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Communication

A new synthetic method for perfluorocycloimines

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Abstract

Pyrolysis of alkali salts of perfluoro(cycloamino-substituted acetic) acids provided perfluorocycloimines; a countercation effect was also studied.

Keywords: Perfluoropyrrolidino; Perfluoropiperidino; Perfluoromorphorino; Pyrolysis; Counter cation effect

Perfluoroazaalkenes are of interest as precursors for making various functional materials [1], for example engineering polymers, inert liquids, and chlorofluorocarbon (CFC) alternatives. Perfluorocycloimines are particularly useful reagents for introduction of perfluorocycloamino [2] and -imino [3] groups. Nonafluoro-2,3,4,5-tetrahydro-pyridine (**2b**) has already been synthesized by pyrolysis of undecafluoropiperidine with or without catalysts [4–6]. Although heptafluoro-3,4-dihydro-2*H*-pyrrole (**2c**) [4] and heptafluoro-3,6-dihydro-2*H*-[1,4]oxazine (**2a**) [5] were also prepared by such methods, their starting materials, that is nonafluoropyrrolidine and nonafluoromorpholine respectively, are obtained only in low yields by electrochemical fluorination and other reported methods [4,7].

We have already reported the pyrolysis of alkali metal salts of perfluoro(dialkylaminopropionic) acids. These pyrolyses easily provided perfluorovinylamines in excellent yields; they are difficult to prepare unless multistep syntheses are used [8,9]. In our continuing study, we now wish to describe an improved synthetic route to the perfluorocycloimines **2** by pyrolysis of alkali metal salts (**1**) of perfluoro(cycloamino-substituted acetic) acids.

Starting materials for the alkali salts **1** were easily prepared according to the previous literature [10]. The perfluoro(cycloamino-substituted acetic) acids were obtained by hydrolysis of the corresponding perfluoroacyl fluorides, which were prepared from methyl esters of cycloamino-substituted acetic acids by electrochemical fluorination. The alkali salts **1** were quantitatively obtained by neutralization of the perfluoro acids with alkali hydroxide in aqueous solution. A typical experimental procedure for the pyrolysis of the alkali salt **1** is as follows.

Potassium perfluoropyrrodinoacetate (**1c**, M = K), 2.48 g (7.44 mmol), was placed in a 50 ml round-bottomed flask connected with collection traps. Under reduced pressure (50 mmHg), the temperature of the flask was raised to 270 °C over a period of 25 min with a mantle heater and kept at this temperature for 30 min. Products collected in cold traps were fractionated by trap-to-trap distillation with a vacuum system equipped with Heise Bourdon tube and Televac thermocouple gauges. Compound **2c** was isolated in a trap cooled to −110 °C (60% yield) having passed through a trap at −40 °C. Spectral data obtained were as follows: IR (reciprocal centimetres) (gas), 1720 s, 1430 m, 1350 s, 1300 s, 1230 vs, 1150 s, 1110 w, 1040 s, 980 s; ^{19}F (NMR), $\delta = -130.49$ (2F, m, 4-F), 123.78 (2F, m, 3-F), −94.42 (2F, m, 5-F), −70.49 (F, m, 2-F); mass spectroscopy (MS) (EI, 20 eV) (*m/e* (species) intensity), 245 (M^+) 2.0, 226 ($M^+ - F$), 2.3, 195 ($M^+ - CF_2$) 55. (Compound **2b** was mentioned in Ref. [4]; however, there were no descriptions of physical properties except IR.)

The results of pyrolysis of the alkali salts **1** are summarized in Table 1. Compounds **2b** and **5c** were identified by IR, gas chromatography (GC), GC–MS, and ^{19}F NMR. Compound **5c** was characterized as follows: IR (gas) 189 cm^{-1} (CF=CF) (vs); ^{19}F NMR, $\delta = -132.60$ (8F, m, 3-F and 4-F), −115.94 (2F, m, CF=CF), −92.96 (8F, m, 2-F and 5-F); MS (EI, 20 eV) (*m/e* (species) intensity), 490 (M^+) 19, 471 ($M^+ - F$) 19.) Other products shown in Table 1 were determined by comparison with the spectroscopic data of authentic samples prepared according to the previous papers [5,8]. All samples for analyses were collected with the vacuum line systems.

