Brief Communications

Polyfluorinated hydrazones in organic synthesis
1. Oxidation of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione dihydrazone with bromine

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A preparative one-step method for the synthesis of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione dihydrazone from perfluoro-4-methylpent-2-ene and hydrazine hydrate has been developed. Oxidation of this dihydrazone with bromine in water gives 3-diazo-1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2-one. The same product is obtained from 3-hydrazono-1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2-one under similar conditions.

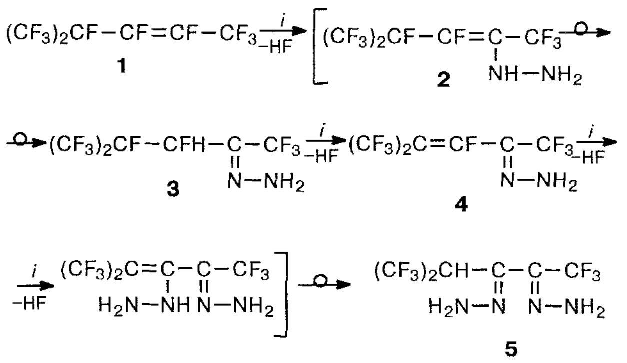
Key words: hydrolysis, oxidation, bromine, hydrazine hydrate, perfluoro-4-methylpent-2-ene, 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione dihydrazone, 3-hydrazono-1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2-one, 3-diazo-1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2-one.

Oxidation of *N*,*N*-unsubstituted hydrazones of aliphatic α-diketones as a result of complete dehydrogenation and elimination of nitrogen is known to lead to formation of dialkylacetylenes[1], whereas the behavior of their fluorine-containing analogs with respect to oxidizing agents was not investigated.

This paper opens a series of publications devoted to the oxidation of *N*,*N*-unsubstituted hydrazones of polyfluorinated aliphatic α-diketones with various oxidants and deals with the synthesis and oxidation of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2-dione dihydrazone (**5**) with bromine in water.

We have developed a one-step preparative method for synthesis of dihydrazone **5** from perfluoro-4-methylpent-2-ene (**1**) and hydrazine hydrate (Scheme 1) (for preliminary communication, see Ref. 2).

Scheme 1



i. $N_2H_4 \cdot H_2O$

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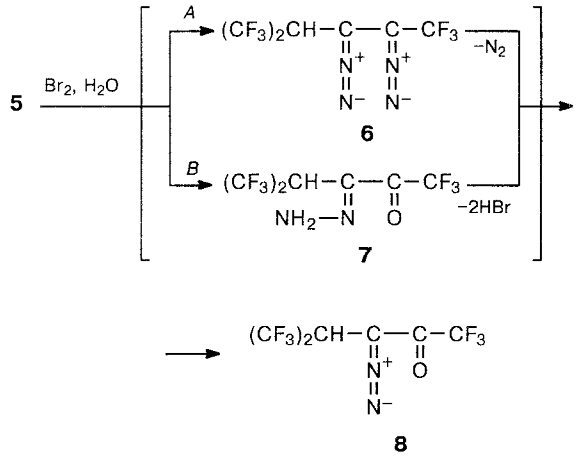
The process involves a number of successive steps: nucleophilic substitution of the vinyl fluorine atom, isomerization of the intermediate enehydrazine (**2**), dehydrofluorination of monohydrazone (**3**), and similar conversions of the olefin (**4**) with the second equivalent of hydrazine hydrate. It should be noted that compound **5** is the first representative of α-dihydrazones of aliphatic polyfluorinated α-diketones.

We have shown previously that oxidation of monohydrazones of polyfluorinated ketones with bromine in water (unlike their unfluorinated analogs) give the corresponding substituted diazomethanes in high yields[3].

The same oxidizing system proved to be applicable to α-dihydrazones.

Thus, the oxidation of dihydrazone **5** at room temperature affords 3-diazo-1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2-one (**8**) as the only product of the reaction (Scheme 2).

