ELSEVIER

Journal of Fluorine Chemistry 75 (1995) 83–86

JOURNAL OF FLUORINE CHEMISTRY

A facile route to tetrafluoroallene

Hengyao Lu, H. Bruce Friedrich, Donald J. Burton *

Department of Chemistry, The University of Iowa, Iowa City, IA 52242, USA

Received 11 March 1995; accepted 3 June 1995

Abstract

Tetrafluoroallene has been prepared in 72%–75% yield by metallation of either 2-hydropentafluoropropene or 2-bromopentafluoropropene with t-butyllithium followed by thermal elimination of lithium fluoride from the 2-lithiopentafluoropropene. The 2-bromopentafluoropropene route gives the allene free of isobutane.

Keywords: Allenes; Lithium reagents; Metallation reactions; Elimination reactions; IR spectroscopy

1. Introduction

Tetrafluoroallene has been prepared by two routes starting from the addition product of dibromodifluoromethane and vinylidene fluoride [1–3].

$$CF_2Br_2 + H_2C{=}CF_2 \xrightarrow[\substack{\text{110 °C}\\ \text{autoclave}}]{\substack{\text{benzoyl}\\ \text{peroxide,}}} \underset{(51\%)}{CF_2BrCH_2CF_2Br} \qquad (1)$$

Although route A is the shorter route, experimental difficulties in the dehydrobromination step resulted in low overall yield of the allene. Route B involves two extra stages but has been suggested as the preferred method:

Route A:

$$CF_2BrCH_2CF_2Br \xrightarrow[\text{60 °C/35 mmHg}]{\text{KOH (s)}} \underset{(89\%)}{CF_2BrCH{=}CF_2} \xrightarrow[\text{110 °C}]{\text{KOH (s)}} \underset{(\mathbf{2},\ 34\%)}{F_2C{=}C{=}CF_2} \qquad (2)$$

Route B:

$$CF_2BrCH_2CF_2Br \xrightarrow[\substack{\text{charcoal}\\ \text{300 °C/1 mmHg}}]{\text{silica tube}} \qquad (3)$$

$$\begin{tikzcd}
\underset{(86\%)}{CF_2BrCH{=}CF_2} \arrow[r, "Br_2", "\substack{h\nu,\\ \text{RT,}\\ \text{6 h}}"'] & \underset{(92\%)}{CF_2BrCHBrCF_2Br} \arrow[d, "\substack{\text{50\% aq. KOH,}\\ \text{RT}}"] \\
\underset{(74\%)}{F_2C{=}C{=}CF_2} & \underset{(91\%)}{CF_2BrCBr{=}CF_2} \arrow[l, "Mg"', "\substack{\text{THF,}\\ \text{0 °C, 4 h}}"]
\end{tikzcd}$$

2. Results and discussion

Recent work in our laboratory has involved the generation, trapping and functionalization of 2-metallated pentafluoropropenes [4,5]. In the course of our work with the 2-lithio reagent **1**, it became of interest to determine the mode of thermal decomposition of **1**. Elimination of the allylic fluorine from **1** would give tetrafluoroallene **2**; whereas elimination of vinylic fluorine would produce tetrafluoropropyne (**3**). If either mode of elimination predominated, this simple route could provide ready access to interesting compounds previously obtained only with difficulty or via multistep synthesis.

$$CF_3CH{=}CF_2 \xrightarrow[\substack{Et_2O,\\ -78\ °C}]{{}^tBuLi}$$

$$\begin{tikzcd}
\underset{(\mathbf{1})}{[CF_3C(Li){=}CF_2]} \arrow[r, "-LiF"] \arrow[d, "-LiF"] & \underset{(\mathbf{2})}{F_2C{=}C{=}CF_2} \\
\underset{(\mathbf{3})}{CF_3C{\equiv}CF} &
\end{tikzcd} \qquad (4)$$

Consequently, after metallation of 2-hydropentafluoropropene with ${}^tBuLi$ in ether at −78 °C, the reaction mixture was warmed to −50 °C and then to room temperature (with concomitant vacuum removal of all volatile materials). Trap-to-trap distillation of the volatiles gave a 75% yield of **2**, 94% pure by NMR analysis, indicating that allylic fluoride elimination is the preferred mode of elimination. ^{13}C NMR, ^1H

---

* Corresponding author.

