been seen in metal–indenyl complexes where the M–bridgehead C distances are significantly longer than the other M–C distances.[14] This slipping of the Fe atom from $\eta^5$-coordination to the pentalene ring may be interpreted as maximization of the interaction of the Fe with $\pi$-electron density of the delocalized fused ring system. The longer C–C bond (1.464 (5) Å) between the two bridgehead carbon atoms supports this delocalization of $\pi$-electron density about the perimeter of the pentalene ligand with less electron density shared between the two bridgehead carbon atoms (Figure 1).

Strong coupling between the metal centers in these dinuclear compounds is evidenced by the diamagnetism of the compounds **1b** and **1c**[11] and by the large values of $\Delta E_{1/2}$ for their one- and two-electron oxidations (Table I).[15] Indeed, the $\Delta E_{1/2}$ values for **1a–c** are the largest yet observed for homodinuclear compounds.[16]

The anti conformation of the two iron atoms in **1a** and the large distance between them (3.98 Å), as confirmed by the X-ray structure determination, precludes the possibility that a metal-to-metal interaction is responsible for the diamagnetism of compounds **1b** and **1c**. We propose, instead, that the effect comes about because of a strong through-bond interaction facilitated by the bridging ligand. Extended Hückel molecular orbital calculations on $(CpFe)_2$(pentalene) support this assertion.[17] The MO diagram of this compound along with a fragment analysis based on an obvious partition of the molecule is shown in Figure 2. Owing to the large number of orbitals involved, the interaction diagram is simplified by focusing on the Cp–Fe frontier d-orbitals and the ligand $\pi$-orbitals. It is interesting to note that even though the destabilization of the $d_{xz}$ and $d_{yz}$ orbital combinations appears to be dominated by the interaction with the $\pi$-orbitals of pentalene, there is also a substantial contribution from the occupied $\sigma$-orbitals of the pentalene ligand (the effect of the orbitals, although not shown in the diagram, can be seen in the destabilization of the $a_g$ (s, $d_{z^2}$) metal hybrid combination of the Cp–Fe units). The significant gap between the bonding and antibonding combinations, as depicted in Figure 2, represents the strength of the interaction between the Cp*Fe systems and the central pentalene ligand by which the electrons of the two Cp–Fe units are effectively coupled. This type of through-bond coupling provides a unique mechanism for delocalization in a mixed-valent system.

**Acknowledgment.** We are greatly indebted to Professor John E. Bercaw for helpful discussions, Pamela J. Shapiro for her help in the writing of this manuscript, and the DPD Computer Center of the Universidad Tecnica Federico Santa Maria (UTFSM). Partial support for this work from Project Number 871302 of the UTFSM is gratefully acknowledged.

**Supplementary Material Available:** A stereoview of the crystal packing of **1a**, table of analytical data and $^1H$ and $^{13}C$ NMR data for **1a–c**, tables of data collection and structure solution details, atomic positional parameters, thermal parameters, root-mean-square amplitudes of vibration, and bond distances and angles for **1a** (12 pages); a listing of observed and calculated structure factors for **1a** (5 pages). Ordering information is given on any current masthead page.

---

(14) Smith, D. E.; Welch, A. J. *Organometallics* **1986**, *5*, 760. Mlekuz, M.; Bougeard, P.; Sayer, B. G.; McGlinchey, M. J.; Rodger, C. A.; Churchill, M. R.; Ziller, J. W.; Kang, S.-K.; Albright, T. A. *Organometallics* **1986**, *5*, 1656.

(15) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(16) Le Vanda, C.; Cowan, D. O.; Leitch, C.; Bechgaard, K. *J. Am. Chem. Soc.* **1974**, *96*, 6788.

(17) Extended Hückel calculations with the modified Wolfsberg–Helmholz formula were performed. Parameters for the calculations were taken from the following: Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805. Hoffmann, R.; Summerville, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 7240. Crystallographic distances for **1a** were used, symmetrized to conform to full $C_{2h}$ symmetry. Methyl groups on the Cp* ligand were not included in the calculations and were replaced by hydrogen atoms.

