

Annulation of propargylic dithioacetals leading to furan-containing oligoaryls*

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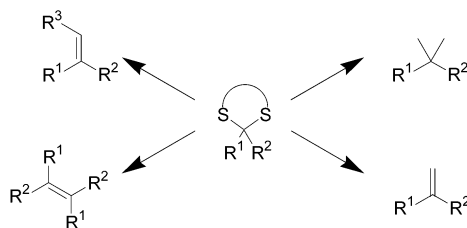
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Abstract: Reaction of propargylic dithioacetals with BuLi followed by treatment with di-aldehydes yields the corresponding allenyl carbinols which can be cyclized to give the 2,3,5-trisubstituted furans. The use of this strategy for the synthesis of a range of alternating benzene-furan oligoaryls is described.

Keywords: annulation; propargylic dithioacetals; oligoaryls; furans; optoelectronic applications; cyclophanes; convergent synthesis.

INTRODUCTION

Direct conversion of carbon–sulfur bonds in dithioacetal functionality into the corresponding carbon–carbon bonds has been extensively studied in recent years [1]. Representative examples are shown in Scheme 1. The substituents R¹ and/or R² can be aryl, alkenyl alkynyl, or, more recently, alkyl groups. Since carbon and sulfur atoms have similar electronegativities, the polarity of the carbon–sulfur bond can vary depending on the nature of the substrates and reaction conditions. In general, the carbon end of a carbon–sulfur bond can serve as a carbocationic equivalent to reaction with a nucleophile. Alternatively, the nucleophile can attack at the sulfur end of a carbon–sulfur bond to generate the carbanion, which can then react with an electrophile leading to the corresponding substitution product. In this case, the carbanionic moiety must be stabilized by a neighboring stabilizing substituent(s). Ikehira and Krief have shown that benzylic dithiolanes react with butyllithium followed by protonolysis to give the corresponding mono-desulfurized products (eq. 1) [2]. Apparently, the remaining sulfur moiety and the aryl substituent may facilitate such umpolung processes. We have recently extended this reaction to allylic and propargylic systems, leading to a variety of fascinating transformation. In this account, recent advances in the use of propargylic and allylic dithioacetals are presented.



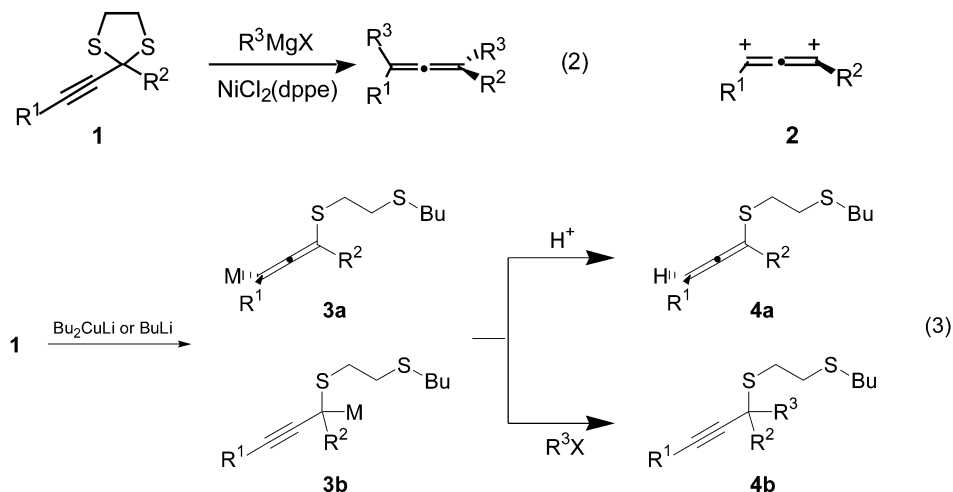
Scheme 1

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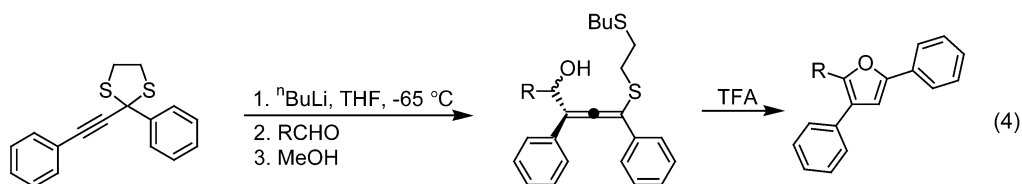
SYNTHESIS OF POLYSUBSTITUTED ALLENES