0022-1139/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 0022-1139(95)03310-6

NMR and FT-IR analysis of the product indicated that the major impurity was $(CH_3)_3CH$ (formed in the initial exchange reaction); pentane and diethyl ether were trace impurities.

$$\underset{(\mathbf{1})}{[CF_3C(Li){=}CF_2]} \xrightarrow[(2)\ \mathrm{RT,\ vacuum}]{(1)\ -50\ ^\circ\mathrm{C}} \underset{(75\%)}{\mathbf{2}} \qquad (5)$$

In order to avoid the isobutane contaminant, an alternative approach was devised, starting from 2-bromopentafluoropropene (**4**). The by-product in this metallation reaction is 2-bromo-2-methylpropane (b.p. 91 °C), which is easily separated from **2**. Under these conditions, **2** is isolated in 72% yield (via trap-to-trap distillation). The purity of **2** was 98% as determined by quantitative FT-IR analysis (cf. Experimental details). Only a trace (2%) of $CF_3C{\equiv}CF$ was detected by FT-IR analysis. Thus, metallation of **4** followed by thermal elimination of LiF provides ready access to **2** in high purity.

$$\underset{(\mathbf{4})}{CF_3CBr{=}CF_2} + {}^tBuLi \xrightarrow[-78\ ^\circ\mathrm{C}]{Et_2O} \qquad (6)$$

$$\begin{array}{l} \underset{(\mathbf{1})}{[CF_3C(Li){=}CF_2]} + (CH_3)_3CBr \\ \quad\Big\downarrow \begin{array}{l}(1)\ -50\ ^\circ\mathrm{C}\\(2)\ \mathrm{RT/vacuum}\end{array} \\ \quad\underset{(72\%)}{\mathbf{2}} \end{array}$$

The requisite precursor, **4**, has been reported by Zeifman et al. [6] from 2-hydropentafluoropropene via a tedious route and by Morken and Burton [5] from 2,2-dibromohexafluoropropane. Herein we describe two alternative routes to **4** that are facile and amenable to scale-up. Bromination of 2-hydropentafluoropropene followed by elimination of hydrogen bromide with tri-butylamine gives **4** in an overall yield of 81% as outlined below:

Method A:

$$CF_3CH{=}CF_2 + Br_2 \xrightarrow[\substack{\mathrm{to}\\ \mathrm{RT}\\ 10\ \mathrm{h}}]{78\ ^\circ\mathrm{C}}$$

$$\underset{(95\%)}{CF_3CHBrCF_2Br} \xrightarrow[\substack{Bu_2O,\\ \mathrm{RT}}]{Bu_3N} \underset{(\mathbf{4},\ 85\%)}{CF_3CBr{=}CF_2} \qquad (7)$$

Alternatively, **4** can be prepared in 89% yield via a one-pot procedure by in situ conversion of **1** to the corresponding organozinc reagent, followed by cleavage of the zinc reagent with bromine to **4**.

Method B:

$$CF_3CH{=}CF_2 \xrightarrow[\substack{-78\ ^\circ\mathrm{C}\\ (2)\ ZnCl_2,\\ -78\ ^\circ\mathrm{C}}]{(1)\ {}^tBuLi,}$$

$$[CF_3C(ZnCl){=}CF_2] \xrightarrow[\substack{-20\ ^\circ\mathrm{C\ to}\\ \mathrm{RT}\\ \mathrm{TG}}]{Br_2} \underset{(\mathbf{4},\ 89\%)}{CF_3CBr{=}CF_2} \qquad (8)$$

Thus, **2** can be readily prepared in high yield and high purity from the commercially available 2-hydropentafluoropropene either in a one- or two-step procedure.

3. Experimental details

3.1. General

All reactions were performed in oven-dried glassware. ^{19}F NMR spectra were recorded on a JEOL FX 90Q (83.81 MHz) spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer. Unless otherwise indicated, all NMR spectra were recorded in $CDCl_3$ using approximately 10% (by volume) solutions. All chemical shifts are reported in parts per million (ppm) downfield (positive) of the standard. ^{19}F NMR spectra are referenced against internal $CFCl_3$, ^1H and ^{13}C against internal tetramethylsilane. FT-IR spectra of CCl_4 solutions were recorded using a solution cell with a 0.1-cm path length. GC–MS spectra were obtained at 70 eV in the electron impact mode on a VG Trio-1 GC/MS instrument. GLPC analyses were carried out on an HP 5890 A gas chromatograph using a DB-1 15 m (methyl silicone) capillary column with a thermal conductivity detector.

