig. F). The Teflon barrel of the tap was replaced. The tube charged with SbF_5 was then connected to the tube containing the E-1,2,3,3,3-pentafluoropropene via a tee which was also connected to a vacuum line. Both tubes were cooled in liquid nitrogen and the entire system was evacuated. The stopcock on the vacuum line was closed, and the tube containing the E-1,2,3,3,3-pentafluoropropene was allowed to slowly warm to room temperature. When the transfer was completed, the tap on the tube containing the reagents was closed and the rest of the system was repressurized. The tube was allowed to warm to room temperature in a safe area.[6] After 1 hour at room temperature with occasional shaking the product was transferred as described previously into a Rotaflo tube containing several grams of sodium fluoride. This tube was allowed to stand at room temperature for several hours. Finally the product was transferred to a clean tared Rotaflo tube for storage. 32.6 g (96% yield) of Z-1,2,3,3,3-pentafluoropropene resulted. ^{19}F NMR (Triglyme solvent, $CFCl_3$ reference): $CF^a{}_3CF^c=CF^bH$ -72.0 ppm (a, ddd), -154.4 ppm (b, ddq), -161.6 ppm (c, dqd), J(ab)=5.8 Hz, J(ac)=14.1 Hz, J(bc)=8.8 Hz, J(aH)=1.2 Hz J(bH)=67.0 Hz J(cH)=15.8 Hz.

PREPARATION OF E-1-IODOPENTAFLUOROPROPENE

A 500 ml three-necked round bottomed flask with a septum port was equipped with a magnetic stirbar, Dry Ice condenser, low temperature thermometer in a Teflon thermometer adaptor, and a glass stopper. The apparatus was dried with a Bunsen burner under a stream of nitrogen. The flask was charged with 40 ml of dry ether[1] and 80 ml THF,[7] and cooled to

-100°C using a pentane/liquid nitrogen slush.[8] The condenser was cooled with Dry Ice/isopropyl alcohol, and the Z-1,2,3,3,3-pentafluoropropene (18.6 g, 141 mmol) was added dropwise via the condenser (Fig. G). The actual amount of propene added was determined by the weight difference of the Rotaflo tube. A 2.5 M hexane solution of n-BuLi (135 mmoles) was added dropwise via syringe at a rate which allowed the temperature of the solution to remain below -95°C. This addition required approximately 70 minutes. After the addition was completed, the reaction mixture was stirred for an additional 20 minutes at -100°C.

A solution of ZnI_2[9] (43 g, 135 mmoles) in THF (100 ml) was added to the lithium reagent via syringe at a rate which allowed the temperature to rise to -70°C. A large amount of tan precipitate formed during this addition, making stirring difficult (alternatively a mechanical stirrer could be used). If stirring stopped, the apparatus was swirled to prevent hot spot generation during the addition. The solution was once again allowed to cool to -100°C before the cooling bath was finally removed. As the mixture slowly warmed to room temperature, a brown solution developed.

The thermometer and thermometer adapter were replaced with a glass stopper, and the condenser was replaced with a flash distillation apparatus fitted with a 500 ml Dry Ice/isopropyl alcohol cooled receiver. All of the volatile material was distilled from the reaction flask under full vacuum. When the transfer of the volatile materials was no longer detected with the reaction flask at room temperature, 120 ml of triglyme was added via syringe and the reaction flask was heated to 70°C with an oil bath.[10] When triglyme began distilling, the heat was removed, but the system was left under full vacuum for an additional 2 hours at room temperature.