---

# 3,4-Di-*tert*-butylthiophene 1,1-Dioxide, a Convenient Precursor of *o*-Di-*tert*-butylbenzene and Its Derivatives

Juzo Nakayama,* Shoji Yamaoka, Tomoko Nakanishi, and Masamatsu Hoshino

*Department of Chemistry, Faculty of Science*
*Saitama University, Urawa, Saitama 338, Japan*

*Received April 7, 1988*

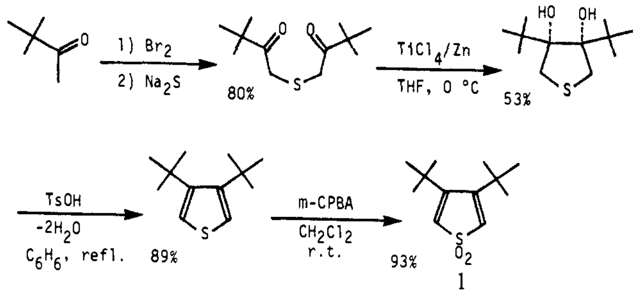
We have recently developed a surprisingly simple synthesis of 3,4-di-*tert*-butylthiophene and its oxidative conversion to 3,4-di-*tert*-butylthiophene 1,1-dioxide (**1**) in high yield (Scheme I).[1-3] This procedure allows the easy preparation of **1** in large quantities. Herein we report that the Diels–Alder reaction of **1**[4] with acetylenes and their synthetic equivalents provides a simple synthesis of *o*-di-*tert*-butylbenzene (**2a**) and its many derivatives having a variety of functional groups, which are otherwise very difficult to prepare.

Syntheses, reactivities, and structures of **2a** and related compounds have attracted much attention.[5] 1,2,4-Tri-*tert*-butylbenzene, the first compound to have *o*-*tert*-butyl groups, was obtained in 1961 from $Co_2(CO)_4(t\text{-BuC}{\equiv}\text{CH})_3$ either by reaction with bromine or by thermolysis.[6] Parent compound **2a** was also obtained in low to moderate yields through cyclization of acetylene with $Co_2(CO)_6(t\text{-BuC}{\equiv}\text{CBu-}t)$.[7,8] Although purely organic routes are also available, they are lengthy and suffer from low overall yields.[9,10] Introduction of a functional group to **2a** by electrophilic aromatic substitution is often accompanied by rearrangement of the *tert*-butyl group,[11] which makes it difficult to prepare functionalized derivatives of **2a**. A literature survey reveals that synthetic methods of **2a** and related compounds have scarcely developed thereafter,[12,13] though their physical and chemical properties have been a matter of extensive investigation.

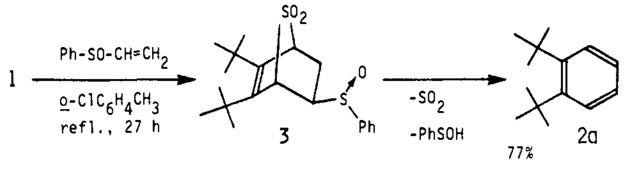
The parent compound **2a** was cleanly obtained in 77% yield by heating **1** with phenyl vinyl sulfoxide (2.2 equiv) in refluxing *o*-chlorotoluene (Scheme II). Under the applied conditions, the initial adduct **3** extrudes sulfur dioxide and benzenesulfenic acid to give **2a**, thereby phenyl vinyl sulfoxide acting as an acetylene equivalent.[14]

A variety of acetylenes satisfactorily react with **1** to give the corresponding functionalized *o*-di-*tert*-butylbenzenes with elimination of sulfur dioxide from the initial Diels–Alder adducts (Scheme III). Acetylenes, activated by electron-withdrawing group(s) (dimethyl acetylenedicarboxylate, methyl propiolate, and 3-butyn-2-one) and acetylenes, activated by angle strain (benzyne

