

The first synthesis and X-ray structures of polyfluorinated 1,2-, 2,3- and 2,4a-dihydro-1,3-diazafluorenes

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Abstract

Acetic acid-catalyzed condensation of 2-amino-3-(1-imino-2,2,2-trifluoroethyl)-1,1,4,5,6,7-hexafluoroindene (**1b**) with acetone and cyclopentanone gives 5,6,7,8,9,9-hexafluoro-2,2-dimethyl-4-trifluoromethyl-2,3-dihydro-1,3-diazafluorene (**2a**) and 5,6,7,8,9,9-hexafluoro-4-trifluoromethyl-2,3-dihydro-1,3-diazafluorene-2-spiro-1'-cyclopentane (**3a**) together with small amounts of 5,6,7,8,9,9-hexafluoro-2,2-dimethyl-4-trifluoromethyl-1,2-dihydro-1,3-diazafluorene (**2b**) and 5,6,7,8,9,9-hexafluoro-4-trifluoromethyl-1,2-dihydro-1,3-diazafluorene-2-spiro-1'-cyclopentane (**3b**), respectively. When acted upon by $(\text{CH}_3)_2\text{SO}_4$ compounds **2**, **3** were converted into corresponding fluorine-containing 1-methyl-1,2-dihydro-1,3-diazafluorenes **6**, **7**. 4a-Chloro-5,6,7,8,9,9-hexafluoro-2,2-dimethyl-4-trifluoromethyl-2,4a-dihydro-1,3-diazafluorene (**8**) has been synthesized by the interaction of compound **2** with SOCl_2 . Solution of compound **2** as well as **8** in $\text{CF}_3\text{SO}_3\text{H}\text{-CD}_2\text{Cl}_2$ generated 5,6,7,8,9,9-hexafluoro-2,2-dimethyl-4-trifluoromethyl-1,2,3,4-tetrahydro-1,3-diazafluorene-4-yl cation (**2c**). The structures of compounds **2**, **3**, **6–8** have been determined by single crystal X-ray diffraction.

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1. Introduction

Fluorine-containing en-amino-imines can be used for the synthesis of nitrogen containing heterocyclic systems. Thus, the reaction of polyfluorinated en-amino-imines with aromatic aldehydes is known to give 2-aryl-4,6-bis(perfluoroalkyl)pyrimidines [1]. The condensation of 2-amino-4-iminoheptafluoropent-2-ene with anhydrides and chloroanhydrides of perfluorinated alkanic acids leads to the formation of 5-fluoro-2,4,6-tris(perfluoroalkyl)-pyrimidines [2]. 2-Alkyl(aryl)-5,6,7,8,9,9-hexafluoro-4-trifluoromethyl-1,3-diazafluorenes [3] and fluorine-containing derivatives of 2-selena-1,3-diazafluorene [4] have been synthesized by the interaction of 2-amino-3-(1-imino-2,2,2-trifluoroethyl)-1,1,4,5,6,7-hexafluoroindene (**1**) with anhydrides and chloroanhydrides of carboxylic acids [3] and SeCl_4 [4], respectively. 1-Alkyl-5,6,7,8,9,9-hexafluoro-4-trifluoromethyl-1,2,3,4-tetrahydro-1,3-diazafluorenes have been prepared by the isomerization of 2-dialkylamino-(1-imino-2,2,2-

trifluoroethyl)-1,1,4,5,6,7-hexafluoroindenes in the presence of $\text{N}(\text{C}_2\text{H}_5)_3$ or $(\text{CH}_3)_2\text{SO}$ [5]. Furthermore, for the first time X-ray structures of 1,3-diazafluorene derivatives were defined [3].

