Polyfluorinated hydrazones in organic synthesis
4.* The oxidation of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione bishydrazone with compounds of Se and Hg

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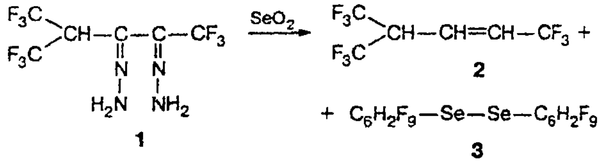
The oxidation of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione bishydrazone (**1**) with SeO_2, HgO, and $Hg(OAc)_2$ was studied. The use of selenium dioxide leads to 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpent-2-ene (**2**) and $C_{12}H_4F_{18}Se_2$. 1,1,1,5,5,5-Hexafluoro-4-trifluoromethylpent-2-yne (**4**) and $C_6H_2F_9HgC_6H_2F_9$ were obtained by the oxidation of bishydrazone **1** with mercuric oxide. The oxidation of compound **1** with mercuric acetate in diglyme affords 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpenta-2,3-diene (**6**). Alkyne **4** is isomerized to allene **6** at 130 °C.

Key words: oxidation; selenium dioxide; mercuric oxide; mercuric acetate; 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione bishydrazone; 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpent-2-ene; 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpent-2-yne; 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpenta-2,3-diene.

Previously, the oxidation of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione bishydrazone (**1**) with bromine in water,[2] with bromine under anhydrous conditions, or with sulfuryl chloride,[3] and with an H_2SO_4—P_2O_5 mixture[1] has been studied.

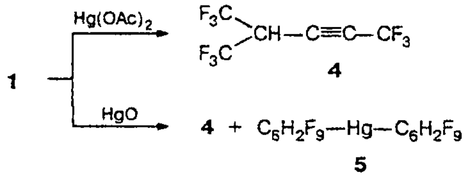
In the present work, the oxidation of bishydrazone **1** with selenium and mercury compounds was studied.

Our experiments showed that the oxidation of bishydrazone **1** (for its synthesis see Ref. 2) with selenium dioxide in diglyme affords 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpent-2-ene (**2**) in a ~60% yield.

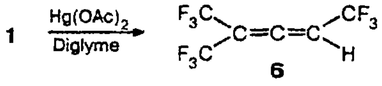


In this reaction, $C_6H_2F_9$—Se—Se—$C_6H_2F_9$ (**3**) was isolated in a ~20% yield along with compound **2**. According to GC/MS data, compound **3** is a mixture of seven isomers, each having the same molecular ion (650 $[M]^+$) and fission ions: 325 $[1/2\ M]^+$, 245 $[C_6H_2F_9]^+$, and 160 $[Se_2]^+$.

1,1,1,5,5,5-Hexafluoro-4-trifluoromethylpent-2-yne (**4**) was obtained (62% yield) by the oxidation of bishydrazone **1** with Hg^{II} acetate in the absence of solvent. A similar product is formed in the reaction with yellow HgO as the oxidant. Apart from alkyne **4**, $C_6H_2F_9$—Hg—$C_6H_2F_9$ (**5**) was isolated in minor yield in this reaction. According to GC/MS data, compound **5** is a mixture of seven isomers. All isomers have the same molecular ion and fission ions characteristic of the linear structure: 692 $[M]^+$, 673 $[M-F]^+$, 447 $[C_6F_9H_2Hg]^+$, and 245 $[C_6F_9H_2]^+$.



When bishydrazone **1** is oxidized by Hg^{II} acetate in diglyme, the main reaction product is 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpenta-2,3-diene (**6**). Alkyne **4** is formed only as a minor admixture (~10%).



The structures of compounds **2**, **4**, and **6** were confirmed by MS, ^1H and ^{19}F NMR, and IR spectroscopy. An intense absorption maximum at 2290 cm^{-1} corresponding to the C≡C bond (*cf.* Ref. 4) is found in the IR spectrum of compound **4**, while an absorption maximum at 2015 cm^{-1} corresponding to antisymmetric vibrations of the allene system is observed for compound

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* For Part 3, see Ref. 1

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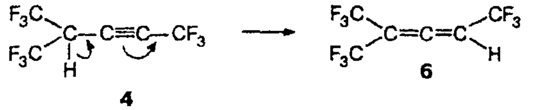
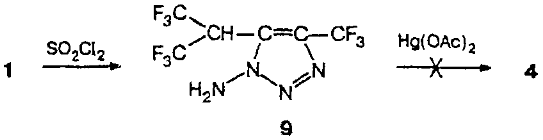
6 (*cf.* Ref. 5). It is interesting to note that alkyne **4** is completely converted to allene **6** on heating to 130 °C.