3.2. Materials

2-Hydropentafluoropropene was obtained from PCR, Inc. and used without further purification. Diethyl ether was distilled from Na/benzophenone ketyl at atmospheric pressure prior to use. Triglyme (TG) was distilled from Na/benzophenone ketyl at approximately 70 °C/1 mmHg and stored over 4 Å molecular sieves in a brown bottle. t-Butyllithium (1.7 M solution in pentane) was obtained from Aldrich Chemical Co. and used directly. Zinc chloride was obtained from Aldrich Chemical Co. and dried by heating to 150 °C overnight under full vacuum. All other reagents were commercially available materials and used without further purification.

3.3. Preparation of tetrafluoroallene (2) from $CF_3CH{=}CF_2$

A 150 ml three-necked flask equipped with a Teflon-coated magnetic stir bar, a rubber septum port, a low temperature thermometer and a Dry Ice/IPA condenser connected with a tee tube leading to a source of N_2 was charged with 50 ml of dry diethyl ether. The ether was cooled to −78 °C and 2.6 g (20 mmol) of 2-hydropentafluoropropene was condensed into the flask via the Dry Ice/IPA condenser. To the resultant solution (at −78 °C) was added (dropwise) 11.8 ml (20 mmol) of a 1.7 M solution of t-butyllithium in pentane via a syringe. The reaction mixture was stirred at −78 °C for 30 min; then allowed to warm to −50 °C over 2 h. The thermometer was replaced with a glass stopper, and the condenser was replaced with a flash distillation apparatus fitted with a

150 ml liquid-nitrogen-cooled receiver. All the volatile material was distilled from the reaction mixture under full vacuum at room temperature. The distilled material was purified by trap-to-trap distillation (traps at − 15 °C, − 35 °C and − 78 °C) to give 1.7 g (75%) of **2** in the third trap. NMR analysis of this material indicated a purity of 94%; the major impurity was 2-methylpropane as determined by ^{1}H NMR and FT-IR. For **2**: ^{19}F NMR δ: -64.2 (s) ppm. ^{13}C NMR δ: 117.9 (pentet, $J=39$ Hz, $=C=$); 140.1 (tdd, $J=276$, 14, 5 Hz, $=CF_2$) ppm. Reported [7] for **2**, δ: 118.1, 140.6 ppm. FT-IR (gas, 2–10 Torr) (cm^{-1}): 1040 (s); 1250 (s); 2071 (s).

3.4. Preparation of 2-bromopentafluoropropene (4) (Method A)

A 150 ml three-necked flask was equipped with a Teflon-coated magnetic stir bar, a glass stopper, a rubber septum port and a Dry Ice/IPA condenser with a tee tube to a source of N_2. The flask was cooled to − 78 °C and 6.6 g (50 mmol) of 2-hydropentafluoropropene was condensed into the flask via the Dry Ice/IPA condenser. Bromine (8.1 g, 51 mmol) was added to the 2-hydropentafluoropropene via a syringe at a rate to gently reflux the 2-hydropentafluoropropene. When the bromine addition was completed, the reaction mixture was warmed to room temperature and any excess Br_2 was removed via addition of 10 ml of a saturated solution of sodium bisulfite. The resultant colorless organic phase was washed with ice water (2 × 10 ml), dried and distilled through a short-path apparatus to give 13.8 g (47 mmol, 95%) of 2,3-dibromo-1,1,1,3,3-pentafluoropropane, b.p. 90–92 °C 1 atm; GLPC > 99% (reported [6]: b.p. 89–91 °C). ^{19}F NMR ($CFCl_3$, external standard) δ: -50.4 (pentet, 2F, $J=10$ Hz); -67.8 (td, 3F, $J=10$, 7 Hz) ppm. Reported [6] (CF_3COOH, external standard) δ: -28.8 (m, 2F); -11.8 (td, 3F, $J=9.4$, 5.6 Hz) ppm. ^{1}H NMR δ: 4.67 (m) ppm. Reported [6] δ: 4.27 (tq, 1H, $J=9.4$, 5.6 Hz) ppm. ^{13}C NMR δ: 121.2 (1, $J=281$ Hz, CF_3); 115.5 (t, $J=308$ Hz, CF_2Br); 50.5 (qt, $J=34$, 28 Hz, $CHBr$) ppm. GC–MS m/z % abundance; 213 ($M^+ - Br$, 81.3); 211 (85.0); 131 (26.6); 129 (25.7); 113 (17.5); 69 (100). FT-IR (cm^{-1}): 1340 (m); 1334 (m); 1256 (vs); 1231 (vs); 1209 (vs); 1195 (s); 1149 (w); 1127 (vs); 1110 (m); 1096 (m); 1021 (m); 961 (m); 951 (m).

