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The Synthesis of Pentafluoroacetyl Derivatives based on Iodopentafluoroacetone

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Abstract: Iodopentafluoroacetone smoothly undergoes dimerization in the presence of Cu-powder yielding perfluoroacetylpropenyl ether. The adducts of iodopentafluoroacetone with ethylene and tetrafluoroethylene were obtained under the conditions of thermal initiation. The transformations of 2-(perfluoroacetyl)ethyl iodide have been studied.

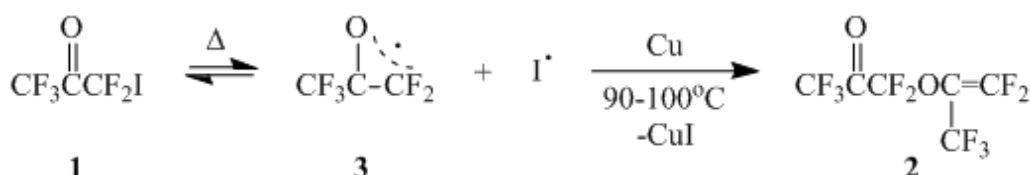
Keywords: iodopentafluoroacetone, ethylene, tetrafluoroethylene.

Earlier it was found that the thermolysis of iodopentafluoroacetone (**1**) (autoclave, 250B°C/25 h) led to the formation of perfluoroacetylpropenyl ether (**2**) – the product of O-C-dimerization of **1** [1]. The authors assumed that the reaction proceeded according to the scheme comprising the homolytic dissociation of C-I-bond in **1** with subsequent addition of perfluoroacetyl radical (**3**) to oxygen atom of carbonyl group of another molecule **1** accompanied by elimination of iodine radical from ICF₂-group.

In spite of the expected easiness of the homolysis C-I-bond in **1**, that should lead to the generation of relatively stable heteroallyl radical **3**, the reaction conditions appeared to be very severe that was most probably connected with the reversible character of homolytic rupture.

In the given work we have found that in the presence of Cu-powder as iodine acceptor acetone **1** formed dimer **2** in quantitative yield at 90-100B°C.

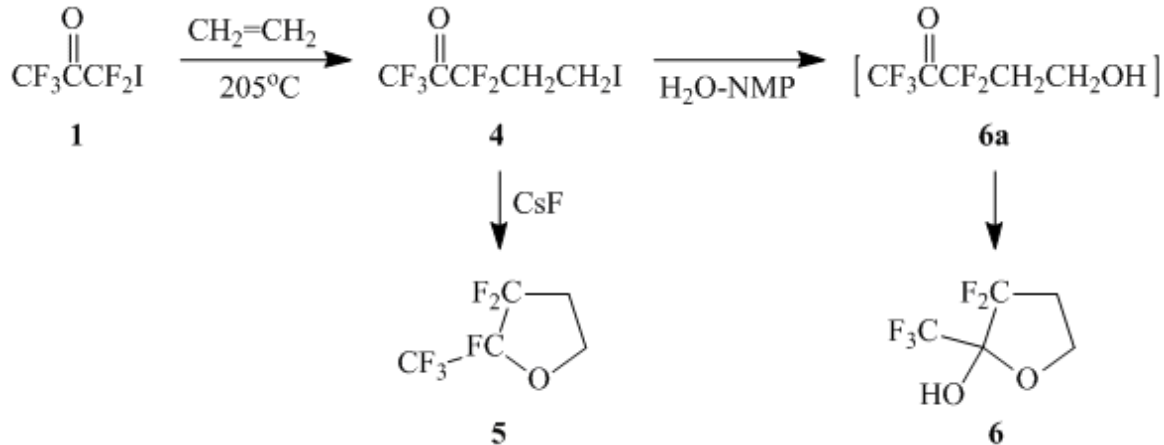
Scheme 1



The easiness of acetone **1** homolysis allows to apply the radical addition reactions of **1** to unsaturated compounds as a convenient method of introducing perfluoroacetyl moiety into different classes of organic compounds.

Indeed, under the conditions of thermal initiation acetone **1** adds smoothly to ethylene affording adduct **4** – a starting material for preparing oxolane **5** by intramolecular cyclization of iodide **4** in the presence of CsF. The saponification of **4** under the conditions described in [2] resulted in formation of oxyoxolane **6** – the product of intramolecular cyclization of initially formed alcohol **6a**.

