Hypohalites as reagents for the macrocyclization of diamines of the furazan series

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The possibility of using hypohalites for the oxidative cyclocondensation of diamines was demonstrated for the first time by the example of 3,4-diaminofurazan and 4,4'-diamino-3,3'-azofurazan and the series of macrocyclic polydiazenofurazans, including previously unknown difurazano[c,g]-1,2,5,6-tetrazocine, was synthesized.

A series of new macrocyclic systems, polydiazenofurazans,[1,2] has been synthesized during a study of the oxidative cyclocondensation of 3,4-diaminofurazan (DAF) and 4,4'--diamino-3,3'-azofurazan (DAAF) under the action of DBI or mixtures of $Pb(OAc)_4$ with bromine-containing components (Bu_4NBr, Br_2, or $NaBr$). It has been supposed in ref. 1 that acetyl hypobromite (AcOBr) is the oxidant that directly reacts with diamines in their reactions with oxidizing mixtures based on $Pb(OAc)_4$. In the present work, in order to confirm this assumption, the possibility of the oxidative macrocyclocondensation of DAF and DAAF under the action of AcOBr and other hypohalites ($NaOBr$, $AcOCl$ and $NaOCl$) was studied.[†]

In fact, it turned out that the reactions of DAAF and DAF with AcOBr or NaOBr (high excess) in MeCN or EtOAc and of DAAF with these hypobromites in aqueous-methanol solutions result in the cyclocondensation of the diamines studied to form polydiazenofurazan macrocycles 1–3[1,2] from DAAF and macrocycles 1–5[1,2] from DAF (Scheme 1).[‡]

It is noteworthy that the formation of the four-membered macrocycle 1, which was isolated in the majority of the reactions in high yields (55 to 93%), is the preferential process

under the conditions studied upon both the action of DBI[2] and $Pb(OAc)_4$ with Bu_4NBr.[1] Macrocycles 2–5 were not isolated. They were identified in the mixtures by comparison with known samples,[1] by mass spectral and TLC data.

The study of the oxidation of DAAF in MeCN by a small excess AcOBr (1:4) shows that DAAF does not react

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† Acetyl hypohalites were obtained by a procedure similar to that described in ref. 3 from AcONa and the corresponding halogen in a particular solvent and were used *in situ*. The reactions with aqueous solutions of NaOCl or NaOBr were performed in homogeneous (aqueous–methanol) or heterogeneous (water–organic solvent–MeCN, EtOAc) media. The reaction was controlled by TLC with Silufol UV-254, C_6H_6–EtOAc (5:1) as eluent.

‡ Compound 1 or a mixture of macrocycles was isolated by chromatography on a column (silica gel LS 40/100) using benzene or CH_2Cl_2–hexane (3:1) as eluent, respectively. A mixture of benzene–EtOAc (3:1) was used as eluent for the isolation of compound 6. Compound 7: mp 232 °C (decomp.), R_f 0.9 (benzene–EtOAc, 5:1); R_f 0.78 (CH_2Cl_2–hexane, 1:1); MS m/z (I, %): 192 (70) [M⁺]; IR (KBr) ν/cm^{-1}: 1635, 1410, 1260, 1035, 910, 760; ^{13}C NMR (HNO_3, δ 1.5, external standard $^2[H_6]$acetone), δ 158.30 ppm.

	n
1	1
2	3
3	5
4	0
5	2
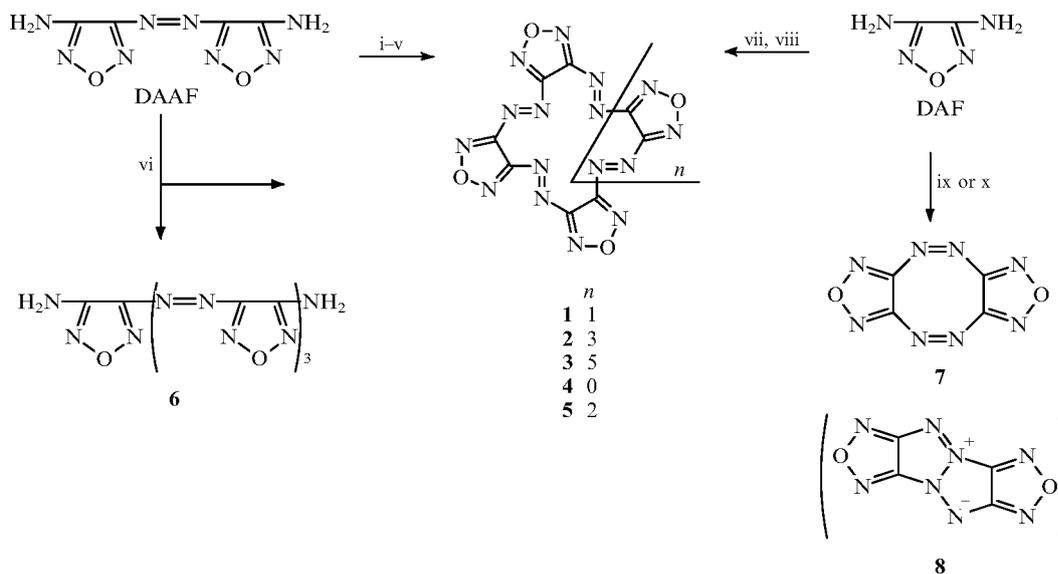
Scheme 1 *Reagents and conditions*: i, AcOBr (40 mmol), MeCN (EtOAc), 5–10 °C, 15 min, **1**: 90% (85%); ii, AcOBr (40 mmol), MeCN, 5–10 °C, 30 min, **1**: 67%, mixture **1**, **3**; iii, AcOCl (10 mmol), MeCN, 5–10 °C, 4 h, **1**: 90%, iv, NaOBr (50 mmol), MeCN (EtOAc, MeOH), 0–2 °C, 1 h, **1**: 93% (85%, 50%); v, NaOCl (45 mmol), MeCN (EtOAc), 0–2 °C, 4 h, **1**: 90% (1 h, **1**: 65%, mixture **1**, **3**, **6**); vi, AcOBr (4 mmol), MeCN, 5–10 °C, 20 h, **6**: 37%, **1**: 6%; vii AcOBr (20 mmol), MeCN, 10–15 °C, 30 min, **1**: 55%, mixture **2–5**; viii, NaOBr (25 mmol), MeCN, 0–2 °C, 30 min, **1**: 41%, mixture **2–5**; ix, AcOCl, MeCN, 20 °C, 15 min, **7**: 70%; x, NaOCl, MeCN (5–7 °C, 30 min, **7**: 65%), EtOAc (5–7 °C, 4 h, **7**: 40%).