A 50 ml three-necked flask equipped with a Teflon-coated magnetic stir bar, a glass stopper, a rubber septum port, a 12 in Vigreaux column connected to a trap cooled in Dry Ice/IPA was charged with 7.4 g (40 mmol) of tri-n-butylamine and 10 ml of di-n-butyl ether. To this solution was added (dropwise) via a syringe 10.0 g (34.2 mmol) of 2,3-dibromo-1,1,1,3,3-pentafluoropropane at room temperature. The 2-bromopentafluoropropene formed immediately (visible bubbles). After the addition of the dibromide was completed, the reaction mixture was stirred and heated at 40 °C for 1 h to distil all the 2-bromopentafluoropropene from the reaction mixture. The crude olefin (collected in the trap) was purified by trap-to-trap distillation (25 °C/1 mmHg) (traps at − 15 °C, − 78 °C, − 120 °C). From the second trap was obtained 6.1 g (29 mmol, 85%) of 2-bromopentafluoropropene as a colorless liquid (GLPC > 99%). The ^{19}F and ^{13}C NMR and FT-IR spectra were identical to a previously prepared sample [5] by an alternative method.

3.5. Preparation of 2-bromopentafluoropropene (4) (Method B)

A 500 ml three-necked flask equipped with a Teflon-coated magnetic stir bar, a rubber septum port, a low-temperature thermometer and a Dry Ice/IPA condenser connected with a tee tube leading to a source of nitrogen was charged with 150 ml of dry diethyl ether. The ether was cooled to − 78 °C and 8.0 g (60 mmol) of 2-hydropentafluoropropene was condensed into the flask via the Dry Ice/IPA condenser. To this solution was added (dropwise) via a syringe 35.0 ml (59.5 mmol) of a 1.7 M solution of t-butyllithium in pentane. After the addition of the t-butyllithium solution was completed, the reaction mixture was stirred at − 78 °C for 30 min. Then 8.3 g (61 mmol) of $ZnCl_2$ in THF (30 ml) was added via a syringe at a rate to maintain a temperature of − 75 °C. A large amount of tan precipitate formed — occasionally making stirring difficult. After the addition of the $ZnCl_2$ solution was completed, the reaction mixture was stirred at − 78 °C for 1 h and then allowed to warm to room temperature to give a brown colored solution. The thermometer was replaced with a glass stopper and the condenser was replaced with a flash distillation apparatus fitted with a 500 ml Dry Ice/IPA cooled receiver. All the volatile materials were removed under vacuum at room temperature; then 50 ml of triglyme (TG) was added to the reaction mixture via a syringe and the reaction mixture heated to 70 °C under vacuum until triglyme began to distil. The reaction mixture was then cooled to room temperature and repressurized with dry N_2. ^{19}F NMR δ: -50.7 (dd, 3F, $J=17$, 13 Hz); -62.8 (dq, 1F, $J=34$, 13 Hz); -74.3 (m, 1F) ppm.

To the reaction mixture (in TG) was slowly added via a syringe 9.3 g (58 mmol) of Br_2. After the addition of Br_2 was completed, the resultant solution was again evacuated and the volatile product collected in a receiver cooled with liquid nitrogen. When gas evolution had slowed, the reaction mixture was slowly heated to 70 °C (under vacuum) until TG began to distil. The distillate was purified by trap-to-trap distillation (as noted in Method A) to give in the second trap, 10.9 g (51.9 mmol, 89%) of 2-bromopentafluoropropene (GLPC > 99%).

