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POLYHALOGENO-ALLENES AND -ACETYLENES. PART XII[1]. FURTHER STUDIES ON ROUTES TO TETRAFLUOROALLENE AND TETRAFLUOROPROPYNE

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SUMMARY

Passage of the 2,3-dibromopropene $CF_2BrCBr{=}CF_2$ over hot catalytic grade silica causes it to isomerize to its 1,2-dibromo analogue $CF_3CBr{=}CFBr$. Flow pyrolysis of these dibromopropenes over copper yields tetrafluoroallene (39%) and tetrafluoropropyne (11%). Isomerization (with catalytic grade silica, boron tribromide, or aluminium tri-bromide or -chloride) of the 3-bromopropene $CF_2BrCH{=}CF_2$ followed by KOH-dehydrohalogenation of the resulting (E)/(Z) mixture of the 1-bromopropene $CF_3CH{=}CFBr$ gives low yields of the propynes $CF_3C{\equiv}CBr$ and $CF_3C{\equiv}CF$.

INTRODUCTION

Difficulties associated with the synthesis of tetrafluoroallene and tetrafluoropropyne have seriously hindered studies on these compounds. Tetrafluoroallene is best prepared by the five-stage route $CF_2Br_2 + CH_2{=}CF_2 \longrightarrow CF_2BrCH_2CF_2Br \longrightarrow CF_2BrCH{=}CF_2 \longrightarrow CF_2BrCHBrCF_2Br \longrightarrow CF_2BrCBr{=}CF_2$ (I) $\longrightarrow CF_2{=}C{=}CF_2$ [2], the first four of which are common to the synthesis of tetrafluoropropyne $\{ \dashrightarrow CF_2BrCBr{=}CF_2$ (I) $\longrightarrow CF_3CBr{=}CFBr$ (II) $\longrightarrow CF_3C{\equiv}CF$ [2] $\}$. Efforts to improve these methods led to the results now presented.

RESULTS AND DISCUSSION

The final stages in the preferred (see above) syntheses of tetrafluoroallene and tetrafluoropropyne are batchwise debrominations, effected with magnesium in tetrahydrofuran (74% yield of $CF_2=C=CF_2$) and zinc in dioxan (43% yield of $CF_3C\equiv CF$), respectively [2]. Attempts were made to improve both processes in terms of yield and throughput by using hot copper in a flow apparatus as the bromine acceptor; a similar technique was employed previously [3] to effect the debromination $CF_2BrCFBrSF_5 \longrightarrow CF_2=CFSF_5$ in 88% yield (conversion 56%). Despite numerous experiments, however, the best yield of tetrafluoroallene was only 39%, and acceptable conversions (≥60%) of 2,3-dibromotetrafluoropropene (I) could not be achieved. Debromination of 1,2-dibromotetrafluoropropene (II) by this method also proved unsatisfactory: good conversions (ca. 70%) were achieved but yields of tetrafluoropropyne were poor (ca. 10%).

During the search for ways to increase the efficiency of the copper-initiated debromination of 2,3-dibromotetrafluoropropene, it was observed that isomerization of the dibromo-compound to 1,2-dibromo-1,3,3,3-tetrafluoropropene occurred ($CF_2BrCBr=CF_2 \xrightarrow{\ell} CF_3CBr=CFBr$) when mixtures of copper and catalytic grade silica were used. Quantitative conversion of the 2,3-dibromide to a ca. 3:2 mixture (65% yield) of (*Z*)- and (*E*)-1,2-dibromotetrafluoropropene was achieved by passing it at 5 mmHg pressure over only fresh silica at 240°C, and the yield increased to 86% after the silica had become 'seasoned'. Thus an efficient flow method was developed for obtaining the immediate precursor of tetrafluoropropyne, the activity of the catalytic grade silica possibly stemming from the traces of alumina it contained. Previously the isomerization of 2,3- to 1,2-dibromotetrafluoropropene was effected batchwise with aluminium tribromide [2].

