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Formation of Fluoroderivatives of 1,2,3,4-Tetrahydro-1,3-diazafluorene from 2-Dialkylamino-3-(1-imino-2,2,2-trifluoroethyl)hexafluoroindenes

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Abstract—2-Dimethylamino-3-(1-imino-2,2,2-trifluoroethyl)hexafluoroindene in the presence of DMSO or NEt_3 undergoes isomerization into 1-methyl-4-trifluoromethyl-5,6,7,8,9,9-hexafluoro-1,2,3,4-tetrahydro-1,3-diazafluorene, and from 1-(1-amino-2,2,2-trifluoroethylidene)octafluoroindane by the treatment with water solution of $NHEt_2$ 2-methyl-4-trifluoromethyl-1-ethyl-5,6,7,8,9,9-hexafluoro-1,2,3,4-tetrahydro-1,3-diazafluorene was obtained.

We studied formerly reactions of polyfluorinated 1-alkylideneindanes and 3-alkylindenes with ammonia and aliphatic amines [1]. In particular, it was established that 1-(1-amino-2,2,2-trifluoroethylidene)-octafluoroindane (**I**) treated with water solution of $NHMe_2$ afforded 2-dimethylamino-3-(1-imino-2,2,2-trifluoroethyl)hexafluoroindene (**II**) [1].

In the present study we demonstrated that unlike reaction with $NHMe_2$ under the treatment with $NHEt_2$ enamine **I** instead of expected 2-diethylamino-3-(1-imino-2,2,2-trifluoroethyl)hexafluoroindene (**III**) yielded its cyclic isomer, 2-methyl-4-trifluoromethyl-1-ethyl-5,6,7,8,9,9-hexafluoro-1,2,3,4-tetrahydro-1,3-diazafluorene (**IV**) (Scheme 1).

It is presumable that in this reaction enamine **I** under the action of $NHEt_2$ first gives rise to compound **III** which in the presence of a base transforms into diazafluorene **IV**. This assumption is not at variance with the known fact that dimethylamino derivative **II** in NEt_3 solution undergoes cyclization into 1-methyl-4-trifluoromethyl-5,6,7,8,9,9-hexafluoro-1,2,3,4-tetrahydro-1,3-diazafluorene (**V**).

One possible way of compound **V** formation may be the following (Scheme 1, cf. [2]). In compound **II** (in a resonance form **IIa**) under the action of a base might occur proton abstraction from the dimethylamino group providing anion **VI**. Addition of a H^+ to the nitrogen of iminotrifluoroethyl group of anion **VI** results in ion **VII** which isomerizes into a zwitterion **VIII** and then through intramolecular cyclization affords diazafluorene **V**. It should be noted that in keeping with Woodward–Hoffmann rules and Evans principle the thermal transformation of compound **II** (resonance form **IIa**) into intermediate **VIII** is permissible and may occur by concerted mechanism as 1,5-sigmatropic proton shift ("aromatic" transition state); the 1,6-shift to nitrogen ("antiaromatic" transition state) is forbidden.

Besides a possibility of a process occurring by a chain radical mechanism cannot be disregarded. Actually, since the reaction was carried out in air the oxidation of anion **VI** with the air oxygen might occur providing radical **IX**. The latter may undergo intramolecular cyclization into radical **X** which abstracts a hydrogen atom from a dimethylamino group of compound **II** thus affording compound **V** and regenerating the radical **IX**. Apparently the radical mechanism is not at variance with the easier cyclization of diethylamino derivative **III** as compared to dimethylamino derivative **II**, and also with the formation of diazafluorene **V** at storage of compound **II** solution in dichloromethane containing DMSO.

2-Methylamino-3-(1-methylimino-2,2,2-trifluoroethyl)hexafluoroindene (XI) in the NEt_3 medium does not change under conditions that bring about cyclization of its isomer **II**, and also 2-ethylamino-3-(1-methylimino-2,2,2-trifluoroethyl)hexafluoroindene (**XII**), isomer of compound **III**, does not suffer any changes under conditions of reaction between enamine **I** and aqueous diethylamine. Compounds **XII** and **XI** were obtained by reaction of perfluoro-1-ethylideneindane **XIII** with excess aqueous NH_2Et [1] and NH_2Me respectively (Scheme 2).

