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Suzuki and Heck Processes for the Synthesis of New Anthraquinone-Based Glycoconjugated Dyes

Lorenzo Calugi,*[a] Marco Bonanni,[b] Massimo Corsi,[a] Stefano Chimichi,[a] and Roberto Bianchini*[a]

Starting from a bromo-anthraquinone dye, different aryl- and styril- derivates are obtained following Suzuki and Heck procedures. Bathochromic shifts are displayed for the products, if compared to the starting anthraquinone dye. Two of these dyes, coming from either the Suzuki and the Heck processes, have been glycosylated with a piperazinyl-lactose derivative, so that two naturalized species are finally obtained. Therefore, the disperse chromophores were transformed in water soluble direct species. These kinds of dyes allow to avoid azo-structures, that are object of growing criticism in the European Union due to their environmental impact.

Introduction

Anthraquinones are valuable compounds of continuous attraction among researchers, due to their broad use at industrial level and basic research. Differently substituted anthraquinones have been examined for the development of organic light-emitting diodes,[1] molecular electronic devices,[2] selective anion sensors,[3–5] and Dye-Sensitized Solar Cells (DSSCs),[6] but in this particular case the anthracene-9,10-dione moiety is more a limiting factor rather than a boost.[7] However, the main field of application is in the dyeing industry, where anthraquinones encompass a vast group of colorants across the different classes of dyes.[8] They possess good fastness properties and hue intensity, that are key parameters in the search of the ideal colorant.[9] Recently, we have disclosed a new class of naturalised dyes,[10–12] that are glycoconjugate derivatives of chromophores, including anthraquinones.[13,14] In this relevant case, anthraquinones bearing a phenolic group were O-alkylated, to introduce an ethanoic acid C-substituent suitable for dye "naturalization".[10] The only limitation is the presence of a ready available hydroxy group in the molecule, so it's impossible to naturalize every tinctorial dye. Our work is an attempt to extend naturalized dyes palette with the modification of commercial available anthraquinones dyes. It is well known that the dicarbonyl moiety of anthraquinones is accomplished by Friedel-Crafts acylation,[15–18] but there are also some reports involving Diels-Alder cycloadditions.[19–21] As the

tricyclic structure is assembled, further elaboration may regard the carbonyls,[22–25] the introduction of halogens[26,27] and other substituents via either C-heteroatom[28–30] or C–C bond formation,[31,32] quite often requiring transition metal catalysis.[33–39] Our interest in expanding this arena of sugar derived dyes led us to consider commercial 1-amino-2-bromo-4-hydroxyanthracene-9,10-dione **1** (Figure 1) as an interesting building block for
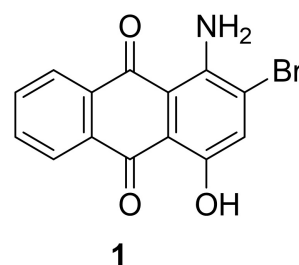

Figure 1. 1-amino-2-bromo-4-hydroxy-anthracen-9,10-dione.

the rapid generation of differently substituted aryl and alkenyl derivatives at position two.

Suzuki[40] and Heck[41] reactions were examined in this respect as they were already performed on other anthraquinone derivatives.[34,39] To the best of our knowledge, little exploration has been reported for the elaboration of **1** with palladium based catalysis,[42,43] but surprisingly no reports for the Suzuki and Heck coupling were found, although Okita and Isobe[44] reported an intramolecular Heck process on a derivative related to **1** en route towards Dynemicin A. Thus, we were intrigued to explore the potential of those palladium mediated processes, within the naturalization approach towards water soluble dyes.[13,14]

[a] L. Calugi, Dr. M. Corsi, Prof. S. Chimichi, Prof. R. Bianchini
Department of Chemistry "Ugo Schiff"
Università degli Studi di Firenze
Via della Lastruccia 3–13, 50019, Sesto Fiorentino (FI)
E-mail: lorenzo.calugi@unifi.it
        roberto.bianchini@unifi.it
[b] Dr. M. Bonanni
Glycolor s.r.l.
Via Madonna del Piano 6, 50019, Sesto Fiorentino (FI)

