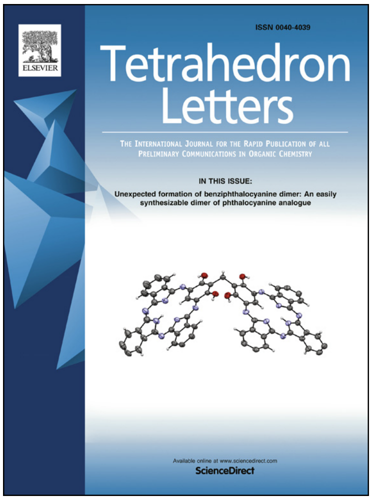

Unprecedented acid-catalyzed Wurtz-type coupling of *meso*-bromoindodicarbocyanine dyes

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Unprecedented acid-catalyzed Wurtz-type coupling of *meso*-bromoindodicarbocyanine dyes

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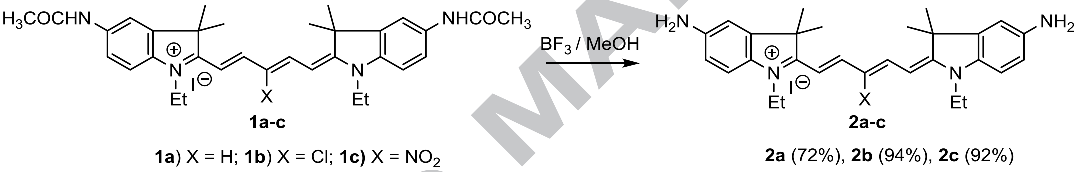
Abstract

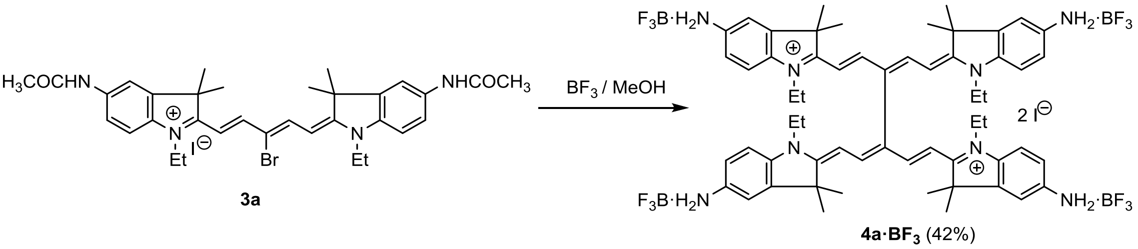
meso-Bromosubstituted indodicarbocyanine dyes produce dimeric molecules, together with the debrominated species, under acid catalysis. The relationship between the dimerization and hydrodebromination routes depends on the aryl substitution of the dyes. A possible reaction mechanism is also proposed.

In course of our research regarding the synthesis of long-wave absorbing diaminosubstituted indocyanine dyes, suitable for the preparation of polymeric materials with nonlinear properties,[1,2] boron trifluoride in methanol was used for the deprotection of acetylated precursors, including *meso*-substituted 5,5'-diacetylaminoindodicarbocyanines **1a**-**c**, to give the corresponding free diamines **2a**-**c** in high yields[3-5] (Scheme 1). The deacetylation reagent was prepared by the addition of an appropriate amount of $BF_3 \cdot MeOH$ (50%) or $BF_3 \cdot Et_2O$ (6 equiv. of BF_3 per amino group) to absolute methanol (10 mL per 1 mmol of dye).



Scheme 1. Deacetylation of meso-substituted dicarbocyanines **1a-c**.[4] *Reagents and conditions*: dye (1 mmol), 50% BF_3-MeOH (12 mmol, 1.5 mL), MeOH (10 mL), 2 h, reflux.

In an attempt to employ this procedure for the deprotection of *meso*-brominated acetamide **3a** (X = Br) we observed the formation of a product, which in the ES-MS$^+$ spectra contained only the significant signal of a doubly-charged species with *M/Z* = 440.2942 [$M^{2+} = (2M^+_{3a} - 2Br)/2$ (cal. 440.2940)], that could be assigned to the product of Wurtz-type dimerization (Scheme 2). The ^{1}H NMR spectrum of crude product **4a** revealed considerable variations in the chemical shifts of most protons in comparison with the *meso*-chlorinated diaminosubstituted dye **2b**, without any changes in the spin system of the pentamethine chain; this indicated that the *meso*-position remained substituted. The greatest difference was observed for the methine proton signals in positions 1 and 5, whose interactions with the *meso*-substituent are the most intense (δ 5.65 in **4a** *vs* δ 6.13 for **2b**). The same changes were previously observed when bulky fragments were introduced to the *meso*-positions of tricarbocyanines.[5,6] It should be noted that the chemical shifts of the protons in positions 1 and 5 of the acetylated precursors **1b** (X = Cl) and **3a** (X = Br) are very similar (δ 6.29 in **3a** *vs* δ 6.24 for **1b**). We failed to obtain the free tetraaminocyanine **4a** in pure form and therefore evaluated it as the boron trifluoride complex (**4a·BF$_3$**).[5] The proposed structure, confirmed by ^{1}H and ^{13}C NMR and ES-MS$^+$ data, is depicted in Scheme 2.



Scheme 2. Attempted deacetylation of dicarbocyanine **3a**. *Reagents and conditions*: dye (1 mmol), 50% BF_3-MeOH (16 mmol, 2 mL), MeOH (20 mL), 2 h, reflux.

In order to explore the scope of this reaction, a set of substituted *meso*-bromodicarbocyanines **3b-f** were prepared and their behavior examined under the above conditions.[7] It was found that the introduction of electron-withdrawing substituents onto the