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The Sonogashira coupling of 2- and 4-ethynyl derivatives of proton sponge with 1,8-diiodonaphthalene: Novel cascade transformations into naphtho[1,2-*k*]fluoranthenes and acenaphtho[1,2-*b*]benzo[*g*]indoles

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ABSTRACT

The Sonogashira coupling of 2-ethynyl, 4-ethynyl and 2,7-diethynyl derivatives of 1,8-bis(dimethylamino)naphthalene (proton sponge) with 1-iodo- and 1,8-diiodonaphthalenes has been studied. The reaction of the above alkynes with 1-iodonaphthalene gave the expected naphthylethynyl derivatives of proton sponge. At the same time, the coupling of 2-ethynyl- and 2,7-diethynyl-1,8-bis(dimethylamino)naphthalenes with 1,8-diiodonaphthalene resulted in the formation of *N*,*N*,7-trimethyl-7*H*-acenaphtho[1,2-*b*]benzo[*g*]indol-8-amines. The reaction of 1,8-diiodonaphthalene with 4-ethynyl-1,8-bis(dimethylamino)naphthalene produced 14-(4,5-bis(dimethylamino)naphthalen-1-yl)-N^{11},N^{11},N^{12},N^{12}-tetramethylnaphtho[1,2-*k*]fluoranthene-11,12-diamine together with 4-((8-iodonaphthalen-1-yl)ethynyl)-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine. It was suggested that the mechanisms of the two novel cascade transformations stem from the specific nature of the proton sponge substrates.

1. Introduction

π-π Interactions are ubiquitous in chemistry. They contribute to a variety of phenomena including the specific structure of proteins,[1] nucleic acids,[2] drug binding[3] and charge transport in semiconducting materials.[4] Gaining an understanding of the tendency for π-systems to stack with one another and the influence of intermolecular interactions on the properties of such assemblies is crucial to the further development of these diverse fields of research.[5]

The 1,8-disubstituted naphthalene unit represents a useful scaffold for study of π−π interactions. Taking the van der Waals radius of a π-bonded carbon atom (1.7 Å) into account, the introduction of two π-electronic systems at the *peri*-positions of the naphthalene ring would predictably introduce strong attractive or repulsive π−π interactions between the substituents depending on their electronic nature. To understand these interactions, various compounds have been synthesized including 1,8-diarylnaphthalenes[6] and 1,8-dialkynylnaphthalenes.[7]

Another interesting aspect of *peri*-alkynyl naphthalenes is the potential bond formation between the closely located triple bonds leading to the formation of polycyclic aromatic compounds by intramolecular cyclization reactions.[7a,b,d,h,8]

From this and following our interest in proton sponge chemistry[9] we reasoned that the Sonogashira coupling of 1,8-diiodonaphthalene with 2-ethynyl and 4-ethynyl derivatives of N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine (proton sponge, PS) could result in the formation of 1,8-dialkynylnaphthalenes **1** and **2** (Scheme 1). It seemed rather intriguing to examine what kind of reactivity would prevail in such compounds: π,π-interaction with the following cyclization or common proton sponge behavior. In the latter case, one could expect the participation of compounds

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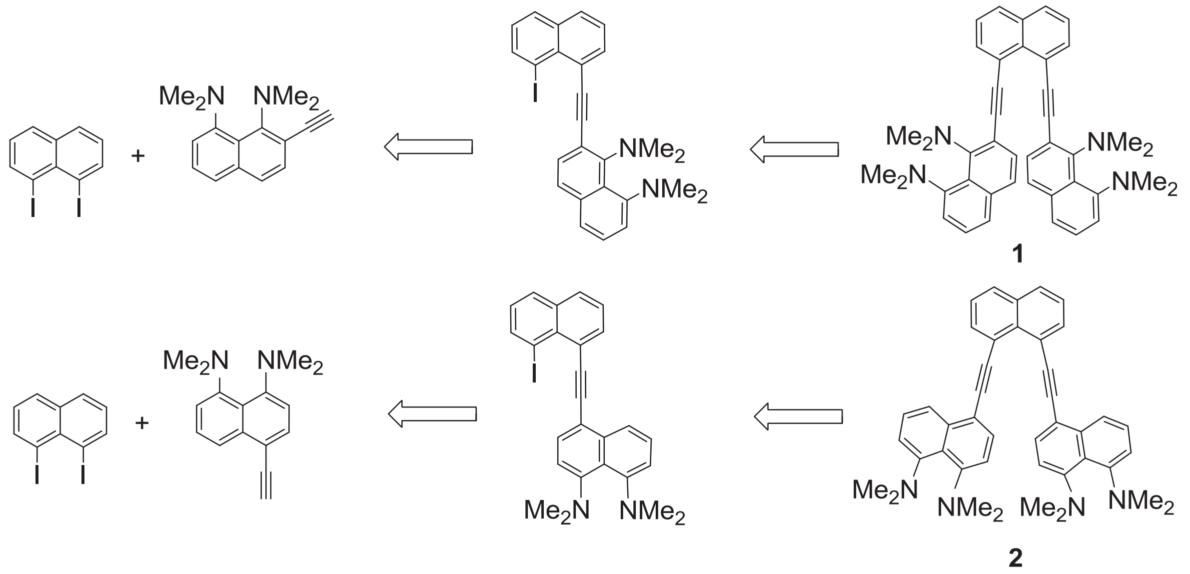