Scheme 2



Obviously, the formation of **8** occurs as a result of either partial hydrolysis of the intermediate — α-bisdiazomethane **6** (route *A*) or conversion of starting **5** to the monohydrazone **7** followed by its oxidation (route *B*). The latter route seems to be more probable, because the special experiment showed that ketohydrazone **7** (obtained by acidic hydrolysis of the dihydrazone **5**)[4] can be readily oxidized into the ketodiazomethane **8**, under conditions similar to those used for dihydrazone **5**.

$$7 \xrightarrow[H_2O]{Br_2} 8$$

The compounds of type **8** were synthesized earlier from not easily available trifluoromethyldiazomethane and a perfluorocarboxilic acid anhydride[5].

Experimental

The ^1H and ^{19}F NMR spectra were recorded using a Perkin-Elmer R-32 (90 and 84.6 MHz, respectively); TMS and CF_3COOH were used as external standards. IR spectra were recorded using an UR-20 instrument. Mass-spectra (EI, 70 eV) were obtained on a 7070 E chromato-mass spectrometer.

1,1,1,5,5,5-Hexafluoro-4-trifluoromethylpentane-2-dione dihydrazone (5). To a mixture of olefin **1** (40 g, 133 mmol) with monoglyme (80 mL), $N_2H_4 \cdot H_2O$ (26 g, 520 mmol) was added dropwise with stirring at 20—25 °C. The reaction mixture was stirred until homogenization was complete, then poured into water; the organic layer was separated, washed several times with water with shaking, and distilled *in vacuo* to give starting olefin **1** (9 g) in a trap (−78 °C) after drying with calcined $MgSO_4$ and product **5** (22 g, 73 %). Product **5** was obtained as a colorless liquid, b.p. 89—90 °C (1 Torr), which crystallized immediately, m.p. 85—86 °C (CCl_4). IR spectrum, (ν/cм$^{-1}$): 1580 and 1640 s (C=N); 2940 and 3000 m (CH); 3245, 3330, and 3445 s (NH_2). ^1H NMR spectrum (CCl_4, δ, ppm, a mixture of two isomers): 6.3 and 6.1 (br. s, 2 H, NH_2), 3.67 (hept, 1 H, $CH(CF_3)_2$, J = 10 Hz). ^{19}F NMR spectrum (CCl_4, δ, ppm): −14.7 and −13.8 (m, 3 F, CF_3), −11.3 (dq, 6 F, $(CF_3)_2CH$, J = 10 Hz). Mass spectrum, *m/z* [*I* (%)]: 304 $[M]^+$ (19.6); 288 $[M-NH_2]^+$(32.7); 287 $[M-NH_3]^+$(15.1); 285 $[M-F]^+$(13.5); 268 $[M-HF, NH_2]^+$(15.5); 259 $[M-N_3H_3]^+$(14.7); 256 $[M-HF, N_2]^+$(37.4); 248 $[M-2N_2]^+$(22.5); 193 $[(CF_3)_2CH-C{=}N-NH_2]^+$(66.7); 111 $[CF_3-C{=}N-NH_2]^+$(55.6); 69 $[CF_3]^+$(100); 42 $[C{=}N-NH_2]^+$(50.0). Found (%): C, 23.59; H, 1.66; N, 18.67; $C_6H_5F_9N_4$. Calculated (%): C, 23.68; H, 1.64; N, 18.42.

3-Diazo-1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2-one (8). To a mixture of the dihydrazone **5** (9.6 g, 31.4 mmol) with H_2O (50 mL) bromine (11.4 g, 71.5 mmol) was added dropwise with stirring. The mixture was stirred until HBr evolution ceased; the organic layer was separated, washed with 1% solution of $Na_2S_2O_3 \cdot 5H_2O$ and water, dried over $MgSO_4$, and distilled. Diazoketone **8** (4.4 g, 70 %) was obtained as a greenish-yellow liquid, b.p. 32 °C (40 Torr); and the residue contained the starting dihydrazone **5** (3 g). IR spectrum (ν/cм$^{-1}$): 1690 s (C=O); 2140 s ($-C{=}N^+{=}N^-$); 2970 w (CH). ^1H NMR spectrum (δ, ppm.): 3.6 (hept, 1 H, $CH(CF_3)_2$, J =7 Hz). ^{19}F NMR (δ, ppm.): −10.2 (dm, 6 F, $(CF_3)_2CH$, J =7 Hz); −2.9 (m, 3 F, CF_3). Found (%): C, 24.69; H, 0.57; F, 59.12 $C_6F_9HN_4$. Calculated (%): C, 25.00; H, 0.34; F, 59.37. Mass-spectrum, *m/z* [*I* (%)]: 288 $[M]^+$ (19.3); 269 $[M-F]^+$ (1.2); 260 $[M-N_2]^+$ (10.1); 193 $[M-COCF_3]^+$ (11.4); 97 $[COCF_3]^+$ (1.6); 69 $[CF_3]^+$ (100). Product **8** (6.5 g, 83 %) was obtained in a similar manner from α-ketohydrazone **7** (9.8 g, 33.8 mmol), water (20 mL), and Br_2 (6 g, 37.6 mmol) ; 2 g of the starting **7** remained unchanged.