The composition and structure of compounds obtained were confirmed by elemental analysis and spectral characteristics. The assignment of signals in the ^{19}F NMR spectra was carried out proceeding from the chemical shifts, fine structure, and integral

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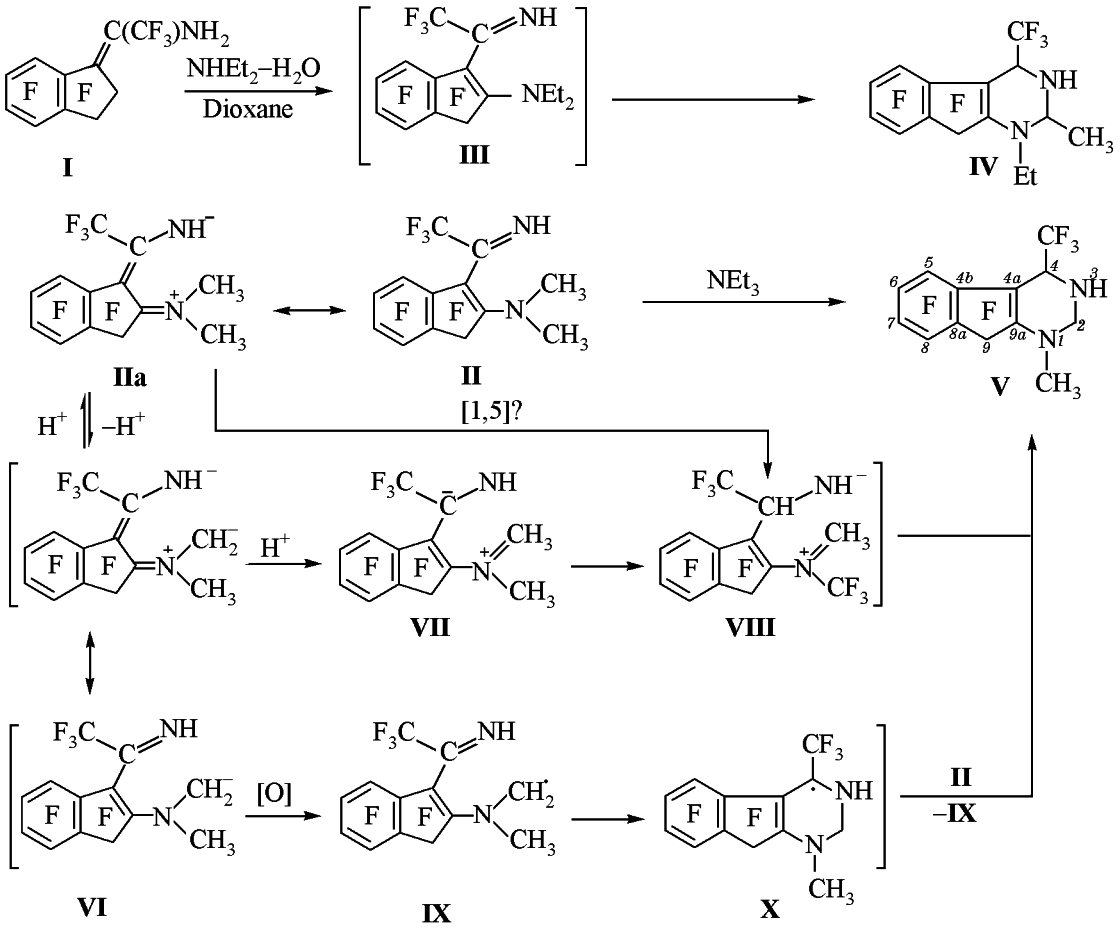
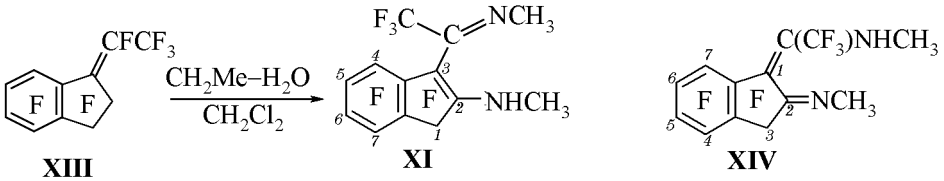
Scheme 1.



Scheme 2.



intensity analogously to assignment performed for enamines and enaminoimines of **I** and **II** types and for 2-aminopolyfluoroindenes [1]. It should be noted that in the spectra of compounds **II** and 2-aminopolyfluoroindenes the chemical shift of F^6 atom (−0.7 ÷ 2.5 ppm) considerably differs from the chemical shift (6.3 ÷ 10.9 ppm) of the signal from the similar fluorine atom (F^5) in compounds of type **I** [1]. Taking the above into account the ^{19}F NMR spectrum of compound **XI** indicates that the compound in solution has the assigned structure [$\delta(F^6)$ 0.5 ppm] and not tautomeric structure **XIV**. In the compound an intramolecular hydrogen bond is lacking for the coupling constant $J_{CF3\text{-}F}{}^4$ is 7 Hz, and in the presence of such hydrogen bond the expected coupling constant should amount to ~40 Hz [1].