$$CF_2Br_2 + CH_2=CF_2 \xrightarrow[\Delta]{Bz_2O_2} CF_2BrCH_2CF_2Br \xrightarrow[\Delta]{C}$$

$$CF_2BrCH=CF_2 \xrightarrow{\ell} CF_3CH=CFBr \xrightarrow{-HBr} CF_3C\equiv CF$$

In an attempt to shorten the six-step synthesis [2] of tetrafluoropropyne, the possibility of branching the route to tetrafluoroallene at the 3-bromo-1,1,3,3-tetrafluoropropene stage as shown above was examined. Efficient isomerization of the 3-bromo-compound to a ca. 3:2 mixture of (E)- and (Z)-1-bromo-1,3,3,3-tetrafluoropropene (isomers which, under certain conditions are formed in small amounts during the carbon-catalysed thermal dehydrobromination of 1,3-dibromo-1,1,3,3-tetrafluoropropane in step 2) was effected with boron tribromide (92% yield), aluminium halides ($AlBr_3$, 91%; $AlCl_3$, 91%), or fresh catalytic grade silica (71%). Dehydrohalogenation of the mixture of (E)- and (Z)-1-bromo-1,3,3,3-tetrafluoropropene with solid potassium hydroxide at 120°C, however, gave tetrafluoropropyne in only 1% yield, the major product being 1-bromo-3,3,3-trifluoropropyne (15%). Separate experiments with the two geometric isomers of the bromopropene indicated that the major source of the bromopropyne was the (E)-isomer, i.e. that a trans-elimination mechanism had predominated.

EXPERIMENTAL

^{19}F N.m.r. spectra were obtained with a Perkin-Elmer R10 (56.46 MHz) spectrometer using external CF_3CO_2H as reference (low field shifts designated positive). Unless stated otherwise, products were identified only by g.l.c. and i.r. spectroscopy.

Debrominations

(a) 2,3-Dibromo-1,1,3,3-tetrafluoropropene

The propene (1.05 g, 3.86 mmol) was passed at 5 mmHg pressure during 1.5 h through a silica tube (80 cm x 1 cm. i.d.), the central section (38 cm) of which was packed with copper turnings and heated to 260°C. The product, collected at -196°C, was fractionated, *in vacuo*, to give tetrafluoroallene (0.024 g, 0.217 mmol, 39%) and starting material (0.900 g, 3.30 mmol, 86% recovery).

Passage of 2,3-dibromotetrafluoropropene (1.46 g, 5.36 mmol) at 5 mmHg pressure during 3 h through a hot (370°C) copper tube (0.8 cm i.d.) packed with copper turnings (heated length 50 cm) gave tetrafluoroallene (0.124 mmol, 33%) and starting material (4.99 mmol, 93%).

(b) 1,2-Dibromo-1,3,3,3-tetrafluoropropene

The propene (1.08 g, 3.97 mmol) was passed at 15 mmHg pressure during 5 min through a silica tube (80 x 1 cm i.d.), the central section (15 cm) of which was packed with copper bronze supported on copper turnings and heated to 330°C. Fractionation of the product gave tetrafluoropropyne (0.035 g, 0.31 mmol, 11% based on $CF_3CBr=CFBr$ consumed) contaminated (*ca.* 2% by i.r. analysis) with tetrafluoroallene, and starting material (0.345 g, 32% recovery).

Isomerizations

(a) 2,3-Dibromo-1,1,3,3-tetrafluoropropene

The propene (2.09 g) was passed at 5 mmHg pressure during 2 h through a pyrolysis train comprising a Pyrex preheater (50 cm x 0.8 cm i.d., 100°C) attached to a silica tube (80 cm x 1 cm i.d.) the central section (50 cm) of which was packed with a 1:4 w/w mixture of copper turnings and catalytic-grade silica (particle size 5 mm: Unilever Ltd., wide-pore gel, 380 m^2/g) and heated to 245°C. The product, collected at -196°C, was shown by ^{19}F n.m.r. spectroscopy to be a 59:41 mixture of (*Z*)- and (*E*)-1,2-dibromo-1,3,3,3-tetrafluoropropene (1.39 g, 67%).