It has been known that reactions of allylic dithioacetals with MeMgI in the presence of a catalytic amount of NiCl₂(dppe) give the corresponding geminal dimethylation products [3]. In contrast, propargylic dithioacetal serves as allene-1,3-dication synthetic equivalent **2** [4]. Thus, treatment of **1** with the Grignard reagent in the presence of a nickel catalyst (eq. 2) results in the replacement of the two carbon–sulfur bonds by two carbon–carbon bonds. The reaction would be more versatile if the two carbon–sulfur bonds in **1** could be sequentially substituted by different moieties. It is well documented that propargylic acetals react readily with organocopper reagents via an S_N2'-like mechanism to give the corresponding allenyl ethers [5]. Copper moiety is thiophilic. As such, the transfer of an alkyl nucleophile from the organocopper reagent to the sulfur moiety of the dithioacetal group might generate intermediate **3** (eq. 3) [6]. It is noteworthy that anion **3** is stabilized by the remaining thioether moiety and by the triple bond. There is an equilibrium between allenyl **3a** and alkynyl **3b** organometallic intermediates. Further reactions with electrophiles can afford either substituted allene **4a** or propyne **4b** derivatives, depending on the nature of the electrophiles. When proton and hard electrophiles are employed, allenes are obtained exclusively in excellent yield. On the other hand, alkyne derivatives are the only products when soft electrophiles such as alkyl halides are used (eq. 3). The remaining carbon–sulfur bond in allenes or alkynes can be converted into the corresponding carbon–carbon bond via the nickel-catalyzed cross-coupling reactions with Grignard reagents.



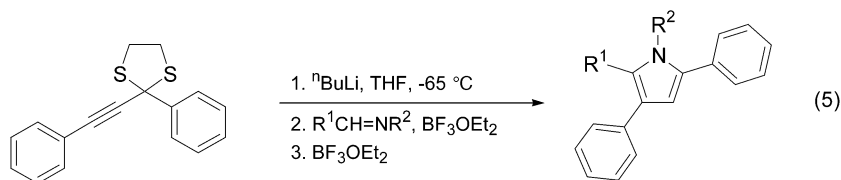
ANNULATION TO TRISUBSTITUTED FURANS AND PYRROLES

When an aldehyde is allowed to react with the allenyl copper or lithium intermediate, the corresponding allenyl carbinol is obtained in good yield. Further reactions of the carbinols with TFA yields the corresponding 2,3,5-trisubstituted furan derivatives (eq. 4) [7]. The reaction can also be preceded in one pot. It is worthy to note that R³ comes from the electrophile and R² arises from the propargylic dithioacetal. If both R² and R³ are aryl groups, the reaction provides a convenient route for the synthesis of furan-containing conjugated teraryls. Furthermore, the substituent R¹ originates from the substituent at the triple bond in the starting material. It can be a simple aliphatic moiety so that the solubility of the teraryl products can be improved significantly.



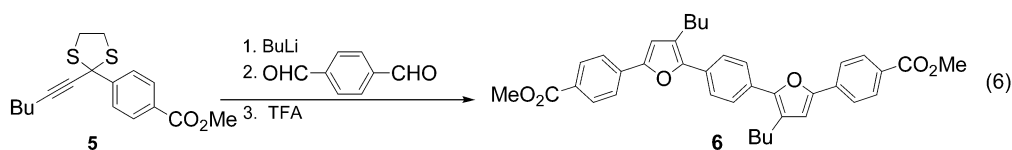
A range of functional groups are stable under the reaction conditions. It is particularly noteworthy that an ester group remains intact upon treatment with BuLi or the corresponding copper reagents. Since an ester group can later be transformed into the corresponding aldehyde, further treatment using similar procedures may lead to an extension of aryl linkage, leading to a convenient synthesis of furan-containing oligoaryls.

