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Polydiazenofurazans: novel macrocyclic systems

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The oxidative intermolecular cyclocondensation of 3,4-diaminofurazan and 4,4′-diamino-3,3′-azofurazan has been carried out by treating them with mixtures of $Pb(OAc)_4$ and Bu_4NBr, Br_2 or NaBr to give previously unknown macrocyclic compounds: polydiazenofurazans possessing differing numbers of units.

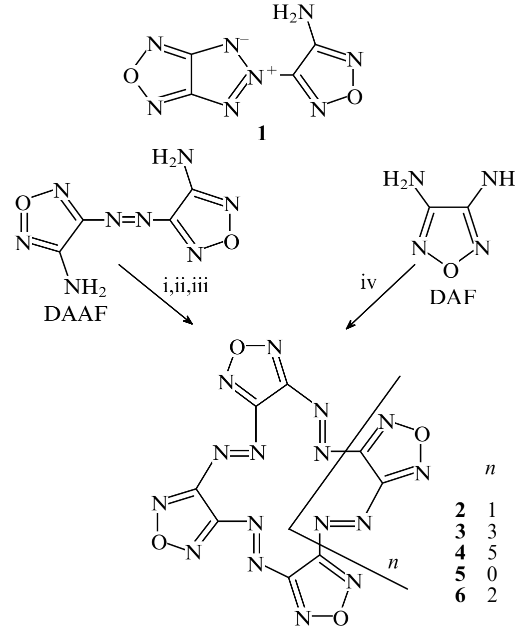
It has been shown previously[1] that the treatment of 4,4′-diamino-3,3′-azofurazan (DAAF) with $Pb(OAc)_4$ in chloro- and *o*-dichlorobenzenes at high temperatures gives 5-[4-amino-1,2,5-oxadiazol-3-yl]-5*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazole **1** as a result of intramolecular oxidative cyclisation involving the diazene fragment and one of the amino groups of DAAF.

In the present work we have found that the oxidation of DAAF with $Pb(OAc)_4$ in the presence of Bu_4NBr results in an essential change in the reaction pathway: instead of **1**, previously unknown macrocyclic compounds **2**–**4** are formed, products of intermolecular oxidative condensation of two, three and four DAAF molecules, respectively (Scheme 1). The cyclocondensation of DAAF occurs at room temperature.[†] As well as chlorobenzenes used in the syntheses of **1**, other aprotic solvents can also be used (MeCN, EtOAc, CH_2Cl_2, C_6H_6). Macrocycle **2** is the main reaction product and can be isolated in 60–70% yields, while compounds **3** and **4** are formed under the conditions studied only in small quantities and can be isolated in $<1\%$ yields.[‡]

In addition to DAAF, we also studied the reaction of 3,4-diaminofurazan (DAF) with $Pb(OAc)_4$ in the presence of Bu_4NBr.[†] This reaction results in a mixture of macrocycles not only with an even number of diazenofurazan units, as is the case in the cyclocondensation of DAAF (**2**–**4**) but also with an odd number of diazenofurazan units, macrocycles **5** and **6**[†] (Scheme 1). It should be noted that compound **2** again predominates in this reaction.

Polydiazenofurazans **2–5** were isolated by column chromatography and identified by a combination of elemental analysis data (corresponding to general formula C_2N_4O), ^{13}C NMR spectra (**2–4**, one signal from each of the carbon atoms in the furazan rings), IR spectra (the absence of absorption in the region 3200–3600 cm^{-1}), mass spectra (the presence of peaks with masses corresponding to the molecular ions of the target macrocycles)[§] and X-ray diffraction analysis (**2–4**).[¶] We did not manage to isolate compound **6** individually; it was detected as a mixture with compounds **2–4**, which, according to TLC data, contained four compounds; the mass spectrum of this mixture contained peaks with masses corresponding to molecular ions of polydiazenofurazans **2–4** along with a peak with a mass corresponding to the molecular ion of compound **6**. It should be noted that separation of macrocycles on a column or on plates with silica gel is complicated by destructive transformations, which makes their isolation much more difficult.

A comparison of IR spectra of compounds **2–5** shows one particular feature: the region of 1450–1600 cm^{-1} either scarcely contains absorption bands usually observed as intense peaks in the IR spectra of various furazans, or contains very weak absorption bands.



Scheme 1 *Reagents and conditions*: i, $Pb(OAc)_4$ (4.6 mmol), Bu_4NBr (0.6 mmol), 30 ml MeCN (EtOAc, CH_2Cl_2, C_6H_6), 15 min; 30 ml o-$Cl_2C_6H_4$, 3 h; ii, $Pb(OAc)_4$ (4.6 mmol), Br_2 (6 mmol), 60 ml C_6H_6, 20 h (60 ml MeCN, 1 h); iii, $Pb(OAc)_4$ (4.6 mmol), NaBr (8 mmol), 60 ml MeCN, 10 min; iv, $Pb(OAc)_4$ (9 mmol), Bu_4NBr (2 mmol), 30 ml MeCN, 3 h; i–iv, 20 °C.

