Brief Communications

Reaction of 3*H*-perfluoroalk-2-enes with ammonia

O. E. Petrova and M. A. Kurykin★

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

3*H*-Perfluoroalk-2-enes react with aqueous ammonia to form polyfluorinated iminoenamines, from which hexafluoroacetylacetone and its analogs were synthesized.

Key words: monohydroperfluoroolefins, 3*H*-perfluoroalk-2-enes, ammonolysis; polyfluorinated iminoenamines, synthesis; polyfluorinated β-diketones, hexafluoroacetylacetone.

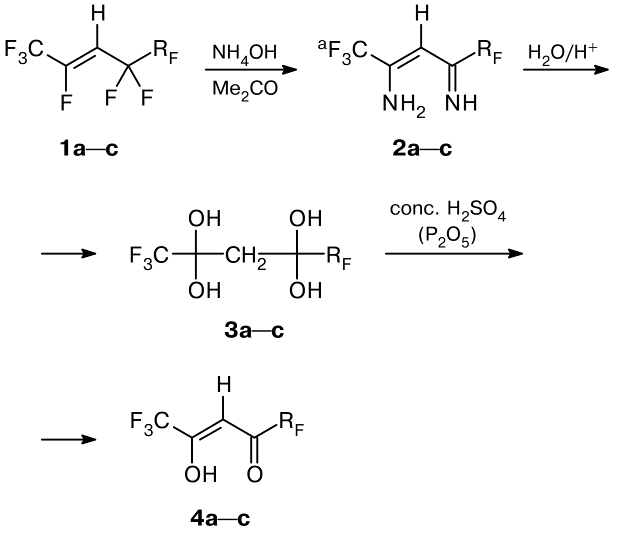
We have previously shown that perfluoroalk-2-enes (perfluoropentene, perfluorohexene, perfluoroheptene, and perfluorooctene) react with aqueous NH_3 to form iminoenamines, whose hydrolysis gives heptafluoroacetylacetone and its homologs.[1] It seemed reasonable to extend this reaction to 3*H*-perfluoroalk-2-enes,[2] which would provide earlier inaccessible bis-aza analogs of hexafluoroacetylacetone and its homologs.

We found that monohydroperfluoroalk-2-enes, such as 3*H*-perfluoropent-2-ene, 3*H*-perfluorohex-2-ene, and 3*H*-perfluorohept-2-ene (**1a**—**c**), also react readily with aqueous NH_3 in acetone under atmospheric pressure to form iminoenamines **2** (Scheme 1, Tables 1 and 2).

Compounds **2a**—**c** are mobile light-yellow liquids with chelate structure, as follows from their ^1H and ^{19}F spectra. The spectra of diimines **2a**—**c** contain one signal common for all three NH protons. Both trifluoromethyl groups in **2a** are magnetically equivalent.

We studied some chemical properties of the synthesized iminoenamines. Under hydrolysis (heating with conc. HCl), compounds **2a**—**c** are transformed into dihydrates of the corresponding diketones **3a**—**c**. Note

Scheme 1



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

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 149—150, January, 2001.

Table 1. Yields and elemental analysis data of compounds **2a—c**

Compound	Yield (%)	B.p. /°C	Found / Calculated (%) C	H	F	Molecular formula
2a	86.8	96—99	29.0 29.1	1.8 1.9	55.6 55.3	$C_5H_4F_6N_2$
2b	72.4	110—113	28.4 28.1	1.6 1.6	59.4 59.4	$C_6H_4F_8N_2$
2c	76.2	122—123	27.3 27.5	1.3 1.3	61.9 62.1	$C_7H_4F_{10}N_2$

Table 2. Spectral parameters of compounds **2a—c**

Compound, R_F	IR, ν/cm^{-1}	^{1}H NMR, δ (*J*/Hz) ^{19}F	^{1}H
2a, CF_3	1562, 1600, 1665, 3332, 3519	−2.5 (s, 6 F)	5.7 (s, 1 H); 8.7 (br.s, 3 H)
2b, $CF_2{}^bCF_3{}^c$	1560, 1604, 1659, 3335, 3519	−3.6 (s, 3F$_a$); 6.6 (t, 3 F$_c$, *J* = 2) 45.9 (q, 2 F$_b$, *J* = 2)	5.3 (s, 1 H); 7.9 (br.s, 3 H)
2c, $CF_2{}^bCF_2{}^cCF^d{}_3$	1557, 1606, 1665, 3336, 3517	−1.5 (s, 3 F$_a$); 5.0 (t, 3 F$_d$, *J* = 9); 45.0 (q, 2 F$_b$, *J* = 9); 51.0 (s, 2 F$_c$);	5.5 (s, 1 H); 8.1 (br.s, 3 H)

that dihydrate **3c** is stable below ~15 °C and melts with decomposition to diketone and water at higher temperatures. By contrast, dihydrates **3a**,**b** are colorless crystalline substances stable at a room temperature. This distinction in stability of **3a**,**b** and **3c** has previously been observed.[3]