Compound **IV** is a mixture of nearly equal amounts of *cis* and trans isomers as follows from the analysis of the fine structure of the methylene part of ethyl group signal in the ^1H NMR spectrum. The ^{19}F NMR spectra of isomers **IV** coincide. The signal of C^4 d.q.d ($^1J_{CH}$ 140, $^2J_{CF}$ *32*, J_{CH} 8 Hz) in ^{13}C NMR spectrum of compound **V** unambiguously confirms the structure **V** and allows rejection of an alternative isomeric structure with a five-membered heterocycle that should have formed at intramolecular attack by the carbanion site on the carbon atom of iminotrifluoroethyl group in ion **VI**.

EXPERIMENTAL

^{19}F and ^{1}H NMR spectra were registered on spectrometers Varian A-56/60A (56.4 and 60 MHz respectively) and Bruker WP-200SY (188.3 and 200 MHz respectively. ^{13}C NMR spectrum was recorded on Bruker AC-200 instrument at operating frequency 50.3 MHz. The chemical shifts are measured in δ scale from internal references C_6F_6, HMDS (δ 0.04 ppm), and $CDCl_3$ (δ_C 76.9 ppm) respectively. Elemental composition of compound **XI** was determined by high-resolution mass spectrometry performed on Finnigan MAT 8200 instrument.

2-Methyl-4-trifluoromethyl-1-ethyl-5,6,7,8,9,9-hexafluoro-1,2,3,4-tetrahydro-1,3-diazafluorene (IV). To a solution of compound **I** (0.26 g, 0.73 mmol) in 1 ml of dioxane was added dropwise at stirring a solution of $NHEt_2$ (0.16 g, 2.18 mmol) in 0.4 ml of water at ~20°C within 5 min. The stirring at ~20°C continued for 1.5 h, then the reaction mixture was treated with water and extracted with dichloromethane. The extract was washed with water, dried with $MgSO_4$, the solvent was distilled off. We obtained 0.27 g of dark residue that was subjected to column chromatography on silica gel (eluent dichloromethane) to isolate 0.21 g (0.54 mmol, 74%) of a mixture of *cis*- and *trans*-isomers of compound **IV**, mp 90–93°C after sublimation in a vacuum (80°C, 1 mm Hg) and recrystallization from hexane.

^{1}H NMR spectrum (CCl_4, 60 MHz), δ, ppm: 4.48 q ($2\underline{H}CH_3$, *J* 6Hz), 4.13 q ($2C\underline{H}CF_3$, *J* 7 Hz), 3.61 q ($1C\underline{H}_2CH_3$, *J* 7 Hz), 1.74 d ($2CHC\underline{H}_3$, *J* 6 Hz), 1.18 t ($2CH_2C\underline{H}_3$, *J* 7Hz). ^{19}F NMR spectrum (CCl_4, 56.4 MHz), δ, ppm: 90.9 d.d (CH_3, $J_{CF3\text{-}F}^{5}$ 18, $J_{CF3\text{-}CH}$ 7 Hz), 48.7 (CF_2), 20.6 (F^{8}), 13.9 (F^{6}), 12.9 (F^{5}), –0.9 (F^{7}). Found, %: C 46.33; H 2.70; F 44.33; N 7.25. $C_{15}H_{11}F_9N_2$. Calculated, %: C 46.16; H 2.84; F 43.82; N 7.18.

1-Methyl-4-trifluoromethyl-5,6,7,8,9,9-hexafluoro-1,2,3,4-tetrahydro-1,3-diazafluorene (V). (a) A solution of 0.3 g of compound **II** in 2 ml of NEt_3 was stored at ~20°C for 24 h, then NEt_3 was distilled off in a vacuum at ~20°C, and the ^{19}F NMR spectrum of the reaction mixture was recorded. The mixture contained according to the ^{19}F NMR spectrum compounds **II** and **V** in ~2 : 1 ratio. Then the mixture was dissolved in ~2 ml of NEt_3 and stored at ~20°C for 7 days. NEt_3 was distilled off in a vacuum, and the residue was subjected to column chromatography on silica gel (eluent dichloromethane) to isolate 0.26 g (87%) of compound **V** as viscous yellow fluid.

