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Amination of octafluoronaphthalene in liquid ammonia 2,6- and 2,7-Diaminohexafluoronaphthalenes selective preparation

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Abstract

Monoamination of octafluoronaphthalene by liquid ammonia affords 2-aminoheptafluoronaphthalene mainly (isolated yield 85–90%). Diamination of octafluoronaphthalene or amination of 2-aminoheptafluoronaphthalene affords a mixture of isomeric 1,6-, 1,7-, 2,6-, and 2,7-diaminohexafluoronaphthalenes with considerable prevalence of the 2,7-isomer (~70%), thus being the first example of the predominant substitution at position 7 in 2-substituted polyfluoronaphthalenes. The 2,7/2,6 ratio of 2-*X*-heptafluoronaphthalene ($X = {}^{-}NH$, NH_2 and NHAc) amination diminishes with the decrease of electron-donating effect of the substituent; 2,7-diaminohexafluoronaphthalene forms in the reactions of 2-aminoheptafluoronaphthalene or octafluoronaphthalene with excess of $NaNH_2$ in liquid ammonia and 2,6-diaminohexafluoronaphthalene—in the reaction of 2-acetylamidoheptafluoronaphthalene with liquid ammonia followed by acetylamido group hydrolysis. The method of the selective preparation of these diamines based on the reversible transformation of amino group and a convenient technique of their high purity isolation by complexation with crown ether have been elaborated.

Keywords: Octafluoronaphthalene; Diaminohexafluoronaphthalenes; Liquid ammonia; Aminodefluorination; Nucleophilic substitution; Regioselectivity

1. Introduction

The known reactions of octafluoronaphthalene (**1**) with both charged and neutral nucleophiles [1,2] proceed mainly by fluorine displacement at the β-carbon atom (β/α > 9/1). Nucleophilic substitution in β-*X*-heptafluoronaphthalenes or insertion of two substituents into **1** results in the mixture of β,β-disubstituted isomers with the 2,6 being predominant (>75%) [3–8]. Only some of the individual 2,6-disubstituted hexafluoronaphthalenes have been reported (2-methoxy-6-thiomethoxyhexafluoronaphthalene [3], 2-methoxy-6-piperidinohexafluoronaphthalene [4], 1,3,4,5,7,8-hexafluoronaphthalene [5], perfluoro-2,6-diphenylnaphthalene [6]), while 2,7-isomers have not been isolated at all. Diamination of **1** has not been reported, though polyfluoroaromatic diamines and diaminohexafluoronaphthalenes in particular are prospective monomers for condensation polymers, whose physicochemical characteristics depend strongly on the framework as well as presence of fluorine atoms [9].

We have shown [10] the use of liquid ammonia as a reagent/medium system provides for selective preparation of mono- and diaminopolyfluoro(get)arenes with high purity and yields. The present work goals are (i) the investigation of the direct amination of **1** by liquid ammonia or its solutions as the shortest route to diaminohexafluoronaphthalenes; (ii) the development of the methods for 2,6- and 2,7-diaminohexafluoronaphthalenes selective preparation based on the reversible transformation of 2-aminoheptafluoronaphthalene (**2a**); (iii) the elaboration of the procedure for product isolation and purification based on complexation with crown ether.

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Table 1
Experimental conditions and product yields for reactions of octafluoronaphthalene (**1**) with amination reagents

Entry	Reactant amounts		Reaction conditions		Product mixture yields (g)	Product mixture composition (%, GC data)[a]							Product isolated yields (g/% calculated to **1**); purification method
	1 (g)	NH_3 (ml)	Temperature (°C, ±5)	Time (h)		**1**	**2a**	**2b**	**3a**	**3b**	**3c**	**3d**	
1	10.0	50 (liq)	15	9	9.5		95	2	<1				**2a** 8.5/87; crystallization
2	10.0	50 (liq)	90	24	8.0		1		71	12	10	3	**3a** + **3b** (9:1) 6.2/63; complexation
3	5.0	30 (aq)	120	5	4.8	19	72	6	2	<1			
4	5.0	30 (aq)	120	8	4.7	5	81	6	5	1			**2a** 3.0/61; complexation
5[b]	10.0	60 (aq)	130	48	8.6				62	16	8	3	**3a** + **3b** (7:2) 5.9/60; complexation
6[c]	5.0	30 (aq)	110	5	4.7		81	9	1				
7[c]	5.0	30 (liq)	90	5	4.6	4	45		31	5	7	2	
8[d]	2.0	80 (liq)	−55	0.15	1.9	1	64						**2a** 1.0/52; sublimation
9[e]	2.0	80 (liq)	−55	1	1.8				72		4		**3a** 1.1/55; complexation

[a] Average values from the results of at least three experiments, the error for the main products does not exceed 2%.