3.6. Preparation of tetrafluoroallene (2) from $CF_3CBr{=}CF_2$

A 150 ml three-necked flask equipped with a Teflon-coated magnetic stir bar, a rubber septum port, a low-temperature thermometer and a Dry Ice/IPA condenser connected with a tee tube to a source of N_2 was charged with 20 ml of dry diethyl ether. The ether was cooled to − 78 °C; then 1.3 g

(6.1 mmol) of 2 bromopentafluoropropene was condensed into the flask via the Dry Ice/IPA condenser. To the resultant solution was added (−78 °C) 3.6 ml (6.1 mmol) of a 1.7 M solution of t-butyllithium in pentane via a syringe at a rate to maintain the temperature of the reaction mixture at −78 °C. After the addition of the t-butyllithium solution was completed, the reaction mixture was stirred at −78 °C for 30 min and then allowed to warm to −50 °C. The thermometer was replaced with a glass stopper and the condenser was replaced with a flash distillation apparatus fitted with a 50 ml liquid-nitrogen-cooled receiver. All the volatile materials were distilled from the reaction mixture under full vacuum at room temperature. The distillate was purified by trap-to-trap distillation (cf. Method A) to give 0.5 g (72%) of **2** in the third trap. The purity of this sample was >99% as determined by FT-IR analysis (cf. below).

3.7. *FT-IR analysis*

Infrared spectra of gas samples were recorded on an IBM 98 instrument (1 cm^{-1} resolution, 64 scans per spectrum) using a gas cell with a 10-cm path length. The spectra of **2** and **3** were identical to those reported in previous work [8,9].

The purity of **2** prepared from $CF_3CH{=}CF_2$ was determined using the total pressures and absorbance spectra of mixtures of **2** and hydrocarbons. Sixteen samples which contained different ratios of **2** to hydrocarbons were obtained by fractional distillation of the preparation described in Section 3.3. The total pressures of these samples were measured with an MKS Baratron (222BHS) capacitance manometer and varied from 2.1 to 9.5 Torr. The pressures of **2** and the hydrocarbons were obtained from $P_{\mathrm{total}} = k_a A_a + k_h A_h = P_a + P_h$, where P_{total} is the total pressure, A_a is the area of an absorption band due to **2** only, A_h is the area of a band due to hydrocarbons only, and k_a and k_h are constants. The values of k_a and k_h were determined by classical least-squares methods using either the absorbance band in the 2195–1965 cm^{-1} or the 1065–1055 cm^{-1} range for **2** and the 3050–2825 cm^{-1} range for the hydrocarbons. The average error in the calculated total pressure was 1.3%, so there was no detectable contribution to the total pressure from gases other than **2** and the hydrocarbons.

The value of k_a was then used to determine the purity of **2** prepared from $CF_3CBr{=}CF_2$. The total pressures of five samples were measured with the capacitance manometer, and the pressures of **2** in these samples were calculated from the absorbance spectra. The average calculated purity of **2** was 98.1% ± 0.4%. The remaining 1.9% was due to **3**; no hydrocarbons were detectable in the IR spectrum.

Acknowledgement

We thank the National Science Foundation for support of this work.

References

[1] R.E. Banks, R.N. Haszeldine and D.R. Taylor, *J. Chem. Soc.*, (1965) 978.

[2] T.L. Jacobs and R.S. Bauer, *J. Am. Chem. Soc.*, *81* (1959) 606.

[3] R.E. Banks, M.G. Barlow, R.N. Haszeldine and D.R. Taylor, *J. Chem. Soc. C*, (1969) 1104; R.E. Banks, W.D. Davies, R.N. Haszeldine and D.R. Taylor, *J. Fluorine Chem.*, *10* (1977) 487.

[4] P.A. Morken, H. Lu, A. Nakamura and D.J. Burton, *Tetrahedron Lett.*, *32* (1991) 4271.

[5] P.A. Morken and D.J. Burton, *J. Org. Chem.*, *58* (1993) 1167.

[6] Y.V. Zeifman, L.T. Lantseva and S.A. Postovoi, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1981) 1350 (Eng. Transl.).

[7] R.W. Saalfrank, *Isr. J. Chem.*, *26* (1985) 181.

[8] H.B. Friedrich, D.J. Burton and D.C. Tardy, *J. Phys. Chem.*, *91* (1987) 6334.

[9] H.B. Friedrich, D.J. Burton and P.A. Schemmer, *Spectrochim. Acta*, *45A* (1989) 181.