



Versatile synthesis of 3,4-*b* diheteropentalenes

Tanmoy Dey, Daminda Navarathne, Michael A. Invernale, Ian D. Berghorn, Gregory A. Sotzing*

University of Connecticut, Department of Chemistry and the Polymer Program, 97 North Eagleville Road U-3136, Storrs, CT 06269-3136, United States

ARTICLE INFO

Article history:

Received 23 October 2009

Revised 4 February 2010

Accepted 7 February 2010

Available online 11 February 2010

ABSTRACT

We describe a new route for the synthesis of thieno[3,4-*b*]thiophene, alkyl derivatives thereof, seleno[3,4-*b*]thiophene, and thieno[3,4-*b*]furan made from inexpensive starting materials, such as thiophene-2-carboxylic acid and furan-2-carboxylic acid. Such fused heterocycles are of great interest for low band gap organic semiconductors and applications including OLEDs, organic photovoltaic cells, and electrochromics.

© 2010 Published by Elsevier Ltd.

During recent years, many research groups have been involved in the preparation of a variety of heterocycles and fused heterocycles,¹ including thienothiophenes² and thienofurans,³ for different applications. Many of these methodologies have involved expensive starting materials and difficult synthetic procedures, sometimes with undesirable yields. Herein, we focus on the synthesis and characterization of the fused heterocycles thieno[3,4-*b*]thiophene (T34bT), thieno[3,4-*b*]furan (T34bF), seleno[3,4-*b*]thiophene (S34bT), and related compounds using inexpensive chemical reagents, lowering synthetic difficulty, as well as providing a versatile route to a myriad of fused heterocycles and derivatives thereof. Selenium, oxygen, and sulfur were used as the heteroatoms, and different-length alkyl chain derivatives were prepared; these routes are amenable to the inclusion of different heteroatoms, various combinations thereof, and other substituents, as well.

Five-membered fused heterocyclic structures (Fig. 1) are commonly known as the A, B-diheteropentalenes. They are created by replacing a CH group from each of the pentalene rings with a heteroatom, typically oxygen, nitrogen, sulfur, selenium, or tellurium.⁴ A pair of electrons is donated by the heteroatom, resulting in 10 π -electron systems, which are isoelectronic with the aromatic pentalene dianion.^{5,6} The stability of the π -electrons within the A, B-diheteropentalene rings depends on the relative orientation of the two heteroatoms.^{7–9} The resonance energy value and heats of formation obtained from MNDO calculations¹¹ suggested that the heterocycles with [2,3-*b*] and [3,2-*b*] ring fusion would be more stable than the [3,4-*b*] isomer, while the [3,4-*c*]-fused isomer was predicted to be extremely unstable. Research efforts in the thienothiophene series confirmed these predictions; both thieno[2,3-*b*]thiophene (T23bT) and thieno[3,2-*b*]thiophene (T32bT) were stable and underwent electrophilic substitution¹⁰ while thieno[3,4-*b*]thiophene (T34bT) was more reactive and more easily underwent oxidation in air; none of these heterocycles were

completely immune to such oxidation.¹¹ To date, the parent thieno[3,4-*c*]thiophene (T34cT) has not been isolated.

Any thienothiophene possesses two fused thiophene rings, the orientations of which vary depending on the locations of the sulfur atom in the peripheral thiophene. Whereas in any thienofuran (A = S, B = O), a furan ring is attached to another thiophene. Thus far, two furan-containing diheteropentalenes have been reported, namely thieno[3,4-*b*]furan¹² (T34bF) and thieno[2,3-*c*]furan (T23cF).¹³ Approaches to the furo[2,3-*c*]furan (F23cF) ring system have not been investigated. Figure 1 shows the structures of the various molecules synthesized herein.

In the growing field of organic semiconductors, thiophene-based fused heterocyclic materials play an important role. These materials display promising optical and electrical properties for use in electrochromics,¹⁴ organic light-emitting diodes (OLEDs),¹⁵ and organic photovoltaics (OPVs).¹⁶ T34bT and T34bF are notable monomers as they can be used in the preparation of intrinsically conducting, low band gap polymers. Indeed, polymeric forms of T34bT have been used as conductors and as ion storage layers for electrochromic devices.^{17,18} Derivatization of these heterocycles

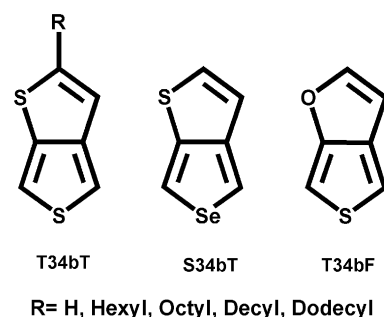


Figure 1. Structure of thieno[3,4-*b*]thiophene (T34bT), its derivatives, seleno[3,4-*b*]thiophene (S34bT), and thieno[3,4-*b*]furan (T34bF).