Imines can also react with the sulfur-substituted allenyl anions in the presence of BF_3OEt_2 to give the corresponding pyrroles (eq. 5). This reaction again can be used in the incorporation of pyrrole rings into the oligoaryls [7].

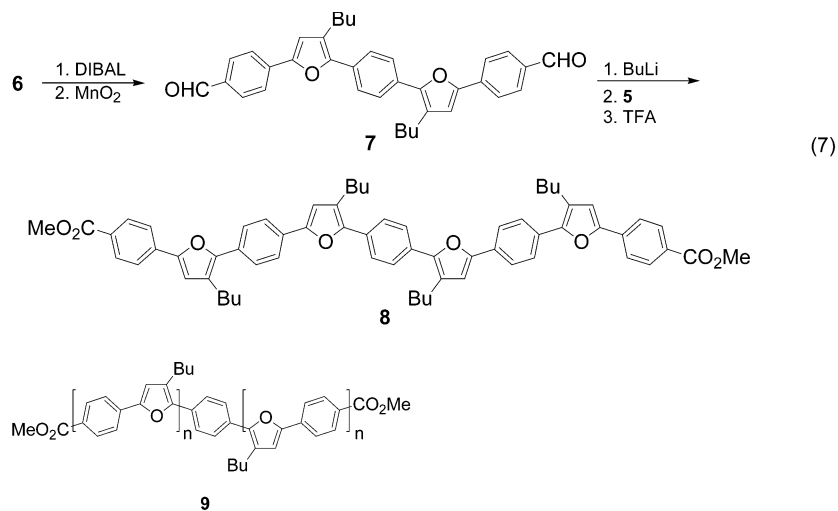


SYNTHESIS OF FURAN-CONTAINING OLIGOARYLS

Treatment of **5** with terephthalaldehyde yields the corresponding pentaaryl **6** in satisfactory yield (eq. 6). This procedure will add four aromatic rings (two phenyl and two furan rings) upon each of such treatment [7,8].

