Reaction of 1,1,2,3,3-pentafluoro-1,5-hexadiene with methanol in the presence of a base

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The reaction of 1,1,2,3,3-pentafluoro-1,5-hexadiene (**1**) with MeOH in the presence of MeONa results in products of substitution, rearrangement, hydro-, or dehydrofluorination, depending on the reaction conditions.

Key words: polyfluorolefins, nucleophilic rearrangement, hydro- and dehydrofluorination.

It is known that polyfluorolefins generally react with alcohols in the presence of bases by the S_N2 mechanism[1] to give products of the substitution of the vinylic F atoms by a RO group.[2] In neutral and weakly-acidic media, the addition of the alcohol to the double bond occurs.[3]

Terminal polyfluorolefins react with alcohols and alcoholates with subsequent rearrangement *via* the action of the fluoride anion formed in the reaction medium. This pathway is often preferable to direct substitution.[1]

The literature contains almost no data on the reactivity of partially fluorinated unconjugated dienes. Nucleophilic isomerization through the action of F^- of 1,1,2,3,3-pentafluoro-1,5-hexadiene (**1**) obtained by us[4] has been studied.[5] In the present work, the reactions of diene **1** with MeOH in the presence of a base were studied.

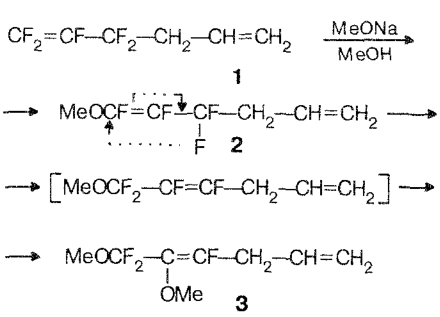
We reacted compound **1** with MeOH in the presence of an equimolar amount of MeONa.[6] Two products were found in the resulting mixture, *viz.*, dienes **2** and **3**. Diene **2**, the product the substitution of the fluorine atom of the terminal difluoromethylene group with a MeO group, is formed initially. Then rearrangement of the fluorallyl group into the thermodynamically more stable fluoropropenyl group, followed by substitution of the more reactive F atom with a MeO group, occur[5] through the action of F^- according to Scheme 1.

The preferential occurrence of this reaction pathway may be regarded as a confirmation of the assumption[7] that the stability of polyfluorolefins increases as the number of fluorine atoms at the double bond decreases.

When compound **1** is refluxed with an excess of a base, dienes **2** and **3** formed initially undergo further transformations according to Scheme 2.

In molecule **2**, substitution of the second vinylic F atom with a MeO group followed by addition of F^- and stabilization of the carbanion with a proton occur. This results in stable compound **5**. The F^- ion is readily added to organofluorine compounds in alcoholic media.[8] The possibility of hydrofluorination has been discussed by us previously.[5]

Scheme 1



$$CF_2{=}CF{-}CF_2{-}CH_2{-}CH{=}CH_2 \ (\mathbf{1}) \xrightarrow[\text{MeOH}]{\text{MeONa}} MeOCF{=}CF{-}CF_2{-}CH_2{-}CH{=}CH_2 \ (\mathbf{2}) \longrightarrow [MeOCF_2{-}CF{=}CF{-}CH_2{-}CH{=}CH_2] \longrightarrow MeOCF_2{-}\underset{OMe}{C}{=}CF{-}CH_2{-}CH{=}CH_2 \ (\mathbf{3})$$

Under more vigorous conditions, compound **3** also turns out to be unstable, and the reaction equilibrium is shifted towards the formation of a rearrangement product, which, as has already been mentioned, is thermodynamically unstable and undergoes stabilization by dehydrofluorination to give triene **6**.

Experimental

IR spectra were recorded in thin films on a Specord IR-75 spectrophotometer. ^1H (100 MHz) and ^{19}F (75.3 MHz) NMR spectra were recorded on a Tesla BS-567A spectrometer relative to TMS and hexafluorobenzene as internal standards. Fluorine shifts are reported relative to $CFCl_3$ regarding the strong-field shifts as positive. GLC analyses were performed on a LKhM-72 chromatograph with a thermal conductivity detector using helium as the carrier gas and a steel column (6000×4 mm) with 20 % SKTFT-50 on Chromosorb W.

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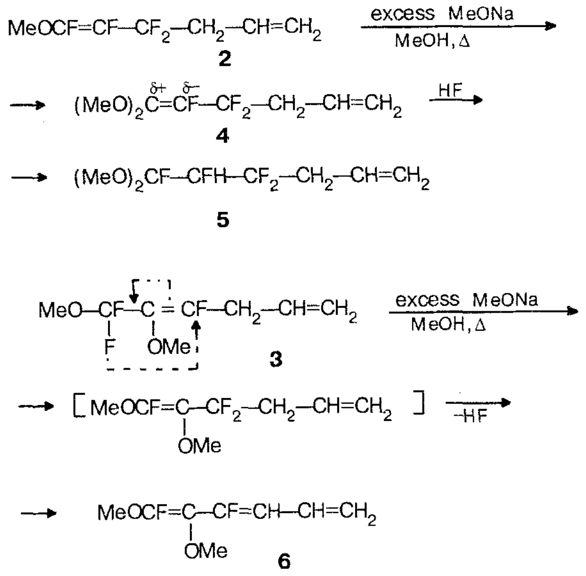
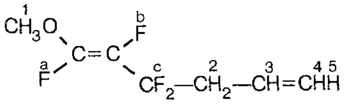
1066-5285/94/4304-0711 $12.50

Scheme 2



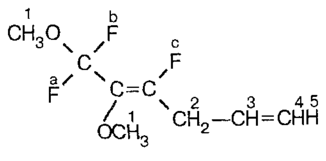
Reaction of diene 1 with MeOH in the presence of an equimolar amount of MeONa. MeONa (2.7 g, 50 mmol) in MeOH (20 mL) was added dropwise with stirring to compound **1** (8.5, 50 mmol). Then the mixture was brought to neutral pH by adding dilute HCl. The lower layer was separated, washed with H_2O, and dried with $CaCl_2$. Distillation gave 4.2 g (50 %) of a mixture containing 34 % of diene **2** and 66 % of diene **3**, b.p. 155—162 °C. IR, ν/cm^{-1}: 1725, 1675 (C=C).

