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SHORT COMMUNICATION

Polyhalogeno-allenes and -acetylenes. Part XIII [1]. Dechlorination of 1,2,2,3-Tetrachloro-1,1,3,3-tetrafluoropropane as a Route to Tetrafluoroallene

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During their pioneering work on the synthesis of tetrafluoroallene [2,3], which established the 'bromo routes' subsequently developed further in these laboratories [4,5], Jacobs and Bauer tried unsuccessfully to effect exhaustive dechlorination of 1,2,2,3-tetrachloro-1,1,3,3-tetrafluoropropane ($CF_2ClCCl_2CF_2Cl$) [3]. Re-examination of this method, using starting material obtained by treatment of commercial sym-dichlorotetrafluoroacetone with phosphorus pentachloride [6,7], was commenced in 1967 [8] as part of a search for a less expensive route to tetrafluoroallene than those based on dibromodifluoromethane.

Tetrafluoroallene was obtained, but in only miserable yield (7% in each case), when 1,2,2,3-tetrachlorotetrafluoropropane was treated with magnesium in boiling tetrahydrofuran or vaporized and passed at low pressure over mild steel at 520 °C; the product of partial dechlorination, 2,3-dichloro-1,1,3,3-tetrafluoropropene ($CF_2ClCCl{=}CF_2$) was also produced (4 and 18% yield, respectively). No reaction appeared to occur when the propene, prepared in 72% yield by treating the propane with zinc in hot dioxan, was subjected to the action of magnesium in boiling tetrahydrofuran. Also, no tetrafluoroallene was detected amongst the products of pyrolysis of the propane over copper turnings at 300 °C or of the propane and the propene over heated copper powder of the type used in work on the synthesis of perfluoro-(3-methylbuta-1,2-diene) via dehalogenofluorination of the halogeno-olefins $(CF_3)_2C{=}CXCF_3$ (X = I, Br, or Cl) [9].

1,2,2,3-Tetrachlorotetrafluoropropane was recovered in 86% yield when its vapour was passed slowly at low pressure over copper turnings housed in a silica tube at 300 °C, the material consumed being converted into 2,3-dichlorotetrafluoropropene (46%). At 400 °C, with freshly-precipitated copper powder as dehalogenating agent, 51% of the propane was converted into a complex tetrafluoroallene-free mixture containing the compounds $CF_2ClCCl{=}CF_2$ (21%), $CF_3CCl{=}CF_2$ (28%), *E*- and *Z*-$CF_3CCl{=}CFCl$ (3%), CO_2, and SiF_4; similar pyrolysis of 2,3-dichlorotetrafluoropropene gave $CF_3CCl{=}CF_2$, CO_2, and SiF_4, the last two products again being produced in appreciable amounts. Fluoride ion generated during these pyrolyses is presumed to have led to the conversion of 2,3-dichlorotetrafluoropropene into 2-chloropentafluoropropene, a change known [10] to be brought about by tetraethylammonium fluoride in chloroform at 0 °C and shown in the present work to occur almost quantitatively when the dichloropropene is passed over heated potassium fluoride. Formation of the 1,2-dichlorotetrafluoropropenes during the passage of 1,2,2,3-tetrachlorotetrafluoropropane over hot copper in silica can be ascribed to isomerization of 2,3-dichlorotetrafluoropropene, a reaction which finds analogy in the silica-induced conversion $CF_2BrCBr{=}CF_2$ $\xrightarrow{\ell}$ *E*- and *Z*-$CF_3CBr{=}CFBr$ [1].

Attempts to dechlorofluorinate 2-chloropentafluoropropene at 405 and 500 °C over freshly-precipitated copper powder in a nickel pyrolysis tube failed, the olefin being recovered in 100 and 88% yield, respectively {*cf.* the failure to convert $(CF_3)_2C{=}CClCF_3$ into $(CF_3)_2C{=}C{=}CF_2$ with the same reagent at 450 °C [9] }.

EXPERIMENTAL

Reactions of 1,2,2,3-Tetrachloro-1,1,3,3-tetrafluoropropane

(a) With zinc

Treatment of the propane (74.3 g, 0.29 mole) with activated zinc dust (45 g) in boiling dioxan (500 cm^3) for 5 h gave only 2,3-dichlorotetrafluoropropene (38.3 g, 0.21 mole; 72%), identified by i.r. and ^{19}F n.m.r. analysis.

(b) With magnesium

A solution of the propane (7.56 g, 29.7 mmole) in dry tetrahydrofuran (50 cm^3) was added slowly (1 h) to a stirred mixture of magnesium turnings (3.0 g) and boiling tetrahydrofuran (300 cm^3). The volatile product, swept by a slow flow of nitrogen into cold traps (-72 and -196 °C), was fractionated *in vacuo* to give tetrafluoroallene (0.219 g, 1.96 mmole, 7%) and 2,3-dichloro-1,1,3,3-tetrafluoropropene (0.225 g, 1.22 mmole, 4%), both of which were identified by i.r. spectroscopy.

