NEW FLUORINE-CONTAINING POLYAZAHETEROCYCLES

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Interaction of perfluoropentene-2 with ethylenediamine, diethylenetriamine, and triethylenetetramine forms previously unknown fluorine-containing azaheterocycles in yields of 25-74%. The structure of the compounds obtained has been confirmed by ^1H and ^{19}F NMR methods and mass spectrometry.

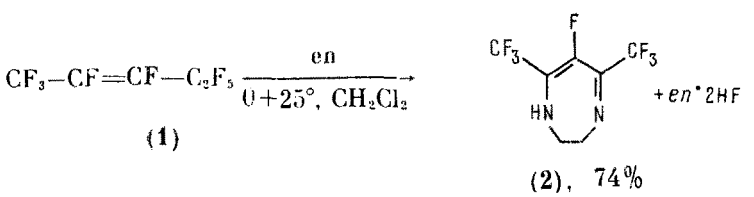
Keywords: *ethylenediamine, diethylenetriamine, triethylenetetramine, perfluoropentene-2, azaheterocycles.*

Unlike 1,3-diketones with one fluorinated substituent [1, 2], hexafluoroacetylacetone (HFAA) reacts with ethylenediamine (en) to form 5,7-trifluoromethyl-2,3-dihydro-1H-1,4-diazepine [3], but in a template reaction with triethylenetetramine (trien) the product is not a macrocyclic tetradentate ligand similar to that produced from hexafluoroacetylacetone (TFAA) [4, 5], but a linear bis(hexafluoroacetylacetone)-triethylenetetramine [6].

It is known that aza analogs of HFAA (imino-enamines) are readily formed by the reaction of perfluoropentene-2 with ammonia [7]. We considered that the reaction of this olefin with polyamines could be used to obtain fluorine-containing macrocyclic ligands related to heterocycles based on 1,3-dicarbonyl compounds.

The present study is concerned with the interaction of perfluoropentene-2 (**1**) with en, diethylenetriamine (dien), and trien.

Perfluoropentene-2 **1** reacts with en in CH_2Cl_2 to from 5,7-trifluoromethyl-6-fluoro-2,3-dihydro-1H-1,4-diazepine (**2**).



(**1**) (**2**), 74%

The PMR spectrum of **2** contains signals from methylene protons in ethylenediamine and the secondary amine, like the spectrum of 5,7-trifluoromethyl-2,3-dihydro-1H-1,4-diazepine [8], but no signal from a methenyl proton. The ^{19}F NMR spectrum of **2** contains doublets from the nonequivalent CF_3 groups (−66.03 and −69.33 ppm) as well as a multiplet from the CF group (−159.64 ppm). In the IR spectrum of **2** the absorption of NH valence and deformation vibration (3200, 1580 cm^{-1}) is characteristic of diazepines [8] but bands corresponding to absorption of C=N and C=C conjugate bond are in a higher frequency region (1710, 1640 cm^{-1}) than those in [8] due to the fluorine atom in position 6.

With dien and trien reaction **1** gives the polyazaheterocycles **3** and **4**.

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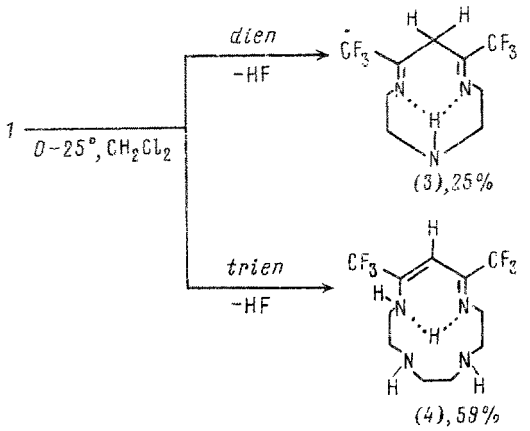

The PMR spectrum of **3** contains, apart from the NH bands (1.64 ppm), three multiplets due to resonance absorption of methylene groups (3.10, 3.42, and 3.76 ppm) and the ^{19}F NMR spectrum contains one signal from equivalent CF_3 groups at −66.90 ppm, suggesting that **3** lacks a vinyl fluorine atom and exists in a diimino form. The PMR spectra of **4** contain multiplets from methylene and amino-group protons and a signal at 5.38 ppm corresponding to absorption of a methenyl proton; the ^{19}F NMR spectrum has two CF_3 signals (−60.56 and −64.81 ppm). Thus ligand **4** has no vinyl fluorine atom but, unlike **3**, **4** exists in a tautomeric enamineimino form like the macrocylcic complexes obtained from TFAA and trien on a Ni^{2+} matrix [4].