Results and Discussion

The reactivity of **1** in the Suzuki-Miyaura coupling reaction was first studied with phenyl boronic acid as model reagent, adopting the experimental conditions of Thiemann et al.,[21] but only starting material was recovered. Changing the solvent to THF, DMF or DMSO did not aid the formation of the desired product, despite the several reported examples of Suzuki-Miyaura processes on bromo-phenols[45] and bromo-anilines.[46] Deprotonation of the phenol group of **1** (K_2CO_3 was typically used) may be responsible for an intermediate hampering the catalytic cycle of the process. Therefore, we reckoned to circumvent this issue by analysing the chemical behaviour of compounds **2** and **3** (Scheme 1) as key intermediates in the synthesis of naturalised dyes.[13,14]
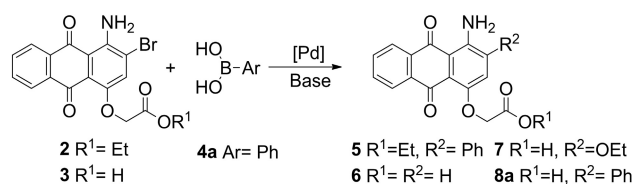
Scheme 1. Suzuki reaction on compounds 2 and 3

A preliminary test in THF at 66 °C using aq. K_2CO_3 succeeded on the two species, giving in both cases the carboxylic acid **8 a**. No analytical evidence was found for compound **5**, which was expected to come from **2**, neither for derivative **7**, which may be generated by the interference of ethanol in the catalytic process.[47] However, species like **2** are usually transitory intermediates in the naturalization process of hydroxy-anthraquinones, since the hydrolysis of the ester group follows up in situ conveniently after the completion of the alkylation of the phenol group of **1**.[14] Therefore, we embarked on the exploration of the scope and limitations of the Suzuki coupling on **3**, focusing mainly on the contribution of the base and the solvent to the formation of compound **8 a** (Table 1).

Use of KOH was more effective than K_2CO_3 and Cs_2CO_3 whereas KF and NaOAc were not able to activate the catalytic cycle. When *N,N*-dimethylacetamide (DMA) was used without adding water, the undesired dehalogenated product **6** was recovered. In this case the strong alkaline conditions and the high temperature tend to favour the decomposition of the solvent forming dimethylamine.[48] This amine coordinates Pd, and once the complex is formed, it can undergo β-hydride elimination, to produce **6** instead of **8 a**.[49] Formation of **6** seemed to be independent from the nature of the catalyst[50] since the combination of DMA/H_2O led to the formation of **8 a** regardless of the source of Pd. Other Pd catalysts did not improve the best result obtained and neither did other phosphine ligands like tri(*o*-tolyl) phosphine (P(o-tolyl)₃), Xant-phos or XPhos. Thus, the combination described in the second entry were replicated on **3** with different aromatic and heteroaromatic boronic acids with electron donor and acceptor groups (Table 2).

Crude materials obtained by Suzuki reaction were purified by chromatography on silica gel. The λ_{max} of compounds **8 a-8 i** were close to that of **3** with higher values for the molar extinction coefficients (λ_{max} 490 nm and ε 7500 cm^{-1} mol^{-1} for compound **3**). We refer to our anthraquinone derivatives as donor-acceptor systems. Aryl unit is the electron donor group while the anthraquinone core is the electron deficient one. Results shown in Table 2 indicated that the contribution of the

Table 1. Optimization of reaction conditions for the Suzuki process on compound 3				
Base	Solvent	Catalyst	Time (h)	Product (Yield %)
K2CO3	THF/H2O 4:1[a]	Pd(OAc)2	18	8 a (56)
KOH	THF/H2O 4:1[a]	Pd(OAc)2	1	8 a (71)
NaOAc	THF/H2O 4:1[a]	Pd(OAc)2	18	-
Cs2CO3	THF/H2O 4:1[a]	Pd(OAc)2	3	8 a (64)
KF	THF[a]	Pd(OAc)2	18	-
KF	Toluene[a]	Pd(OAc)2	18	-
K2CO3	DMA[b]	Pd(OAc)2	5	6 (50)
K2CO3	DMA/H2O 4:1[b]	Pd(OAc)2	4	8 a (51)
K2CO3	DMA[b]	Pd/C	4	6 (25)
K2CO3	DMA/H2O 4:1[b]	Pd/C	4	8 a (15)
KOH	THF/H2O 4:1[a]	Pd(dba)	3	8 a (70)
KOH	THF/H2O 4:1[a]	Pd(dppf)	3	8 a (71)
[a] Reflux; [b] 110 °C				