Usually, such a prototropic isomerization, which is characteristic of acetylene derivatives, occurs in the presence of bases. In our case, the H atom in compound **4** readily migrates to the allyl C atom even in the absence of catalyst because of an electron-acceptor effect of the fluoroalkyl groups. As a result, allene **6**, a thermodynamically more stable isomer, forms. Assumed pathways for the synthesis of compounds **2**, **4**, and **6** are given in Scheme 1.

When bishydrazone **1** reacts with selenium dioxide, only one hydrazone group is oxidized. An intermediate α-diazohydrazone **7** is transformed under the reaction conditions to olefin **2**, following pathway *a* or *b*. When the oxidant is Hg^{II} acetate, both hydrazone groups enter the reaction to give intermediate bisdiazo compound **8**, whose decomposition leads to either alkyne **4** or allene **6** (pathways *c* and *d*). The scheme proposed for the synthesis of alkyne **4** differs from that described in the literature, which includes the oxidation of intermediate 1-amino-1,2,3-triazole (Scheme 2).[6]

Scheme 1 proposed by us seems to be more likely. Special-purpose experiments demonstrated that triazole **9**, which was first isolated by us upon oxidation of bishydrazone **1** with sulfuryl chloride,[3] is not oxidized under both the reaction conditions described for the synthesis of alkyne **4** and the more drastic conditions (heating to 100 °C, $Hg(OAc)_2$ as the oxidant).

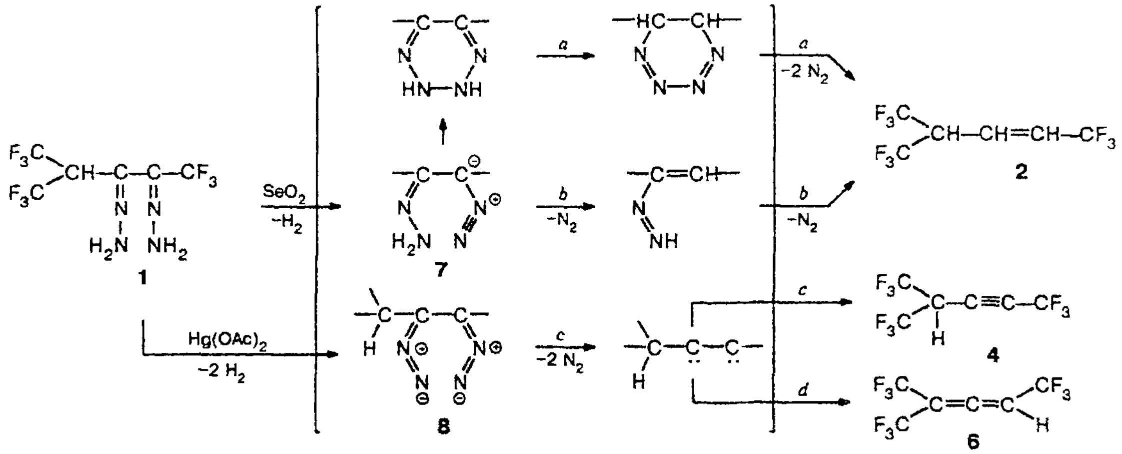


Experimental

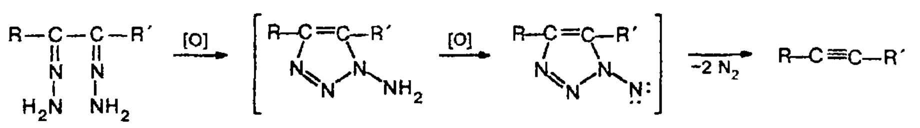
^1H and ^{19}F NMR spectra were recorded on a Perkin—Elmer 32 spectrometer (90 and 84.6 MHz, respectively) with Me_4Si and CF_3COOH as the external standards. IR spectra were recorded on a UR-20 spectrophotometer. Mass spectra (electron impact, 70 eV) were obtained on a VG-7070E chromato-mass spectrometer.

1,1,1,5,5,5-Hexafluoro-4-trifluoromethylpent-2-ene (2). A solution of bishydrazone **1** (11 g, 36 mmol) in 20 mL of anhydrous diglyme was added at 0 °C with stirring for 2 h to a mixture of SeO_2 (9 g, 80 mmol) and 50 mL of anhydrous diglyme. The reaction mixture was heated to ~20 °C and stirred for an extra 2 h until N_2 evolution ceased. The precipitate was filtered off and washed with anhydrous diglyme. The volatile compounds were condensed from the filtrate *in vacuo* (1 Torr) at ~20 °C into a trap cooled to −78 °C. The content of the trap was distilled on a column to obtain alkene **2** (5 g, 56%). B.p. 68—70 °C, IR, ν/cm^{-1}: 1700 s (C=C); 2990 w (CH). Found (%): C, 29.26; H, 1.22; F, 69.30. $C_6F_9H_3$. Calculated (%): C, 29.69; H, 1.21; F, 69.51. MS (EI, 70 eV),