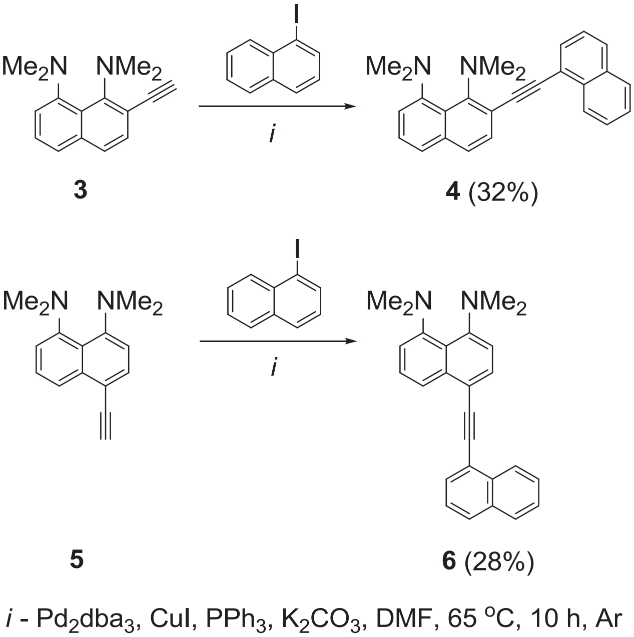
Scheme 1.

1 and **2** in various supramolecular interactions, for example, with bifunctional proton donors, such as 1,2-diols, 1,2-diamines or pyrocatechols.

Herein, we wish to report on the results of the above approach and the unusual cascade cyclizations that occurred on coupling 2-ethynyl-PS, 4-ethynyl-PS and 2,7-diethynyl-PS with 1,8-diiodonaphthalene.

2. Results and discussion

The palladium-catalyzed Sonogashira coupling has become a lynchpin methodology to prepare arylalkynes and conjugated enynes.[10] Earlier, we have synthesized some alkynyl derivatives of proton sponge, including 2-ethynyl-, 4-ethynyl- and 2,7-diethynyl-PS.[11] They were obtained via Sonogashira reactions of 2-, 4-iodo- or 2,7-diiodo-PS with terminal alkynes. Before the synthesis of the target compounds **1** and **2**, we examined the possibility of using 2-ethynyl- and 4-ethynyl-PS as a nucleophilic coupling partner in the Sonogashira reaction with 1-iodonaphthalene. The reactions were performed using a $Pd_2dba_3/CuI/PPh_3/K_2CO_3$/DMF catalytic system at 65 °C for 10 h and resulted in the formation of 2- and 4-naphthylethynyl derivatives **4** and **6** in 32 and 28%, respectively (Scheme 2).



Scheme 2.

The coupling of 4-ethynyl-PS **5** (1.5 equiv.) with 1,8-diiodonaphthalene under similar conditions led to the incorporation of one alkynyl group in the *peri* position of the naphthalene ring leaving the second *peri* iodine atom intact (Scheme 3). The reaction was somewhat more effective than the previous ones producing 4-((8-iodonaphthalen-1-yl)ethynyl)-PS **7** in 35% yield. When using 2.5 equiv. of 4-ethynyl-PS **5** and under more forcing conditions (75–80 °C, 24 h), the reaction gave a mixture of alkyne **7** (39%) and, unexpectedly, polynuclear aromatic compound **8** (42%). The structure of the latter was determined based on spectral and analytical data. It is a red-colored substance with a long-wavelength absorption band (λ_{max} 354 nm) and absorption cut off at 518 nm. The ^{13}C NMR spectrum of **8** indicated the absence of the triple bonds in this compound (see Supporting Information). In its ^1H NMR spectrum (Fig. 1), signals of four different NMe_2 groups were observed, as well as signals from sixteen aromatic protons. Among them a singlet at δ 6.73, assigned to the proton H(13), and a singlet at δ 9.17 ppm belonging to the “bay region” proton H(7) were the most characteristic. The mass-spectrum (ESI) of **8** included an intense peak $[M+2H]^{2+}$ at 301.1702. This is consistent with structure **8** and the superbasic nature of this molecule, containing two fragments of proton sponge. The structure of 14-(4,5-bis(dimethylamino)naphthalen-1-yl)-N^{11},N^{11},N^{12},N^{12}-tetramethylnaphtho[1,2-*k*]fluoranthene-11,12-diamine **8** was proved unambiguously by X-ray single crystal study (Fig. 2).

It is well known that *peri*-dialkynyl naphthalenes tend to undergo intramolecular thermal cyclization into benzo[*k*]fluoranthene derivatives (Scheme 4, ***a***) to relieve the severe electronic and steric congestion between the *peri* triple bonds.[7a,b,i,j] A free-radical mechanism was hypothesized for this cyclization. On the other hand, ionic bromo-[7a,i] or iodocyclizations[8f] of 1,8-dialkynylnaphthalenes furnished acenaphthylenes (Scheme 4, ***b***) or indeno[2,1-*a*]phenalenes (Scheme 4, ***c***). Scheme 4 demonstrates