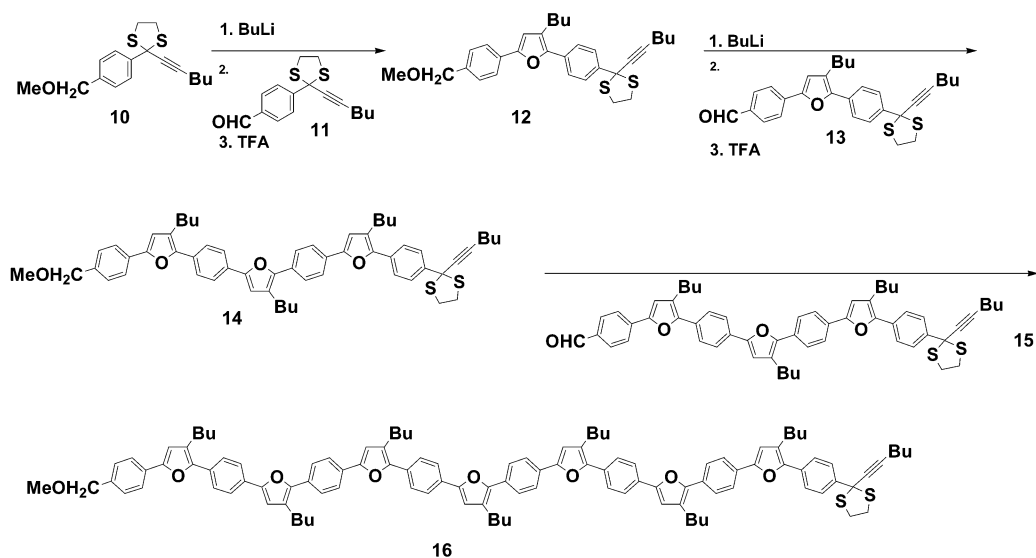


It is noteworthy that ester groups are stable under the furan annulation conditions. Since the ester function can easily be reduced into the corresponding aldehyde, further annulation can occur, leading to the synthesis of a range of furan- or pyrrole-containing oligoaryls. Accordingly, nonamer **8** is obtained from annulation of pentamer dialdehyde **7** with **5** (eq. 7). Similarly, 13-mer **9** ($n = 3$) is synthesized from the corresponding nonamer dialdehyde. However, this procedure is no more applicable when the conjugation length reached 13-mer. Oxidation of furan rings may occur when MnO_2 or DDQ are employed. Alternatively, conversion of an ester group into an aldehyde group can be achieved via a Weinreb amide [9]. By using such a strategy, 17-mer **9** ($n = 4$) containing eight substituted furan rings is conveniently synthesized. Since each of the furan moieties contains a butyl substituent, these oligoaryls are soluble in organic solvent and can easily be purified by crystallization.



CONVERGENT SYNTHESIS

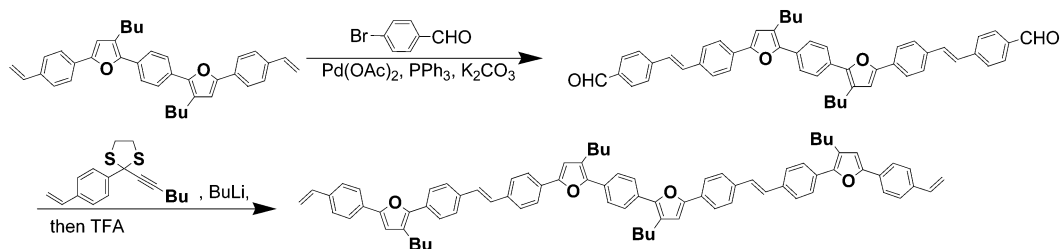
The reaction sequence shown in eq. 7 can add two furan and two benzene rings on each annulation procedure. A more expedited procedure is desirable for the synthesis of higher homologues of furan-containing oligoaryls. Since the ester group is stable under the reaction conditions, treatment of **10** with BuLi gives the corresponding allenyl lithium, which is allowed to react with **11** and which can generate tetrayl **12** having propargylic dithioacetal functionality. The alkoxyethyl group in **12** can be converted into aldehyde **13**, which in turn can react with allenyl lithium generated from **12** by same procedure to produce hepta-aryl **14**. In a similar manner, 15-mer **16** can be obtained from the coupling reaction of two heptamers **14** and **15** (Scheme 2) [10].



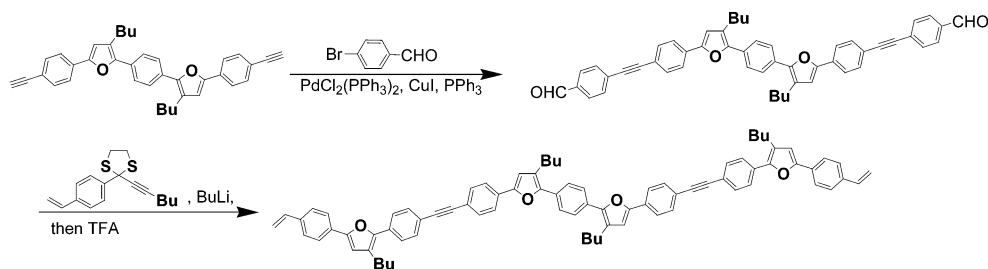
Scheme 2

INTRODUCTION OF DOUBLE AND TRIPLE BONDS INTO OLIGOARYLS

As shown in eq. 7, the key intermediates to elongate the oligoaryl chains are the corresponding dialdehydes. Since double and triple bonds are stable under the furan annulation conditions, Heck and Sonogashira reactions can thus be used to introduce araldehyde moieties at the terminals for further annulation reactions. These procedures provide useful entries to incorporate double or triple bonds into the oligoaryl chains (Scheme 3 and 4) [11].



