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3,4-Epoxyperfluorooxolane in the synthesis of new fluorine-containing furo[3,4-*b*]quinoxaline derivatives

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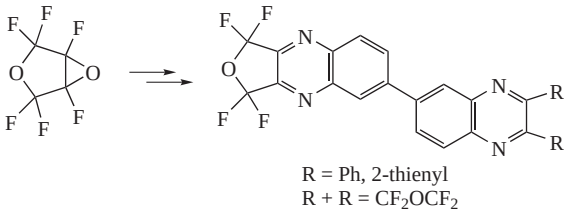
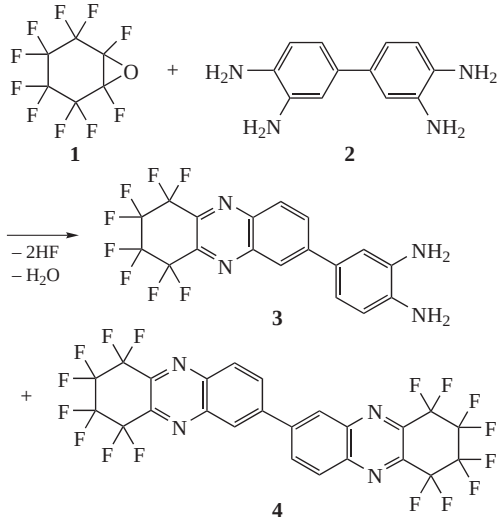
The reaction between equimolar amounts of 3,4-epoxyperfluorooxolane and 3,3′,4,4′-tetraaminobiphenyl provided a new fluorine-containing diamino derivative of furoquinoxaline, namely, 6-(3,4-diaminophenyl)-1,1,3,3-tetrafluoro-1,3-dihydrofuro[3,4-*b*]quinoxaline. Its reactions with 3,4-epoxyperfluorooxolane, 1,2-diphenylethanedione, or di(2-thienyl)ethanedione yielded new quinoxaline fluorine-containing polycyclic compounds whose structures were confirmed by X-ray diffraction.



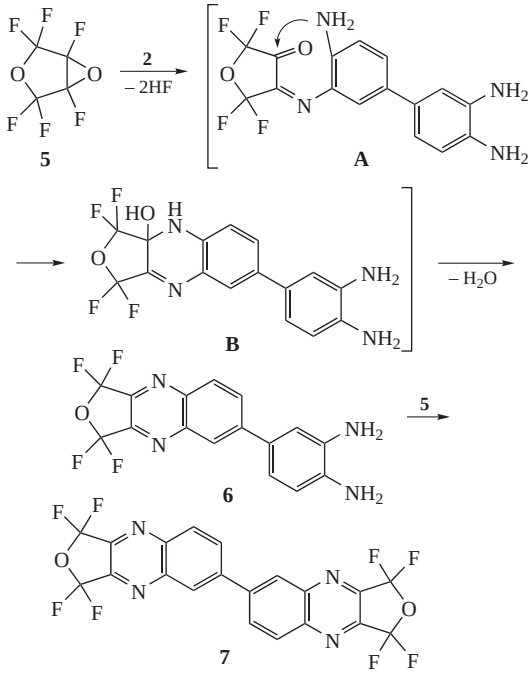
Perfluoroxiranes are widely used in the synthesis of various fluorinated polyfunctional and heterocyclic systems, the mostly used co-reactants having been binucleophiles.[1–6] However, the reactivity of cyclic perfluoroalkene oxides compared to linear ones remains insufficiently studied. The scarce reports exemplify reactions of 1,2-epoxyperfluorocyclohexane **1**[7] and 3,4-epoxyperfluorooxolane[8] with binucleophiles that proceed with the epoxide ring opening and the subsequent formation of new fluorine-containing heterocycles. The previously reported[9] reaction between oxirane **1** and 3,3′,4,4′-tetraaminobiphenyl **2** afforded product of mono-condensation **3** and small amounts of bis-adduct **4** (Scheme 1). Compound **3** seems to be an interesting building block for the syntheses of polycyclic structures[9] with luminescent and biological properties.[10]

Here, we report on the reaction between tetraamine **2** and fluorooxolane **5**. Compound **5** contains two rings capable of opening, the oxirane and oxolane ones. We have observed the opening of both cycles of compound **5** when it was treated with SbF_5 giving pentafluoroacetoacetic acid fluoride $CF_3C(O)CF_2C(O)F$. During the preparation of epoxyoxolane **5** by hypohalogenite epoxidation of perfluoro-3-oxolene, small amounts of by-products, sodium polyfluorooxacarboxylates, were formed as a result of the oxolane cycle opening under the action of hypochlorite anion.[11] However, reactions of perfluoro oxirane **5** with binucleophiles such as thiourea or *o*-phenylenediamine proceed exclusively with epoxy cycle opening.[8]

In our experiments, epoxyoxolane **5** reacts with an equimolar amount of tetraamine **2** only *via* the oxirane ring opening to give product **6** (Scheme 2), which would further add the second



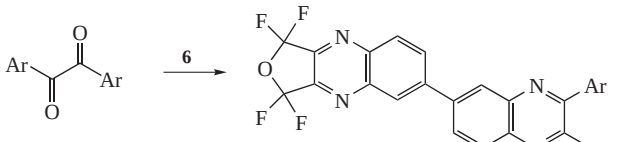
Scheme 1



Scheme 2

molecule of **5** to provide compound **7** (Scheme 2). The new fluorine-containing quinoxalines **6** and **7** were isolated in the ratio of ~1:1.† Similarly to oxirane **1**,[9] the reaction apparently occurs *via* formation of intermediates **A** and **B** (see Scheme 2). The final elimination of the water molecule leads to a stable quinooxaline aromatic system.

