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Ring size selective synthesis of *meso*-aryl expanded porphyrins

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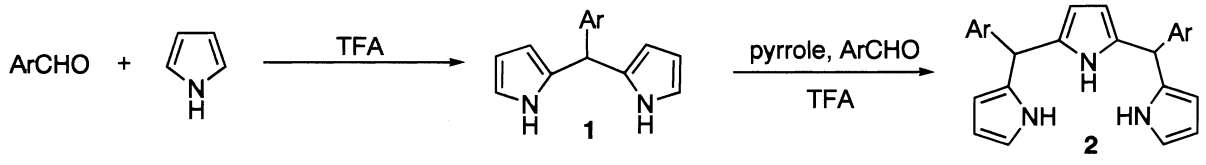
Abstract—*meso*-Aryl expanded porphyrins were prepared in a ring size selective manner from methanesulfonic acid-catalyzed reaction of dipyrromethane and tripyrromethane with aryl aldehydes. © 2003 Elsevier Science Ltd. All rights reserved.

Expanded porphyrins having a macrocycle larger than porphyrins have attracted considerable attention in light of their unique and fascinating optical, electrochemical, and coordination properties.[1] As a result, a variety of expanded porphyrins have been prepared differing in ring size, ring connectivity, and hetero atom replacement.[2] However, the synthesis of *meso*-aryl substituted expanded porphyrins, which may be regarded as the 'legitimated' members of *meso*-aryl-substituted expanded porphyrin in respect of the alternate arrangement of a pyrrole and a *meso*-methine carbon, has still remained very limited. Recently we found that a series of *meso*-aryl substituted expanded porphyrins were formed in the reaction of 2,6-disubstituted aryl aldehyde and pyrrole under modified Rothemund–Lindsey conditions.[3,4] Although this method is convenient and effective, the simultaneous formation of every size of expanded porphyrins at least up to dodecamer inevitably causes serious separation difficulties. Thus, ring size selective synthesis of *meso*-aryl expanded porphyrins is strongly desirable, since it will lead to facile product isolation. Another favorable improvement may be more production of larger *meso*-aryl expanded porphyrins, since our original method tend to provide smaller ones as major products. Typically, our original synthesis of the *meso*-aryl expanded porphyrins by the reaction of pyrrole and pentafluorobenzaldehyde (67 mM each) in dry CH_2Cl_2 with $BF_3{\cdot}OEt_2$ followed by the oxidation with DDQ led to isolation of porphyrin (11 ~ 12%), *N*-fused pentaphyrin **NFP$_5$**[4] (14 ~ 15%), hexaphyrin[5] (16 ~ 20%), heptaphyrin (4 ~ 5%), octaphyrin (5 ~ 6%), and nonaphyrin (2 ~ 3%). Among these products, octaphyrin and nonaphyrin are expected to exhibit novel reactivities due to their unique symmetric structures,[3] but separation of heptaphyrin, octaphyrin, and nonaphyrin is usually very difficult due to their close R_f values on silica gel and alumina columns. In this paper we report ring-size selective synthesis of expanded porphyrins using dipyrromethane **1** and tripyrromethane **2** as the starting materials in place of pyrrole.

Dipyrromethane **1** and tripyrromethane **2** were prepared by TFA-catalyzed reaction of pentafluoro-benzaldehyde with excess pyrrole following the method reported by Lee (Scheme 1).[6]

A solution of **1** and pentafluorobenzaldehyde (33 mM each) in CH_2Cl_2 was treated with acid for 2 h followed by oxidation with DDQ (Scheme 2, Table 1). Use of $BF_3{\cdot}OEt_2$ as an acid catalyst led to scrambling, as indicated by the formation of expanded porphyrins



Scheme 1.

Keywords: porphyrinoids; expanded porphyrin; size selective synthesis.