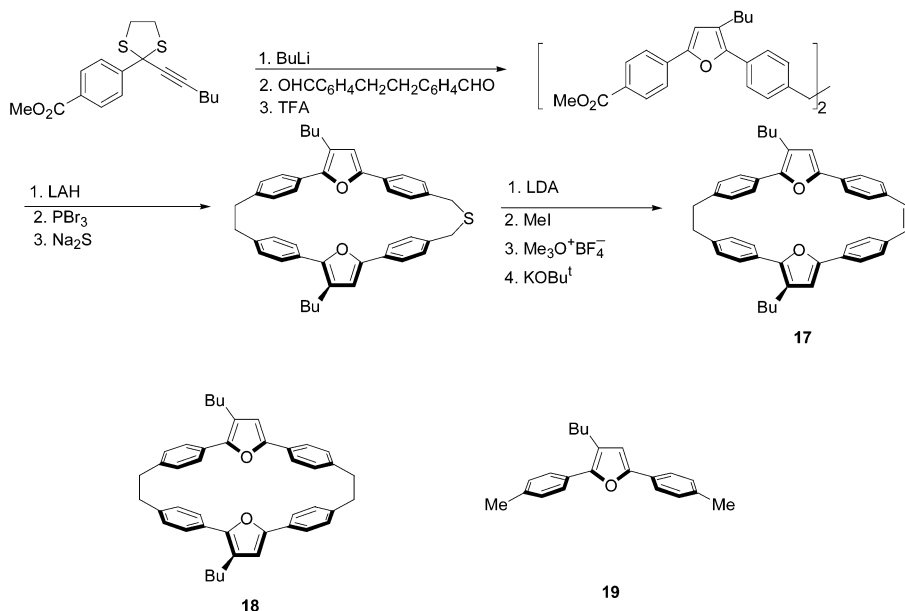
Scheme 3



Scheme 4

FURAN-CONTAINING OLIGOARYL CYCLOPHANES

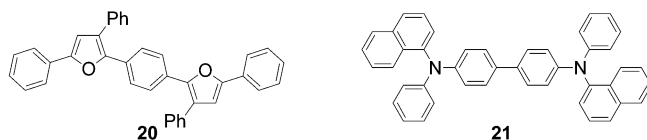
The use of cyclophanes as models to elucidate the nature of interactions between chromophores abounds. The strategy used for furan annulation may provide a convenient route leading to the synthesis of furan-containing cyclophanes **17** (Scheme 5) [12]. Both **17** and its saturated analog **18** are highly fluxional, and barriers are about 10 Kcal/mol. Cyclophanene **17** exhibits large red-shift in the emission spectrum (499 nm) in comparison with those of **18** (389 nm) and **19** (379 nm). Presumably, the presence of the double bond in **17** may result in extension of conjugation in the excited state. This point has been supported by theoretical calculations.



Scheme 5

FURAN-CONTAINING OLIGOARYLS AS HOLE-TRANSPORTING MATERIALS

It has recently been found that a new class of highly stable furan-based hole-transporting oligomeric materials (e.g., **20**) serve as efficient hole-transporting materials in electroluminescent devices. The performance of the devices using these furan materials is comparable with or somewhat better than those employing the conventional triarylaminnes (**21**) [14].



CONCLUSIONS

This account summarizes the recent advances on the use of propargylic dithioacetals in organic synthesis. Based on the similarity of the electronegativities of sulfur and carbon, the reactions with BuLi provide useful routes for the synthesis of polysubstituted allenes and trisubstituted furans and pyrroles. This strategy has been extended to the preparation of a range of furan-containing oligoaryls which exhibit interesting photophysical properties for optoelectronic applications.

ACKNOWLEDGMENTS

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