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Thermal degradation of silver 2-hydroperfluoro-3-methylcrotonoate

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Abstract: It is shown that 1,1,1,6,6,6-hexafluoro-2,5-bis(trifluoromethyl)-2,4-hexadiene – the main product of silver 2-hydroperfluoro-3-methylcrotonoate thermolysis – undergoes prototropic rearrangement and dehydrofluorination under the reaction conditions to give a mixture of polyunsaturated compounds.

Keywords: silver 2-hydroperfluoro-3-methylcrotonoate; 1,1,1,6,6,6-hexafluoro-2,5-bis(trifluoromethyl)-2,4-hexadiene; tetrakis(trifluoromethyl)butatriene; 1,2-bis(perfluoropent-2-yl)acetylene.

Earlier in the course of study devoted to the synthesis of gem-bis(trifluoromethyl) substituted olefines and dienes it was shown that 4,4,4-trifluoro-3-(trifluoromethyl)-2-butenal reacts with hexafluoropropylidene triphenylphosphoran generated *in situ* to give 1,1,1,6,6,6-hexafluoro-2,5-bis(trifluoromethyl)-2,4-hexadiene (**1**) [1].

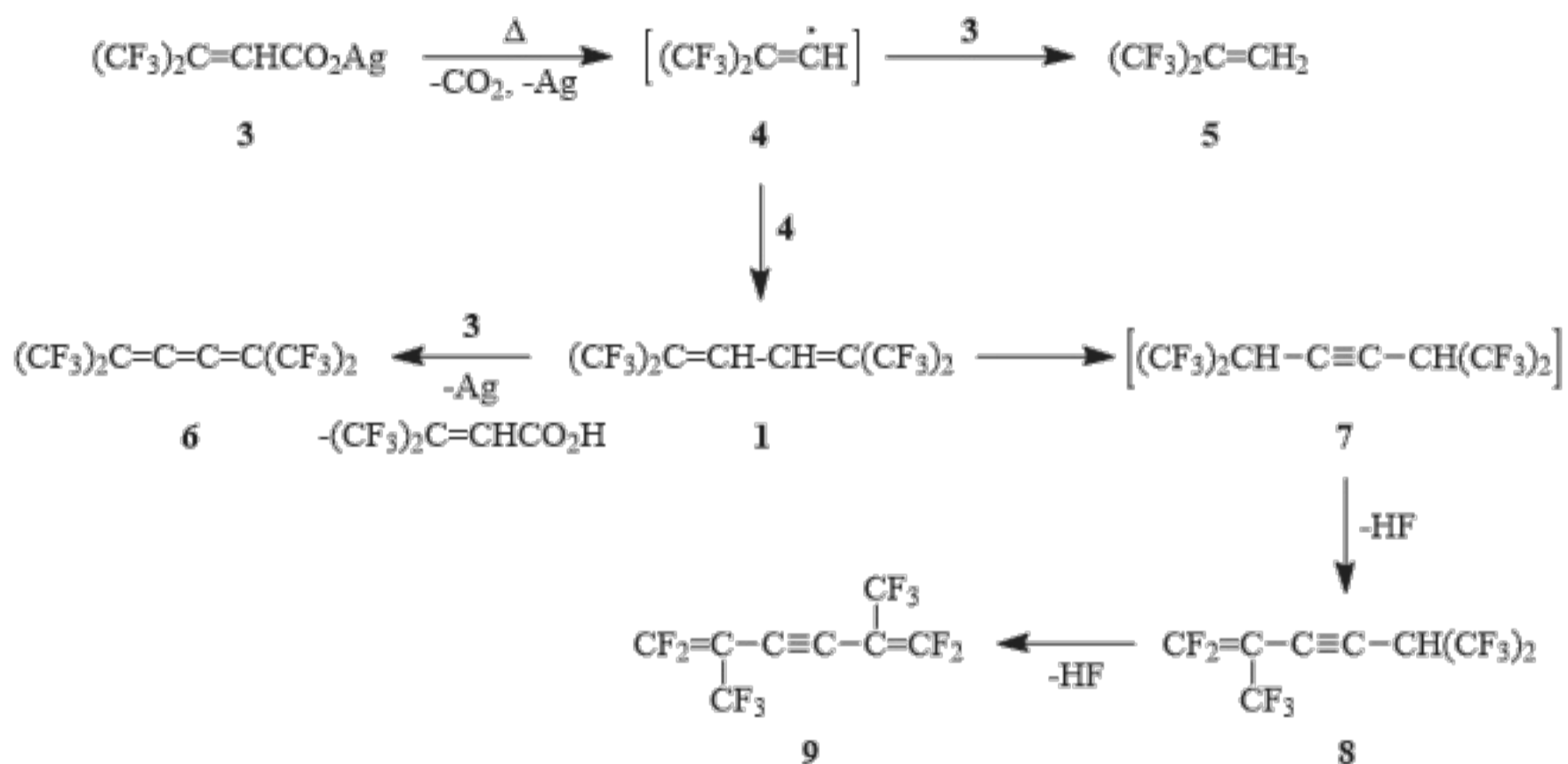
It is known that degradation of silver salts of perfluoro- α,β -unsaturated carboxylic acids of general formula $R_FCF=CFCO_2Ag$ ($R_F = i-C_3F_7$; *tert*- C_4F_9) (**2**) at 210-220°C leads to the formation of the corresponding α -dienes in 80-85% yields [2]. It could be assumed that thermolysis of silver 2-hydroperfluoro-3-methylcrotonoate (**3**) would appear to be a convenient method of preparing diene **1**.