(c) With iron

The propane (4.20 g, 16.54 mmole) was passed at 10 mmHg pressure during 1.25 h through a silica tube (80 x 1 cm) packed with 'silver' steel wool (Stephenson Mills Ltd., grade 5, previously activated *in situ* with hydrogen at 500 °C) and heated to 520 °C over 50 cm. of its length. The volatile product, collected in two traps cooled to -196 °C, was fractionated *in vacuo* to provide tetrafluoroallene (0.119 g, 1.07 mmole, 7%), 2,3-dichloro-1,1,3,3-tetrafluoropropene (0.553 g, 3.02 mmole, 18%), two (by g.l.c.) unidentified products (total: 0.017 g), and silicon tetrafluoride.

(d) With copper

Passage of 1,2,2,3-tetrachlorotetrafluoropropane vapour (7.30 g, 28.7 mmole) at 15 mmHg pressure during 4.5 h over hot (300 °C) copper turnings (previously activated with hydrogen as above) in the apparatus used in experiment (c) above gave a mixture of starting material (6.305 g, 24.8 mmole, 86% recovery) and 2,3-dichlorotetrafluoropropene (0.333 g, 1.82 mmole, 46% based on $CF_2ClCCl_2CF_2Cl$ consumed).

In another experiment, 5.83 g (22.95 mmole) of the propane was passed (10 mmHg; 4 h) through a silica tube (100 x 1 cm; heated length 60 cm) loosely packed with freshly-precipitated copper powder (*ca.* 40 g, prepared as described in ref. 9) and heated to 400 °C. The volatile product was condensed at -196 °C then subjected to trap-to-trap fractional condensatio *in vacuo*; analysis of the fractions by coupled g.l.c.-i.r. and ^{19}F n.m.r. methods showed the products to be 1,2,2,3-tetrachlorotetrafluoropropane (11.35 mmole, 49% recovery), 2,3-dichlorotetrafluoropropene (2.4 mmole, 21% based on $CF_2ClCCl_2CF_2Cl$ consumed), *E*- and *Z*-1,2-dichlorotetrafluoropropene (0.36 mmole, 3%), 2-chloropentafluoropropene (3.23 mmole, 28%), traces of at least three unidentified compounds, and carbon dioxide and silicon tetrafluoride (total: 4.0 mmole).

Reactions of 2,3-Dichloro-1,1,3,3-tetrafluoropropene

(a) With copper

Using the apparatus described in the second part of (d) above, 2,3-dichlorotetrafluoropropene (3.27 g, 17.9 mmole) was passed at 12 mmHg pressure during 0.5 h over hot (405 °C) freshly-precipitated copper powder. The volatile product, collected at -196 °C, was shown by standard techniques to comprise starting material (12.2 mmole, 68%), 2-chloropentafluoropropene (0.80 mmole, 14% based on $CF_2ClCCl=CF_2$ consumed), carbon dioxide, and silicon tetrafluoride.

(b) With potassium fluoride

During 0.5 h, 2.09 g (11.4 mmole) of vaporized 2,3-dichlorotetrafluoropropene was passed, at 1 mmHg pressure, through a hot (400 °C) silica tube (100 x 1 cm), the heated section (60 cm) of which was loosely packed with anhydrous potassium fluoride. Fractionation of the volatile product (collected at -196 °C) gave 2-chloropentafluoropropene (1.68 g, 10.1 mmole, 97%; condensed at -132 °C in a trap-to-trap train) and starting material (0.19 g, 1.04 mmole, 9% recovery; -72 °C trap). The identity of the 2-chloropentafluoropropene was confirmed by ^{19}F n.m.r. spectroscopy [11].

A similar fluorination at 200 °C and 5 mmHg gave 2-chloropentafluoropropene in 95% yield based on 63% recovery of starting material.

REFERENCES

1 R. E. Banks, W. D. Davies, R. N. Haszeldine, and D. R. Taylor, J.Fluorine Chem., 10 (1977) 487.

2 T. L. Jacobs and R. S. Bauer, J.Amer.Chem.Soc., 78 (1956) 4815.

3 T. L. Jacobs and R. S. Bauer, J.Amer.Chem.Soc., 81 (1959) 606.

4 R. E. Banks, R. N. Haszeldine, and D. R. Taylor, J.Chem.Soc., (1965) 978.

5 R. E. Banks, M. G. Barlow, W. D. Davies, R. N. Haszeldine, and D. R. Taylor, J.Chem.Soc. Perkin Trans. I, (1969) 1104.

6 B. S. Farah and E. E. Gilbert, J.Org.Chem., 30 (1965) 1241.

7 J. E. Bissey, H. Goldwhite, and D. G. Rowsell, J.Org.Chem., 32 (1967) 1542.

8 W. D. Davies, Ph.D. Thesis, University of Manchester, 1968.

9 P. W. Bosbury, R. Fields, R. N. Haszeldine, and D. Moran, J.Chem.Soc. Perkin Trans. I, (1976) 1173.

10 W. T. Miller, J. H. Fried, and H. Goldwhite, J.Amer.Chem.Soc., 82 (1960) 3091.

11 J. D. Swalen and C. A. Reilly, J.Chem.Phys., 34 (1961) 2122.