Scheme 1



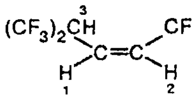
Scheme 2



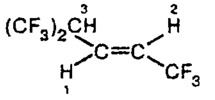
R = R′ = Me; R = Me, R′ = Ph; R = Me, Ph, CH_2Ph, R′ = H, Me

m/z (I_{rel} (%)): 246 $[M]^+$ (13.1), 227 $[M-F]^+$ (23.8), 207 $[M-F, HF]^+$ (3.3), 177 $[M-CF_3]^+$ (4.6), 163 $[C_4F_6H]^+$ (5.7), 158 $[C_4F_5H_3]^+$ (7.1), 132 $[C_3F_5H]^+$ (14.8), 113 $[C_3F_4H]^+$ (20.4), 95 $[M-(CF_3)_2CH]^+$ (25.7), 69 $[CF_3]^+$ (100), 51 $[CF_2H]^+$ (9.6).

^{1}H NMR, δ (a mixture of *cis*- and *trans*-isomers in a 1 : 2 ratio): 6.6—6.4 (ddq, H(1)); 6.3—6.2 (dq, H(2)); 3.8 (dhept, H(3), $J_{H(1)-H(2)}$ = 16 Hz, $J_{H(1)-H(3)}$ = 9 Hz, $J_{H(2)-CF_3}$ = 6 Hz, $J_{H(1)-CF_3}$ = 2 Hz, $J_{H(3)-C(CF_3)_2}$ = 8 Hz). ^{19}F NMR, δ: −8.9 (dm, 3 F, $J_{CF_3-H(2)}$ = 6 Hz); −8.4 (dm, 6 F, $J_{(CF_3)_2C-H(3)}$ = 8 Hz).



cis-**2**



trans-**2**

The residue of the reaction mixture (after volatile products were removed *in vacuo* (1 Torr)) was washed with water, dried with $MgSO_4$, and distilled *in vacuo*. Compound **3** (4 g, 17%) was obtained as a viscous yellowish liquid (b.p. 59—60 °C/1 Torr). The mass spectrum of compound **3** is a superposition of the spectra of seven isomers with similar molecular and fission ions but of different intensities. Mass spectrum (m/z (I_{rel} (%)) of the isomer whose content in the mixture is maximum (~60%): 650 $[M]^+$ (50%), 631 $[M-F]^+$ (5.5), 325 $[1/2\ M]^+$ (100), 305 $[1/2\ M-HF]^+$ (30.3), 245 $[C_6H_2F_9]^+$ (35.7), 225 $[C_6HF_8]^+$ (31.3), 193 $[C_5F_7]^+$ (40.3), 174 $[C_5F_6]^+$ (10.1), 160 $[Se_2]^+$ (15.7), 137 $[C_5F_4H]^+$ (10.2), 113 $[C_3F_4H]^+$ (40.3), 69 $[CF_3]^+$ (80).

1,1,1,5,5,5-Hexafluoro-4-trifluoromethylpent-2-yne (4). ***A.*** Bishydrazone **1** (9 g, 29 mmol) was carefully added in portions to Hg^{II} acetate (17 g, 53 mmol). The gas that evolved violently was successively passed through a trap cooled to −100 °C and a bubble counter. When evolution of the gas had ceased, the reaction mixture was heated on a boiling water bath for 2 h. The liquid condensed in the trap was distilled on a column. Compound **4** (9.4 g, 62%) was obtained, b.p. 49—50 °C. IR, ν/cm^{-1}: 2290 s (C≡C); 2995 w (CH). Found (%): C, 29.05; H, 0.35; F, 69.07. C_6HF_9. Calculated (%): C, 29.50; H, 0.40; F, 70.08. MS (EI, 70 eV), m/z (I_{rel} (%)): 244 $[M]^+$ (30.1), 225 $[M-F]^+$ (35.2), 205 $[M-F-HF]^+$ (2.3), 194 $[M-CF_2]^+$ (6.0), 175 $[M-CF_3]^+$ (4.3), 156 $[M-CF_4]^+$ (12.4), 137 $[M-CF_4-F]^+$ (10.2), 125 $[C_4F_4H]^+$ (5.0), 113 $[C_3F_4H]^+$ (30.1), 106 $[C_4F_3H]^+$ (20.3), 87 $[C_4F_2H]^+$ (5.1), 75 $[C_3F_2H]^+$ (10.4), 69 $[CF_3]^+$ (100), 56 $[C_3HF]^+$ (3.0), 37 $[C_3H]^+$ (4.9), 31 $[CF]^+$ (7.0). ^{19}F NMR, δ: −22.5 (dm, 3 F, J = 4.36 Hz); −8.4 (dm, 6 F, J = 6.54 Hz). ^{1}H NMR, δ: 4.48 (1 H, J = 6.6 Hz).