Table 2. Suzuki reaction on 3 with different boronic acids			
Ar =	Time (h)	Product (yield %)	λ_{max}[a] (ε[b])
(phenyl)	2	8 a (71)	506 (8100)
(4-methylphenyl)	2	8 b (67)	509 (10300)
(4-methoxyphenyl)	3	8 c (65)	516 (3800)
(4-fluorophenyl)	4	8 d (69)	504 (9300)
(4-chlorophenyl)	12	8 e (68)	504 (9500)
(4-cyanophenyl)	12	8 f (63)	505 (7800)
(naphthyl)	2	8 g (75)	511 (10600)
(pyridyl)	4	8 h (73)	506 (7000)
(thienyl)	3	8 i (67)	512 (9200)
[a] λ_{max} determined in THF and expressed in nm; [b] ε in cm^{-1} mol^{-1}			

aryl substituent was negligible to the variation of absorption. For compounds **8 d**, **8 f** and **8 h** the electrowithdrawing features of the aryl substituents were expected to cause a blue shift in λ_{max}, but the information provided by the little red shift seen for the absorption of **8 c** and **8 i** highlighted that the aryl group and the anthraquinone moiety of those two compounds are likely to determine a dihedral angle similar to that of a typical biphenyl structure. This would obstruct any potential mesomeric conjugation and thus limiting the electrodonating effect from the aryl ring to the anthraquinone. This evidence was also an indirect confirmation for the λ_{max} of **8 d**, **8 e** and **8 f**, whose values were rather constant despite the different electrowithdrawing nature of the substituent at 4-position of the phenyl group. The good results observed in the Suzuki coupling, prompted us to move the study of compound **3** in different conditions such as those of the Heck reaction (Table 3), using 4-chlorostyrene **9 b** as model reagent and keeping catalyst Pd(OAc)$_2$ (Scheme 2).

Table 3. Optimization of reaction conditions for the Heck process on compound **3**

Base	Solvent	Ligand	Yield (%)
TEA	THF[a]	PPh$_3$	-
TEA	DMSO[b]	PPh$_3$	-
TEA	NMP[b]	PPh$_3$	-
DIPEA	DMSO[b]	PPh$_3$	-
TEA	DMSO[b]	P(o-tolyl)$_3$	70
TEA	DMSO[b]	Xantphos	59
TEA	DMSO[b]	XPhos	66
TEA	DMSO[b]	DPEPhos	32

[a] Reflux; [b] 110 °C

3   **9 b** Ar= p-ClC$_6$H$_4$ **10 b** R^1= p-ClC$_6$H$_4$
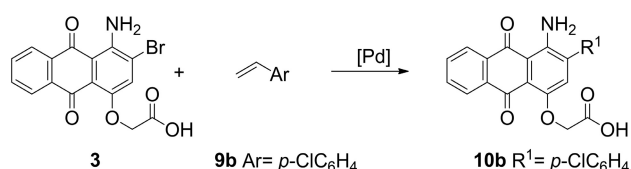
Scheme 2. Heck reaction on compound **3**

Despite the good dissolving properties of THF towards anthraquinones, the combination triethylamine (TEA)/Ph$_3$P failed in the formation of **10 b**. Even the replacement of THF with more polar solvents or TEA with a higher boiling point amine like *N,N*-diisopropylethylamine (DIPEA) did not aid the formation of **10 b**. Thus, we were rather pleased to find the usefulness of tri(*o*-tolyl) phosphine (P(*o*-tolyl)$_3$) which furnished the desired product in good yield. Other phosphine ligands did not bring along any advantage.

The combination TEA/DMSO/P(*o*-tolyl)$_3$ was extended to a group of commercial 4-substituted styrenes to obtain Heck derivatives of 3 (Table 4).

In this case, it was difficult to isolate the products through a chromatographic step, since the powder technique for the loading of the column had to be used, but poor yields were

Table 4. Heck reaction on **3** with different styril groups

Ar =	Product (yield %)	λ_{max}[a] (ε[b])
	10 a (71)	529 (12700)
Cl	**10 b** (67)	531 (11500)
	10 c (65)	532 (11600)
O	**10 d** (69)	537 (13700)
NH$_2$	**10 e** (68)	557 (9500)
F	**10 f** (63)	528 (10100)
	10 g (75)	533 (12200)
CN	**10 h** (73)	527 (9500)

[a] λ_{max} determined in THF and expressed in nm; [b] ε in cm^{-1} mol^{-1}

obtained. It was decided to recover the products taking advantage from the poor solubility of the reference compound **3** in common solvents. Thus, the whole reaction mixtures were diluted with EtOH and the slurries obtained were filtered, recovering **10 a–h** in good purity. These all possessed the alkene moiety in the E configuration, as demonstrated by the vicinal coupling constant (J = 16 Hz) in the ^{1}H-NMR spectra. Also, they showed higher extinction coefficients than those observed for the Suzuki derivatives and a more pronounced red shift for the λ_{max} (Table 4).