**Scheme I**

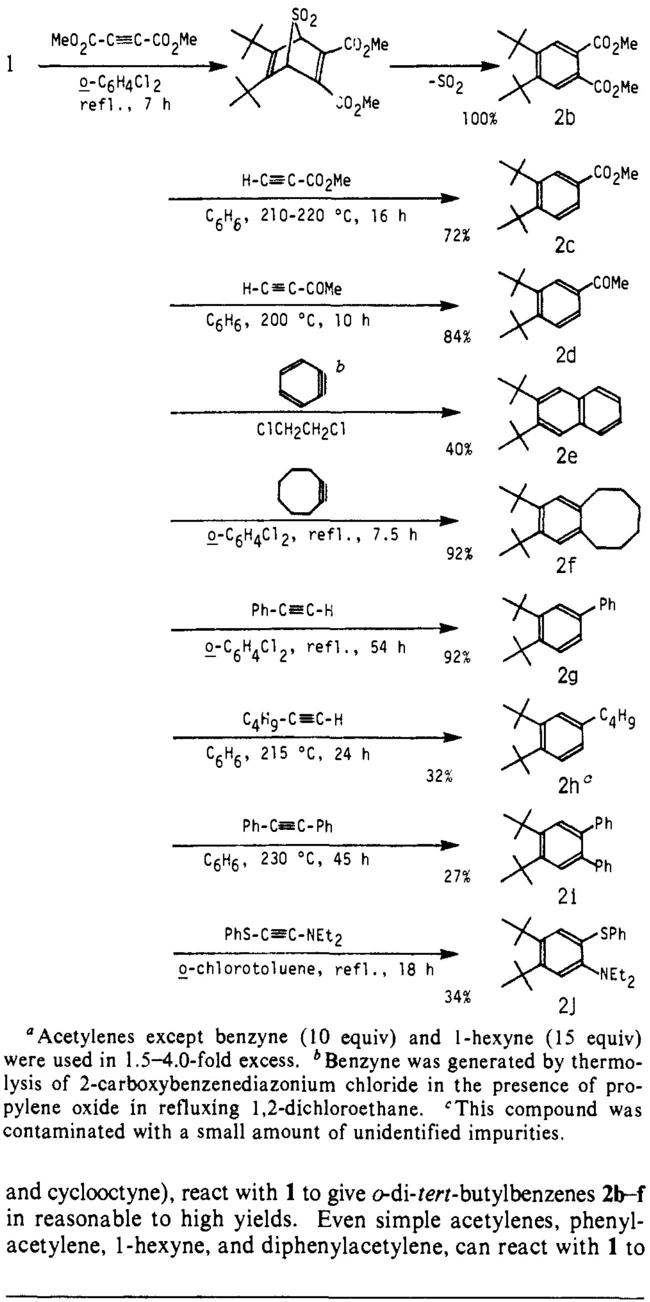


**Scheme II**



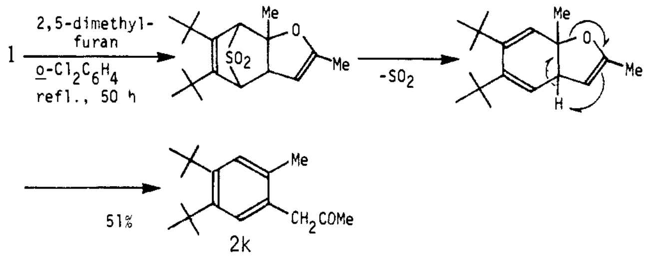
0002-7863/88/1510-6598$01.50/0 © 1988 American Chemical Society

**Scheme III**[a]



[a] Acetylenes except benzyne (10 equiv) and 1-hexyne (15 equiv) were used in 1.5–4.0-fold excess. [b] Benzyne was generated by thermolysis of 2-carboxybenzenediazonium chloride in the presence of propylene oxide in refluxing 1,2-dichloroethane. [c] This compound was contaminated with a small amount of unidentified impurities.

**Scheme IV**



and cyclooctyne), react with **1** to give *o*-di-*tert*-butylbenzenes **2b–f** in reasonable to high yields. Even simple acetylenes, phenylacetylene, 1-hexyne, and diphenylacetylene, can react with **1** to afford compounds **2g–i**. Relatively low yield of **2j** observed by reaction with a ynamine may come from the steric repulsion between substrates.

Finally reaction of **1** with excess 2,5-dimethylfuran afforded **2k** in 51% yield (Scheme IV). In this case 2,5-dimethylfuran acts as an equivalent of 4-hexyn-2-one. This type of reaction is precedented.[15]

In conclusion the reaction of **1** with acetylenes and their synthetic equivalents provides a very facile synthesis of *o*-di-*tert*-butylbenzene and its many derivatives.

**Supplementary Material Available:** Experimental procedures for the preparation of compounds **1** and **2a–k** and characterization data for these compounds ($^1$H NMR, $^{13}$C NMR, and high resolution MS) (8 pages). Ordering information is given on any current masthead page.

---

(1) Nakayama, J.; Yamaoka, S.; Hoshino, M. *Tetrahedron Lett.* **1988**, *29*, 1161–1164.