Scheme 2



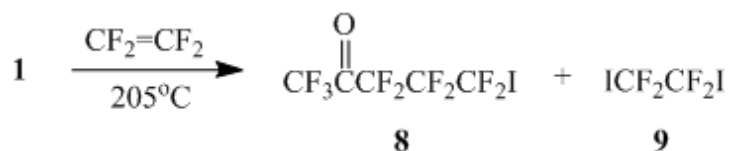
The dehydration of oxyxolane **6** under the action of P_2O_5 led to olefine **7**. Evidently alcohol **6a** is the immediate precursor of ketoolefine **7**, and in order to shift the equilibrium **6** \rightleftharpoons **6a** to the right the reaction mixture was heated up to $\sim 300^\circ\text{C}$ by Bunsen burner.

Scheme 3



The reaction of **1** with tetrafluoroethylene (autoclave, 205°C) gave adduct **8** (Scheme 4), but in this case 1,2-diiidotetrafluoroethane (**9**) was formed as a by-product. We failed to isolate analytical sample of adduct **8** from azeotrope **8-9**. The structure of compound **8** was established on the basis of CMS and ^{19}F NMR data.

Scheme 4



Thus the above examples show that the radical addition of iodopentafluoroacetone to nonfluorinated and fluorinated ethylenes and further transformations of the adducts obtained poses convenient method of introducing perfluoroacetyl group in to different classes of organic compounds.

Experimental

^1H , ^{19}F NMR spectra were recorded on Bruker AVANCE-300 spectrometer at 300 and 282 MHz, accordingly; the external standard was CDCl_3 or D_2O . Chemical shifts for ^1H spectra are presented vs. the residual signal of the solvent (O^\dagger 7.25; 4.79) and are given in ppm vs. tetramethylsilane. Chemical shifts in ^{19}F spectra are given in ppm vs. $\text{CF}_3\text{CO}_2\text{H}$. Downfield shifts are positive. The Raman spectra were recorded on Jobin Yvon LabRam Raman spectrometer. The mass spectra were recorded on Finnigan Polaris Q (Trace GC ultra) Mass spectrometer.

Iodopentafluoroacetone (**1**) was obtained by method [3].

Dimerization of iodopentafluoroacetone in the presence of Cu-powder

The mixture of iodopentafluoroacetone (**1**) (30 g, 0.109 mol) and Cu-powder (7 g, 0.11 g-atom) was heated at $100^\circ\text{C}/3$ h in a sealed glass tube. The reaction product **2** (16.1g, quantitative yield) was evacuated under reduced pressure into receiver (-78°C). ^{19}F NMR-spectrum of the product obtained corresponded of that described in [1]. Further distillation gave 15.5 g of **2**, b.p. $69-70^\circ\text{C}$ (lit. data: b.p. $65-72^\circ\text{C}$ [1]).

The reaction of iodopentafluoroacetone with ethylene

The mixture of acetone **1** (25 g, 91 mmol) and ethylene (6 l, 240 mmol) was shaken in 100 ml stainless steel autoclave at 200B°C/10 h, then the liquid part of reaction mixture (27 g) was distilled to give 24.6 g (89%) of adduct **4**, b.p. 70-79B°C (85 Torr).

The analytical sample was isolated by redistillation, b.p. 71-72B°C (85 Torr). Found (%): C, 19.86; H, 1.33; F, 31.46. C₅H₄F₅O. Calculated (%): C, 19.85; H, 1.33; F, 31.23. IR-spectrum (OS, C_fm⁻¹): 1788 (C=O). ¹H NMR Or': 2.53, (s, 2H, CH₂), 2.98, (s, 2H, CF₂CH₂); ¹⁹F NMR Or': -1.83, (s, 3F, CF₃), 31.25 (s, 2F, CF₂).

The preparation of oxolane **5**

The mixture of ketoidide **4** (9 g, 30 mmol), CsF (5 g, 33 mmol) and 25 ml of diglyme was stirred at 35-40B°C/6 h, filtered, the filtrate was washed with dilute aq. HCl, extracted with ether, extract was dried MgSO₄, the ether was evaporated to give a residue (3.9 g), which contained compounds **4** : **5** = 1 : 9. Its distillation afforded 3.5 g of a fraction (106-135B°C) that contained ~95% of oxolane **5** (GLC, ¹⁹F NMR), yield 75% based on **4** entered the reaction.

The analytical sample of **5** was obtained by redistillation, b.p. 114-115B°C. Found (%): C, 30.72; H, 2.06; F, 58.43. C₅H₄F₆O. Calculated (%): C, 30.92; H, 2.06; F, 58.76. ¹⁹F NMR Or': 2.45 (dt, 3F, ³J_{CF₃-CF} = 13 Hz, ⁴J_{CF₃-CF₂} = 2.9 Hz, CF₃), AB-pattern with centrum 36.35 (2F, J_{AB} = 245.3 Hz, CF₂), 44.8 (br.s, 1F, CF).

