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# Facile Construction of Furanoacenes by a Three-step Sequence Going Through Disilyl-*exo*-cyclic Dienes

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**Abstract:** Facile synthesis of various benzonaphthofurans was achieved by intramolecular hydroarylation of 1,4-disilyl-2-aryloxy-1,3-enynes followed by cycloaddition with arynes or alkenes and finally desilylaromatization. The three-step transformation can be operated sequentially in one-pot, providing with a range of furanoacenes easily and highly effectively.

Polycondensed heteroaromatics (PCHA) have become an important and challenging class of synthetic targets in material chemistry. PCHA show unique functional properties based on their own structures. A typical example is thienoacenes that have a carrier mobility in many instances and are applied to ptype organic semiconductors for organic field-effect transistors.<sup>[1]</sup> Recently, furanoacenes are attracting much interest due to novel bioactivity and physical properties as functional materials (Figure 1)<sup>[2]</sup> and a building block for polyaromatic hydrocarbons.<sup>[3]</sup> Accordingly, facile preparative methods of furanoacenes are disclosed, taking advantage of intramolecular C-O or C-C bond forming reactions of biaryls or diaryl ethers or annulation with benzofuran,<sup>[4,5]</sup> whereas the conventional methods require multistep preparation and/or uncontrolled condensations in a late stage. Thus, invention of convenient synthetic methods for various kinds of acenes is an urgent research target for the future material chemistry.



 $\ensuremath{\mbox{Figure 1.}}$  Fused dibenzofuran derivatives in material and medicinal compounds

Cycloaddition reaction is a powerful method for the construction of condensed cycles. In particular, exo-cyclic dienes like isobenzofurans are a useful building block for the construction of various polycondenced acenes through the cycloaddition with various dienophiles followed by aromatization (Figure 2a).<sup>[6]</sup> Unlike its simplicity, this particular system is not directly applicable to the synthesis of heteroacenes such as furanoacenes. Furthermore, 2,3-bismethylene-2,3-dihydrofurans, as an ideal building block for furanoacenes, are unstable and quickly undergo undesired transformations.<sup>[7]</sup> Thus, for the construction of heteroacenes, stable but conveniently reactive building blocks are strongly required. Recently, we reported intramolecular exo-hydroarylation of envnes under palladium/carboxylic acid catalytic system, giving variously substituted 2,3-bis(silylmethylene)-2,3-dihydrobenzofurans kinetically-stabilized by two bulky silyl groups.<sup>[8,9]</sup> We envisaged that the cyclic bis(silylmethylene) cycles<sup>[10]</sup> have a potential to work as building intermediates for various furanoacenes employing arynes as a representative reaction partner. For example, cycloadducts resulting from the bis(silylmethylene)dihydrobenzofurans and arynes, are expected to show high solubility and convertibility to a variety of furanoacenes via silyl-promoted aromatization reactions.[11,12,13] From these viewpoints, we pursued the facile construction of furanoacenes by sequential transformations based on the 1,4disilylated oxacyclic dienes as a key building intermediate (Figure 2b).

a Isobenzofuran as a intermediate for acenes



b This work: Construction of furanoacenes via disilylated precursors



Figure 2. Utility of exo-cyclic dienes for the construction of condensed cycles



Initially, we examined the reaction of 2-TIPSmethylene-3-TESmethylene-2,3-dihydrobenzofuran with 1a generated from 2-trimethylsilylphenyl triflate (2a) and CsF in acetonitrile at room temperature.<sup>[14]</sup> To our delight, the desired disilyl dihydorbenzonaphthofuran 3a was obtained in 74% yield

with 6,11-anti configuration (Scheme 1). The two silyl groups in 1a tolerated the presence of CsF due possibly to the steric crowding without any steric retardation toward the cycloaddition. 3a could be aromatized by treatment with I<sub>2</sub> at room temperature to give benzonaphthofuran 4a.[11e] On the other hand, DDQ oxidatively removed the TES group only to provide TIPSsubstituted benzonaphthofuran 5a.[11g]



Scheme 1. Construction of disilyl precursor 3a and benzonaphthofuran 4a and 5a from disilyl exo-oxacyclic diene 1a. Conditions A: I2 (2 eq) and CH2CI2 (0.1 M) at 25 °C. Conditions B: DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone, 2 eq) and toluene (0.1 M) at 80 °C.

The successful transformation led us to improve this protocol to an easier one. We first synthesized 3a from disilyl enyne 6a in one-pot by Pd/acid-catalyzed hydroarylation<sup>[15]</sup> to generate 1a and by cycloaddition with in situ generated benzyne, as shown in Eq. (1) in an overall yield similar to the stepwise synthesis.<sup>[16]</sup> Based on this observation, we examined a true one-pot three-step sequence and obtained 4a in 52% total yield (Scheme 2 upside). This one-pot protocol is quite simple and effective. However, we worried that reaction mess generated by the cycloaddition might complicate the last aromatization step. Therefore, we modified the protocol to the one involving the first two-step one-pot sequence, filtration through Celite, and the treatment with I2. As a result, yield of 4a was enhanced up to 62% (Scheme 2 lower equation), showing this protocol is highly effective to construct the furanoacenes via 1.