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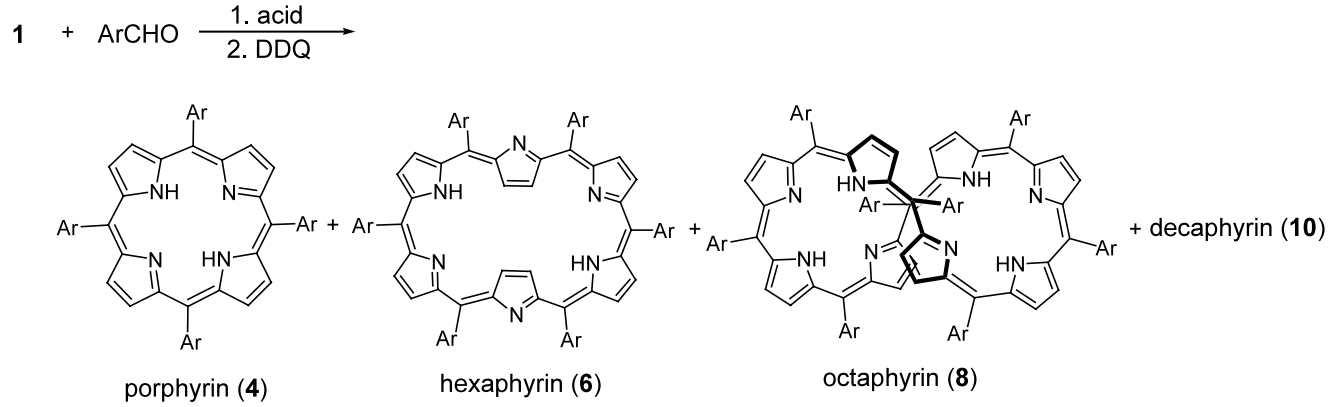
with odd number of the pyrrole subunits at room temperature (entry 1). Lowering the reaction temperature to 0°C did not suppress scrambling (entry 2). Methanesulfonic acid (MSA) was found more suitable for ring size selective synthesis of *meso*-aryl expanded porphyrins when used at 0°C (entry 4), which allowed the formation of *meso*-aryl expanded porphyrins including porphyrin (9%), hexaphyrin (19%), octaphyrin (38%) and decaphyrin (15%), while the scrambling was observed at room temperature (entry 3). High yields of octaphyrin and decaphyrin should be noted, since the original method did not achieve such yields. Isolation of octaphyrin and decaphyrin from this reaction mixture now became much easier. Similar ring size selective synthesis of *meso*-aryl expanded porphyrins was also effected with trichloroacetic acid. MSA gave expanded porphyrins in the reaction of 5-(2,6-difluorophenyl)dipyrromethane and 5-(2,6-dichlorophenyl)dipyrromethane, also in a ring-size selective manner.

In the next step, we examined the similar reaction of 5,10-bis(pentafluorophenyl)tripyrromethane **2** with aldehyde (Scheme 3 and Table 2). As was the case for **1**, the use of $BF_3{\cdot}OEt_2$ also led to entire scrambling both at room temperature and 0°C (entries 1 and 2),

