Journal of Fluorine Chemistry, 28 (1985) 417–423

Received: November 12, 1984; accepted: January 3, 1985

FLUOROVINYLKETONES FROM PERFLUOROPENTENE-2

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SUMMARY

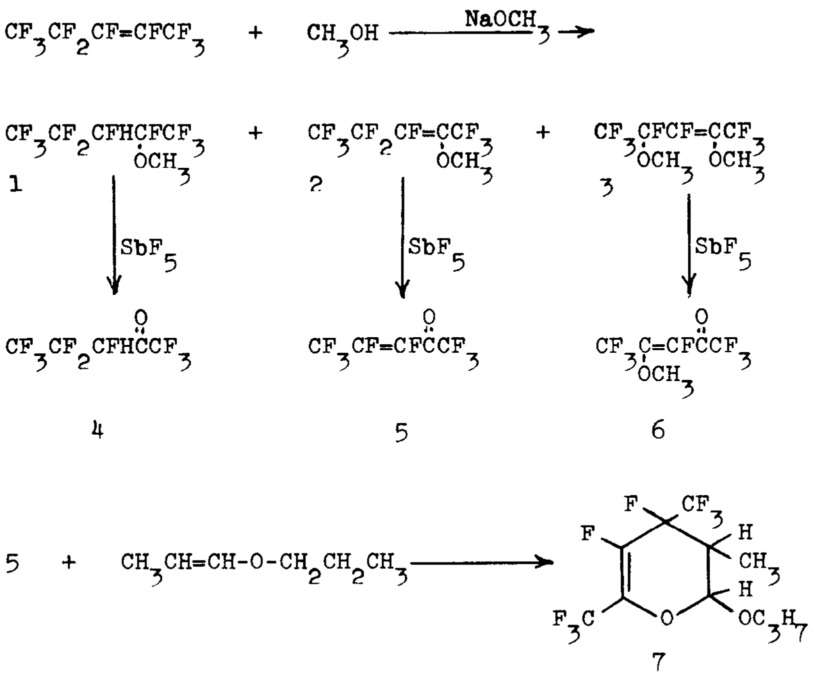
Two fluorovinylketones have been prepared from methoxyperfluoropentenes using a new reaction involving catalytic loss of methyl fluoride. One of these vinylketones reacted as a diene with propenyl propyl ether.

INTRODUCTION

Perfluoropentene-2 is available from the antimony pentafluoride catalyzed reaction of hexafluoropropene (HFP) with tetrafluoroethylene (TFE) reported by German and coworkers [1]. They and others [2-9] have prepared a number of derivatives from this fluoroolefin starting with nucleophilic or radical additions to the double bond.

0022-1139/85/$3.30

RESULTS AND DISCUSSION



$CF_3CF_2CF{=}CFCF_3 + CH_3OH \xrightarrow{NaOCH_3}$

$CF_3CF_2CFHCFCF_3(OCH_3)$ (1) + $CF_3CF_2CF{=}C(OCH_3)CF_3$ (2) + $CF_3CF(OCH_3)CF{=}C(OCH_3)CF_3$ (3)

$\xrightarrow{SbF_5}$ $CF_3CF_2CFHC(O)CF_3$ (4), $CF_3CF{=}CFC(O)CF_3$ (5), $CF_3C(OCH_3){=}CFC(O)CF_3$ (6)

5 + $CH_3CH{=}CH{-}O{-}CH_2CH_2CH_3 \longrightarrow$ 7

The reaction of perfluoropentene-2 with alkoxide ions has been reported [5] to give mixtures containing mono- and dialkoxy addition-elimination products. In this work the reaction of perfluoropentene-2 with methoxide ion in methanol gave three major products (1,2 and 3 above). They have been subjected to the recently reported [10] catalytic reaction for the preparation of carbonyl compounds by loss of methyl fluoride.

The methanol adduct of perfluoropentene-2 (1) gave the monohydroketone 4. This ketone has been reported earlier as a product of sulfuric acid hydrolysis of the unsaturated tert-butoxy derivative analogous to 2 above [5] and from sulfuric acid hydrolysis of the corresponding dialkylamino derivatives [3]. Compound 2 with antimony pentafluoride catalyst lost methyl fluoride to give the vinylketone 5. This vinylketone was reported [3] as prepared by sulfuric acid hydrolysis of a perfluoropentene-2 derivative substituted in the allylic position with a dialkylamino group. Although much less reactive than a terminally unsaturated perfluorovinylketone reported earlier [11], this vinylketone did undergo Diels Alder addition to propenyl propyl ether to give the dihydropyran 7 above.

The unsaturated dimethoxy derivative 3 with antimony pentafluoride catalyst gave the methoxyvinyl ketone 6. Both vinylketones were separated into their cis and trans isomers by gas chromatography.