^{1}H NMR spectrum (CCl_4, 200 MHz), δ, ppm: 4.15 and 3.96 ($2H^{2}$, *AB* system, J_{AB} 13 Hz), 4.15 ($C\underline{H}CF_3$), 3.05 s (CH_3), 2.11 (NH). ^{19}F NMR spectrum (CCl_4, 188.3 MHz), δ, ppm: 88.5 d.d (CF_3, $J_{CF3\text{-}F}^{5}$ 18, $J_{CF3\text{-}CH}$ 7 Hz), 45.8 and 44.6 (CH_2^{9}, AB system, J_{AB} 290 Hz), 19.4 (F^{8}), 12.4 (F^{6}), 11.3 (F^{5}), –0.6 (F^{7}). ^{13}C NMR spectrum ($CDCl_3$, 50.3 MHz), δ, ppm: 145.3 t (C^{9a}, $^{2}J_{CF}$ 21 Hz), 144.2 d.t (C^{6}, $^{1}J_{CF}$ 250, $^{2}J_{CF}$ 13 Hz), 144.0 d.d (C^{8}, $^{1}J_{CF}$ *257*, $^{2}J_{CF}$ 13 Hz), 138.9 d.d (C^{5}, $^{1}J_{CF}$ 247, $^{2}J_{CF}$ 11 Hz), 137.0 d.t (C^{7}, $^{1}J_{CF}$ 251, $^{2}J_{CF}$ 15 Hz), 124.6 (C^{4b}), 124.5 q.d (CF_3, $^{1}J_{CF}$ 282, J_{CH} 8 Hz), 120.6 t (CF_2^{9}, $^{1}J_{CF}$ 250 Hz), 112.3 (C^{8a}), 94.4 (C^{4a}), 60.4 (C^{2}, $^{1}J_{CH}$ 151 Hz), 50.9 d.q.d (C^{4}, $^{1}J_{CH}$ 140, $^{2}J_{CF}$ 32, J_{CH} 8 Hz), 34.4 q (CH_3^{1}, $^{1}J_{CH}$ 139 Hz). Found, %: C 43.46; H 1.82; N 8.12. $C_{13}H_7F_9N_2$. Calculated, %: C 43.11; H 1.95; N 7.74.

(b) Compound **II** (0.13 g) was dissolved in ~0.5 ml of DMSO, and the ^{19}F NMR spectrum was registered. In the spectrum alongside the signals of initial compound **II** appeared small resonances belonging to reaction product **V**. The mixture was treated with water, extracted with dichloromethane, and the extract was dried on $MgSO_4$. After 3 weeks of storage the solution was evaporated, and the residue was sublimed in a vacuum (70°C, 1 mm Hg). We obtained 0.09 g (69%) of viscous yellow substance **V** (according to ^{19}F and ^{1}H NMR spectra) containing a little DMSO as an impurity (^{1}H NMR spectrum).

2-Methylamino-3-(1-methylimino-2,2,2-trifluoroethyl)hexafluoroindene (XI). To a solution of 0.2 g (0.56 mmol) of compound **XIII** in 0.8 ml of CH_2Cl_2 cooled with ice water was added dropwise while stirring 0.9 g (5.8 mmol) of 20% water solution of $NHMe_2$ within 5 min. Then the stirring was continued at ~20°C for 3.5 h, 2 ml of dichloromethane was added, the solution was washed with water, the organic solution was placed on a watch glass, and the separated precipitate was dissolved in acetone and put on the same watch glass. The resulting solution was evaporated and dried in air. We obtained 0.19 g (94%) of compound **XI**, mp 153–154°C (from acetone–hexane mixture, melting in a sealed capillary).

^{1}H NMR spectrum ($CDCl_3$, 200 MHz), δ, ppm: 4.67 ($N\underline{H}CH_3$), 3.43 q ($=NC\underline{H}_3$, $J_{CH3\text{-}CF3}$ 1.8 Hz), 2.88 d ($NHC\underline{H}_3$, $J_{CH3\text{-}H}$ 5.5 Hz). ^{19}F NMR spectrum ($CDCl_3$, 188.3 MHz), δ, ppm: 90.6 d (CF_3, $J_{CF3\text{-}F}^{4}$ 7 Hz), 49.1 and 48.7 (CF_2^{1}, AB system, J_{AB} *285 Hz)*, *20.3 (*F^{7}), 13.5 (F^{5}), 10.2 (F^{4}), 0.5 (F^{6}). Found: 362.04635 $[M]^+$. $C_{13}H_7F_9N_2$. Calcd.: 362.04654 *M*.

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