Pyrolysis of 2,3-dibromo-1,1,3,3-tetrafluoropropene (2.10 g) at 240°C during 45 min as above, but with the silica tube packed with only fresh silica particles, also gave only a *ca.* 3:2 mixture of (*Z*)- and (*E*)-1,2-dibromotetrafluoropropenes (1.37 g, 65%): the silica packing turned yellowish brown. Pyrolysis of 2,3-dibromotetrafluoropropene (7.20 g) during 7 h at 235°C and 5 mmHg pressure over 'seasoned' silica (used four times previously) gave 1,2-dibromotetrafluoropropenes (6.20 g) in 86% yield.

(b) 3-Bromo-1,1,3,3-tetrafluoropropene

(i) With silica. Passage of the propene (1.47 g) over fresh catalytic-grade silica [as in (a) above] at 240°C and 5 mmHg pressure during 45 min gave a mixture (16:9 by ^{19}F n.m.r. spectroscopy) of (*E*)- and (*Z*)-1-bromo-1,3,3,3-tetrafluoropropene (1.05 g, 71%).

(ii) With boron tribromide. A mixture of 3-bromo-1,1,3,3-tetrafluoropropene (4.911 g, 25.40 mmol) and boron tribromide (0.450 g, 1.79 mmol) was stored at 20°C in a Pyrex ampoule (10 cm^3) in the absence of air for 48 h. The product was a *ca.* 3:2 mixture of (*E*)- and (*Z*)-1-bromo-1,3,3,3-tetrafluoropropene (4.517 g, 92%).

(iii) With aluminium trihalides. 3-Bromo-1,1,3,3-tetrafluoropropene (8.14 g, 42.2 mmol) was condensed, *in vacuo*, on to anhydrous aluminium tribromide (1.9 g, 7.1 mmol) contained in a Pyrex tube (60 cm^3) at -196°C. The tube was sealed, allowed to warm to 20°C, and then shaken for 24 h. The volatile product was a *ca.* 3:2 mixture of (*E*)- and (*Z*)-1-bromo-1,3,3,3-tetrafluoropropene (7.39 g, 91%).

Similarly, 3-bromo-1,1,3,3-tetrafluoropropene (19.68 g, 0.102 mol) and aluminium chloride (1.5 g, 11 mmol) interacted exothermically at room temperature to yield a 16:9 mixture of (*E*)- and (*Z*)-1-bromo-1,3,3,3-tetrafluoropropene (17.82 g, 91%).

The following ^{19}F n.m.r. parameters were obtained by examination of a **16:9** mixture of (*E*)- and (*Z*)-1-bromo-1,3,3,3-tetrafluoropropene: (i) (*E*)-*isomer*: δ_F 22.3 (CFBr; $|\underline{J}_{F,H}|$ 26.9, $|\underline{J}_{F,CF_3}|$ 17.2 Hz) and 17.7 p.p.m. (CF_3; $|\underline{J}_{CF_3,H}|$ 6.7 Hz), and τ4.55: (ii) (*Z*)-*isomer*: δ_F 21.0 (CFBr: $|\underline{J}_{F,H}|$ 10.8, $|\underline{J}_{F,CF_3}|$ 13.4 Hz) and 17.85 p.p.m. (CF_3: $|\underline{J}_{CF_3,H}|$ 6.4 Hz), and τ4.06.