Compound **6** contains perfluorooxolane, quinoxaline, and also 1,2-diaminobenzene moieties and, analogously to diamine **3**, should be of interest as a building block for the preparation of new fluorine-containing conjugated heterocyclic systems. Indeed, diamine **6** readily interacts not only with epoxyoxolane **5** (see Scheme 2), but also with 1,2-diphenylethanedione **8a** and di(2-thienyl)ethanedione **8b** to afford new polycyclic derivatives **9a**,**b** (Scheme 3).



8a,**b** **9a**,**b**

a Ar = Ph
b Ar = 2-thienyl

Scheme 3

The structures of products **6**, **7** and **9a**,**b** were confirmed by elemental analysis, IR and NMR (^{1}H, ^{19}F, and ^{13}C) spectroscopy. The molecular and crystalline structures of compounds **6** and **7** were determined by the single-crystal X-ray analysis (Figure 1).‡

In summary, we have synthesized the new fluorine-containing diamino derivative of furoqinoxaline, 6-(3,4-diaminophenyl)-1,1,3,3-tetrafluoro-1,3-dihydrofuro[3,4-*b*]quinoxaline, from available fluorinated synthon, 3,4-epoxyperfluorooxolane and converted it into new promising polycyclic compounds.

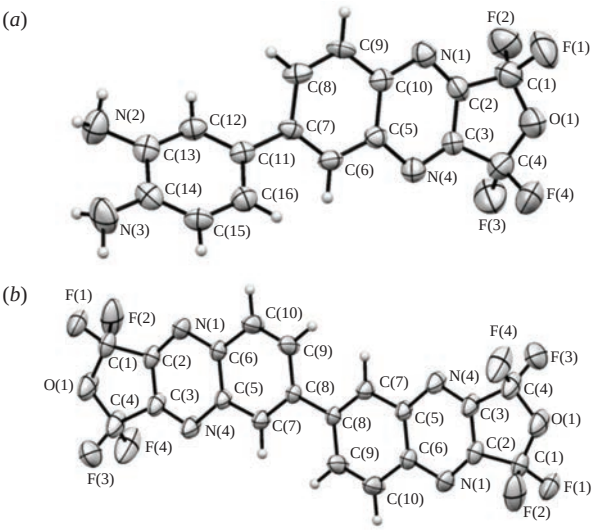


Figure 1 Molecular structure of compounds (*a*) **6** and (*b*) **7** showing thermal ellipsoids at the 50% probability level.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.09.020.

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† Note that no more than 10% of compound **4** was formed in the reaction of oxirane **1** with tetraamine **2** under the similar conditions,[9] which was apparently caused by a decreased nucleophilicity of the amino groups in diamine **3** as compared to diamine **6** due to the larger number of fluorine atoms in the molecule.

‡ The XRD analyses were accomplished on an Xcalibur 3 automated four-circled diffractometer with CCD-detector by standard procedure [295(2) K, MoKα-irradiation, graphite monochromator, ω-scans with 1° steps], empirical absorption correction was applied. The solution and refinement of the structure were accomplished using SHELXTL program package.[12] All non-hydrogen atoms were refined in anisotropic approximation; the H atoms at C–H bonds were placed in the calculated positions and refined in the 'riding' model with dependent isotropic displacement parameters. The H atoms at NH-bonds were localized by direct method and refined isotropically.

Crystal data for **6**: $C_{16}H_{10}F_4N_4O$, M = 350.28, monoclinic, space group $C2/c$, a = 31.887(5), b = 7.5349(13) and c = 12.459(3) Å, β = 106.296(19)°, V = 1743.8(3) Å^3, Z = 8, μ(MoKα) = 0.141 mm^{-1}. Total of 6376 reflections were measured (2.78 < θ < 26.38°), 2796 unique (R_{int} = 0.0840), which were used in all calculations. The final R_1 = 0.2051, wR_2 = 0.0633 (all data) and R_1 = 0.0692, wR_2 = 0.0532 [$I > 2\sigma(I)$]. Largest diff. peak/hole: 0.184/–0.190 eÅ^{-3}.

Crystal data for **7**: $C_{20}H_6F_8N_4O_2$, M = 486.29, monoclinic, space group $P2_1/c$, a = 8.3315(8), b = 7.0390(12) and c = 16.147(3) Å, β = 99.652(11)°, V = 933.5(2) Å^3, Z = 2, μ(MoKα) = 0.169 mm^{-1}. Total of 6331 reflections were measured (3.16 < θ < 33.63°), 3098 unique (R_{int} = 0.0218) which were used in all calculations. The final R_1 = 0.0988, wR_2 = 0.1367 (all data) and R_1 = 0.0505, wR_2 = 0.1263 [$I > 2\sigma(I)$]. Largest diff. peak/hole: 0.235/–0.329 eÅ^{-3}.

CCDC 1838023 and 1838024 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.