

SYNTHETIC TRANSFORMATIONS OF DIMETHYL PERFLUORO-4-METHYL-2-PENTENEDIOATE*

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Received November 26th, 1981

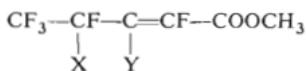
Reaction of the title compound *I* with methanolic sodium methoxide proceeded with decarboxylation and substitution of the vinylic fluorine atom, the resulting product being methyl 2,4,5,5,5-pentafluoro-3-methoxy-2-pentenoate (*II*). Compound *I* reacted with chlorine to give dimethyl 2,3-dichloro-2,3,4-trifluoro-4-trifluoromethylpentanedioate (*III*) which was selectively hydrolyzed to potassium 1-methyl 2,3-dichloro-2,3,4-trifluoro-4-trifluoromethylpentanedioate (*IV*). This ester salt was transformed in two steps into methyl 2,3-dichloro-4-fluoroformylhexafluoropentanoate (*VIII*). Pyrolysis of *IV* afforded methyl 2-chlorohexafluoro-3-pentanoate (*V*). Reduction of the diester *III* with sodium borohydride led to 3-chloro-2,3,4-trifluoro-2-hydroxymethyl-4-trifluoromethylloxolane (*IX*) and 2,3-dichloro-2,3,4-trifluoro-4-trifluoromethyl-1,5-pentane diol (*X*).

In this communication we compare reactions of dimethyl perfluoro-4-methyl-2-pentenedioate (*I*), prepared by anionic dimerization¹ of methyl trifluoropropenoate, with those of halogenoacrylates. We used the dimer *I* in syntheses of some new compounds.

We studied qualitatively²⁻⁴ the reactivity of fluorinated propenoates towards nucleophilic reagents using the base-catalyzed reaction with methanol. It was found²⁻⁴ that propenoates with a terminal difluoromethylene group added methanol even in the presence of weak bases such as fluoride ions. On the contrary, propenoates containing a chlorine atom⁴ or a methoxycarbonyl group⁵ in position 3 did not react under these conditions. In accord with these findings, no addition of methanol to the double bond of the dimer *I* occurred in the presence of potassium fluoride. With sodium methoxide as catalyst the reaction afforded methyl 2,4,5,5,5-pentafluoro-3-methoxy-2-pentenoate (*II*) as the only isolated product. Its structure shows that the dimer *I* underwent a substitution at the double bond together with replacement of the methoxycarbonyl group by hydrogen. The fluorine atom at the double bond was substituted probably by a multistep vinyl substitution mechanism⁶, similarly as in the case of the mentioned difluoropropenoates^{4,5} with substituents in position 3. Perfluorocarboxylic acids or esters are known to lose the carboxyl carbon in both

* Part XIX in the series Haloacrylic Acids; Part XVIII: This Journal 47, 54 (1982).

acid and alkaline medium. Perfluorocarboxylic acids with unbranched chain are quite stable in solution^{7,8} whereas carboxyl groups bonded to secondary carbon atoms in perfluoroalkyl⁹ or perfluorocycloalkyl¹⁰ systems tend to be split off. On the other hand, ester of unbranched perfluorocarboxylic acids lose the ester group on reflux with sodium ethoxide^{11,12} under formation of 1-hydrylperfluoroalkanes. The reaction proceeds *via* a carbanion intermediate which was isolated¹² in high yield. Since the ester group in compound *I* was split off very smoothly, we assume that the intermediate has a relatively high stability. Solvolysis of the dimer *I* with potassium hydroxide in aqueous 1,2-dimethoxyethane afforded only a mixture of salts but no product *II*. The dichloro derivative *III* was also not decarboxylated when treated with methanolic potassium hydroxide. We therefore assume that the observed facile decarboxylation may be the property of β,γ -unsaturated perfluoroacids.