Dehydrobromination of 1,3-Dibromo-1,1,3,3-tetrafluoropropane

The propane (6.90 g, 25.2 mmol) was pyrolysed at 290°C and 1 mmHg pressure during 1 h as described previously [2] except that the granular charcoal was contained in a new Pyrex tube. Separation of the product by g.l.c. (4 m dimethylsulpholane-Celite, 40°C) afforded 3-bromo-1,1,3,3-tetrafluoropropene (2.79 g, 14.4 mmol, 57%), (*Z*)-1-bromo-1,3,3,3-tetrafluoropropene (nc) (0.155 g, 0.80 mmol, 3%) [Found: C, 18.8; H, 0.8%; *M* (Regnault) 193. C_3HBrF_4 requires C, 18.7; H, 0.5%; *M*, 193], b.p. 31.6°C (isoteniscope), $\lambda_{max.}$ (vapour) 5.93 µm (C=C str.), and m/e 194 ($C_3H^{81}BrF_4^{+\bullet}$, 62), 192 ($C_3H^{79}BrF_4^{+\bullet}$, 65%), 69 ($CF_3^{+\bullet}$, 100%), and (*E*)-1-bromo-1,3,3,3-tetrafluoropropene (nc) (0.155 g, 0.80 mmol, 3%) [Found: C, 18.8; H, 0.8: *M* (Regnault) 193. C_3HBrF_4 requires C, 18.7; H, 0.5%; *M*, 193], b.p. 36.0°C (isoteniscope), $\lambda_{max.}$ (vapour) 5.95 µm (C=C str.).

Dehydrohalogenation of 1-Bromo-1,3,3,3-tetrafluoropropene

A 3:2 mixture of (*E*)- and (*Z*)-1-bromo-1,3,3,3-tetrafluoropropene (4.01 g, 20.8 mmol) contaminated with 3-bromo-1,1,3,3-tetrafluoropropene (0.54 g, 2.8 mmol) was added dropwise to a stirred bed of potassium hydroxide pellets (80 g) heated to 120°C in a vessel swept with a slow stream of nitrogen and attached to two cold traps (-72 and -140°C) *via* a cooled (-23°C) reflux condenser. Trap-to-trap fractional condensation of the product, *in vacuo*, afforded a mixture (-196°C trap) of 2*H*-pentafluoropropene (0.107 g, 0.81 mmol) (presumably derived from tetrafluoroallene), tetrafluoropropyne (0.015 g, 0.14 mmol, 1% based on $CF_3CH{=}CFBr$ consumed), and a trace of tetrafluoroallene(from the $CF_2BrCH{=}CF_2$ impurity), and a mixture (-95°C trap) of 1-bromo-1,3,3,3-tetrafluoropropene (0.53 g, 2.75 mmol, 13% recovery) and 1-bromo-3,3,3-trifluoropropyne (0.475 g, 2.75 mmol, 15%). A sample of 1-bromo-3,3,3-trifluoropropyne, b.p. (isoteniscope) 26.8°C (lit. [4], 25-25.5°C), $\lambda_{max.}$ (vapour) 4.47 μm ($C\equiv C$ str.), *m/e* (peaks with >30% rel. abund.) 174 ($C_3{}^{81}BrF_3{}^{+\bullet}$, 87), 172 ($C_3{}^{79}BrF_3{}^{+\bullet}$, 91), 155 ($C_3{}^{81}BrF_2{}^{+}$, 33), 153 ($C_3{}^{79}BrF_2{}^{+}$, 35), 131 ($C^{81}BrF_2$, 97), 129 ($C^{79}BrF_2$, 100), 93 ($C_3F_3{}^{+}$, 87), 69 ($CF_3{}^{+}$, 52), 55 ($C_3F^{+}$, 71), 43 ($C_2F^{+}$, 54%), was isolated by g.l.c. (4 m dimethylsulpholane-Celite, 40°C).

When a mixture of powdered potassium hydroxide (78 g) and (*Z*)-1-bromo-1,3,3,3-tetrafluoropropene (1.08 g, 5.62 mmol) was heated at 90°C for 30 min., the product comprised 2*H*-pentafluoropropene (0.08 mol, 2% based on $CF_3CH{:}CFBr$ consumed), tetrafluoropropyne (0.12 mmol, 3%), a trace of 1-bromo-3,3,3-trifluoropropyne, and starting material (1.38 mmol, 25% recovery). Similar treatment of (*E*)-1-bromo-1,3,3,3-tetrafluoropropene (14.4 mmol) provided 1-bromo-3,3,3-trifluoropropyne (0.28 mmol, 2% based on $CF_3CH{=}CFBr$ consumed), a trace of tetrafluoropropyne, and starting material (2.22 mmol, 15%).

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