* Corresponding author. Tel.: +1 860 486 4619; fax: +1 860 486 4745.

E-mail address: sotzing@mail.ims.uconn.edu (G.A. Sotzing).

is an effective method of property-tuning for the resultant polymers. Limitations, with respect to derivatization, in the established syntheses of these monomers have led to the development of the alternate routes described herein.

In 1991, Brandsma and Verkruijse¹⁹ reported the synthesis of T34bT via the conversion of 3,4-dibromothiophene to the monotrimethylsilyl acetylenic derivative, which was then ring closed to form T34bT after forming the thiolate on the 3-position. We reported a modified synthetic procedure where we obtained as high as 55–60% yield in the final ring-closing step²⁰, however we were able to obtain a maximum yield of only 8% using the conditions reported by Brandsma.¹⁹ In 1986, Moursounidi and coworkers first reported the synthesis of T34bF. For many applications, derivatization at the 2-position is important, since the substituent can affect the band gap and solubility of the resultant polymer. This concept was shown by Pomerantz et al. with the synthesis of poly(2-decylthieno[3,4-*b*]thiophene).²¹ Ferraris extended this concept by introducing a phenyl group in the 2-position.²² Yu et al.,²³ have synthesized T34bT with electron-withdrawing ester groups in the 2-position; however, thus far no one has reported substituents with an electron-donating character stronger than that of an alkyl chain.

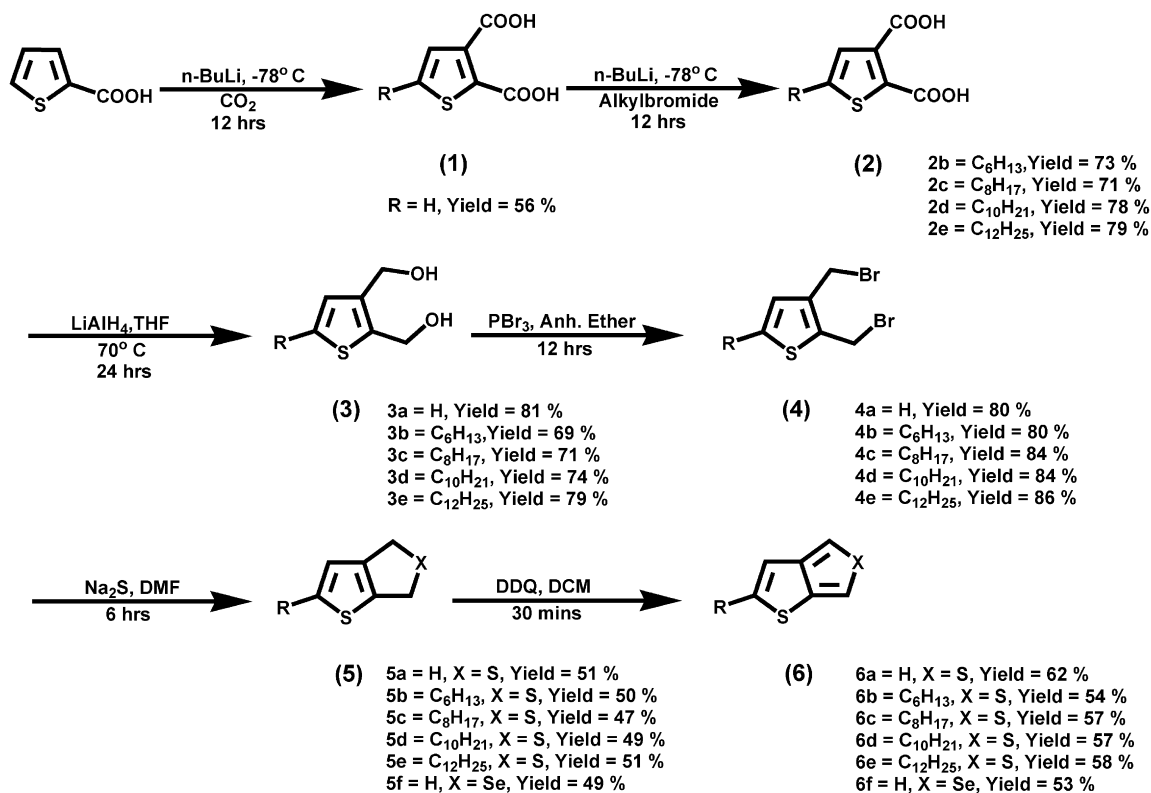
We were able to extend and expand the versatility of fused heterocycles by our new routes. The alkyl substituents reported in this work are weak electron-donating groups, which will result in lower oxidation potentials for polymerization. In addition, the lengthy alkyl groups will also contribute towards making the resultant polymer organic soluble. Our use of the selenium heteroatom further broadens the utility of this synthetic approach.