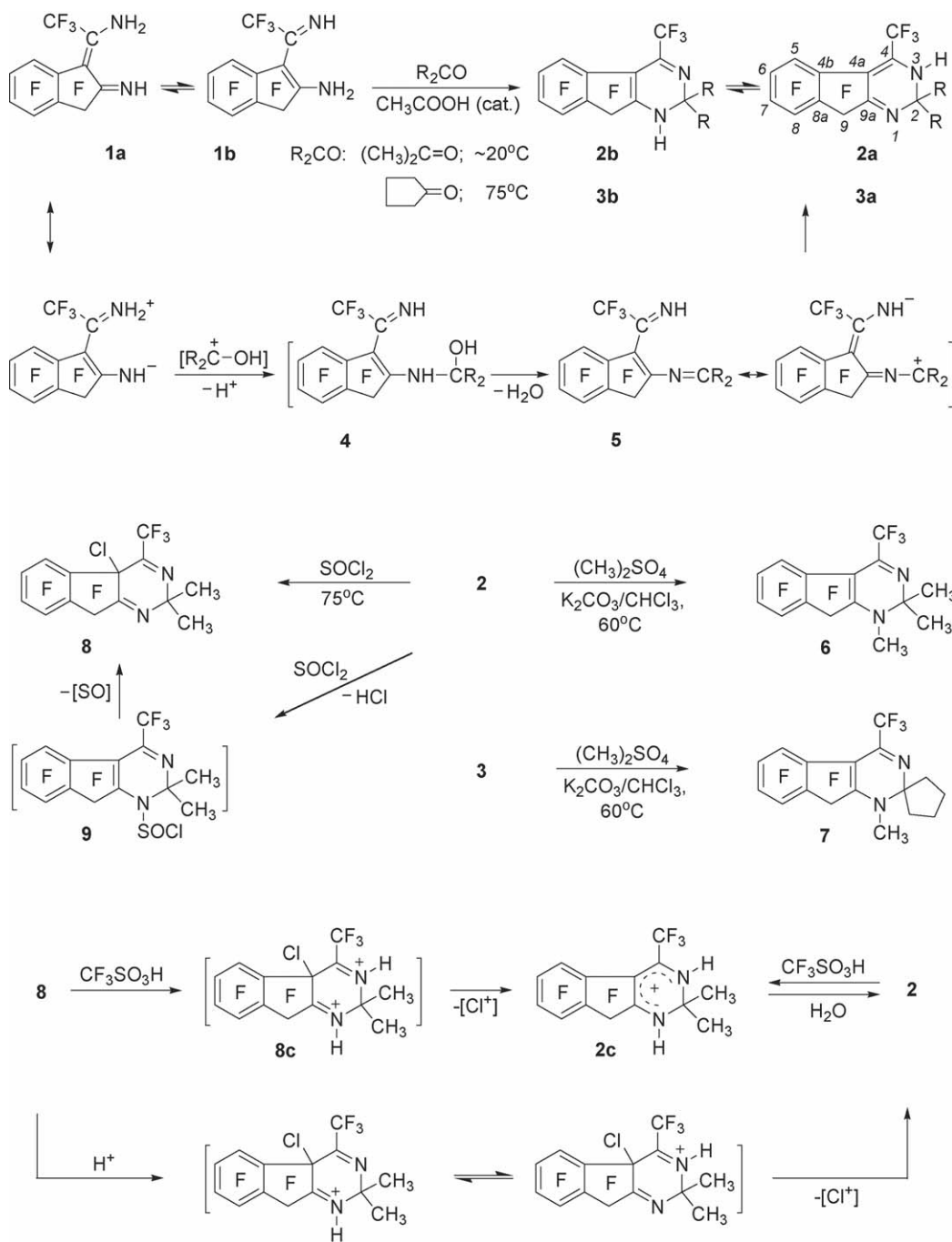
Thus, first fluorine-containing 4-trifluoromethyl-1,3-diazafluorenes [3] and their 1,2,3,4-tetrahydroderivatives [5] were synthesized and characterized. At the same time polyfluorinated dihydro-1,3-diazafluorenes are unknown. In this connection, for logical progress in chemistry of this type of compounds it seemed reasonable to study the reaction of compound **1** with alkanones for synthesis of polyfluorinated derivatives of dihydro-1,3-diazafluorenes. This work describes the reactions of compound **1** with acetone and cyclopentanone and transformations of condensation products under the action of $(\text{CH}_3)_2\text{SO}_4$ and SOCl_2 . The work describes X-ray structures of prepared fluorine-containing 4-trifluoromethyl-1,2-, 2,3- and 2,4a-dihydro-1,3-diazafluorenes as well.

2. Results and discussion

In the presence of catalytic amounts of acetic acid, compound **1** reacts with acetone at room temperature to give 5,6,7,8,9,9-hexafluoro-2,2-dimethyl-4-trifluoromethyl-2,3-dihydro-1,3-dia-

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Scheme 1.

zafluorene (**2a**). The reaction mixture also contains small amounts of 5,6,7,8,9,9-hexafluoro-2,2-dimethyl-4-trifluoromethyl-1,2-dihydro-1,3-diazafluorene (**2b**). Acetic acid-catalyzed condensation of compound (**1**) with cyclopentanone proceeds under more rigid conditions to form 5,6,7,8,9,9-hexafluoro-4-trifluoromethyl-2,3-dihydro-1,3-diazafluorene-2-spiro-1'-cyclopentane (**3a**) together with 5,6,7,8,9,9-hexafluoro-4-trifluoromethyl-1,2-dihydro-1,3-diazafluorene-2-spiro-1'-cyclopentane (**3b**) (Scheme 1).

The probable mechanism for the condensation of compound **1** with alkanones can be formulated as shown in Scheme 1. At first protonated form of alkanone reacts with compound **1** to

give adduct **4**; this assumption is in accordance with data for orientation of methylation of en-amino-imine **1** under the action of $(\text{CH}_3)_2\text{SO}_4$ [6]. Dehydration of adduct **4** and subsequent intramolecular cyclization of product **5** yields compounds **2**, **3**. It should be noted that compounds **2**, **3** exist in the solid state as **2a** and **3a** while in solution there is the equilibrium of tautomers **a** and **b** similar to that for en-amino-imine **1** [6]. These data are in agreement with gas phase DFT (PBE/TZ2P, PRIRODA program [7]) calculations, which show that tautomer **2a** is more stable by $2.8 \text{ kcal mol}^{-1}$ than **2b**.

When acted upon by $(\text{CH}_3)_2\text{SO}_4$ compounds **2**, **3** were converted into 5,6,7,8,9,9-hexafluoro-1,2,2-trimethyl-4-tri-

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