[b] The product mixture contains three additional diaminopentafluoronaphthalenes ~7% in total (M 248, GC–MS data).

[c] EtOH (30 mL) was used as co-solvent. The product mixture contains additional isomeric aminoethoxyhexafluoronaphthalenes ~5% in total (M 295, GC–MS data).

[d] Na (0.35 g) was used for $NaNH_2$ preparation ($NaNH_2$/**1** mole ratio = 2). The product mixture also contains *N,N*-bis(heptafluoro-2-naphthyl)amine, 7% (M 521), 2-amino-7-(N-heptafluoro-2-naphthylamino) naphthalene, 8% (M 518) (GC–MS data), and non-volatile compounds (~20%).

[e] Na (0.85 g) was used for $NaNH_2$ preparation ($NaNH_2$/**1** mole ratio = 5). The product mixture also contains non-volatile compounds (~25%).

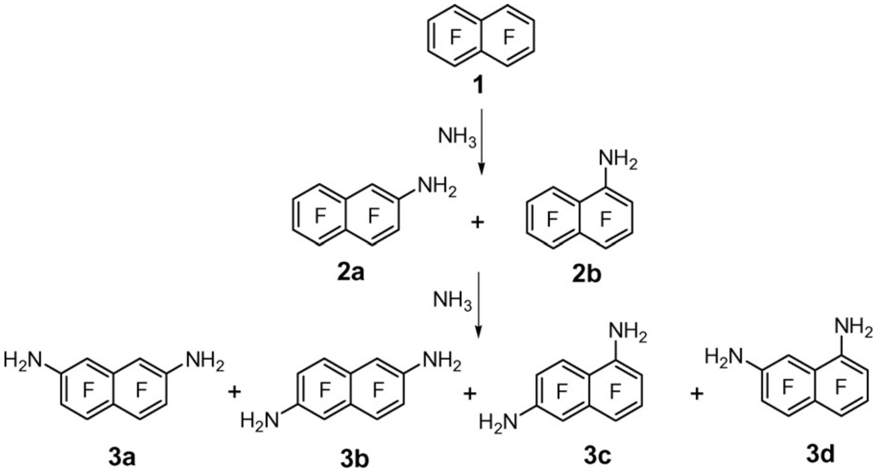
2. Results and discussion

2.1. Amination of octafluoronaphthalene by liquid ammonia and its solutions

The processes were carried out in a steel autoclave under pressure to keep ammonia as a liquid up to ~120 °C ($t_{crit}NH_3 = 132°C$ [11]). Both mono- and diamination of **1** by liquid ammonia can be realized selectively due to the large difference in temperature conditions required (Entries 1 and 2, Table 1, Scheme 1). Proportion of β/α substitution in monoamination of **1** is 95/2, and so the major product – **2a** – has been isolated from the product mixture with yield >85% by crystallization. Thus, this mode of **2a** preparation has a clear advantage towards the known method (via amination of **1** by aqueous-ethanolic ammonia), which is characterized by low yield (44%) [4].

Under the optimal conditions of **1** bis-aminodefluorination (Entry 2, Table 1, Scheme 1) content of isomeric diaminohexafluoronaphthalenes is ≥96%, at that 2,7-diaminohexafluoronaphthalene (**3a**) is the major product. The proportions of 2,6-diaminohexafluoronaphthalene (**3b**) and 1,6-diaminohexafluoronaphthalene (**3c**) in the product mixture are considerably lower, and the minor product is 1,7-diaminohexafluoronaphthalene (**3d**). Aminodefluorination of **2a** affords the same result (Entry 1, Table 2), *i.e.* the ratio of diamines **3a–d** does not depend on the identity of starting compound (**1** or **2a**). Isomeric diamines **3a–d** obtained for the first time have been isolated and characterized.

Aqueous or ethanolic ammonia are widespread amination systems for polyfluoroarenes in spite of their lower efficiency as compared with liquid ammonia ([10] and references therein) caused by hydrogen bonding [12]. Actually, amination of **1** by aqueous ammonia occurs at harder conditions. The reaction becomes efficient only at 120 °C, however under this temperature, mono- and diamination processes cannot be separated. Thus, diamination is appreciable at 80% conversion of **1** (Entry 3, Table 1), and an increase of the reaction duration



Scheme 1.