The synthesis of oxyoxolane **6**

The mixture of ketoidide **4** (24.6 g, 81.46 mmol), 3.8 g (210 mmol) H₂O and 160 g NMP was stirred at 150B°C/13 h, then the reaction mixture was poured into 400 ml of water, extracted with ether (4x50 ml), extract was evaporated, the residue was distilled under reduced pressure (60-110B°C (17 Torr)) to give 19 g of a fraction, which was redistilled yielding 12.5 g (78%) **6**, b.p. 72-98B°C (30 Torr).

Found (%): C, 30.27; H, 2.77; F, 48.12. C₅H₅F₅O₂·0.25H₂O. Calculated (%): C, 30.53; H, 2.80; F, 48.35. ¹H NMR Or': 2.25Γ-2.40 (m, 2H), 3.94Γ-4.01 (m, 2H). ¹⁹F NMR Or': 3.93 + 3.94 (d, 3F, J_{CF₃-OH} = 14 Hz, CF₃), AB-pattern with centrum 36.5 (2F, J_{AB} = 240.6 Hz, CF₂). Mass-spectrum **6** (m/z, reference): 193 [M+H]⁺; 175 [M-OH]⁺; 153 [C₅H₄F₃O₂]⁺; 148 [C₃HF₅O]⁺; 135 [C₅H₂F₃O]⁺; 123 [M-CF₃]⁺; 103 [C₄H₄FO₂]⁺; 95 [C₃H₅F₂O]⁺; 83 [C₄H₃O₂]⁺; 77 [C₃H₃F₂]⁺ (100%); 75 [C₃HF₂]⁺; 69 [CF₃]⁺; 64 [C₂H₂F₂]⁺; 55 [C₃F]⁺; 51 [CHF₂]⁺; 45 [C₂H₅O]⁺; 39 [C₃H₃]⁺.

The preparation of ketoolefine **7**

The mixture of oxyoxalane **6** (13.2 g, 70 mmol) and P₂O₅ (9.5 g, 77 mmol) was heated by Bunsen burner, collecting the distillate into receiver cooled with ice. The distillation of distillate afforded 6.1 g (51%) of ketoolefine **7**, b.p. 48-50B°C.

Found (%): C, 34.65; H, 1.67; F, 54.88. C₅H₃F₅O. Calculated (%): C, 34.48; H, 1.72; F, 54.60. IR-spectrum (OS, cm⁻¹): 1651.0 (C=C); 1788.6 (C=O). ¹H NMR Or': 6.27Γ-6.55 (m). ¹⁹F NMR Or': 1.96 (s, 3F, CF₃), 30.38 (s, 2F, CF₂).

The reaction of iodopentafluoroacetone with tetrafluoroethylene

The mixture of acetone **1** (29 g, 106 mmol) and tetrafluoroethylene (3.25 l, 130 mmol) was shaken in 100 ml stainless steel autoclave at 205B°C/11 h. The liquid part of the reaction mixture (34.1 g) contained 10% of starting ketone **1**, 20% of 1,2-diiodotetrafluoroethane (**9**) and 70% of Oi-hexafluoropropyltrifluoromethyl ketone (**8**) (yield 68% based on **1** entered the reaction). The further distillation gave 30.5 g of a fraction (98-115B°C), which contained compounds **8** : **9** = 78 : 22 couldn't be divided by rectification. The structure of adduct **8** was established according to CMS and ¹⁹F NMR data.

¹⁹F NMR Or': -17.8 (s, 2F, CF₂l), 1.5 (s, 3F, CF₃), 36.5 (s, 2F, C(O)CF₂), 40.5 (s, 2F, CF₂). Mass-spectrum **8** (m/z, reference): 375 [M+H]⁺; 355 [M-F]⁺; 277 [C₃F₆l]⁺; 247 [M-l]⁺ (100%); 239 [C₃F₄l]⁺; 227 [C₂F₄l]⁺; 208 [C₂F₃l]⁺; 181 [C₄F₇]⁺; 177 [CF₂l]⁺; 169 [C₃F₇]⁺; 131 [C₃F₅]⁺; 100 [C₂F₄l]⁺; 97 [C₂F₃O]⁺; 69 [CF₃]⁺.

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Recommended for publication by Prof. S. Sterlin