We have found that thermal degradation of salt **3** at 170-240°C/10-12 Torr leads to the formation of product mixture that contains, along with the expected diene **1**, compounds **5**, **6**, **8**, **9** which structures were suggested based on GC-MS-data. The comparison of molecular ions of compounds **1**, **6**, **8**, **9** leads to the evident conclusion that the compounds **6-9** are the diene **1** derivatives, formed either as a result of its oxidation (butatriene **6**) or sequential mono- or didehydrofluorination (propenyl acetylene **8** and bis(propenyl) acetylene **9**).

Hence it appears that diene **1** is in fact the main product of salt **3** thermal degradation, and complex mixture of the reaction products is determined by oxidation of two C-H-bonds in 2,3-positions of butadiene fragment of the molecule under the action of Ag⁺-ions as well as prototropic migration of hydrogen atoms that leads to the intermediate formation of bis(hexafluoroisopropyl) acetylene **7** - precursor of acetylenes **8-9**.

Most probably the driving power of prototropic allylic rearrangement of α -diene **1** is a high polarization of double bonds under the influence of four CF₃-groups in 1,4-positions of butadiene fragment. The quantum-chemical calculation shows that enthalpy of acetylene **7** formation as a consequence of diene **1** prototropic isomerisation is 14 kJ/mol. Taking into consideration that decarboxylation of crotonoate **3** begins at 170°C the formation of acetylene **7** as the intermediate appears to be highly probable.

Scheme 1



Experimental

Mass spectra are recorded using a Finnigan Polaris Q mass spectrometer (Trace GC ultra).

Quantum-chemical calculations were performed by TPSSh/6-311++G(d, p) method assisted by program complex GAMESS-US at supercomputer BlueGene/P of CM&C faculty (Moscow University) [4, 5]. According to calculation data the enthalpy of diene **1** isomerization into acetylene **7** is 14 kJ/mol. The gauche conformation of appeared to be energetically favorable.

Thermolysis of salt **3**.

Sodium carbonate (3.76 g, 35.5 mmol) was added to solution of 16 g (71 mmol) 4,4,4-trifluoro-3-(trifluoromethyl)crotonic acid monohydrate in 100 ml of water, when the evolution of CO₂ ceased the solution of 12.05 g (71 mmol) AgNO₃ in 20 ml of water was added under stirring, the precipitate was extracted with ether, the extract was evaporated, the residue (salt **3**) was dried over P₂O₅ at 100°C/1-2 Torr. The salt **3** obtained (19.2 g, 61 mmol) was heated at 170-240°C/10-12 Torr, the volatile products were collected into receiver (-78°C). According to CG-MS-data the distillate (8.2 g) for ~90% consists of compounds **1** : **5** : **6** : **8** : **9** in approximate ratio 10 : 5 : 5 : 1 : 3. The attempt to fractionate the mixture obtained led

to intensive tarring; no analytically pure compounds were isolated.

Mass-spectrum of **1** (m/z, reference): 326[M]⁺; 307[M-F]⁺; 287[M-H-2F]⁺; 257[M-CF₃]⁺; 237[C₇HF₈]⁺; 219[C₇H₂F₇]⁺; 207[C₆H₂F₇]⁺; 191[C₈F₅]⁺(100%); 181[C₇H₂F₅]⁺; 163[C₄HF₆]⁺; 113[C₃HF₄]⁺; 75[C₃HF₂]⁺; 69[CF₃]⁺ (cf. [1, 8]).

Mass-spectrum of **5** (m/z, reference): 164[M]⁺; 163[M-H]⁺; 145[M-F]⁺(100%); 113[C₃HF₄]⁺; 95[M-CF₃]⁺; 75[C₃HF₂]⁺; 69[CF₃]⁺.

Mass-spectrum of **6** (m/z, reference): 324[M]⁺; 305[M-F]⁺; 286[M-2F]⁺; 267[C₈F₉]⁺; 255[M-CF₃]⁺(100%); 236[C₇F₈]⁺; 217[C₇F₇]⁺; 205[C₆F₇]⁺; 186[C₆F₆]⁺; 167[C₆F₅]⁺; 148[C₆F₄]⁺; 117[C₅F₃]⁺; 69[CF₃]⁺ (cf. [6, 7]).

Mass-spectrum of **8** (m/z, reference): 306[M]⁺; 287[M-F]⁺; 267[C₈F₉]⁺; 237[M-CF₃]⁺; 218[C₇HF₇]⁺; 199[C₇HF₆]⁺; 187[C₆HF₆]⁺; 168[C₆HF₅]⁺(100%); 148[C₆F₄]⁺; 137[C₅HF₄]⁺; 117[C₅F₃]⁺; 99[C₅HF₂]⁺; 93[C₃F₃]⁺; 75[M-CF₃]⁺; 69[CF₃]⁺.

Mass-spectrum of **9** (m/z, reference): 286[M]⁺(100%); 267[M-F]⁺; 236[C₇F₈]⁺; 217[C₇F₇]⁺; 186[C₆F₆]⁺; 167[C₆F₅]⁺; 148[C₆F₄]⁺; 129[C₆F₃]⁺; 117[C₅F₃]⁺; 98[C₅F₂]⁺; 79[C₅F]⁺; 69[CF₃]⁺; 43[C₂F]⁺.

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