In particular, the stronger the electrodonating properties of the aromatic group, the deeper the red shift observed. This was obviously absent in the case of compound **10 f** and **10 h**, due to the electrowithdraing nature of the fluorine and nitrile group, since the anthraquinone moiety is an electron poor tricyclic moiety. On the other hand, the λ value of compound **10 a**, **10 c**, **10 d** and **10 g** indicated the limited electrodonating activity of the aryl substituent, which was a bit more pronounced in the case of **10 e**. It can be assumed that the planarity and the π-structure of the C=C contributes to a better conjugation effect between the substituent on the aryl group and the anthraquinone core than in the case of the Suzuki derivatives, whose aryl substituent directly linked to the anthraquinone is likely to assume a skewed position. Compounds **8 b** and **10 c** were chosen as representative examples for each group of derivatives in the naturalization process[34] with the so called 6′-deoxy-6′-(piperazinyl)lactose building block **11** (Scheme 3).[51]
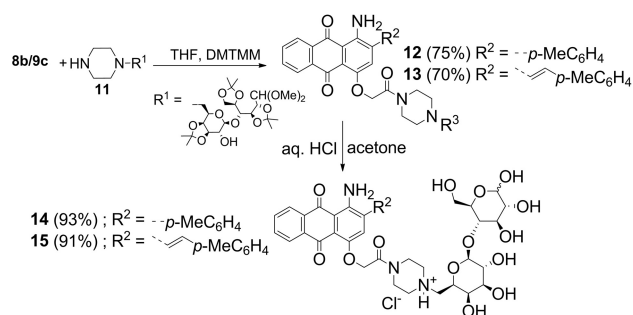
Scheme 3. Naturalization process

Amides formation was accomplished in THF using 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride (DMTMM),[52] providing products **12** and **13** in good yield. Next deprotection was carried out with the HCl/acetone combination, which has been developed by our research group as a cheaper alternative to the known aq. TFA method.[32] Products **14** and **15**[53] precipitated out of the reaction mixture and were recovered along with a small amount of the corresponding methyl glycoside, as observed by ESI-MS analysis. The persistence of the incomplete deprotected methyl glycoside species proved to be irrelevant for tinctorial properties.[54] As a matter of fact, the naturalized species become water soluble, and therefore allow dyeing process in water without dispersing agents. These dyes become "multi-purpose dyes", able to dye textiles, leather, wood, hair and so on.[14] The deprotection step involving the ring closure of the glucosyl part gives α- and β-anomers. However, only product **14** showed good water solubility properties even at 20–25 °C, whereas **15** could not dissolve in water even at very low concentration. This may be explained by a quite compact macroaggregate structure of the product, favoured by the planarity of the molecule and so by the π-stacking interaction between the aromatic units of the chromophore that aren't affected either by the soluble part of the molecule.

Conclusions

The application of Pd-mediated process on anthraquinone **3**, which is related to the chromophore species present in commercial Disperse Violet 17 dye, allowed the installation of aryl groups both in their simple form (Suzuki type coupling) and in the presence of a π-bond based spacer (Heck type coupling). The two processes required some little tuning to reach the desired compounds: in the Heck case, the use of a more electrodonating phosphine than PPh3 was crucial, whereas in the Suzuki process the alkylation of **1** was sufficient to start the investigation. The analysis of the two groups of products by visible spectroscopy revealed the role of the π-bond spacer, influencing the λ_{max} towards longer wavelengths. This evidence was ascribed to the E-configured C=C bond, which tends to minimize the potential steric interaction between the anthraquinone and the aryl group lying on the same plane. All compounds were good candidates for the

naturalization process, which was completed for one representative of each group. However, the unexpected lack of water solubility for the Heck derivative **15** may undermined the potential development of those compounds, towards the achievement of commercial dyes free from additives. This purpose is being pursued for the Suzuki derivatives in current development studies, focusing on the optimization of the fastness properties according to the type of material to dye.[55,56] In addition, since these naturalized dyes are amphiphiles, it's expected they possess a macromolecular organization in water. To better understand the size and shape of these aggregates, a physico-chemical characterization will be performed on water solutions of compound **14**, starting from Circular Dichroism and Small-Angle X-Ray Scattering techniques. Subsequent studies will focus also on the application of the Sonogashira coupling, to generate alkynyl derivatives of **3**. In this case, the presence of the triple C–C bond may offer the opportunity to increase the complexity of the electronic features of the dyes through the generation of enol derivatives in the last deprotection step of the naturalization process.

Supporting information summary

Detailed experimental procedures, product characterization and copies of Visible Absorption, 1H NMR, 13C NMR spectra for all new compounds.

Conflict of Interest

The authors declare no conflict of interest.

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