EXPERIMENTAL

Boiling points are uncorrected. ^{1}H NMR spectra were obtained with a Varian A-60 spectrometer operating at 60 MHz. Chemical shifts are reported in ppm from tetramethylsilane as external standard with the downfield direction taken as positive. ^{19}F NMR spectra were obtained with a Varian XL-100 spectrometer operating at 94.1 MHz using $CFCl_3$ as internal standard. Upfield shifts are reported as negative values.

Preparation of Perfluoropentene-2

Perfluoropentene-2 was prepared in high yield by mixing HFP and TFE in sealed glass tubes at room temperature using impure SbF_5 which had been stored for a long period in a metal cylinder. However, use of pure SbF_5 or $HSbF_6$ in glass tubes gave low yields and considerable TFE polymer. Perhaps the catalytic action of SbF_5 is metal promoted.

A mixture of 32 g. (0.21 m) of HFP, 17.5 g. (0.175 m) of TFE and 5 g. impure SbF_5 (blue from metal cylinder contamination) in a sealed glass tube overnight at room temperature gave 36 g. (82%) of trans-perfluoropentene-2 [1], bp 20°-25°, and very little polymer.

^{19}F NMR: -69.7 ppm (m, 3F), -85.1 ppm (m, 3F), -158.1 ppm (m, 2 C=F), and -122.0 ppm (m, 2F).

Reaction of Perfluoropentene-2 with Sodium Methoxide in Methanol

A mixture of perfluoropentene-2 (75 g., 0.3 m) and 75 ml methanol (not completely miscible) in a 3-neck flask was stirred at -10° to -15° while adding dropwise a solution of 18 g. (0.33 m) of sodium methoxide in 75 ml methanol. When addition was complete and the mixture was still cold, there was added 250 ml of 15% HCl. The lower layer was separated and dried over P_2O_5. Crude product from two such runs was distilled to give 50.5 g., bp 67°-70°, and 61 g., bp 72°-75°. These fractions were largely mixtures of the cis and trans isomers of 2-methoxyperfluoropentene-2 (2) [5]. There was also distilled 18.7 g., bp 76°-80°, and 13.4 g., bp 82°. The latter fraction was largely 2-methoxy-3-hydroperfluoropentane (1).

Anal. Calcd. for $C_6H_4F_{10}O$: C, 25.55; H, 1.43; F, 67.35.
For 1 Found: C, 25.68; H, 1.51; F, 66.91.

When the above reaction was run with more sodium methoxide, there was an added exotherm to 30° when cooling was removed. Higher-boiling products were isolated. The olefin (50 g., 0.2 m) in 50 ml methanol was stirred while adding a solution of 22 g. (0.4 m) of sodium methoxide in 75 ml of methanol. Acidification and work-up as above gave 41 g. of crude oil. There was recovered 3 g., bp 78°-80°, mostly 2; 10 g., bp 108°-112°, and 16 g., bp 115°-117° (these fractions were largely cis and trans isomers of 3); and 11 g., bp 122°-170°.

Synthesis of 3-Hydroperfluoropentanone-2 (4)

To 13.4 g. of 2-methoxy-3-hydroperfluoropentane (1) cooled in a still pot was added 3 g. of SbF_5. On warming to room temperature and above, methyl fluoride was evolved and there was distilled 9.3 g. (79%) of 3-hydroperfluoropentanone-2 (4), bp 53°. [3,5].

IR: 5.55 μ (C=O).

^{1}H NMR: 5.07 ppm (d, 45 Hz.; d, 15.6 Hz.,; d, 4.8 Hz.; 1 H).

^{19}F NMR: -77.16 ppm (m, 3F), -83.09 ppm (m, 3F), -121.84 ppm (J_A=293 Hz., m, 1F), -127.31 ppm (J_B=293 Hz., m, 1F) and -211.81 ppm (m, 1F).

Synthesis of Perfluoro-2-pentene-4-one (5)

To 50.5 g. of a mixture containing cis- and trans-2-methoxyperfluoropentene-2 (2) cooled in a still pot was added 3 g. SbF_5. On warming to room temperature and above, methyl fluoride was evolved, and the product was rapidly distilled. On redistillation it boiled at 45°-50° and was a mixture of about equal amounts of *cis*- and *trans*-perfluoro-2-penten-4-one (5)(37 g., 84%). The isomers were separated by gas chromatography. [3].

IR: 5.60 μ (C=O), 5.90 μ (C=C).

^{19}F NMR for *cis* : -67.80 ppm (t, 9 Hz., 3F), -77.15 ppm (d, 15.5 Hz., 3F), -129.43 ppm (d, 10.5 Hz., q, 9.0 Hz., 1F), and -145.76 ppm (q, 15.5 Hz., q, 9 Hz., d, 10.5 Hz., 1F).

