A convenient method for the synthesis of polyfluorinated β-diimines

O. E. Petrova, M. A. Kurykin, and D. V. Gorlov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085. E-mail: mak@ineos.ac.ru

The higher internal perfluoroalk-2-enes react with ammonium hydroxide at atmospheric pressure to give the corresponding iminoenamines, whose further transformations yield heptafluoroacetylacetone analogs.

Key words: internal perfluoroolefins, ammonolysis; polyfluorinated iminoenamines, polyfluorinated β-diketones, synthesis; heptafluoroacetylacetone.

It was shown earlier that some linear internal perfluoroolefins such as perfluorobut-2-ene[1] and perfluoropent-2-ene[2] react with gaseous ammonia under pressure (autoclave) to give respective monoamine (in the former case) and 2-amino-4-iminoperfluoropent-2-ene (**1a**) (in the latter case). Iminoenamine **1a** thus obtained is the first bisaza analog of polyfluorinated β-diketones; on the one hand, it is a ligand of a new type and, on the other, it can be used for the synthesis of various heterocyclic compounds.

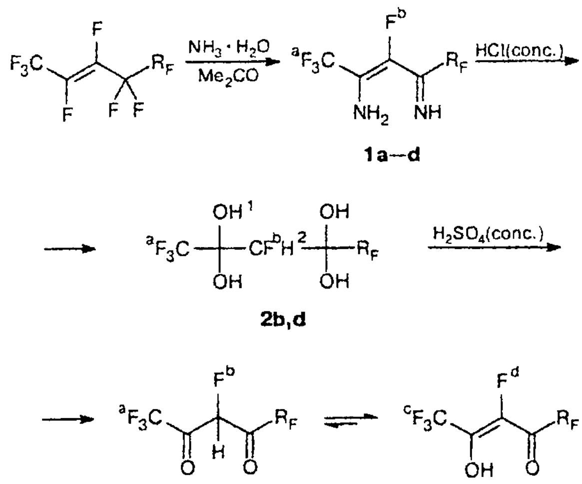
Thus, a study of the reactivity of compounds of type **1** is a long-term problem. However, the published[2] method for the synthesis of this iminoenamine is quite laborious because of the complexity of the equipment required.

For the purpose of modifying the described[2] procedure for the synthesis of β-diimines, we investigated the reactions of perfluoroalk-2-enes with ammonium hydroxide at atmospheric pressure. It was established that such linear internal perfluoroolefins as perfluoropent-2-ene, perfluorohex-2-ene, perfluorohept-2-ene, and perfluorooct-2-ene easily react with ammonium hydroxide in acetone at atmospheric pressure to give the corresponding iminoenamines **1a—d** (Scheme 1, Table 1). To homogenize the reaction mixture, a number of organic solvents (THF, monoglyme, acetone, and acetonitrile) were used, the highest yield being reached with acetone.

It should be noted that the ^1H NMR spectra of iminoenamines **1a—d** contain only one broadened singlet (Table 2), which is caused, on the one hand, by the degeneracy of structure **1** and, on the other, by rapid proton exchange.

The hydrolysis of compounds **1b,d** results in the corresponding diketone dihydrates **2b,d**, whose dehydration, as with heptafluoroacetylacetone dihydrate,[2] gives the corresponding diketones **3b,d**. According to ^1H and ^{19}F NMR spectral data, compounds **3b,d** at room temperature are mixtures of ketone and enol forms, the former being predominant. The content of enol at the instant of isolation varies from 14 to 28%, depending on the reaction conditions. With time, the enol : ketone ratio becomes equal to 90 : 10 and remains unchanged, which may suggest that an equilibrium is established.

Scheme 1



R_F = CF_3 (**a**), C_2F_5 (**b**), C_3F_7 (**c**), C_4F_9 (**d**)

Hence, the reaction of internal perfluoroolefins with aqueous ammonia can be recommended as a convenient method for the preparation of polyfluorinated iminoenamines, which, in turn, are the starting compounds for the synthesis of polyfluorinated β-diketones containing the fluorine atom in the α-position.

