Dyes and Pigments 131 (2016) 264–267

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Short communication

One-step construction of aminosquaraine backbone

Hanze Ying, Jianjun Cheng*

Department of Materials Science and Engineering, University of Illinois at Urbana–Champaign, 1304 W. Green Street, Urbana, IL 61801, USA

ARTICLE INFO

Article history:
Received 4 March 2016
Received in revised form
10 April 2016
Accepted 11 April 2016
Available online 12 April 2016

Keywords:
Squaraine
Aminosquaraine
One-step
Amidation
Oxidation
Dye functionalization

ABSTRACT

One-step construction of the amino-substituted squaraine dye backbone was discovered unexpectedly in an amidation reaction. Under the catalysis of Mukaiyama's reagent, (4-dimethylamino)phenylacetic acid and bulky secondary amine 2,2,6,6-tetramethylpiperidine give the reduced form of aminosquaraine instead of amide as the major product. The reduced form of aminosquaraine can be oxidized to a dark-colored conjugated aminosquaraine within seconds. The method provides a novel and facile way to functionalize the four-membered core of squaraine dye.

1. Introduction

Squaraine dyes are a class of conjugated organic dyes with strong absorption in visible to near-infrared region (low band-gap), which features a four-membered aromatic ring structure as the core (see one example in Scheme 1a). Over the past few decades, squaraine dyes have been developed for many different applications [1,2], including sensors [3,4], organic electronics [5–7], and photo dynamic therapies (PDT) [8,9]. Squaraine dyes are usually synthesized through condensation reaction of electron-rich arenes and squaric acid (Scheme 1b) [1]. Structure tuning of squaraine dyes are mostly focused on interchanging and modifying the arenes, while the functionalization of the squaric core (Scheme 1a) is challenging [1]. It has been reported that the squaric core can be modified with a substituted methylene group via a semisquarate intermediate [10]. The squaric core can also be modified by amino group through post-modification using sequential reduction-substitution-oxidation reactions (Scheme 1b) [11]. However, both routes involve tedious multi-step syntheses. Herein, we report a new method to synthesize amino substituted squaraine (also named as aminosquaraine), which is discovered unexpectedly in a simple amidation reaction (Scheme 1b), and takes only one step to construct the aminosquaraine backbone.