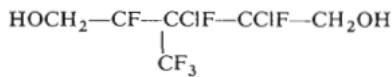
I, X = COOCH₃, Y = F
II, X = H, Y = OCH₃



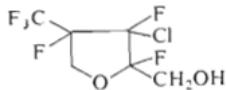
III, Z = OCH₃ *VII*, Z = Cl
IV, Z = OK *VIII*, Z = F
VI, Z = OH



V



X



IX

Ultraviolet light-initiated radical addition of chlorine to the double bond in the dimer *I* afforded dimethyl 2,3-dichloro-2,3,4-trifluoro-4-trifluoromethylpentanedioate (*III*) which served as starting material for synthesis of some new compounds. As expected, the compound *III* was selectively hydrolyzed with potassium hydroxide at the ester function in the position 5, since it follows from the Hammett constants¹³ that secondary perfluoroalkyls have a stronger inductive effect than primary and unbranched ones. The inductive effect of secondary perfluoroalkyls influences markedly the acidity of the O—H and C—H bonds. Thus, *e.g.* the pK_a values of fluorinated hydroxylamines¹⁴ and fluorinated alcohols¹⁵⁻¹⁸ increase by three orders of magnitude on going from primary to secondary perfluoroalkyls. This effect is even more pronounced in the monohydrylperfluoroalkane series^{19,20}. The length of the perfluoroalkyl chain affects the pK of acids only little^{21,22}. At room tempera-

ture, the diester *III* was hydrolyzed to the ester salt *IV* practically immediately, the excess base being consumed only very slowly. The fact that hydrolysis of the compound *III* was not accompanied by decarboxylation shows the dominant role of the double bond in the decarboxylation mechanism (as observed with the dimer *I*). The reactivity of the second carboxyl in compound *I* is suppressed by its conjugation with the double bond^{23,24}. The diester *III* was converted into the ester salt *IV* also by reaction with carbonates or alkali metal hydroxides²⁵ under similar conditions.

The ester salt *IV* was transformed into methyl 2,3-dichloro-4-fluoroformylhexafluoropentanoate (*VIII*) by the following series of reactions. Acidification of *IV* with sulfuric acid liberated 1-methyl hydrogen 2,3-dichloro-2,3,4-trifluoro-4-trifluoromethylpentanedioate (*VI*) which was converted into methyl 2,3-dichloro-4-chloroformylhexafluoropentanoate (*VII*) by pyridine-catalyzed reaction with thionyl chloride²⁶. Nucleophilic replacement of chlorine by fluorine (with potassium fluoride) gave the ester fluoride *VIII*.

Pyrolysis of alkali metal salts of perfluorocarboxylic acids affords fluorinated olefins²⁷⁻²⁹. This decomposition obviously proceeds by a carbanion mechanism in which the last step consists in elimination of fluoride ion. Usually, potassium salts afford a mixture of isomeric olefins^{27,28}. In the case of compound *IV* the halogen could be in principle cleaved off from the trifluoromethyl or chlorofluoromethylene group. In actual fact, pyrolysis of the ester salt *IV* at 300°C gave methyl 2-chlorohexafluoro-3-pentenoate (*V*) as the sole product. This result confirmed⁶ that elimination of chloride ions is much more facile than that of fluoride ions.

Reduction of the diester *III* with sodium borohydride afforded a 2 : 1 mixture of 3-chloro-2,3,4-trifluoro-2-hydroxymethyl-4-trifluoromethyloxolane (*IX*) and 2,3-dichloro-2,3,4-trifluoro-4-trifluoromethyl-1,5-pentanediol (*X*).

EXPERIMENTAL

The temperature data are uncorrected. IR spectra were measured on a Perkin-Elmer 325 spectrometer (Bodenseewerk), NMR spectra on a Varian XL-100-15 instrument (Palo Alto, USA) in deuteriochloroform (¹⁹F NMR spectra with CCl_3F as standard). Gas-liquid chromatography was carried out on a Chrom 41 chromatograph (Laboratorní přístroje, Prague); flame-ionization detector, Chromaton N-AW-DMCS (Lachema, Brno). Chemicals: Dimethyl perfluoro-4-methyl-2-pentenedioate (*I*) was prepared as described previously^{1,2}. Acetonitrile was purified and dried as described in our previous work¹. Structure of the new compounds *II*, *III*, *V*, *IX* and *X* was confirmed by NMR and IR spectra and elemental analyses.