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Table 1. Yields and physicochemical characteristics of compounds **1b—d**, **2b**,**d**, and **3b**,**d**

Compound	Yield (%)	B.p./°C (p/Torr) [M.p./°C]	Found/Calculated (%) C	H	F	N	Molecular formula
1b	66.2	52—54 (31)	27.30 / 26.28	1.28 / 1.09	60.85 / 62.41	—	$C_6H_3F_9N_2$
1c	46.0	64 (32)	26.23 / 25.93	1.10 / 0.93	—	8.67 / 8.62	$C_7H_3F_{11}N_2$
1d	74.0	53—55 (9)	26.89 / 25.67	1.04 / 0.80	63.42 / 66.04	7.58 / 7.49	$C_8H_3F_{13}N_2$
2b	73.0	[66.0—67.5]	22.81 / 23.08	1.60 / 1.60	54.34 / 54.81	—	$C_6H_5F_9O_4$
2d	70.0	[64.0—65.0]	23.74 / 23.30	1.40 / 1.21	59.66 / 59.95	—	$C_8H_5F_{13}O_4$
3b	81.1	87	25.90 / 26.07	0.38 / 0.36	61.64 / 61.96	—	$C_6H_1F_9O_2$
3d	79.0	123	25.28 / 25.53	0.34 / 0.27	65.82 / 65.69	—	$C_8H_1F_{13}O_2$

Table 2. Spectral characteristics of compounds **1b—d**, **2b**,**d**, and **3b**,**d**

Compound, R_F	IR, ν/cm^{-1}	MS, m/z (I_{rel} (%))	NMR, δ (J/Hz) δ ^{1}H	NMR, δ (J/Hz) δ ^{19}F
1b, $CF_2^cCF_3^d$	1555 m, 1605 s, 1625 m	274 [M]$^+$ (66), 255 [$C_6H_3F_8N_2$] (8), 205 [$C_5H_3F_6N_2$] (32), 155 [$C_4H_3F_4N_2$] (100), 135 [$C_4H_2F_3N_2$] (55), 69 [CF_3] (42)	7.0 (s, 3 H, NH, NH_2)	−4.0 (d, 3 F_a); 8.7 (d, 3 F_d); 44.5 (d, 2 F_c); 96.0 (m, 1 F_b); J_{ab} = 17.5, J_{db} = 16.0, J_{bc} = 25.0
1c, $CF_2^cCF_2^dCF_3^e$	1555 m, 1605 s, 1625 m	324 [M]$^+$ (100), 305 [$C_7H_3F_{10}N_2$] (20), 255 [$C_6H_3F_8N_2$] (46), 155 [$C_4H_3F_4N_2$] (99), 136 [$C_4H_3F_3N_2$] (36), 135 [$C_4H_2F_3N_2$] (64), 69 [CF_3] (53)	7.7 (s, 3 H, NH, NH_2)	−4.0 (d, 3 F_a); 5.5 (t, 3 F_e); 41.5 (dq, 2 F_c); 51.5 (d, 2 F_d); 96.0 (m, 1 F_b); J_{ab} = 17.5, J_{cb} = 25.0, J_{db} = 22.0, J_{ce} = 10
1d, $CF_2^cCF_2^dCF_2^eCF_3^f$	1555 m, 1605 s, 1625 m	374 [M]$^+$ (38), 355 [$C_8H_3F_{12}N_2$] (10), 305 [$C_7H_3F_{10}N_2$] (15), 155 [$C_4H_3F_4N_2$] (100), 135 [$C_4H_2F_3N_2$] (34), 69 [CF_3] (40)	7.7 (s, 3 H, NH, NH_2)	−4.0 (d, 3 F_a); 5.2 (m, 3 F_f); 41.0 (dt, 2 F_c); 47.5 (dq, 2 F_d); 51.0 (m, 2 F_e); 96.0 (m, 1 F_b); J_{ab} = 17.5, J_{db} = 22.0, J_{cb} = 25.0, J_{ce} = 12.0, J_{df} = 11.0
2b, $CF_2^cCF_3^d$	1350 w, 3400 sh		7.7 (s, 4 H, H(1)); 5.4 (d, 1 H, H(2), $J_{F_b-H(2)}$ = 44.4)	2.9 (d, 3 F_d); 6.9 (d, 3 F_a); 48.9 (d, 2 F_c); 126.7 (m, 1 F_b); J_{db} = 7.0, J_{ba} = 14.0, J_{cb} = 17.0
2d, $CF_2^cCF_2^dCF_2^eCF_3^f$	1350 w, 3400 sh		8.1 (s, 4 H, H(1)); 5.8 (d, 1 H, H(2), $J_{F_b-H(2)}$ = 44.0)	4.0 (m, 3 F_f); 6.5 (d, 3 F_a); 44.2, 49.0 (m, 2 F_c + 2 F_d + 2 F_e); 126.5 (m, 1 F_b); J_{ab} = 12.0
3b, ketone: $CF_2^eCF_3^f$		276 [M]$^+$ (23), 207 [$C_5H_1F_6O_2$] (31), 157 [$C_4H_1F_4O_2$] (100), 119 [C_2F_5] (36), 88 [C_3HFO_2] (92), 69 [CF_3] (90)	6.7 (d, 1 H, J_{H-F_b} = 44.0)	1.3 (d, 3 F_a); 7.0 (d, 3 F_f); 46.5 (d, 2 F_e); 129.0 (dm, 1 F_b); J_{ab} = 10.5, J_{fb} = 4.0, J_{eb} = 24.0, J_{F_b-H} = 47.0
3b, enol: $CF_2^gCF_3^h$			11.52 (br.s, 1 H)	−1.1 (d, 3 F_c); 8.5 (d, 3 F_h); 46.5 (d, 2 F_g); 96.5 (m, 1 F_d); J_{cd} = 18.0, J_{gd} = 24.0, J_{hd} = 7.0
3d, ketone: $CF_2^eCF_2^fCF_2^gCF_3^h$		376 [M]$^+$ (6), 307 [$C_7H_1F_{10}O_2$] (22), 207 [$C_5H_1F_6O_2$] (18), 157 [$C_4H_1F_4O_2$] (100), 87 [$C_3H_1FO_2$] (39), 69 [CF_3] (69)	5.3 (d, 1 H, J_{H-F_b} = 44.0)	1.4 (d, 3 F_a); 6.1 (m, 3 F_h); 43.5 (m, 2 F_e); 48.0 (m, 2 F_f); 50.8 (m, 2 F_g); 128.2 (dm, 1 F_b); J_{ab} = 10.5, J_{F_b-H} = 47.0
3d, enol: $CF_2^iCF_2^jCF_2^kCF_3^l$			10.6 (br.s, 1 H)	−1.0 (d, 3 F_c); 6.1 (m, 3 F_l); 43.5 (m, 2 F_i); 47.3 (m, 2 F_j); 50.4 (m, 2 F_k); 96.0 (m, 1 F_d); J_{cd} = 17.0