B. A mixture of bishydrazone **1** (5 g, 16 mmol) and HgO (8 g, 37 mmol) was heated on a boiling water bath until the gas evolution ceased. The gas was successively passed through a trap cooled to −100 °C and a bubble counter. The liquid in the trap was distilled in a column. Compound **4** (2.2 g, 50%) was obtained, b.p. 49—50 °C. Data from the ^{19}F NMR spectrum are identical to those known for an authentic sample. The solid residue of the reaction mixture was triply washed with ether. After washing, drying of the ethereal solution, and removal of the solvent on a rotary evaporator, the residue was distilled *in vacuo*. Compound **5** (1.7 g, 15%) was obtained, b.p. 60—61 °C/3 Torr).

The CM/MS of compound **5** showed a superposition of the spectra of seven isomers with similar molecular and fission ions but of different intensities. MS (m/z (I_{rel} (%)) of the isomer whose content in the mixture is maximum (~50%): 692 $[M]^+$ (3.1), 673 $[M-F]^+$ (5.3), 447 $[M-C_6H_2F_9]^+$ (30.3), 245 $[C_6H_2F_9]^+$ (40.0), 225 $[C_6HF_8]^+$ (20.2), 207 $[C_6H_3F_8]^+$ (15.2), 157 $[C_3H_3F_6]^+$ (22.3), 137 $[C_3H_2F_5]^+$ (10.2), 113 $[C_3F_4H]^+$ (100), 69 $[CF_3]^+$ (100).

1,1,1,5,5,5-Hexafluoro-4-trifluoromethylpenta-2,3-diene (6). ***A.*** A solution of bishydrazone **1** (5 g, 16 mmol) in 10 mL of anhydrous diglyme was added at ~20 °C with stirring for 0.5 h to a mixture of Hg^{II} acetate (15 g, 47 mmol) and 20 mL of anhydrous diglyme. The gas that evolved was successively passed through a trap cooled to −100 °C and a bubble counter. The mixture was stirred for 3 h until N_2 evolution ceased, and then the volatile products were recondensed *in vacuo* (1 Torr) at ~20 °C to a trap (−100 °C). The condensates collected in the traps were combined and distilled in a column. Compound **6** (2.4 g, 60%) was obtained, b.p. 52—54 °C. IR, ν/cm^{-1}: 2015 s (C=C=C); 3060 w (CH). Found (%): C, 29.15; H, 0.30; F, 69.20. C_6HF_9. Calculated (%): C, 29.50; H, 0.40; F, 70.08. MS (EI, 70 eV), m/z (I_{rel} (%)): 244 $[M]^+$(3.5), 225 $[M-F]^+$ (5.3), 205 $[M-F-HF]^+$ (1.4), 194 $[M-CF_2]^+$ (1.3), 175 $[M-CF_3]^+$ (2.2), 156 $[M-CF_4]^+$ (11.1), 137 $[M-CF_4-F]^+$ (7.0), 125 $[C_4F_4H]^+$ (2.1), 113 $[C_3F_4H]^+$ (7.4), 106 $[C_4F_3H]^+$ (8.0), 93 $[C_3F_3]^+$ (3.5), 87 $[C_4F_2H]^+$ (4.4), 75 $[C_3F_2H]^+$ (6.1), 69 $[CF_3]^+$ (100), 56 $[C_3FH]^+$ (6.1), 37 $[C_3H]^+$ (7.3), 31 $[CF]^+$ (11.3). ^{19}F NMR, δ: −15.1 (dm, 3 F, J = 4.4 Hz); −14.6 (dm, 6 F, J = 6.6 Hz). ^{1}H NMR, δ: 6.8 (m, 1 H, J = 4.4 Hz).

After removal of volatile products *in vacuo*, the reaction mixture was diluted with ether. The ethereal solution was filtered, and the mother liquor was washed with water and dried. After the solvent was removed on a rotary evaporator and the residue distilled *in vacuo*, a fraction (1.2 g) with b.p. 90—96 °C/1 Torr was obtained, *i.e.*, initial bishydrazone **1** (according to data from ^{19}F NMR and GC/MS).

B. Alkyne **4** (2 g) was heated in a Carius tube at 130 °C for 6 h (the reaction was considered completed when the signals of the F atoms of alkyne **4** disappeared in the ^{19}F NMR spectrum of the reaction mixture). On distillation of the tube contents compound **6** (1.7 g, 88%) was obtained, b.p. 51—52 °C. According to data from ^{1}H and ^{19}F NMR and MS, this compound is identical with the authentic sample.

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