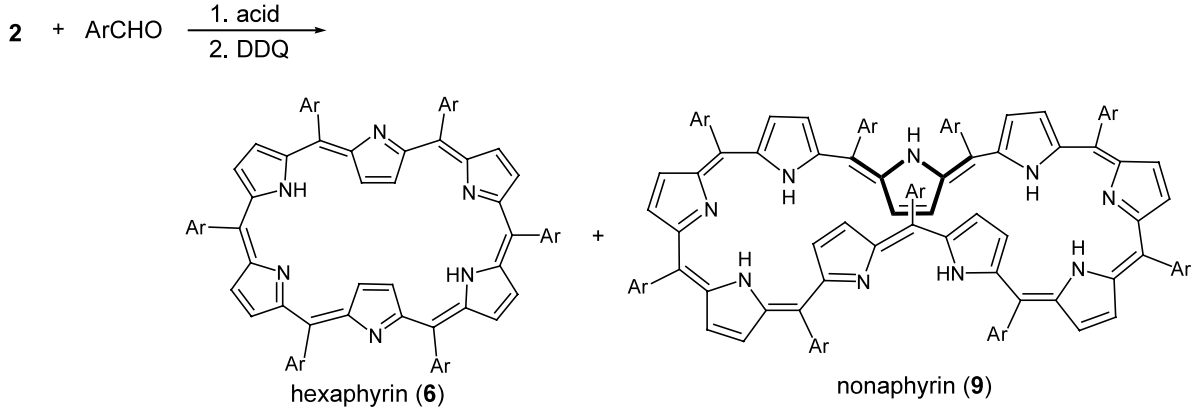


Scheme 2.

Table 1. Yields of expanded porphyrins in the reaction of **1**

Entry	Ar	Acid	Temperature	Cyclization time (h)	Products[a]
1[b]	C_6F_5	$BF_3{\cdot}OEt_2$	rt	2	**4**, **5**, **6**, **7**, **8**, **9**
2	C_6F_5	$BF_3{\cdot}OEt_2$	0°C	2	**4** (8%), **5** (11%), **6** (24%), **7**–**9** (16%, not isolated)
3[b]	C_6F_5	MSA	rt	2	**4**, **5**, **6**, **7**, **8**, **9**
4	C_6F_5	MSA	0°C	2	**4** (9%), **6** (19%), **8** (38%), **10** (15%)
5	C_6F_5	TCA	rt	2	**4** (6%), **6** (14%), **8** (5%), **10** (trace)
6[b]	$C_6F_2H_3$	MSA	rt	2	**4**, **5**, **6**
7	$C_6F_2H_3$	MSA	0°C	2	**4** (4%), **6** (12%)
8	$C_6Cl_2H_3$	MSA	rt	2	**4** (18%), **6** (17%), **8** (12%), **10** (trace)

[a] **4**: porphyrin, **5**: *N*-fused pentaphyrin (NFP_5), **6**: hexaphyrin, **7**: heptaphyrin, **8**: octaphyrin, **9**: nonaphyrin, **10**: decaphyrin.
[b] Not isolated. Yields reported refer to the isolated yields.



Scheme 3.

Table 2. Yields of expanded porphyrins in the reaction of **2**

Entry	Ar	acid	Temperature	Cyclization time (h)	Products[a]
1[b]	C_6F_5	$BF_3{\cdot}OEt_2$	rt	2	**4** (3%), **5** (10%), **6** (16%), **7**–**9** (16%)
2[b]	C_6F_5	$BF_3{\cdot}OEt_2$	0°C	2	**4** (8%), **5** (11%), **6** (24%), **7**–**9** (16%)
3[b]	C_6F_5	MSA	rt	2	**4** (3%), **5** (6%), **6** (23%), **7**–**9** (6%)
4	C_6F_5	MSA	0°C	2	**6** (23%), **7** (3%), **8** (4%), **9** (32%)
5	$C_6Cl_2H_3$	MSA	0°C	2	**4** (12%), **6** (21%), **7** (9%), **9** (22%)

[a] **4**: porphyrin, **5**: *N*-fused pentaphyrin (NFP_5), **6**: hexaphyrin, **7**: heptaphyrin, **8**: octaphyrin, **9**: nonaphyrin.
[b] Not isolated. Yields reported refer to the isolated yields.

though hexaphyrin was a major product. Use of MSA at 0°C gave rise to improved results, giving hexaphyrin (23%) and nonaphyrin (32%) as the major products in addition to the scrambling products, heptaphyrin (3%) and octaphyrin (4%). The reaction of 5,10-bis(2,6-dichlorophenyl)tripyrromethane also gave hexaphyrin (21%) and nonaphyrin (22%) as the major products (entry 5).

In summary, we have developed the ring-size selective synthesis of *meso*-aryl expanded porphyrins by using dipyrromethane **1** and tripyrromethane **2** as the starting substrates. This synthetic method is clearly better than the original one in view of much easier product isolation, particularly providing an easy synthetic access to octaphyrin and nonaphyrin.

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