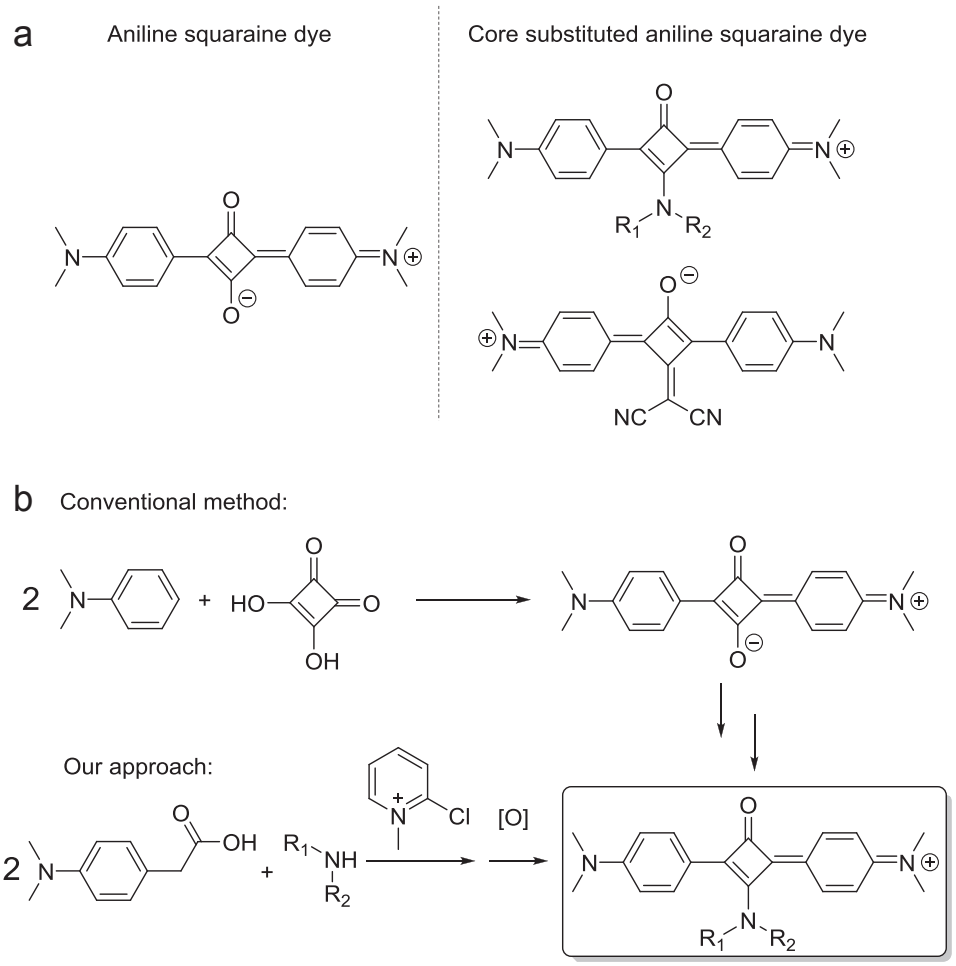
2. Results and discussions

2.1. Unexpected synthesis of aminosquaraine backbone from amidation reaction

(4-Dimethylamino)phenylacetic acid (1, 1.0 equiv.) and bulky secondary amine 2,2,6,6-tetramethylpiperidine (2, 3.0 equiv.) were mixed with Mukaiyama's reagent (3, 1.5 equiv.) as the carboxylic acid activation reagent. After the mixture was vigorously stirred for 12 h, one new major product was observed using thin layer chromatography (TLC). Purification of the compound via column chromatography, and ^{1}H NMR characterization showed that the structure did not match the structure of expected amide product 4 (Fig. 1a). Comparing with simulated ^{1}H NMR spectrum of 4, each peak for protons in phenyl ring and methyl groups in aniline and bulky amine groups splits into two, which manifests that the compound is asymmetric (Figure 1b & S2). Based on integrals of peaks, the compound contains two aniline and one bulky amine structures (or their integer multiples). Integrating the above information and the molecular weight obtained from mass spectrometry (MS), we identified the structure as compound 5 (Fig. 1b). Compound 5 contains characteristic four membered ring core structure, which is the reduced form of 1-(2,2,6,6-tetramethylpiperidinyl) substituted aniline based squaraine dye.

* Corresponding author.
E-mail address: jianjunc@illinois.edu (J. Cheng).

http://dx.doi.org/10.1016/j.dyepig.2016.04.024
0143-7208/



Scheme 1. Squaraine dye derivatives: (a) Structures of squaraine and core-substituted squaraine dyes. (b) Conventional and our new approaches to synthesize amino-substituted squaraine

2.2. Proposed mechanism for the formation of reduced form of aminosquaraine dye

Scheme 2a illustrates the proposed mechanism for the formation of reduced aminosquaraine 5. The carboxylic acid 1 is first activated by Mukaiyama's reagent, followed by substitution with bulky amine 2 giving amide 4, the targeted product. Because of the presence of basic amines in the reaction and the stability of benzyl anions, amide 4 likely undergoes deprotonation followed by Claisen condensation with another molecule of activated carboxylic ester to form ketone 8. Ketone 8 can then undergo intramolecular Aldol condensation, giving the final product 5.

Electron-rich carboxylic acid and bulky amine are required for the reaction to proceed. When 1 was changed to more electron deficient 1′, or 2 was changed to less bulky primary amine 2′ while reaction conditions and reactant molar ratios were kept the same, no aminosquaraine dye was detected. Instead, amides were obtained in high yield (Scheme S2~S5, Figs. S3~S7). It is presumably because: i) For electron deficient amide 4′, the benzylic carbanion is less nucleophilic and tends to form ketene by elimination of bulky amine group (previously reported as dynamic amide) [12], making it less likely for Claisen condensation to occur; ii) Typical ring-closing intramolecular Aldol condensations occur between carbanions and electrophilic carbonyl compounds (aldehydes/ketones). Normally, the more electron-rich amides do not participate in this reaction. However, the bulky amide does not completely adopt the typical amide structure. To avoid the steric hindrance, the C–N bond has lower energy barrier to rotate, which partially breaks the electron delocalization amide bond, making the amide more like a 'ketone' for Aldol reaction [12].

2.3. Synthesis of conjugated aminosquaraine dye

As a reduced form of dye, compound 5 could be easily oxidized to give fully conjugated aminosquaraine dye. Interestingly, it was observed that the spot of 5 on the TLC plate gradually turned green after being exposed to air for several minutes. To further understand the oxidation process of 5, DDQ (6, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone), a widely used organic oxidant for dehydrogenation/aromatization reactions, was used to treat 5. When mixing 5 and 6 in 1:1 molar ratio (Fig. 2a), we observed immediate color change from light yellow to dark blue (Fig. 2c), and the reaction finished within minutes. ^{1}H NMR illustrates that all peaks for 5 moved to downfield, and the 'split' peak pairs merged into singlet peaks (Fig. 2b). It corresponds well to the fact that the asymmetric 5 becomes symmetric and more electron deficient after being oxidized to 7. Also, the peaks became much broader, possibly due to the electrostatic and π-π interactions between cationic 7 and anionic reduced form of 6. The molecular weight measured by MS showed the reduction of molecular weight by 2, which also