^{19}F and ^{1}H NMR spectra (δ) of compounds 2 and 3.



2

1,2,3,3-Tetrafluoro-1-methoxy-1,5-hexadiene (2): 124.60 (td, F^a), 166.81 (td, F^b), 108.05 (um, 2 F^c), 3.85 (s, 3 H-1), 2.80 (ddt, 2 H-2), 5.83 (ddt, H-3), 5.20 (dd, H-4), 5.34 (dd, H-5); $J_{F^a-F^b}$ = 130.0 Hz, $J_{F^a-F^c}$ = 21.7 Hz, $J_{F^b-F^c}$ = 6.0 Hz, $J_{H^2-F^b}$ = 17.3 Hz, $J_{H^2-H^3}$ = 7.5 Hz, $J_{H^2-F^b}$ = 1.4 Hz, $J_{H^3-H^4}$ = 9.5 Hz, $J_{H^4-H^5}$ = 1.8 Hz.

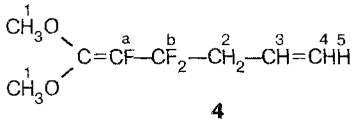


3

1,1,3-Trifluoro-1,3-dimethoxy-2,5-hexadiene (3): 154.57 (s, F^a), 108.28 (um, F^b), 203.07 (td, F^c), 3.85 (s, 6 H-1), 3.53 (ddt, 2 H-2), 5.83 (ddt, H-3), 5.20 (dd, H-4), 5.34 (dd, H-5); $J_{F^b-F^c}$ = 45.3 Hz, $J_{F^c-H^2}$ = 11.8 Hz, $J_{H^3-H^4}$ = 9.5 Hz, $J_{H^4-H^5}$ = 1.8 Hz.

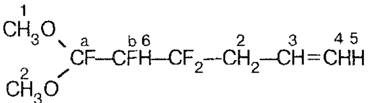
Reaction of diene 1 with MeOH in the presence of an excess of MeONa under reflux. MeONa (5.4 g, 100 mmol) in MeOH (40 mL) was added dropwise with stirring to compound **1** (8.5 g, 50 mmol), and the mixture was refluxed for 2 h. Subsequent treatment was performed as described above. Distillation gave 6.0 g (71 %) of a mixture containing compounds **4** (37 %), **5** (26 %), and **6** (37 %), b.p. 48—49 °C (5—6 Torr). IR, ν/cm^{-1}: 1740, 1675 (C=C).

^{19}F and ^{1}H NMR spectra (δ) of compounds 4—6.



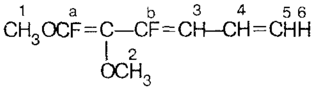
4

2,3,3-Trifluoro-1,1-dimethoxy-1,5-hexadiene (4): 198.92 (udt, F^a), 106.24 (uddt, F^b), 3.63 (s, 6 H-1), 2.77 (ddt, 2 H-2), 5.96 (uddt, H-3), 5.20 (dd, H-4), 5.32 (dd, H-5); $J_{H^4-H^5}$ = 1.8 Hz.



5

4,4,5,6-Tetrafluoro-6,6-dimethoxy-1-hexene (5): 85.20 (dtd, F^a), 211.28 (dtd, F^b), 106.24 (uddt, F^c), 3.63 (s, 6 H-1), 2.77 (ddt, 2 H-2), 5.96 (ddt, H-3), 5.20 (dd, H-4), 5.32 (dd, H-5), 4.79 (ddt, H-6); $J_{F^a-F^c}$ = 14.1 Hz, $J_{F^a-F^b}$ = 50.5 Hz, $J_{F^a-H^6}$ = 8.2 Hz, $J_{F^b-F^c}$ = 17.6 Hz, $J_{F^b-H^6}$ = 10.1 Hz, $J_{H^4-H^5}$ = 1.8 Hz.



$\overset{1}{CH_3}O\overset{a}{C}F{=}\underset{\overset{2}{OCH_3}}{C}{-}\overset{b}{C}F{=}\overset{3}{C}H{-}\overset{4}{C}H{=}\overset{5\,6}{CHH}$

6

1,3-Difluoro-1,2-dimethoxy-1,3,5-hexatriene (6): 87.11 (dd, F^a), 121.51 (ddd, F^b), 3.63 (s, 3 H-1), 3.61 (d, 3 H-2), 5.44 (udd, H-3), 6.61 (uddd, H-4), 5.20 (dd, H-5), 5.32 (dd, H-6); $J_{F^a-F^b}$ = 26.4 Hz, $J_{F^a-H^3}$ = 6.4 Hz, $J_{F^b-H^3}$ = 53.5 Hz, $J_{F^b-H^4}$ = 8.0 Hz, $J_{H^5-H^6}$ = 1.8 Hz.

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