Electrophilic substitution of fluorine by a proton in halophilic attack by the amine in the reaction of **1** with dien and trien probably takes place because they are more basic than en (for en pK_{a1} = 10.0, pK_{a2} = 7.0 [9]; for dien pK_{a1} = 10.1, pK_{a2} = 9.4, pK_{a3} = 4.9 [10]); a similar reaction is also characteristic of vinyl chlorine (bromine) atoms in 1,3-dicarbonyl compounds in reaction of the latter with amines [11, 12]. The significant role played by the basicity of the amine in these reactions is corroborated, in our view, by the fact that perfluoropentene-2 gives no reaction products on heating with *o*-phenylenediamine (pK_a = 4.7 [9]) in CH_2Cl_2, without a solvent, or in an autoclave.

The mass spectra of **2** and **3** contain peaks for the molecular ions $[M]^{+\cdot}$, but the maximum peaks are those for the ion $[M-C_2H_4]^{+\cdot}$ and $[M-H]^{+\cdot}$. The spectrum of **2** contains significant contribution from $[M-F]^{+\cdot}$, $[M-HF]^{+\cdot}$, $[M-HF, C_2H_4]^{+\cdot}$, and $[M-CF_3, C_2H_4]^{+\cdot}$, and the spectrum of **3** contains $[M-H, CF_3]^{+\cdot}$, $[M-CH_2{=}NH]^{+\cdot}$, and $[M-H, CH_2{=}NH]^{+\cdot}$ peaks. In the case of **4** there is a greater tendency for the dimensions of the heterocycle to decrease, the tendency to lose a hydrogen atom being maintained, which accounts for the spectrum having significant contributions from $[M-H, CH_2{=}NH]^{+\cdot}$ and $[M-2H, CH_2{=}NH]^{+\cdot}$ fragments as well as a high intensity for the simplest ion fragments.

The reaction of perfluoropentene-2 with polyamines is unique since it leads to formation of fluorine-containing unsaturated (diene) azaheterocycles with different-sized rings, including the 10-membered ring (**3**) which could not previously be obtained from TFAA [4] as was also the case in attempting to obtain its nonfluorinated analog with one azamethenyl group from acetone [13]. Complexes of a macrocyclic ligand, like **4**, are formed only by template synthesis [4, 5].

The properties of **3** and **4** are still being investigated. However it is already possible to state that **3**, which forms brightly colored salts with acids or complexes with neutral molecules, does not form metal complexes with Cu^{2+} or Ni^{2+} ions, which probably explains the failure to produce it on a matrix of these metals as attempted in [4, 13].

EXPERIMENTAL

The IR spectra of the compounds in suspension in vaseline oil were measured on a Specord 75-IR spectrometer over the range 400-4000 cm^{-1}. The PMR spectra were measured on a Tesla BS-567 A spectrometer (100 MHz, in $CDCl_3$ relative to TMS); ^{19}F NMR spectra were measured on a Tesla BS-587 spectrometer (75 MHz, in $CDCl_3$ relative to $CFCl_3$). Mass spectra were produced in a Varian MAT-311a apparatus using 70 eV ionizing electrons with direct injection of the substance into the ion source. Column chromatography was carried out on L100/250 silica gel using MeOH as eluant. Ultraviolet spectra were recorded in C_2H_5OH on a Specord UV VIS spectrometer.

Perfluoropentene-2 was obtained according to [14]; the content of *trans* and *cis* isomers was 81% and 19% respectively.

5,7-Trifluromethyl-6-fluoro-2,3-dihydro-1H-1,4-diazepine (2). To 15.0 g (0.25 mole) anhydrous en in 250 ml CH_2CL_2 in a 500 ml flask fitted with a stirrer and a low-temperature cooler add 25.0 g (0.10 mole) fresh distilled perfluoropentene-2 (1) by portions over 0.5 h with vigorous stirring and cooling down to 0°C. Stir for 24 h, during which the temperature of the reaction mass rises spontaneously to 25°C. Filter off en·2HF and remove the solvent. Precipitate from MeOH using water. Yield 18.5 g (74%) of **2** in the form of colorless crystals; mp, 98-99°C. Found: C 33.70, H 2.48, F 53.16, N 10.78%. Calculated for $C_7H_5F_7N_2$: C 33.61, H 2.07, F 53.17, N 11.20%. IR spectrum (ν, cm^{-1}): 3200, 1580, 1530 (NH), 1710, 1640 (C=N, C=C). PMR spectrum (δ, ppm; *J*, Hz): 2.26 m (CH_2, 2H), 3.06 m (CH_2, 2H), 4.34 br.s (NH, 1H). ^{19}F NMR spectrum (δ, ppm): −66.03 d (CF_3, $J_{F\text{-}F}$ = 19.5), −69.33 d (CF_3, $J_{F\text{-}F}$ = 19.5), −159.61 m (CF, J_{F-F} = 19.5). Mass spectrum, *m/z* (*I*, %): 250 $[M]^{+\cdot}$ (100), 231 $[M-F]^{+\cdot}$ (19-20), 222 $[M-C_2H_4]^{+\cdot}$ (99.22), 202 $[M-HF, C_2H_4]^{+}$ (47.83), 153 $[M-CF_3, C_2H_2]^{+\cdot}$ (15.98), 69 $[CF_3]^{+\cdot}$ (42.27).