β-Diketones **4a**,**b** can easily be prepared from the corresponding dihydrates **3a**,**b** by dehydration of the latter on heating with P_2O_5 or conc. H_2SO_4.[3]

Thus, we have proposed a method for synthesis of polyfluorinated iminoenamines and developed an alternative method for synthesis of hexafluoroacetylacetone and its homologs from internal polyfluoroalkenes (the known method for synthesis of polyfluorinated β-diketones is based on the Claisen condensation[3,4]).

Experimental

^{1}H and ^{19}F NMR spectra were recorded on a Bruker AC-200F spectrometer (200 and 188.3 MHz) relative to external standards Me_4Si and CF_3COOH, respectively. IR spectra were recorded on an UR-20 spectrometer (in thin layer) in a range of 400—4000 cm^{-1}.

3*H*-Perfluoroalk-2-enes were synthesized according to the published procedure.[2]

2-Amino-3-hydro-4-iminoperfluoropent-2-ene (2a), 2-amino-3-hydro-4-iminoperfluorohex-2-ene (2b), and 2-amino-3-hydro-4-iminoperfluorohept-2-ene (2c). An aqueous 25% ammonia solution (39 g, 0.57 mol) was added dropwise for 1 h with stirring to compound **1a** (23.5 g, 0.10 mol) in acetone (200 mL) at 2—5 °C. The reaction mixture was poured into water. The organic layer was separated, washed with water (2×100 mL), dried over $CaCl_2$, and distilled. Compound **2a** (19.3 g) was obtained. Compounds **2b** and **2c** were prepared similarly. For characteristics of aminoimines **2a—c**, see Tables 1 and 2.

3,3-Dihydroperfluoropentane-2,2,4,4-tetrole (3a) and 3,3-dihydroperfluorohexane-2,2,4,4-tetrole (3b). A mixture of compound **2a** (10.3 g, 0.051 mmol) and conc. HCl (30 mL) was refluxed for ~3 h. The reaction mixture was extracted with diethyl ether (4×20 mL), the extract was dried over $MgSO_4$, the solvent was evaporated, and the residue was recrystallized from CCl_4. Compound **3a** was obtained in 78.7% yield (9.6 g), m.p. 110—111 °C (*cf.* Ref. 5: ~90 °C (decomp.)). Compound **3b** was obtained similarly in 69.4% yield, m.p. 57—59 °C (*cf.* Ref. 3: 60—61 °C).

3,3-Dihydroperfluoroheptane-2,4-dione (4c). A mixture of compound **2c** (15.3 g) and conc. HCl (35 mL) was refluxed for ~2 h. After the reaction mixture was cooled to room temperature, the organic layer was separated, and the aqueous layer was extracted with ether (2×20 mL). The organic layer was combined with the extract, the major portion of the solvent was distilled off, and conc. H_2SO_4 (20 mL) was added to the residue. Compound **4c** was obtained by distillation in 69.5% yield (10.7 g), b.p. 103—105 °C (*cf.* Ref. 3: 103—104 °C).

Hexafluoroacetylacetone (4a) was prepared from compound **3a** by the previously described method[3] in 98.3% yield, b.p. 69—70 °C (*cf.* Ref. 4: 63—65 °C).

3,3-Dihydroperfluorohexane-2,4-dione (4b) was prepared from compound **3b** by the previously described procedure[3] in 89.4% yield, b.p. 85—87 °C (*cf.* Ref. 3: 85—86 °C).

References

1. O. E. Petrova, M. A. Kurykin, and D. V. Gorlov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1710 [*Russ. Chem. Bull.*, 1999, **48**, 1710 (Engl. Transl.)].
2. V. A. Petrov, G. G. Belen'kii, and L. S. German, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1591 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31** (Engl. Transl.)].
3. W. G. Schribner, B. H. Smith, R. W. Moshier, and R. E. Sievers, *J. Org. Chem.*, 1970, **35**, 1696.
4. A. L. Henne, M. S. Newman, L. L. Quill, and R. A. Staniforth, *J. Am. Chem. Soc.*, 1947, **69**, 1819.
5. H. Gilman, R. G. Jones, E. Bindschdler, D. Blume, G. Karmas, G. A. Martin, J. F. Nobis, J. R. Thirtle, H. L. Yale, and F. A. Yoeman, *J. Am. Chem. Soc.*, 1956, **78**, 2790.

Received January 26, 2000;
in revised form May 17 20000