Methyl 2,4,5,5,5-Pentafluoro-3-methoxy-2-pentenoate (*II*)

A solution of sodium methoxide in methanol was added dropwise to a cooled mixture of the dimer *I* (5.5 g; 19.6 mmol) and methanol (6.3 g; 196 mmol) until no starting material was detected by gas liquid chromatography (poly(butanediol succinate), 160°C). The mixture was diluted with 1,1,2-trichlorotrifluoroethane (50 ml), washed with water, dried over anhydrous

calcium chloride and distilled, affording 3.65 g (64%) of compound *II*, b.p. 56–61°C/6.7 kPa; purity 98%. ¹H NMR spectrum: (shift in ppm, s singlet, d doublet, t triplet, q quartet, m multiplet, coupling constants *J* in Hz): s(3), 3.88, d(3) 4.05, dqd(1) 6.52 ²J_{HF} 42, ³J_{HF} 6. ¹⁹F NMR spectrum: dq(1) – 206.4, s(1) – 144.1, dd(3) – 76.4 ³J_{FF} 13. IR spectrum (tetrachloromethane, cm^{−1}): ν(C=C) 1 660 s, ν(C=O), 1 734 s, 1 748 s. For C₇H₇F₅O₃ (234.1) calculated: 35.91% C, 3.01% H, 40.58% F; found: 36.48% C, 2.98% H, 39.58% F.

Dimethyl 2,3-Dichloro-2,3,4-trifluoro-4-trifluoromethylpentanedioate (*III*)

A mixture of the dimer *I* (35.2 g; 0.126 mol) and 1,1,2-trichlorotrifluoroethane (100 ml) was chlorinated under irradiation with a mercury lamp (Pyrex filter) until 90% conversion (gas-liquid chromatography on SE-301; 190°C) was achieved. After washing with a solution of sodium sulfite and water the solution was dried over magnesium sulfate, taken down and distilled, affording 39.0 g (89%) of the diester *III*, b.p. 124–128°C/1.6 kPa; purity 94%. ¹H NMR spectrum: s(6) 3.94. ¹⁹F NMR spectrum: m(1) – 169.2, m(1) – 122.3, m(1) – 120.1, m(3) – 70.9. IR spectrum (tetrachloromethane, cm^{−1}): ν(C=O) 1 795 s. For C₈H₆Cl₂F₆O₄ (351.0) calculated: 27.37% C, 1.72% H, 20.20% Cl, 32.57% F; found: 26.17% C, 1.57% H, 21.06% Cl, 31.89% F.

Potassium 1-Methyl 2,3-Dichloro-2,3,4-trifluoro-4-trifluoromethylpentanedioate (*IV*)

Methanolic potassium hydroxide was added dropwise to a solution of the ester *III* (10.4 g; 26 mmol) in methanol until the red colouration of phenolphthalein (added as an indicator) persisted. The mixture was taken down and the residue crystallized from methanol. Yield 10.1 g (93%) of the ester salt *IV*; m.p. <250°C. For C₇H₃Cl₂F₆KO₄ (374.1) calculated: 22.40% C, 0.80% H, 19.95% Cl, 30.42% F; found 21.72% C, 0.64% H, 19.80% Cl, 30.32% F.

Methyl 2-Chlorohexafluoro-3-pentenoate (*V*)

The ester salt *IV* (4.5 g; 12 mmol) was heated to 300°C at 2.7 kPa for 2.5 h and the volatile products were collected in a receiver cooled with dry ice. Distillation afforded 0.98 g (32%) of the ester *V*, b.p. 58–61°C/2 kPa; purity 95%. ¹H NMR spectrum: s(2) 3.98. ¹⁹F NMR spectrum: *cis*-isomer: m(1) – 143.5, dmm(2) – 108.8, m(3) – 75.3; *trans*-isomer: dmm(2) – 156.9, m(1) – 143.5, m(3) – 75.3. For C₆H₃ClF₆O₂ (256.5) calculated: 28.09% C, 1.18% H, 13.82% Cl, 44.44% F; found: 28.63% C, 1.27% H, 13.18% Cl, 43.22% F.

1-Methyl Hydrogen 2,3-Dichloro-2,3,4-trifluoro-4-trifluoromethylpentanedioate (*VI*)

Sulfuric acid (4.1 ml of 1.4M-H₂SO₄ in 1,2-dimethoxyethane) was added dropwise to the ester salt *IV* (4.3 g; 11.5 mmol) in 1,2-dimethoxyethane (1.5 ml). After stirring for 0.5 h, the insoluble portion was filtered off and distillation of the filtrate gave 3.5 g (86%) of the compound *VI*, b.p. 115–120°C/20 Pa. ¹H NMR spectrum: s(3) 3.88, s(1) 9.94. ¹⁹F NMR spectrum: m(1) – 168.0, m(1) – 123.3, m(1) – 119.4, m(3) – 70.9. For C₇H₄Cl₂F₆O₄ (337.0) calculated: 24.95% C, 1.20% H, 21.04% Cl, 33.82% F; found: 25.48% C, 1.41% H, 21.40% Cl, 33.18% F.