The reported methods of making T34bT, 2-alkyl-derivatized T34bT, and T34bF²⁴ require expensive chemicals such as 3,4-dibromothiophene and 3,6-di(pyridine-2'-yl)-s-tetrazine (DPT).²⁵

This makes the polymers thereof more costly, which is where the bulk of their applications lie. Moreover, current synthetic procedures are limited because of the difficulty in derivatizing the 2-position of T34bT. It is therefore necessary to develop novel synthetic approaches for five-member fused heterocycles. We were interested in developing a common synthetic methodology that combined the strategies of T34bT with 2-alkyl T34bT to ultimately yield a series of 2-substituted molecules. Further, we sought to incorporate another heteroatom, selenium, into these fused to systems to explore the versatility of our approach.

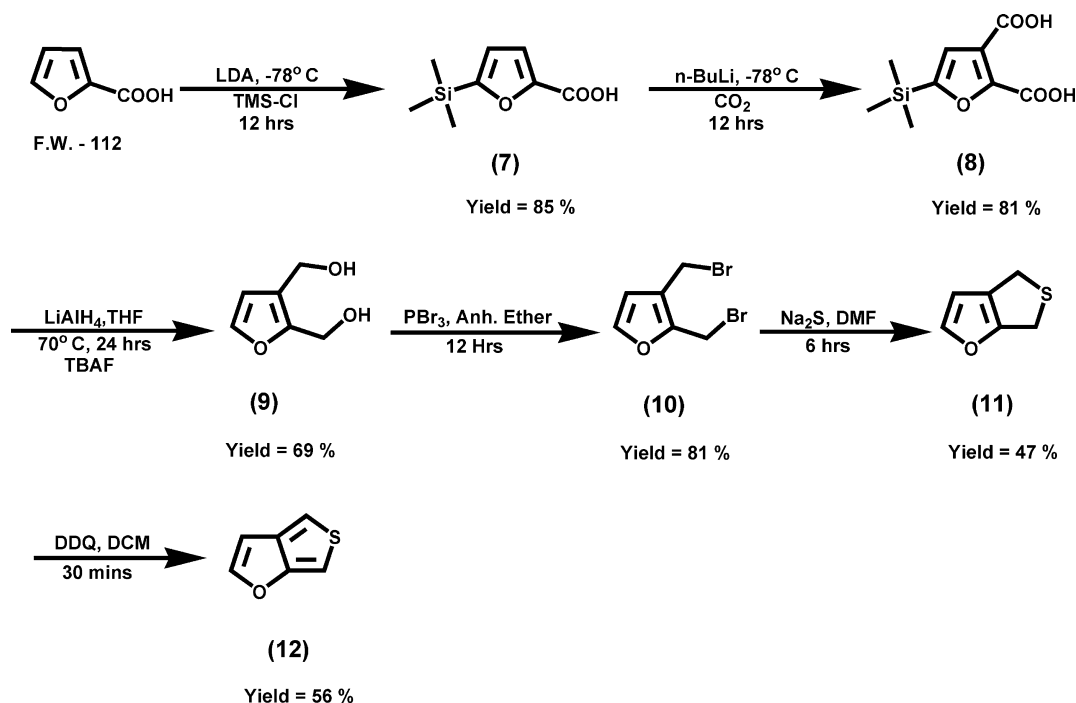
Synthetic schemes, including yields, for the new preparation of T34bT, its derivatives, S34bT, and T34bF appear in Schemes 1 and 2. Scheme 1 shows the new synthesis for T34bT and S34bT, as well as the modified procedure for our alkyl-derivatized T34bT (though it may be adapted to the attachment of other substituents), and Scheme 2 shows the new synthetic route to T34bF.

