

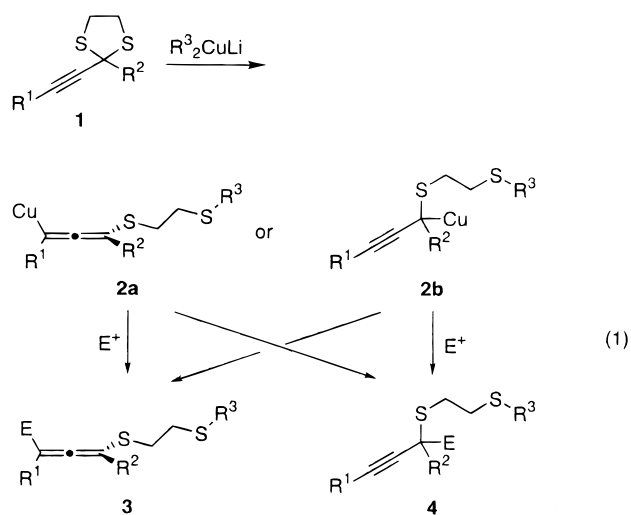
One-Pot Synthesis of Substituted Furans and Pyrroles from Propargylic Dithioacetals. New Annulation Route to Highly Photoluminescent Oligoaryls

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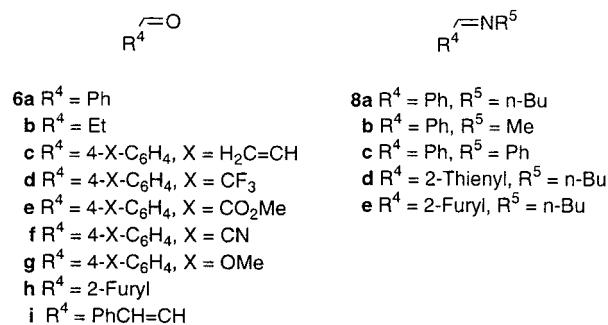
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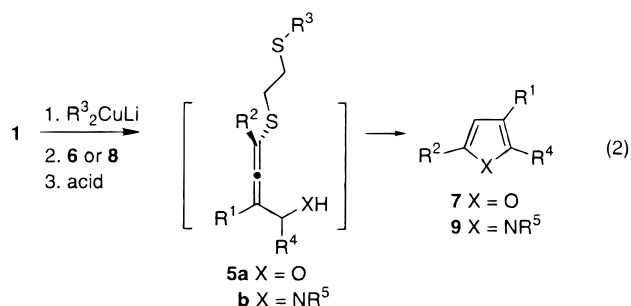
Oligoaryl is an important class of compounds which exhibit a variety of fascinating properties for optoelectronic interests.¹ Incorporation of five-membered heteroaromatic moieties into these conjugated molecules will occasionally increase fluorescence quantum yields and the optoelectronic properties of the oligomers can be tuned.¹ Most syntheses of these heteroaromatic containing oligomers involve the transition-metal catalyzed cross coupling reactions of the corresponding aryl components.² In general, the presence of a long chain aliphatic substituent in these heteroaromatic rings will increase the solubility in organic solvent and hence enhance the processibility of these materials.¹ However, introduction of such alkyl substituent at C₃ and/or C₄ positions in these heteroaromatic rings for further cross coupling reactions is not trivial.³ Cyclization of the 1,4-dicarbonyl moiety with heteroatom-containing reagents provides an alternative procedure for the construction of these five-membered heterocycles.^{3–5} It is known that annulation of allenylmethanols can afford the corresponding five-membered oxygen heterocycles.⁶ In addition, annulation of allenyl carbonyl compounds,⁷ propargylic acetals,⁸ or oxiranes^{9,10} furnishes a powerful arsenal for the synthesis of substituted furans. The applications of propargylic metallic species have paved a useful path for the construction of furan skeletons.¹¹ We recently reported that propargylic dithioacetal **1** can serve as an allene 1,3-zwitterion synthon (eq 1).¹² The interesting feature for this reaction involves an umpolung of one of the two carbon–sulfur bonds in the dithioacetal functionality. The organocopper intermediate **2** can react with a number of electrophiles leading



to either allenyl or alkynyl product **3** or **4**. The chemoselectivity of this reaction depends on the nature of the electrophile. It is envisaged that the reaction of **2** with an aldehyde **6** or an aldimine **8** may yield the intermediate alcohol **5a**, or amine **5b**, respectively.



Since the thioether moiety in **5** could be a good leaving group, cyclization to eliminate the sulfur moiety may lead to the substituted furan **7** or pyrrole **9** (eq 2). In this communication,



we report a convenient one-pot annulation reaction leading to furan or pyrrole moiety as a part of the oligoaryls.