(2) For preparation of polysubstituted thiophenes by this procedure, see: (a) Nakayama, J.; Machida, H.; Saito, R.; Hoshino, M. *Tetrahedron Lett.* **1985**, *26*, 1983–1984. (b) Nakayama, J.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1987**, 26, 2599–2602. See, also: Nakayama, J.; Yamaoka, S.; Hoshino, M. *Tetrahedron Lett.* **1987**, *28*, 1799–1802.

(3) Sterically overcrowded 3,4-di-*tert*-butylthiophene was first synthesized in 1980 after numerous unsuccessful attempts: Brandsma, L.; Meijer, J.; Verkruijsse, H. D.; Bokkers, G.; Duisenberg, A. J. M.; Kroon, J. *J. Chem. Soc., Chem. Commun.* **1980**, 922–923.

(4) For Diels–Alder reaction of thiophene 1,1-dioxides, see: Rajappa, S. In *Comprehensive Heterocyclic Chemistry*; Bird, C. W., Cheeseman, G. W. H., Eds.; Pergamon: New York, 1984; Vol. 4, Chapter 3.14.

(5) (a) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978; Chapter 3. (b) Okazaki, R. *Yuki Gosei Kagaku Kyokai-shi* **1974**, *32*, 704–717.

(6) Krüerke, U.; Hoogzand, C.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2817–2820.

(7) Hoogzand, C.; Hübel, W. *Angew. Chem.* **1961**, *73*, 680.

(8) Arnett, E. M.; Strem, M. *Chem. Ind.* (*London*) **1961**, 2008–2009.

(9) Barclay, L. R. C.; Milligan, C. E.; Hall, N. D. *Can. J. Chem.* **1962**, *40*, 1664–1671.

(10) Burgstahler, A. W.; Abdel-Rahman, M. O. *J. Am. Chem. Soc.* **1963**, *85*, 173–180.

(11) Burgstahler, A. W.; Chien, P.-L.; Abdel-Rahman, M. O. *J. Am. Chem. Soc.* **1964**, *86*, 5281–5290.

(12) For preparation of 1,2,3-tri-*tert*-butylbenzenes, see: (a) Viehe, H. G.; Merenyi, R.; Oth, J. F. M.; Valange, P. *Angew. Chem.* **1964**, *76*, 885. (b) Viehe, H. G. *Angew. Chem.* **1965**, *77*, 768–773. For 1,2,4,5-tetra-*tert*-butylbenzene, see: (a) Hoogzand, C.; Hübel, W. *Tetrahedron Lett.* **1961**, 637–643. (b) Arnett, E. M.; Strem, M. E.; Friedel, R. A. *Tetrahedron Lett.* **1961**, 658–662.

(13) Haefelinger, G.; Marb, M. *New. J. Chem.* **1987**, *11*, 401–402.

(14) Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597–1599.

(15) Raasch, M. S. *J. Org. Chem.* **1980**, *45*, 867–870.

(16) Clandernan, B. H.; Criswell, T. R. *J. Org. Chem.* **1969**, *34*, 3426–3430.

---

# Additions and Corrections

**1-Methyl-4,5-cyclopentenoborepin: A Neutral Boron Analogue of Tropylium** [*J. Am. Chem. Soc.* **1987**, *109*, 1879]. ARTHUR J. ASHE III* and FREDERICK T. DRONE

Pages 1879 and 1880: The $^{11}$B NMR chemical shift value reported for compound **10** is wrong. The correct chemical shift value is $\delta$ 32.1 referenced to external $BF_3 \cdot OEt_2$ at $\delta$ 0. Thus the NMR data suggest that borepin serves as a $\eta^7$ ligand toward $Cr(CO)_3$. We regret any confusion this mistake may have caused.

**Investigations of a Siloxane-Based Polymer Electrolyte Employing $^{13}$C, $^{29}$Si, $^7$Li, and $^{23}$Na Solid-State NMR Spectroscopy** [*J. Am. Chem. Soc.* **1988**, *110*, 3036–3043]. R. SPINDLER and D. F. SHRIVER*

Page 3037, the caption for Figure 2 should read as follows: Figure 2. Solid-state $^{13}$C NMR spectra of siloxane(30) employing (A) MAS and DD (spinning rate = 1400 Hz), (B) MAS, (C) static and DD, and (D) static.