Potassium salts were smoothly decomposed above 270–300 °C to afford only the perfluorocycloimines **2** in 60%–

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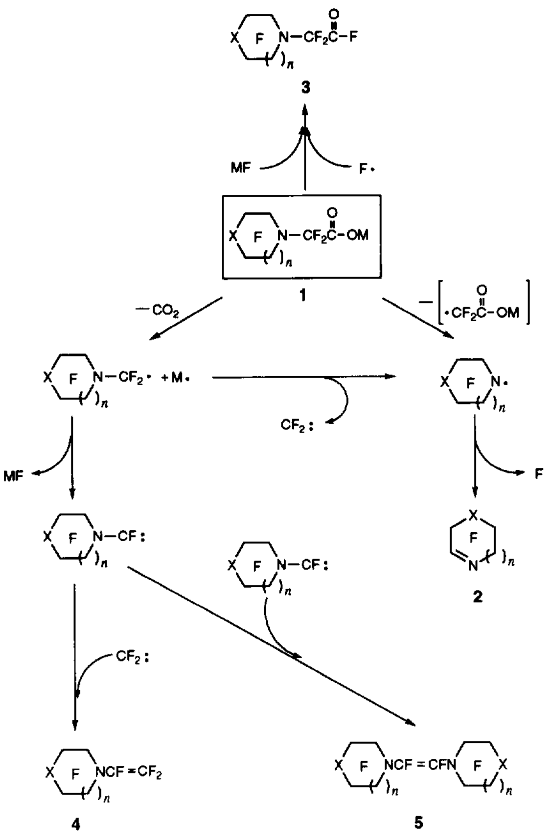
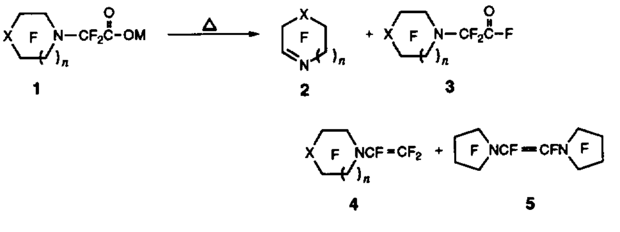
80% yield (entries 1, 4), except for the potassium salt **1c** (M = K) which provided perfluoropyrrolidinovinylamine (**4c**) as a side product (entry 6). Products of pyrolysis of sodium and lithium salts exhibited different tendencies from those of potassium salts: both the sodium salt **1a** (M = Na) and the lithium salt **1a** (M = Li) provided the perfluoroacyl fluoride **3a** together with the cycloimine **2a** (entries 2, 3). Pyrolysis of sodium salts of other ring systems (**1b**, M = Na; **1c**, M = Na) gave the cycloimines (**2b** and **2c**) and the perfluoroacyl fluorides (**3b** and **3c**). These reactions also generated perfluoroazaalkenes, that is perfluoro-(piperidinovinyl)amine (**4b**) and perfluoro-[bis(pyrrolidino)ethylene] (**5**), as a side product (entries 5, 7). Perfluorocycloimines **2** were purified with the vacuum line system, while other products could not be isolated as a pure compound.



Scheme 1. Pyrolysis mechanism of the alkali salts (**1**) of perfluoro(cycloamino-substituted acetic) acids.

Pyrolysis of the alkali salts (**6**) of perfluoro(2-dialkylaminopropionic) acids gave perfluorovinylamines as principal products independently of their countercations [8]. Thermal decomposition points of the alkali salts revealed different orders between the alkali salts **6** (K > Na > Li) and the alkali salts **1** (Na > K > Li). Judging from tendencies of side products and thermal decomposition points, the following decomposition mechanism can be proposed for the alkali salts **1** as shown in Scheme 1. A plausible explanation is available as described below: two initial homolysis steps for formation of the perfluorocycloimines **2** are considered. A predominant step is cleavage of the C–C bond at the position α to the carbonyl group, while cleavage of the C–N bond of the acyclic part also occurred because products having a trifluoroacetyl group were detected by IR. The perfluoroazaalkenes **4** are obtained from fluoro(perfluorocycloamino)methylene with difluoromethylene and the perfluoroazaalkene **5** is obtained by the coupling of two fluoro-(perfluorocycloamino)methylene units. The perfluoroacyl fluorides **3** are obtained by reaction with fluorine radicals, which are generated by not only formation of the perfluorocycloimines **2** but also decomposition of the starting materials **1**. Since the possibility of reaction of metal fluorides with the starting

Table 1
Pyrolysis of the alkali salts (**1**) of perfluoro(cycloamino-substituted acetic) acids



a: X = O, n = 1; b: X = CF_2, n = 1; c: X = CF_2, n = 0

Entry	$(R_F)_2N$	M	Temperature (°C)	Products and yields (%)
1	**1a**	K	280–290	**2a** (71.2)
2	**1a**	Na	300–320	**2a** (20.9), **3a** (24.0)
3	**1a**	Li	250–270	**2a** (15.7), **3a** (5.7)
4	**1b**	K	280–290	**2b** (81.0)
5	**1b**	Na	290–310	**2b** (26.2), **3b** (17.5), **4b** (3.5)
6	**1c**	K	280–300	**2c** (59.9), **4c** (20.5)
7	**1c**	Na	300–320	**2c** (9.8), **3c** (19.5), **5c** (10.3)

materials **1** may not be denied completely, the mechanism of formation of the perfluoroacyl fluoride **3** is still under investigation.

In conclusion, starting from easily available perfluoro(cycloamino-substituted acetic) acids, we have synthesized several perfluorocycloimines in high yield. Studies of the reactions of these cycloimines with various substrates are in progress.

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