A THF solution of **1** was allowed to react with 0.6 equiv of Bu₂CuLi¹³ in THF at –78 °C followed by treatment with an aldehyde **6**. Without workup, the mixture was subsequently treated with trifluoroacetic acid to give the corresponding furans **7** in satisfactory yield. A range of 2,3,5-trisubstituted furans can be conveniently synthesized by this annulation procedure and repre-

(13) Less than a stoichiometric amount of the organocopper reagent (e.g. 0.6 equiv) has been used for the Michael addition of acrolein (Cf.: Matsuzawa, S.; Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Tetrahedron* **1989**, *45*, 349. See also: Lipshutz, B. H. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: Chichester, 1994; p 298).

(1) *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998.

(2) For examples: Pelter, A.; Jenkins, I.; Jones, D. E. *Tetrahedron* **1997**, *53*, 10357. Pelter, A.; Rowlands, M.; Jenkins, I. H. *Tetrahedron* **1987**, *28*, 5213. Pelter, A.; Rowlands, M.; Clements, G. *Synthesis* **1987**, 51. Fanta, P. E. *Synthesis* **1974**, 9. Crisp, G. T. *Synth. Commun.* **1989**, *19*, 307. Gronowitz, S.; Bobosik, V.; Lawitz, K. *Chem. Scr.* **1984**, *24*, 5. Yassar, A.; Garnier, F.; Deloffre, F.; Horowitz, G.; Ricard, L. *Adv. Mater.* **1994**, *6*, 660. Gronowitz, S.; Bobosik, V.; Lawitz, K. *Chem. Scr.* **1984**, *23*, 120.

(3) For reviews, see: Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. Hou, X. L.; Cheung, H. Y.; Hon, T. Y.; Kwan, P. L.; Lo, T. H.; Tong, S. Y.; Wong, H. N. C. *Tetrahedron* **1998**, *54*, 1955.

(4) Bean, G. P. In *Pyrroles*; Jones, R. A., Ed.; Wiley: New York, 1990; p 194. Jackson, A. H. In *Comprehensive Organic Chemistry*; Sammes, P. G., Ed.; Pergamon Press: Oxford, 1979; Vol. 4, p 296.

(5) Wynberg, H.; Metselaar, J. *Synth. Commun.* **1984**, *14*, 1. Moriarty, R. M.; Prakash, O.; Duncan, M. P. *Synth. Commun.* **1985**, *15*, 789. Nakayama, J.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1987**, *26*, 2599. Asano, T.; Ito, S.; Saito, N.; Hatakeda, K. *Heterocycles* **1977**, *6*, 317. Kooreman, H. J.; Wynberg, H. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 37.

(6) Marshall, J. A.; Wang, X.-J. *J. Org. Chem.* **1991**, *56*, 4913. Marshall, J. A.; Barty, G. S. *J. Org. Chem.* **1994**, *59*, 7169.

(7) Marshall, J. A.; Bennett, C. E. *J. Org. Chem.* **1994**, *59*, 6110. Marshall, J. A.; Robinson, E. D. *J. Org. Chem.* **1990**, *55*, 3450. Marshall, J. A.; Wallace, E. M. *J. Org. Chem.* **1995**, *60*, 796.

(8) Kim, S.; Kim, Y. G. *Synlett* **1991**, 869. Obrecht, D. *Helv. Chim. Acta* **1989**, *72*, 447. Ly, N. D.; Schlosser, M. *Helv. Chim. Acta* **1977**, *60*, 2085.

(9) Marshall, J. A.; DuBay, W. J. *J. Org. Chem.* **1991**, *56*, 1685. Marshall, J. A.; DuBay, W. J. *J. Am. Chem. Soc.* **1992**, *114*, 1450. Sham, H. L.; Betebenner, D. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1134.

(10) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363.

(11) Shu, H.-G.; Shiu, L.-H.; Wang, S.-H.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 530. Iwasawa, N.; Maeyama, K.; Saitou, M. *J. Am. Chem. Soc.* **1997**, *119*, 1486.

(12) Tseng, H.-R.; Luh, T.-Y. *J. Org. Chem.* **1997**, *62*, 4568. Tseng, H.-R.; Lee, C.-F.; Yang, L.-M.; Luh, T.-Y. *J. Org. Chem.* **1999**, *64*, 8582.