^{19}F NMR for trans: -69.38 ppm (d, 21.5 Hz., d, 8.0 Hz., 3F), -77.56 ppm (d, 14.0 Hz., d, 7.5 Hz., 3F), -146.36 ppm (d, J_A= 136 Hz., q, 8.0 Hz., q, 7.5 Hz., 1F) and -168.36 ppm (d, J_B= 136 Hz., q, 21.5 Hz., q, 14 Hz., 1F).

Synthesis of 2-Methoxyperfluoro-2-penten-4-one (6)

A mixture of cis and trans-2,4-dimethoxyperfluoropentene-2 (3) (15.6 g.) and 2 g. of SbF_5 when warmed in a still pot gave off methyl fluoride at about 60°. There was distilled 8.9 g. (65%) of a mixture of cis and trans 6, bp 92°-95°. The isomers were separated by gas chromatography.

Anal. Calcd. for $C_6H_3F_7O_2$: C, 30.01; H, 1.26; F, 55.40.
Found : C, 30.19; H, 1.36; F, 55.49.

IR: 5.66 μ (C=O), 6.05 μ (C=C).

^{1}H NMR for cis : 3.5 ppm (s, 3H).

^{19}F NMR for cis : -66.76 ppm (d, 24 Hz., 3F), -77.00 ppm (d, 15 Hz., 3F) and -152.74 ppm (q, 24 Hz., q, 15 Hz., 1F).

^{1}H NMR for trans: 3.3 ppm (s, 3H).

^{19}F NMR for trans: -68.76 ppm (d, 7.0 Hz., 3F), -77.42 ppm (d, 18 Hz., 3F), and -138.83 ppm (q, 18 Hz., q, 7 Hz., 1F).

Synthesis of 3,4-Difluoro-6-propoxy-2,4-bis(trifluoromethyl)-dihydro-4H-pyran (7)

A mixture of the vinyl ketone 5 (10 g.), and 5 g. of propenyl propyl ether after standing at room temperature for about two minutes reacted exothermally and refluxed at about 65°. After standing for two hours there was distilled 5 g. of recovered ketone and 3.8 g., bp 36°/0.2 mm. It was redistilled at 60°/15 mm. and characterized as the pyran 7.

Anal. Calcd for $C_{11}H_{12}F_8O_2$: C, 40.25; H, 3.69; F, 46.31
Found : C, 40.38; H, 3.83; F, 46.39

^1H NMR : 0.70 ppm (m, 6H), 1.40 ppm (m, 2H), 2.12 ppm (m, 1H), 3.49 ppm (m, 2H), and 4.82 ppm (m, 1H).

^{19}F NMR: -68.74 ppm (d, 22 Hz., d, 6 Hz., 3F), -73.63 ppm (d, 8 Hz., d, 10 Hz., m, 3F), -142.22 ppm (m, 1F), and -163.73 ppm (m, 1F).

REFERENCES

1 G.G. Belen'kii, E.P. Lur'e and L.S. German, Izv. Akad. Nauk SSSR, Ser. Khim., (12), (1975) 2728. CA 84 (11): 73567j.

2 M.A. Kurykin, L.S. German, Yu. N. Studnev and A.V. Fokin, Ibid. (7), (1980) 1679. CA 93 (25): 238771x.

3 M.A. Kurykin, L.S. German and I.L. Knunyants, Ibid. (9), (1980) 2172. CA 94 (15): 120780s.

4 M.A. Kurykin, L.S. German and I.L. Knunyants, Ibid. (12), (1980) 2827. CA 95 (1): 6431z.

5 M.A. Kurykin and L.S. German, Ibid. (11), (1981) 2647. CA 96 (13): 103563x.

6 M.A. Kurykin, I.N. Krotovich, Yu. Studnev, L.S. German and A. Y. Fokin, Ibid. (8), (1982) 1861. CA 93 (25): 238771x.

7 I.P. Kolenko, T.I. Filyakova, A.Ya. Zapevalov and E.P. Lur'e, Ibid. (11), (1979) 2509. CA 92 (11): 94148d.

8 R.A. Bekker, Y. Popkova, V.F. Snegirev and I.L. Knunyants Ibid. (3), (1983) 621. CA 98 (23): 197533d.

9 D.J. Burton and Yoshio Inouye, Chem. Lett. (2), (1982) 201. CA 96 (21): 181177p.

10 D.G. Anderson, D.C. England and A.S. Milian, Jr., U.S.P. 4,357,282 (1982).

11 D.C. England, J. Org. Chem. (1981), 46, 147.