The system was repressurized with dry nitrogen, and the receiver was changed to a 100 ml flask. The system was again evacuated, and the receiver cooled with liquid nitrogen. A solution of iodine (38 g, 150 mmoles) in 100 ml of triglyme was added to the zinc reagent solution in 10 ml portions via syringe. As each portion was added the iodine color rapidly dissipated (except for the last portion) and the volatile product distilled from the solution as it was formed, as evidenced by vigorous bubbling. After all of the iodine solution had been added, the flask was slowly heated to 70°C, until triglyme began to distill. The heat was removed and the system was repressurized. The flash distillate was redistilled at atmospheric pressure through a 3" Vigreux column using a short path distillation apparatus to give 30.7 g (88% yield) of E-1-iodopentafluoropropene (bp=55-57°C, 99% pure by GLPC analysis on 5% OV-101). ^{19}F NMR (hexane solvent, $CFCl_3$ reference): $CF^a{}_3CF^c{=}CF^bI$ -66.5 ppm (a, dd), -90.2 ppm (b, qd), -132.8 ppm (c, qd), J(ab)=8.8 Hz, J(ac)=10.2 Hz, J(bc)=8.0 Hz.

Notes

1. Dried over sodium wire.

2. The hexafluoropropene (HFP) was measured by condensing the gas with a Dry Ice/isopropyl alcohol cooled cold finger condenser into a graduated tube cooled in Dry Ice/isopropyl alcohol (see figure A). A rough approximation is 1 ml of HFP is 10 mmol. 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 (figure B). The tube was then carefully removed from the Dry Ice/isopropyl alcohol bath to allow slow transfer of the gas. Care must be taken not to warm the tube rapidly, because rapid volatilization of the gas will pop off the hose or ground glass connections.

3. Distilled from sodium under vacuum.

4. A heavy walled glass tube sealed with a Rotaflo^{TM} tap. The volume of the tubes used in the preparations given here was approximately 300 ml.

5. Do not attempt to help the transfer by warming the trap. This may result in a dangerous rapid pressure increase. The transfer will proceed very smoothly on its own as long as the system was completely evacuated (<0.1 mm Hg) before the transfer was initiated.

6. Warm tubes containing gases only in safe areas, such as in a hood behind a safety shield, or in a metal container. Never fill tubes more than 1/3 full.

7. Dried by distillation from sodium benzophenone ketyl.

8. The pentane slush was prepared by placing a bath containing pentane around the flask. Liquid nitrogen was then slowly poured into the bath with constant stirring with a wood stick. Liquid nitrogen was added until the bath maintained a slushy consistency. Liquid nitrogen was used as necessary to maintain the slush during the reaction.

9. ZnI_2 was prepared from 1 equivalent each of zinc dust and iodine in dry THF. The iodine was added slowly to the zinc and THF. After stirring several hours at room temperature, the THF was removed under reduced pressure.

10. It was important to remove all of the ether and THF at this point, as it would be very difficult to remove these solvents from the volatile vinyl iodide.

[1] Shin-ya, S. Ph.D Thesis, The University of Iowa. Burton, D.J.; Shin-ya, S.; Howells, R.D. J. Fluorine Chem., 15 (1980) 543-546.

ACKNOWLEDGEMENT

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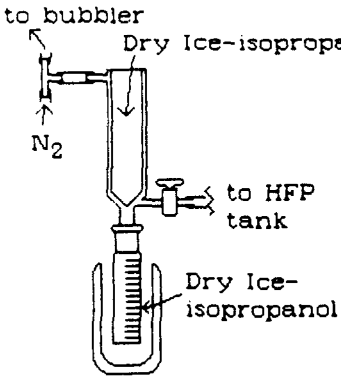

Fig. A.

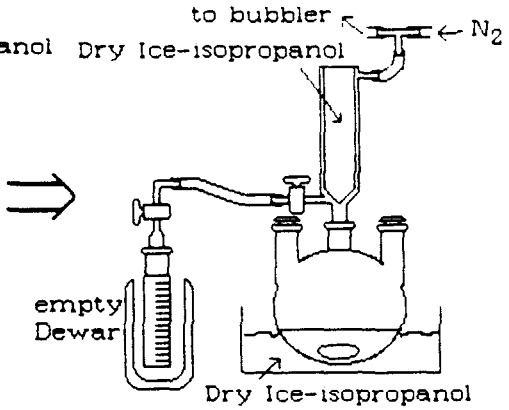

Fig. B.