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Synthesis of 1-(*N*-alkylnitraminomethyl)-3-nitroureas using *N*-alkylsulfamates

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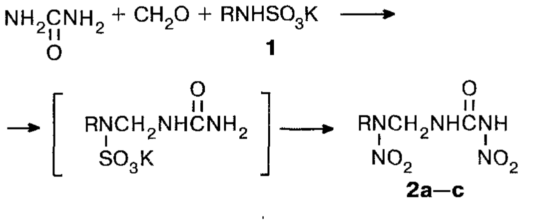
1-(*N*-alkylnitraminomethyl)-3-nitroureas were prepared by nitration of condensation products of urea with formaldehyde and *N*-alkylsulfamate.

Key words: 1-(*N*-alkylnitraminomethyl)-3-nitroureas, N-alkylsulfamates, condensation, nitration.

Previously[1] we demonstrated that the reaction of substitutive nitration of *N*-alkylsulfamates is a convenient method for the synthesis of cyclic nitramine derivatives. In the present work this reaction was used for the preparation of acyclic nitramines: 1-(*N*-alkylnitroaminomethyl)-3-nitroureas.

The literature contains spotty reports about condensation of urea with formaldehyde and sulfaminic acid derivatives[2,3]. The reaction products were not analyzed properly, and the physico-chemical properties were the basis for assigning a polymer structure for these compounds.

We carried out condensation reaction of urea with formaldehyde and primary *N*-alkylderivatives of sulfaminic acid in the form of potassium salts (**1**) in an aqueous medium, with simultaneous distillation of solvent *in vacuo*. The crystalline products do not have definite melting points. The attempts to isolate these products in pure state were unsuccessful. Therefore the product obtained was immediatly nitrated according to the technique we developed earlier.[1]



$$NH_2\underset{\underset{O}{\|}}{C}NH_2 + CH_2O + \underset{\mathbf{1}}{RNHSO_3K} \longrightarrow \left[R\underset{\underset{SO_3K}{|}}{N}CH_2NH\overset{\overset{O}{\|}}{C}NH_2 \right] \longrightarrow R\underset{\underset{NO_2}{|}}{N}CH_2NH\overset{\overset{O}{\|}}{C}\underset{\underset{NO_2}{|}}{N}H$$

2a—c

R = CH_3 (**2a**), Et (**2b**), Pr^i (**2c**)

The nitration products, (1-(*N*-alkylnitraminomethyl)-3-nitroureas (**2**)), were obtained in moderate yields. Their structure was confirmed by spectral data and by elemental analysis. In the case of **2a**, nitration of the terminal NH_2 group of urea is supported by the presence of characteristic coupling constant $^3J_{HCNH}$ = 5.7 Hz.

It is interesting to note that the condensation carried out in similar conditions, but at a different molar ratio of starting compounds (urea : formaldehyde : **1** = 1 : 2 : 2), followed by nitration also gives 1-(*N*-alkylnitraminomethyl)-3-nitroureas **2a—c**.

Experimental

NMR spectra were measured on Bruker AM-300 and Tesla BS-467 spectrophotometers (60 MHz) relative to TMS (^{13}C, ^1H) and CH_3NO_2 (^{14}N). IR spectra were measured in KBr pellets on UR-20 instrument.

General methods of synthesis of 1-(*N*-alkylnitraminomethyl)-3-nitroureas (2). To the solution of 10 mmol of urea in 10 mL water, 10 mmol of the corresponding *N*-alkylsulphamate 1 and 0.9 mL of 33%-formaline were added, pH was adjusted to 6.5 and the mixture was evaporated by a rotating evaporator at the temperature of boiling water. The residue thus obtained (2 g) was added to the mixture of 6 mL

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