Thus, we have demonstrated an efficient, inexpensive, and versatile synthetic approach for preparing T34bT, 2-alkylated T34bT, S34bT, and T34bF. These new routes open the door to a wide variety of potential derivatives. We intend to more fully explore these substituents at the 2-position using this chemistry, particularly with other electron-donating groups. By using the same synthetic methodology, we also intend to make different annelated heterocyclic systems with N and Te. The range of practical applications of isomeric thienothiophene or thienofuran derivatives and their O-, N-, S-, Se-, Te-containing and fused analogues is vast, ranging from prospects in the design of new medicines²⁶ to the design of the previously unknown liquid and clathrate crystals,²⁷ charge-transfer complexes,²⁸ conducting polymers,¹⁸ nonlinear optical materials,²⁹ and dyes,³⁰ among others.



Note : DDQ: 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, Heteroatom (X) = S, Se

Scheme 1. Synthetic procedure for thieno[3,4-*b*]thiophene (T34bT), 2-alkyl substituted thieno[3,4-*b*]thiophenes, and seleno[3,4-*b*]thiophene (S34bT).



Scheme 2. Synthetic procedure for thieno[3,4-b]furan (T34bF).

Acknowledgments

The authors wish to acknowledge Sekisui Chemical Co., Ltd. and the National Science Foundation (NSF Career CHE-0349121) for financial support of this work.

Supplementary data

Supplementary data (fully detailed synthetic steps and characterizations for all intermediate compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.02.036.