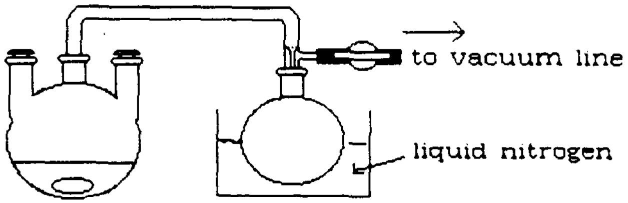

Fig. C.

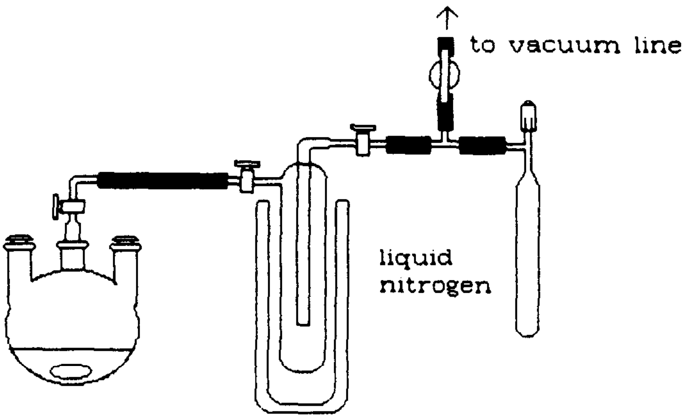

Fig. D.

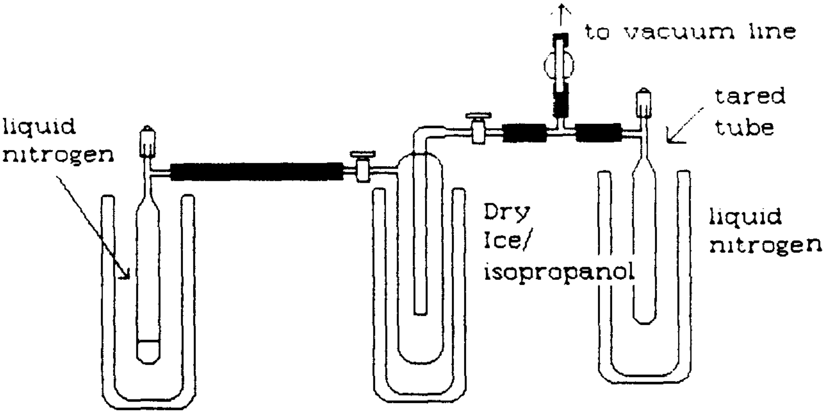

Fig. E.

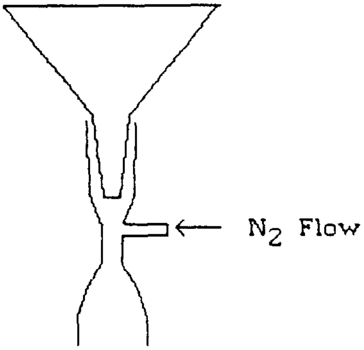

Fig. F.

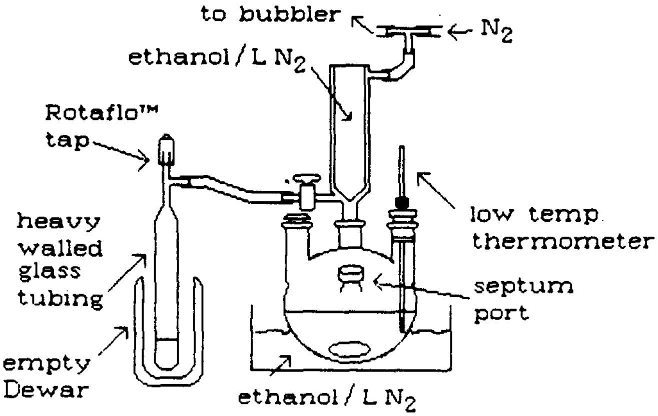

Fig. G.