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The New and Simple 'LEGO' System: Its Application for the Synthesis of 6-Oligopyridyl-1,5,12-triazatriphenylenes

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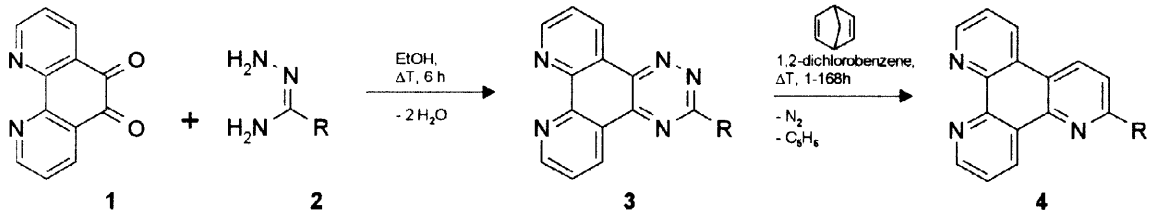
Abstract

The condensation of 1,10-phenanthroline-5,6-dione **1** with amidrazones **2** leads to 6-hetaryl-substituted 1,2,4,8,9-pentaazatriphenylenes **3**. These condensed 1,2,4-triazines can be easily transformed to pyridines by [4+2] cycloaddition with norborna-2,5-diene followed by [4+2] cycloreversions of nitrogen and cyclopentadiene. This reaction sequence offers a new, simple and general access to 6-oligopyridyl-1,5,12-triazatriphenylenes **4**.

Keywords: *Cycloadditions; Oligomers; Pyridines; Triazines*

1,10-Phenanthroline and its derivatives are very important ligands in organometallic chemistry [1,2,3,4]. Some of these complexes, for example, bind to DNA [5]. Our laboratory has developed two novel types of compounds with a 1,10-phenanthroline binding unit using the new and simple 'LEGO'-system for their synthesis [6,7,8].



1 **2** **3** **4**

Scheme 1. Reaction sequence for the synthesis of pyridines via 1,2,4-triazines.

1,2,4,8,9-Pentaazatriphenylenes **3** are easily prepared in good yields by heating of 1,10-phenanthroline-5,6-dione **1** with carboxamidrazones **2** in ethanol under reflux for 4-6 hours.

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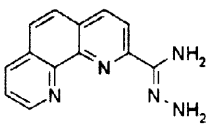
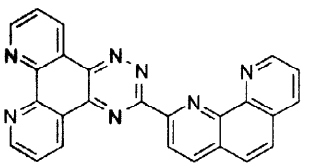
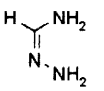
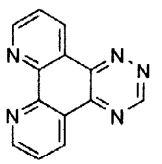
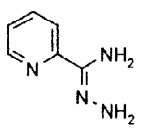
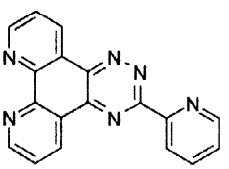
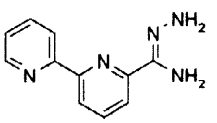
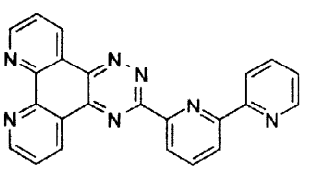
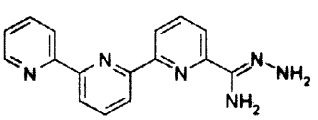
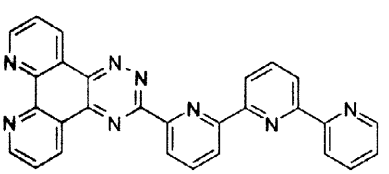
Table 1. 1,2,4,8,9-Pentaazatriphenylenes synthesized according to Scheme 1.