Table 1. Synthesis and Properties of Trisubstituted Furans **7**

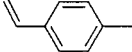
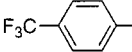
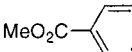
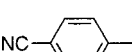
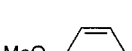


Product	R ¹	R ²	R ⁴	%Yield	λ_{em} (nm)	Φ_f
7a	Ph	Ph	Ph	60	387	52
7b	Ph	Ph	Et	40	345	34
7c	n-Bu	Ph	Ph	73	357	12
7d	Ph	Ph		42	412	66
7e	Ph	Ph		42	401	48
7f	Ph	Ph		45	417	50
7g	Ph	Ph		37	414	46
7h	Ph	Ph		62	394	77
7i	Ph	Ph		66	390	57
7j	n-Bu	Ph		25	421	22

Table 2. Synthesis and Photophysical Properties of Substituted Pyrroles **9** (R¹ = R² = Ph)




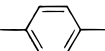
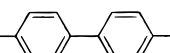

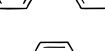
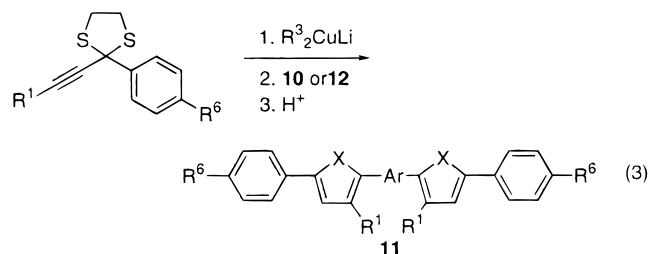
Pyrrole	R ⁵	R ⁴	%Yield	λ_{em} (nm)	Φ_f
9a	n-Bu	Ph	62	391	35
9b	Me	Ph	64	393	35
9c	Ph	Ph	73	395	19
9d	n-Bu		63	423	8
9e	n-Bu		71	387	13

Table 3. Synthesis and Properties of Penta- and Hexaaryls **11**

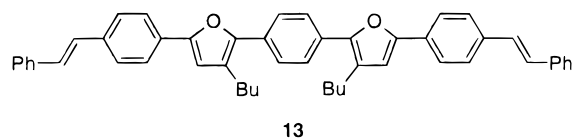
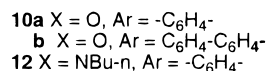
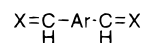
Product	—Ar—	R ¹	R ⁶	X	%Yield	λ_{em} (nm)	Φ_f
11a		n-Bu	H	O	40	414, 439	82
11b		n-Bu	vinyl	O	51	437, 463	100
11c		n-Bu	H	O	59	419, 441	95
11d		n-Bu	vinyl	O	72	433, 458	76
11e		Ph	H	NBu	28	423	65

representative examples are summarized in Table 1. Pyrroles **9** were also obtained in a similar manner when imines **8** were used in place of aldehydes. It is noteworthy that BF₃·OEt₂ appeared to be a better Lewis catalyst for the cyclization in pyrrole synthesis. Results are outlined in Table 2. The structures of **7** and **9** were unambiguously assigned by NOESY, HMQC, and/or HMBC.

As shown in Tables 1 and 2, the reaction is particularly promising to introduce a substituent at C₃. More importantly, this substituent can be a long chain aliphatic moiety. As mentioned earlier, it is a common strategy to have such an alkyl group to increase the solubility for the convenience of processing leading to devices for optoelectronic investigations. Our synthesis indeed provides a very convenient entry for the synthesis of such oligoaryls or polyarylenes with these aliphatic substituents. Starting from the dialdehydes **10**, oligoaryls **11a–d** having two furan moieties were obtained in one pot (eq 3). In a similar manner, when a diimine **12** was employed, bis-pyrrole **11e** was prepared (eq 3). The results are tabulated in Table 3.



As shown in Table 1, a wide range of substituents having different functionalities remains intact under these reaction conditions. Accordingly, further modification of these functionality may lead to a variety of oligoaryls and the lengths of conjugation can thus be tuned. For example, Heck reaction of **11b** with PhI afforded **13** in 83% yield.



The λ_{em} values measured in EtOAc and the fluorescence quantum yields (Φ_f) for these oligomers are also tabulated in Tables 1–3 for comparison. It is noteworthy that penta- or hexaaryl oligomers **11** (Table 3) exhibit very bright emission in the blue light region. As expected, the emission maximum of **13** (λ_{em} 460, 479 nm, Φ_f = 0.67) shifted bathochromically. Thermogravimetric analyses showed that **11c** and **11d** remained intact at 200 °C for at least 24 h and T_d values were 412 and 435 °C, respectively. The potential optoelectronic applications are under investigation.

In summary, we have uncovered a useful annulation procedure starting from the propargylic dithioacetals via the corresponding organocopper intermediates resulting in a convenient synthesis of furan and pyrrole heterocycles. The reaction is particularly appealing for the preparation of a range of oligoaryls containing furan or pyrrole moieties.

Acknowledgment. This work was supported by the National Science Council and the Ministry of Education of the Republic of China.

Supporting Information Available: Experimental procedures for the preparation of **1**, **7**, **9**, **11**, and **13** and their ¹H NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.