References and notes

- (a) Aly, A. A.; Brown, A. B. *Tetrahedron* **2009**, *65*, 8055–8089; (b) Sai Sudhir, V.; Phani Kumar, N. Y.; Nasir Baig, R. B.; Chandrasekaran, S. *J. Org. Chem.* **2009**, *74*, 7588–7591; (c) Sen, S.; Kulkarni, P.; Borate, K.; Pai, N. R. *Tetrahedron Lett.* **2009**, *50*, 4128–4131; (d) Scalzullo, S. M.; Islam, R. U.; Morgans, G. L.; Michael, J. P.; van Otterlo, W. A. L. *Tetrahedron Lett.* **2008**, *49*, 7403–7405; (e) Majumdar, K. C.; Chakravorty, S.; De, N. *Tetrahedron Lett.* **2008**, *49*, 3419–3422; (f) Ozden Kasimogulla, B.; Cesur, Z. *Turk. J. Chem.* **2007**, *31*, 617–622.
- (a) Liang, Y.; Feng, D.; Wu, Y.; Tsai, S.-T.; Li, G.; Ray, C.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 7792–7799; (b) Choudhury, K. R.; Lee, J.; Chopra, N.; Gupta, A.; Jiang, X.; Amy, F.; So, F. *Adv. Funct. Mater.* **2009**, *19*, 491–496; (c) Liang, Y.; Feng, D.; Guo, J.; Szarko, J. M.; Ray, C.; Chen, L. X.; Yu, L. *Macromolecules* **2009**, *42*, 1091–1098; (d) Liang, Y.; Xiao, S.; Feng, D.; Yu, L. *J. Phys. Chem. C* **2008**, *112*, 7866–7871; (e) Yao, Y.; Liang, Y. Y.; Shrotriya, V.; Xiao, S. Q.; Yu, L. P.; Yang, Y. *Adv. Mater.* **2007**, *19*, 3979.
- Kumar, A.; Bokria, J. G.; Buyukmumcu, Z.; Dey, T.; Sotzing, G. A. *Macromolecules* **2008**, *41*, 7098–7108.
- Cava, M. P.; Lakshmikantham, M. V. *Compd. Heterocycl. Chem.* **1984**, *4*, 1037.
- Katz, T. J.; Rosenberger, M. *J. Am. Chem. Soc.* **1962**, *84*, 865.
- Katz, T. J.; Rosenberger, M.; O'Hara, R. K. *J. Am. Chem. Soc.* **1964**, *86*, 249.
- Milun, M.; Trinajstić, N. *Croat. Chem. Acta* **1977**, *49*, 107.
- Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.
- Buemi, G. *J. Chim. Phys.-Chim. Biol.* **1987**, *84*, 1147.
- Litvinov, V. P.; Gol'dfarb, Y. L. *Adv. Heterocycl. Chem.* **1976**, *19*, 123.
- (a) Wynberg, H.; Zwanenburg, D. J. *Tetrahedron Lett.* **1967**, *761*; (b) Heffner, R. J.; Joullie, M. M. *Synth. Commun.* **1991**, *21*, 1055–1069.
- Moursounidis, J.; Wege, D. *Tetrahedron Lett.* **1986**, *27*, 3045–3048.
- (a) Friedrichsen, W.; Schoning, A. *Heterocycles* **1986**, *24*, 307; (b) SchGning, A.; Debaerdemaeker, T.; Zander, M.; Friedrichsen, W. *Chem. Ber.* **1989**, *122*, 1119.
- (a) Schwendeman, I.; Hwang, J.; Welsh, D. M.; Tanner, D. B.; Reynolds, J. R. *Adv. Mater.* **2001**, *13*, 634; (b) Schottland, P.; Zong, K.; Gaupp, C. L.; Thompson, B. C.; Thomas, C. A.; Giurgiu, I.; Hickman, R.; Abboud, K. A.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 7051; (c) Thompson, B. C.; Schottland, P.; Zong, K.; Reynolds, J. R. *Chem. Mater.* **2000**, *12*, 1563.
- Yu, G.; Heeger, A. J. *Synth. Met.* **1997**, *85*, 1183.
- (a) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15; (b) Henckens, A.; Knipper, M.; Polec, I.; Manca, J.; Lutsen, L.; Vanderzande, D. *Thin Solid Films* **2004**, *451*.
- (a) Lee, B.; Seshadri, V.; Sotzing, G. A. *Synth. Met.* **2005**, *152*, 177–180; (b) Lee, B.; Seshadri, V.; Sotzing, G. A. *Langmuir* **2005**, *21*, 10797–10802.
- Invernale, M. A.; Seshadri, V.; Mamangun, D. M. D.; Ding, Y.; Filloramo, F.; Sotzing, G. A. *Chem. Mater.* **2009**, *21*, 3332–3336.
- Brandsma, L.; Verkruisje, H. D. *Synth. Commun.* **1990**, *20*, 2275.
- (a) Lee, K.; Sotzing, G. A. *Macromolecules* **2001**, *34*, 5746–5747; (b) Sotzing, G. A.; Lee, K. *Macromolecules* **2002**, *35*, 7281–7286.
- (a) Pomerantz, M.; Gu, X. *Synth. Met.* **1997**, *84*, 243–244; (b) Pomerantz, M.; Gu, X.; Zhang, S. X. *Macromolecules* **2001**, *34*, 1817–1822.
- Neef, C. J.; Brotherston, I. D.; Ferraris, J. P. *Chem. Mater.* **1999**, *11*, 1957–1958.
- Yao, Y.; Liang, Y. Y.; Shrotriya, V.; Xiao, S. Q.; Yu, L. P.; Yang, Y. *Adv. Mater.* **2007**, *19*, 3979–3983.
- Buttery, J. H.; Moursounidis, J.; Wege, D. *Aust. J. Chem.* **1995**, *48*, 593–607.
- Butte, W. A.; Case, F. H. *J. Org. Chem.* **1961**, *26*, 4690–4692.
- Abdelmoty, S. G.; Heta, H. F. *Bull. Pharm. Sci., Assiut Univ.* **2009**, *32*, 125–140.
- Ha, S.-T.; Koh, T.-M.; Lin, H.-C.; Yeap, G.-Y.; Win, Y.-F.; Ong, S.-T.; Sivasothy, Y.; Ong, L.-K. *Liq. Cryst.* **2009**, *36*, 917–925.
- Hasegawa, M.; Fujioka, A.; Kubo, T.; Honda, T.; Miyamoto, H.; Misaki, Y. *Chem. Lett.* **2008**, *37*, 474–475.
- Matsuo, Y.; Maruyama, M.; Gayathri, S. S.; Uchida, T.; Guldi, D. M.; Kishida, H.; Nakamura, A.; Nakamura, E. *J. Am. Chem. Soc.* **2009**, *131*, 12643–12649.
- Baur, J. W.; Alexander, M. D., Jr.; Banach, M.; Denny, L. R.; Reinhardt, B. A.; Vaia, R. A.; Fleitz, P. A.; Kirkpatrick, S. M. *Chem. Mater.* **1999**, *11*, 2899–2906.