Synthesis of phthalonitrile building blocks using a multicomponent reaction and niobium pentachloride as catalyst

Aloisio de A. Bartolomeu[1] (PG), Timothy J. Brocksom[1] (PQ) and Kleber T. de Oliveira[1*] (PQ)

[1]Department of Chemistry, Federal University of São Carlos – UFSCar, São Carlos-SP, 13565-905, Brazil.

**e-mail: kleber.oliveira@ufscar.br*

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Abstract

The synthesis of a phthalonitrile-quinoline dyad using a multicomponent reaction (MCR) and $NbCl_5$ as catalyst is reported.

Introduction

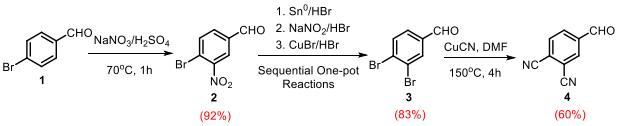
Phthalonitriles are the most common starting materials for phthalocyanine (PCs) synthesis. These dyes (PCs) are used in many technological and medical applications, such as semiconductors, dyes-sensitized solar cells, liquid crystals, catalysts, photodynamic therapy, and others.[1]

Peripheral substituents can be introduced into PC cores using two strategies:[2] (i) by modification of an already existing PC core using aromatic electrophilic substitution reactions, and (ii) by tetramerization of the substituted precursors, e.g., phthalonitriles. In this context, MCRs are a useful synthetic tool for the preparation of functionalized phthalonitriles. Herein, we report the preparation of a 4-formylphthalonitrile, followed by the synthesis of three complex different phthalonitriles using a MCR approach.

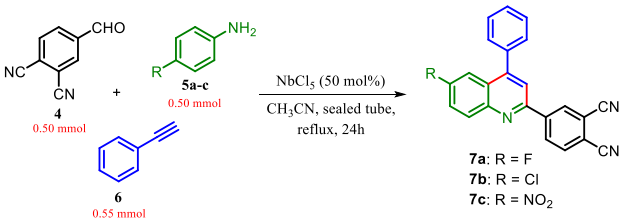
Results and Discussion

4-Formylphthalonitrile (**4**) was synthetized according to the route described in Scheme 1.[3] Nitration of commercially available 4-bromobenzaldehyde (**1**) with a mixture of H_2SO_4 and $NaNO_3$ yielded **2** in 92% yield (10 g scale). Compound **3** was then obtained in 83% yield (10 g scale) by the reduction with tin(II) bromide (generated *in situ* from Sn^0 and HBr), followed by diazotization and reaction with CuBr (sequential one-pot reactions). Finally, compound **3** was converted into **4** by the Rosenmund-von Braun reaction (CuCN) in 60% yield (4.4 g scale).

Phthalonitrile **4** was employed together with aniline derivatives **5a-c** and phenylacetylene (**6**) in MCRs catalyzed by $NbCl_5$ for the preparation of phthalonitriles **7a-c** (Scheme 2 and Table 1).



Scheme 1. Synthetic route for the preparation of 4-formylphthalonitrile (**4**).



Scheme 2. MCRs catalyzed by $NbCl_5$.

Table 1. Results obtained in the MCRs catalyzed by $NbCl_5$.

Phthalonitrile	$NbCl_5$ (mol%)	R	Yield (%)
7a	50	F	42
7b	50	Cl	49
7c	50	NO_2	41

Conclusion

Phthalonitriles **7a-c** were successfully synthesized by using MCRs. We are optimizing these reaction conditions in order to obtain better yields and study the scope for the synthesis of phthalonitriles, thus allowing the preparation of different phthalocyanine derivatives.

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