2,4-Trifluoromethyl[10]1,4-diene-N_3 (3). In a similar fashion mix 24.0 g (0.23 mole) anhydrous dien and 25.0 g (0.10 mole) of **1**, filter off dien·3HF, and evaporate. After column chromatography and recrystallization from CCl_4 a yield of 6.9 g (25%) of **3** is obtained in the form of orange crystals; mp, 129-130°C. Found: C 39.03, H 4.03, F 41.79, N 14.81%. Calculated for $C_9H_{11}F_6N_3$: C 39.28, H 4.03, F 41.42, N 15.27%. IR spectrum (ν, cm^{-1}): 3280, 1580 (NH), 1600 (C=N). PMR spectrum (δ, ppm): 3.10 m (CH_2, 4H), 3.42 m (CH_2, 2H), 3.76 m (CH_2, 4H), 1.64 br.s (NH, 1H). ^{19}F NMR spectrum (δ, ppm): −66.90 s (CF_3). Mass spectrum, *m/z* (*I*, %): 275 $[M]^{+\cdot}$ (10.86), 274 $[M-H]^{+\cdot}$ (100), 273 $[M-2H]^{+\cdot}$ (5.41), 255 $[M-HF]^{+}$ (11.47), 246 $[M-CH_2NH]^{+\cdot}$ (6.92), 245 $[M-CH_2NH, H]^{+\cdot}$ (8.03), 226 $[M-CH_2NH, CF_3]^{+\cdot}$ (7.99), 205 $[M-CF_3, H]^{+\cdot}$ (19.80), 204 $[M-CH_2CH_2NHCH_2CH_2]^{+\cdot}$ (8.09), 202 $[M-NHCH_2CH_2NHCH_2, H]^{+\cdot}$ (9.31), 69 $[CF_3]^{+\cdot}$ (6.40).

11,13-Trifluoromethyl[13]11,13-diene-N_4 (4). Following a similar procedure react 29.2 g (0.20 mole) anhydrous trien with 25.0 (0.10 mole) of **1**. Filter off trien·4HF and evaporate the solvent. Precipitate **4** from $CHCl_3$ using hexane. Yield 18.76 g (59%) of **4** in the form of a yellow powder; mp, 125-126°C. Found: C 41.16, H 5.38, F 35.72, N 17.81%. Calculated for $C_{11}H_{16}F_6N_4$: C 41.51, H 5.06, F 35.82, N 17.61%. IR spectrum (ν, cm^{-1}): 3320, 1515 (NH), 1660 (C=N, C=C). PMR spectrum (δ, ppm): 2.40-3.50 m (CH_2, 12H), 1.30 br.s (NH, 2H), 0.9 br.s (NH, 1H), 5.38 s (CH, 1H). ^{19}F NMR spectrum (δ, ppm): −60.56 (CF_3), −64.85 (CF_3). UV spectrum: λ_{max2} = 295 nm ($\log_{\epsilon 2}$ = 3.08). Mass spectrum, *m/z* (*I*, %): 288 $[M-CH_2{=}NH,H]^{+\cdot}$ (52.97), 287 $[M-CH_2{=}NH, 2H]^{+\cdot}$ (94.21), 274 $[M-CH_2CH_2NH_2]^{+\cdot}$ (11.70), 273 $[M-H, CH_2CH_2NH_2]^{+\cdot}$ (19.87), 161 $[M-CF_3, CH_2CH_2NHCH_2CH_2NH_2, H]^{+\cdot}$ (28.88), 127 $[N{=}CHCH_2NHCH_2CH_2NHCH_2CH_2]^{+\cdot}$ (48.27), 113 $[N{=}CHCH_2NHCH_2CH_2NHCH_2]^{+\cdot}$ (12.49), 101 $[NHCH_2CH_2NHCH_2CH_2NH]^{+\cdot}$ (15.20), 99 $[NCH_2CH_2NHCH_2CH_2N]^{+\cdot}$ (74.07), 85 $[NCH_2CH_2NHCH_2CH_2]^{+\cdot}$ (20.54), 73 $[H_2NCH_2{\cdot}CH_2NHCH_2]^{+\cdot}$ (57.89), 71 $[CH_2CH_2NHCH_2CH_2]^{+\cdot}$ (35.04), 69 $[CF_3]^{+\cdot}$ (65.87), 68 $[NCHCH_2N{=}CH]^{+\cdot}$ (100), 60 $[NH_2CH_2CH_2NH_2]^{+\cdot}$ (52.82).

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