Scheme 2. Facile synthesis of 4a from 6a

benzvne

We propose the mechanism for the oxidative aromatization as shown in Scheme 3. By treatment of I2, 3 should be initially converted into iodonium ion 7 via an interaction of the electronrich vinyloxy moiety in 3. Subsequent attack of an iodide ion to the less-bulky SiEt<sub>3</sub> group occurs to generate  $\alpha$ -iodo intermediate 8 and Et<sub>3</sub>Sil. Oxygen-assisted release of *i*Pr<sub>3</sub>Sil from 8 proceeds through cationic 9 to produce furanoacene 4. On the other hand, DDQ likely undergoes at first one-electron oxidation of the vinyloxy moiety in 3 to form 10. The resulting DDQ anion radical should then nucleophilically attack to the SiEt<sub>3</sub> group to generate 11, which finally loses the methine hydrogen by DDQ-SiEt<sub>3</sub> radical selectively to furnish 5.



Scheme 3. Proposed mechanism of the formation of 4 and 5

We next examined the scope of the furanoacene synthesis by the modified sequence (Figure 3). Non-substituted enyne 6b gave 4b without any problem in 53% total yield. Variously substituted envnes 6c-6j having a methoxy, methyl, phenyl, or trifluoromethyl group, or fluorine at para position of the 2phenoxy group were converted into furanoacenes 4c-4j in good yields. Worthy of note is that the site selectivity of the hydroarylation permitted to control the structure of furanoacenes 4. Specifically, the hydroarylation of meta-fluorinated 6i proceeded via the cleavage of C-H bond ortho to fluorine and provided 4i having fluorine at C1 position exclusively. meta-Trifluoromethylated 6j was converted into 4j substituted at C3 position via less-hindered C-H bond activation. Next, we examined various arynes as shown in Figure 4. The reaction of symmetrical 4,5-dimethoxy benzyne and 2,3-naphthalyne (from 2b and 2c) gave the corresponding acenes in good yields. Unsymmetrical arynes such as 1,2-naphthalyne and 3-methyl benzyne (from 2d and 2e) which are slightly biased sterically, gave the corresponding cycloadducts (3n-3p) as an inseparable isomeric mixture. Final aromatization led to furanoacenes 4n-4p in good yields although with low regioselectivity. On the other hand, 3-methoxybenzyne (from 2f) produced furanoacene 4q and 4r with high regioselectivity (6.8:1, 6.7:1). The observed selectivity can be attributed to the nucleophilic 3-TESmethylidene carbon<sup>[8]</sup> in 1 which attacks to the distal C1position of the highly distorted 3-methoxybenzyne (Scheme 4).<sup>[17]</sup> 3-Morpholinobenzyne (from 2g),<sup>[18]</sup> which have the character similar to 3-methoxy benzyne, gave 7aminobenzonaphthofuran 4s with perfect regioselectivity. Thus, in addition to the site-selective C-H cleavage in the hydroarylation, the difference in the nucleophilicity of the two

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methylidene carbons in **1** also contributes to the site-selective synthesis of furanoacenes. These features suggest advantages of the present enyne **6**-based sequence.<sup>[19]</sup>.



**Figure 3.** Synthesis of **4**. A mixture of **6**,  $Pd_2(dba)_3$  (2.5 mol%),  $PCy_3$  (5 mol%),  $fBuCO_2H$  (20 mol%), 4-octyne (10 mol%), and toluene was stirred at 100 °C for 20 h. Then, **2** (3 eq), CSF (6 eq), and MeCN were added and the solution was stirred at 25 °C for 20 h. After filtration through Celite, a mixture of crude **3**,  $I_2$  (1.6 eq), and  $CH_2CI_2$  (0.1 M) was stirred at 25 °C for 20 h. Isolated total yield based on **6**. <sup>b</sup> Ratio of regioisomers. The displayed structure is the main isomer.



Scheme 4. Regioselective cycloaddition with arynes (from 2f and 2g)

The sequence of the furanoacene synthesis was next extended to alkene dienophiles: aromatization of the cycloadducts was found to be equally feasible, thereby enhancing the potential of the present method (Scheme 5). Methyl  $\alpha$ -chloroacrylate (**12**) could be used for the synthesis of unsymmetrical dibenzofuran **13** by the modified sequence with **6a**.<sup>[20]</sup> 1,4-Epoxy-1,4-dihydronaphthalene (**14**) was used in the two-step sequence formed cycloadduct **15** stereoselectively. Subsequent treatment with TfOH<sup>[21]</sup> gave anthracene-fused benzofuran **16** in 71% yield.



Scheme 5. Sequence using alkene partners

In conclusion, we have disclosed a facile reaction sequence for the modular synthesis of various furanoacenes from aryloxydisilylenynes. This sequence involves catalytic intramolecular hydroarylation, cycloaddition with a dienophile like arynes, αchloroacrylate, and 1,4-epoxy-1,4-dihydronaphthalene, and oxidative desilylaromatization, without isolation of intermediates. The two silyl groups act as the versatile roles in among transformations, endowing high stability and solubility for the diene intermediates, high regioselectivity for the second cycloaddition, and the key functional groups for easy desilylaromatization. As a result, all reactions proceed smoothly, giving the targeted furanoacenes in high yields with excellent site-selectivity. In view that the starting materials are readily accessible, the reaction sequence reported here will find a variety of applications in the smooth preparation of a diverse range of furanoacenes.

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#### Keywords: addition • arene • aromatization • alkyne • diene

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Facile synthesis of various benzonaphthofurans was achieved from 1,4-disilyl-2-aryloxy-1,3-enynes via hydroarylation, cycloaddition with arynes or alkenes, and desilylated aromatization. These three reactions could be operated sequentially in one-pot, being highly effective and providing a range of furanoacene products with ease.