completely under the conditions employed here. Cyclocondensation occurs only insignificantly (**1**, 6%) and largely ceases at the stage of the formation of the linear product of the oxidative dimerization of DAAF (diamine **6** [2]), which was isolated in a yield of 37% . The same compound and DAAF were observed by TLC as intermediates in the oxidation of DAF by hypobromites.

A study of the reactions of DAAF and DAF with hypochlorites (AcOCl, NaOCl) in aqueous-organic (MeCN or EtOAc) media made it possible to establish that the reactivities of the diamines studied with respect to these reagents differ substantially.

Macrocycle **1** was mainly obtained from DAAF under the action of hypobromites, while the reaction of DAF resulted in the formation of the previously unknown compound difurazano[*c,g*]-1,2,5,6-tetrazocine **7** as the sole reaction product, the result of the oxidative cyclocondensation of two DAF molecules.

It follows from this result that the reactivity of DAF with respect to hypochlorites differs from the behaviour of DAAF with respect to these reagents and from that of DAF itself with respect to the corresponding hypobromites and other oxidants used previously.[1,3]

The structure of compound **7** was determined on the basis of elemental analysis (corresponding to the empirical formula C_2N_4O), IR (absorption in the range from 3200 to 3500 cm^{-1}, which is typical of amines, is absent), ^{13}C NMR and mass (an intense peak with the corresponding molecular mass) spectra. The ^{13}C NMR spectrum of **7** exhibits only one signal of the furazan cycle, indicating the equivalence of its carbon atoms, which allows one to exclude the alternative tetraazapentalene structure **8** (Scheme 1).

The formation of the dimer **7** agrees with calculations[5] made on the electrostatic potentials and relative energies of the hypothetical structures **7** and **8**. These calculations show that

structure **7** is considerably more energetically favorable (by 33 kcal mol^{-1})[§] than structure **8**. According to these calculations, structure **7** should have the form of a 'boat' with a *cis*-configuration of the furazan units relative to the diazene bridges.

It is known[6] that the pentalene structure is thermodynamically prefered for the isomeric compounds dibenzo[*c,g*]-1,2,5,6-tetraazocine **9** and the tetraazapentalene **10**. It follows from the calculations presented in ref. 5 that tetraazapentalene itself should also be more energetically favorable than the isomeric 1,2,5,6-tetrazocine. The inverse dependence observed for the corresponding difurazan derivatives **7** and **8** is likely to be related to the instability of the system consisting of four fused five-membered polyheterocycles.[7]

It is significant that compound **7** is not formed from
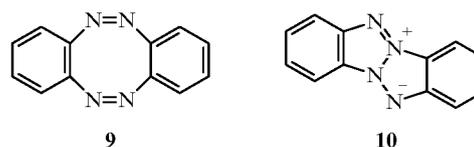
DAAF[1,2] because of its intramolecular cyclization and owing to the treatment of DAF with other reagents favorable for cyclocondensation of these compounds, including hypobromites, *i.e.* in the reactions in which DAAF is observed as an intermediate. In turn, no macrocycles with more than two diazenofurazan units were observed in the reactions of DAF with hypochlorites. It is likely that macrocycle **7** is formed by a different route rather than *via* DAAF in which furazan cycles would be likely to have the *trans*-configuration relative to the diazene fragment (according to the X-ray diffraction data[2,8] of macrocycles obtained from it).

References

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‡ IR spectra were recorded on a UR-20 instrument. Mass spectra of the reaction products were recorded on a Varian MAT CH6 spectrometer, and the mass spectrum of compound **7** was obtained using an aliquot of a solution of the substance in the organic layer that was separated from the aqueous layer after the cessation of the reaction. ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer.

§ 1 cal = 4.184 J.

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