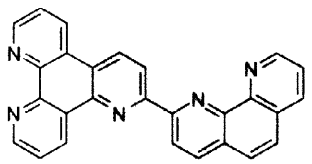
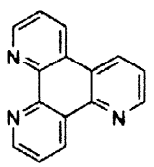
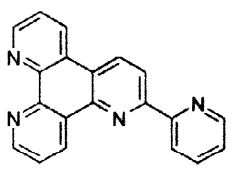
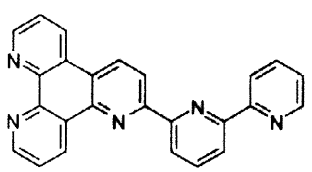
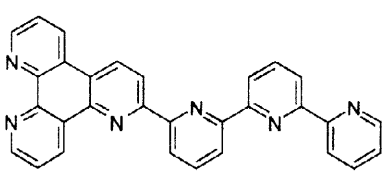
Amidrazone [Ref.]		Triazine		Reaction Times and Conditions	Yield [%]	M.P. [°C]
2a [9]		**3a**		6 h, reflux	83	380-385
2b [10]		**3b**		12 h, r.t.	55	265-267
2c [11]		**3c**		6 h, reflux	87	270-272
2d [12]		**3d**		6 h, reflux	90	275-277
2e analogue to [12]		**3e**		6 h, reflux	86	350-352

Typical procedure for the preparation of **1,2,4-triazines 3**: **1** [13] (500 mg, 2.38 mmol) and **2c** (320 mg, 2.38 mmol) in 40 ml ethanol were heated under reflux for 6h. After cooling the resulting yellow precitipate (**3c**) was collected by suction filtration, washed with cold ethanol and dried for 16 hours at 80°C/0.01 Torr. Recrystallization from *N,N*-dimethylformamide yielded **3c** (641 mg, 2.07 mmol, 87%) as yellow crystals. Analytical data for **3c**: IR (KBr): ν = 3060, 3040, 3000, 1570, 1560, 1490, 1375, 1355, 1050, 775, 725 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.56 (ddd, 1 H, J = 7.6 Hz, J = 4.8 Hz, J = 1.2 Hz), 7.85 (dd, 1 H, J = 8.2 Hz, J = 4.5 Hz), 7.89 (dd, 1 H, J = 8.2 Hz, J = 4.5 Hz), 8.02 (ddd, 1 H, J = 7.9 Hz, J = 7.6 Hz, J = 1.8 Hz), 8.88 (ddd, 1 H, J = 7.9 Hz, J = 1.2 Hz, J = 0.9 Hz), 9.00 (ddd, 1 H, J = 4.8 Hz, J = 1.8 Hz, J = 0.9 Hz), 9.35 (dd, 1 H, J = 4.5 Hz, J = 1.8 Hz), 9.38 (dd, 1 H, J = 4.5 Hz, J = 1.8 Hz), 9.75 (dd, 1 H, J = 8.2 Hz, J = 1.8 Hz), 9.78 (dd, 1 H, J = 8.2 Hz, J = 1.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 124.35 (1 C, +), 124.64 (1 C, +), 124.87 (1 C, +), 125.10 (1 C, +), 125.54 (1 C, +), 125.73 (1 C, +), 132.84 (1 C, +), 134.71 (1 C, +), 137.26 (1 C, +), 142.68 (1 C, 0), 144.67 (1 C, 0), 147.55 (1 C, 0), 149.93 (1 C, 0), 150.74 (1 C, +), 153.13 (1 C, 0), 154.66 (1 C, +), 154.84 (1 C, +), 161.41 (1 C, 0). EI-MS (70eV); m/z (%): 310 (26) [M^+], 282 (100) [M^+ - N_2], 178 (96) [$C_{10}H_6N_2^+$], 152 (55) [$C_{10}H_6N_2^+$ - C_2H_2], 151 (55) [$C_{10}H_6N_2^+$ - HCN], 104 (5) [$C_6H_4N_2^+$], 77 (5) [$C_6H_4N_2^+$ - HCN]. $C_{18}H_{10}N_6$ (310.32): calcd. C 69.97, H 3.25, N 27.08; found C 69.48, H 3.44, N 27.21. All other 1,2,4-triazines were characterized by the same analytical methods.

1,2,4-Triazines participate as electron poor dienes in inverse-type Diels-Alder reactions with electron rich and angle strained dienophiles to yield dihydropyridine and pyridine derivatives after extrusion of molecular nitrogen [6,7,8,14,15]. 1,2,4,8,9-Pentaazatriphenylenes **3** contain a condensed 1,2,4-triazine ring and, therefore, inverse-type Diels-Alder reactions are possible.