Experimental

^1H and ^{19}F NMR spectra were recorded on a Bruker AC-200F spectrometer (200 and 188.3 MHz, respectively) with Me_4Si (^1H) and CF_3COOH (^{19}F) as the external standards. The ^{19}F and ^1H NMR spectra of compounds **2b,d** were recorded in diethyl ether, and the spectra of the other compounds were recorded without a solvent. IR spectra were recorded on a UR-20 spectrometer (thin film) in the range 400—4000 cm^{-1}. Mass spectra were obtained with a VG-7070 E spectrometer (ionizing voltage 70 eV). Elemental analysis of the compounds synthesized was performed at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

2-Amino-4-iminoperfluoropent-2-ene (1a), 2-amino-4-iminoperfluorohex-2-ene (1b), 2-amino-4-iminoperfluorohept-2-ene (1c), and 2-amino-4-iminoperfluorooct-2-ene (1d) (typical procedure). A 25% aqueous solution of ammonia (75 g, 1.12 mol) was added dropwise with continuous stirring to perfluoropent-2-ene (53.8 g, 0.21 mol) in 500 mL of acetone at 2—5 °C for 1.5 h. The reaction mixture was poured into water, and the lower layer was separated. The organic layer was washed with water (2×250 mL), dried over $CaCl_2$, and distilled to give compound **1a** (32.1 g, 68.2%), b.p. 119—120 °C, whose ^{19}F NMR spectrum was identical with that of the compound described earlier.[2] By analogy, compounds **1b**, **1c**, and **1d** were obtained.

2,2,4,4-Tetrahydroxy-3-H-perfluorohexane (2b) and 2,2,4,4-tetrahydroxy-3-H-perfluorooctane (2d). A mixture of compound **1b** (3.0 g, 11 mmol) and conc. HCl (30 mL) was refluxed for ~2 h. The products were extracted from the reaction mixture with ether (3×50 mL). The extract was dried over $CaCl_2$, and most of the solvent was removed. CCl_4 (200 mL) was added to the residue, and the precipitate that formed was separated, washed with CCl_4 (2×30 mL), and dried *in vacuo* to give compound **2b** (2.5 g, 73.0%), m.p. 68 °C. By analogy, compound **2d** was synthesized.

3-H-Perfluorohexane-2,4-dione (3b) and 3-H-perfluorooctane-2,4-dione (3d). A mixture of compound **2b** (2.1 g, 6.7 mmol) and conc. H_2SO_4 (9 mL) was refluxed in a round-bottomed flask equipped with a Liebig condenser for ~1 h. The distilled product was a mixture (1.5 g, 81.1%) of the ketone and enol forms (72 and 28%, respectively, according to ^{19}F NMR spectral data), b.p. 87 °C. By analogy, compound **3d** was obtained.

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