Methyl 2,3-Dichloro-4-chloroformyl-hexafluoropentanoate (*VII*)

A mixture of the compound *VI* (3.5 g; 9.8 mmol), thionyl chloride (2.0 g; 16.8 mmol) and pyridine (50 mg; 0.8 mmol) was refluxed for 8 h. Distillation afforded 2.0 g (55%) of ester chloride *VII*, b.p. 68–76°C/1.3 kPa. Methanolysis of a sample of *VII* gave the diester *III*.

Methyl 2,3-Dichloro-4-fluoroformylhexafluoropentanoate (*VIII*)

A mixture of acetonitrile (4 ml), potassium fluoride (0.62 g; 10.7 mmol) and the ester chloride *VII* (1.09 g; 3.1 mmol) was stirred at 25–30°C under nitrogen for 16 h, the solid was filtered off and the filtrate distilled, yielding 0.58 g (56%) of the ester fluoride *VIII*, b.p. 130–140°C. A sample of the product was hydrolyzed and analyzed for fluorides. For $C_7H_3Cl_2F_7O_4$ (339.0) calculated: 5.61% $F^{(-)}$; found: 5.59% $F^{(-)}$.

Reduction of Dimethyl 2,3-Dichloro-2,3,4-trifluoro-4-trifluoromethylpentanedioate (*III*) with Sodium Borohydride

A solution of the diester *III* (25.0 g; 0.079 mol) in ethanol (50 ml) was added dropwise at 0°C to a stirred solution of sodium borohydride (5.6 g; 0.158 mol) in ethanol (150 ml), the temperature being kept below 10°C. After stirring for 4 h at 35°C, the mixture was decomposed with hydrochloric acid (22 ml; 1:1) and the precipitate dissolved by addition of water. The products were taken up in dichloromethane (4 × 50 ml) and dried over anhydrous magnesium sulfate. Distillation afforded 6.7 g (33%) of 3-chloro-2,3,4-trifluoro-2-hydroxymethyl-4-trifluoromethyl-oxolane (*IX*), b.p. 50–53°/2.7 kPa, purity 90%, and 4.35 g (19%) of 2,3-dichloro-2,3,4-trifluoro-4-trifluoromethyl-1,5-pentanediol (*X*), b.p. 110–114°C/2.7 kPa, purity 90%. Gas-liquid chromatography: poly(butanediol succinate), 180°C. 1H NMR spectra compound *IX*: s(1) 3.23, d(2) 4.01 $^3J_{HF}$ 3, d(2) 4.21 $^3J_{HF}$ 2; compound *X*: s(2) 3.56, m(2) 4.24, m(2) 5.21 $^3J_{HF}$ 11. ^{19}F NMR spectra compound *IX*: ddq(1) – 163.4, dm(1) – 151.7, ddm(1) – 129.5, dd(3) – 68.8; compound *X*: m(1) – 193.7, m(1) – 139.7, m(1) – 123.8, d(3) – 69.8 $^3J_{HF}$ 10. IR spectra (tetrachloromethane, cm^{-1}) compound *IX*: $\nu(\text{OH})$ 3480 m, 3630 m; compound *X*: $\nu(\text{OH})$ 3585 m, 3625 m. For *IX* $C_6H_5ClF_6O_2$ (258.6) calculated: 27.87% C, 1.95% H, 13.71% Cl, 44.09% F; found: 26.99% C, 2.00% H, 14.76% Cl, 44.92% F. For *X* $C_6H_6Cl_2F_6O_2$ (295.1) calculated: 24.20% C, 2.03% H, 23.07% Cl, 38.64% F; found: 25.12% C, 2.36% H, 22.58% Cl, 37.26% F.

The elemental analyses were carried out in the Department of Organic Analysis (Dr L. Helešic, Head), spectral measurements in the Department of NMR Spectroscopy (Dr P. Trška, Head) and Department of Absorption Spectroscopy (Dr A. Muck, Head), all of the Prague Institute of Chemical Technology. We are indebted for this help.

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Translated by M. Tichý.