We used norborna-2,5-diene (10 fold excess) in 1,2-dichlorobenzene as a synthetic equivalent for acetylene (Scheme 1).

Table 2. Synthesis of 1,5,12-triazatriphenylenes according to Scheme 1.

Triazine	1,5,12-triazatriphenylene [Ref.]		Reaction Conditions and Times	Yield [%]	M.P. [°C]
3a	**4a**		reflux, 2 d	84	386-390
3b	**4b** [16]		reflux, 1 d	55	199-201 [199-200]
3c	**4c**		reflux, 1 d	76	204-205
3d	**4d**		reflux, 1 d	69	310-312
3e	**4e**		reflux, 1 d	91	340-342

Typical procedure for the preparation of oligopyridines **4**: **3c** (250 mg, 806 µmol) and norborna-2,5-diene (740 mg, 8.06 mmol) in 10 ml 1,2-dichlorobenzene were heated under reflux in an inert atmosphere for 1 d. The reaction mixture was cooled, treated with petroleum ether 40/60 until it became cloudy and the resulting precitipate was collected by suction filtration, washed with 1 ml cold 1,2-dichlorobenzene and 40 ml petroleum ether 40/60. Recrystallization from acetonitrile yielded **4c** (190 mg, 615µmol, 76%) as colorless crystals. Analytical data for **4c**: IR (KBr): $\tilde{\nu}$ = 3050, 3000, 1585, 1575, 1550, 1520, 1460, 1435, 1410, 1365, 775, 755, 725 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.39 (ddd, 1 H, J = 7.5 Hz, J = 4.8 Hz, J = 1.2 Hz), 7.65 (dd, 1 H, J = 8.2 Hz, J = 4.4 Hz), 7.70 (dd, 1 H, J = 8.2 Hz, J = 4.4 Hz), 7.90 (ddd, 1 H, J = 7.9 Hz, J = 7.5 Hz, J = 1.8 Hz),8.70 (d, 1 H, J = 8.6 Hz), 8.71 (ddd, 1 H, J = 8.0 Hz, J = 1.2 Hz, J = 0.9 Hz), 8.75 (ddd, 1 H, J = 4.8 Hz, J = 1.8 Hz, J = 0.9 Hz), 8.77 (ddd, 1 H, J = 8.2 Hz, J = 1.6 Hz, J = 0.5 Hz), 8.80 (dd, 1 H, J = 4.4 Hz, J = 1.6 Hz), 9.17 (dd, 1 H, J = 8.6 Hz, J = 0.5 Hz), 9.21 (dd, 1 H, J = 4.4 Hz, J = 1.8 Hz), 9.56 (dd, 1 H, J = 8.2 Hz, J = 1.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 120.26 (1 C, +), 121.60 (1 C, +), 123.39 (1 C, +), 123.50 (1 C, 0), 123.653 (1 C, +), 124.23 (1 C, +), 125.48 (1 C, 0), 128.26 (1 C, 0), 130.97 (1 C, +), 131.69 (1 C, +), 133.15 (1 C, +), 136.90 (1 C, +), 144.54 (1 C, 0), 146.13 (1 C, 0), 147.55 (1 C, 0), 149.27 (1 C, +), 150.68 (1 C, +), 151.61 (1 C, +), 155.66 (1 C, 0), 155.68 (1 C, 0). EI-MS (70eV); m/z (%): 308 (100) [M^+], 280 (26) [M^+ - H - HCN], 253 (4) [M^+ - H - 2 HCN], 230 (4) [M^+ - C_5H_4N], 203 (3) [M^+ - C_5H_4N - HCN], 176 (3) [M^+ - C_5H_4N - 2 HCN], 154 (8) [M^{2+}], 78 [$C_5H_4N^+$]. $C_{20}H_{12}N_4$ (308.34): calcd. C 77.91, H 3.92, N 18.17; found C 75.86, H 4.27, N 17.66. All other 1,2,4-triazines were characterized by the same analytical methods.

Recent investigations in our laboratory have shown that 1,2,4,8,9-pentaazatriphenylenes **3** and 1,5,12-triazatriphenylenes **4** act as ligands in ruthenium(II) and silver(I) complexes. Further work and publications on this topic are in progress.

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