A more detailed study of the oxidative cyclocondensation of DAAF occurring on treatment with $Pb(OAc)_4$ + Bu_4NBr showed that the quantity of the latter considerably affects the yield of the product **2**. The quantity of Bu_4NBr should be no less than 0.4–0.5 mol per mol DAAF. On the other hand, it was found that on replacement of Bu_4NBr for Br_2 or NaBr, DAAF also undergoes oxidative cyclocondensation to give a mixture of compounds **2–4**. Treatment of DAAF with only $Pb(OAc)_4$ or with $KMnO_4$ + Bu_4NBr under the conditions specified above does not result in oxidative cyclocondensation.

These data allow us to assume that it is acetyl hypobromite, formed from $Pb(OAc)_4$ and the corresponding bromine-containing component, that is the direct oxidiser of diamines in mixtures of $Pb(OAc)_4$ with Bu_4NBr, Br_2 or NaBr. The results concerning the interaction of DAF and DAAF with acetyl hypohalogenites will be published in a separate communication.

References

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[†] *General procedure for the synthesis of compounds* **2–6**. A mixture of diamine, bromine-containing component and freshly prepared $Pb(OAc)_4$ [2] was stirred in the appropriate solvent for the required period of time. The precipitate was filtered off, the mother liquor was evaporated to dryness, a small amount of C_6H_6 was added and the benzene solution was chromatographed on a column (silica gel LS 40/100, CH_2Cl_2–hexane, 2:1). The following individual macrocycles or their mixtures were isolated: 3,4:7,8:11,12:15,16-tetrafurazano-1,2,5,6,9,10,13,14-octaazacyclohexadeca-1,3,5,7,9,11,13,15-octaene **2** (R_f 0.68); 3,4:7,8:11,12:15,16:19,20:23,24-hexafurazano-1,2,5,6,9,10,13,14,17,18,21,22-dodecaazacyclotetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecaene **3** (R_f 0.51); 3,4:7,8:11,12:15,16:19,20:23,24:27,28:31,32-octafurazano-1,2,5,6,9,10,13,14,17,18,21,22,25,26,29,30-hexadecaaza-cyclodotriconta-1,3,5,7,9,11,13,15,19,21,23,25,27,29,31-hexadecaene **4** (R_f 0.42); 3,4:7,8:11,12-trifurazano-1,2,5,6,9,10-hexaazacyclododeca-1,3,5,7,9,11-hexaene **5** (R_f 0.79); 3,4:7,8:11,12:15,16:19,20-penta-furazano-1,2,5,6,9,10,13,14,17,18-decaazacycloeicosa-1,3,5,7,9,11,13, 15,17,19-decaene **6** (R_f 0.63). TLC monitoring was performed on Silufol UV-254 using CH_2Cl_2–hexane (3:1) as the eluent.

[‡] i: **2**, yields 60–70%; **3**, yield 0.8%; **4**, yield 0.6%; ii: **2**, yields 25% (15%), a mixture of **2–4**; iii: **2**, yield 15%, a mixture of **2–4**; iv: **2**, yield 45 %, **3**, yield 0.9 %, **4**, yield 0.8 %, **5**, yield 0.6 %, a mixture of **2–4**, **6**.

2: mp 208–210 °C (decomp.) ($CHCl_3$–hexane 1:5); R_f 0.68, MS: 384(100) [M^+], 182(32), 152(27), 142(29); IR (KBr): 1498, 1440, 1415, 1240, 1220, 1040, 920, 900, 850, 750, 700; Raman spectrum: 1492, 1417, 920, 856, 792; ^{13}C NMR ([$^2H_6$]acetone): 159.25 (C–C).

3: At 280 °C turns dark, does not melt (C_6H_6); R_f 0.51, MS: 576 [M^+], 546 [M^+–NO], 384 [M^+–2NO–2N_2–2(C–C–N)], 246 [M^+–6NO–2N_2–2(C–C–N)]; IR (KBr): 1560, 1535, 1500, 1445, 1410, 1250, 1230, 1210, 1035, 920, 890, 760, 720; ^{13}C NMR ([$^2H_6$]acetone): 157.59 (C–C).

4: 246 °C (decomp.) (THF–MeOH 1:4); R_f 0.42; MS: 768 [M^+], 510, 345, 235, 217; IR (KBr): 1405, 1240, 1035, 910, 765, 730; ^{13}C NMR (HNO_3 d = 1.5, [$^2H_6$]acetone as the external standard): 167.54 (C–C).

5: mp 116–117 °C (C_6H_6); R_f 0.79; MS: 288 [M^+], 166, 146; IR (KBr): 1405, 1210, 1030, 910, 870, 725.

[§] NMR spectroscopic data were obtained on a Bruker AM-300 spectrometer and are presented in the δ scale (ppm). Mass spectrometric data were obtained on a Varian MAT CH6 spectrometer and presented as m/z values (relative intensity, %). IR and Raman spectral data were obtained on a UR-20 spectrometer and are presented as ν/cm^{-1}.

[¶] X-Ray diffraction data for **2–4** will be published in separate communications.