**2-*tert*-Butoxyallylbenzene (2d).** An oven-dried 100-mL three-necked flask equipped with a magnetic stirring bar, thermometer, and nitrogen inlet was charged with 25 mL of $CH_2Cl_2$ and cooled to -78 °C through the aid of a dry ice-acetone bath. To the flask were added 20 mL of liquified isobutylene and 2.68 g (25 mmol) of *o*-allylphenol (**1d**). To the vigorously stirred reaction mixture was added 177 μL (2 mmol) of trifluoromethanesulfonic acid. After completion of the addition, the resultant homogeneous mixture was stirred for an additional 4.0 at -78 °C. Triethylamine, 0.279 g, (2 mmol) was then added, and the reaction mixture was then allowed to warm to room temperature.

The solution was transferred to a 50-mL flask, and the solvents were evaporated. The oily residue was triturated with 100 mL of petroleum ether, the solids were filtered, and the solvent was evaporated. Analysis of the crude product by gas chromatography on a 5% SE 30 column revealed the product to be 98% pure.

The material obtained in this manner was purified by vacuum distillation, 43-45 °C (0.85 torr), to afford 3.46 g (90%) of pure 2-*tert*-butoxyallylbenzene (**2d**) as a colorless liquid: NMR ($CDCl_3$, $Me_4Si$) δ 1.45 (s, 9, $CH_3$), 3.38 (d, $J$ = 7, 2 H, $CH_2$), 5.05 (m, 2 H, vinyl), 5.95 (m, 1 H, vinyl), 7.1 (m, 3 H, Ar); IR ($cm^{-1}$) (film) 3130-2780, 1390, 1367. Anal. Calcd for $C_9H_{10}O$: C, 82.06; H, 9.00. Found: C, 82.30; H, 9.27).

**1-*tert*-Butoxydodecane (4).** An oven-dried 100-mL three-necked flask equipped with a magnetic stirring bar, thermometer, and nitrogen inlet was charged with 12.5 mL of $CH_2Cl_2$ and cooled to -78 °C with a dry ice-acetone bath. To the flask was added 10 mL of liquified isobutylene and 2.34 g (16.6 mmol) of 1-dodecanol (**3**). To the vigorously stirred reaction mixture was added 235 μL (2.66 mmol) of trifluoromethanesulfonic acid. After the addition, the resultant mixture was stirred for an additional 3.0 at -5 °C, in an ice-salt bath. Triethylamine, 0.557 g (4 mmol), was then added to the reaction mixture.

The solution was transferred to a 50-mL flask, and the solvents were evaporated. The oily residue was triturated with 100 mL of petroleum ether, the solids were filtered, and the solvent was evaporated.

The crude product obtained in this manner was purified by vacuum distillation, 58-61 °C (1.5 mm), to afford 2.24 g (76%) of pure 1-*tert*-butoxydodecane (**4**) as a colorless liquid. Analysis of the purified product by gas chromatography on a 5% SE 30 column revealed the product to be 99% pure: NMR ($CDCl_3$, $Me_4Si$) δ 0.7-1.9 (aliphatic envelope), 1.3 (s, 9 H, $CH_3$), 3.3 (t, $J$ = 7.1, $CH_2$); IR ($cm^{-1}$, film) 3080-2730, 1390, 1365; Anal. Calcd for $C_{16}H_{34}O$: C, 79.27; H, 14.13. Found: C, 79.33; H, 14.08.

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**Registry No.** **1a**, 90-05-1; **1b**, 150-76-5; **1c**, 533-31-3; **1d**, 1745-81-9; **1e**, 591-20-8; **1f**, 121-71-1; **1g**, 97-53-0; **2a**, 16222-38-1; **2b**, 15360-00-6; **2c**, 73673-86-6; **2d**, 99376-82-6; **2e**, 99376-83-7; **2f**, 99376-84-8; **2g**, 99376-85-9; **3**, 112-53-8; **4**, 61548-83-2; $H_2C{=}C(CH_3)_2$, 115-11-7; $F_3CSO_3H$, 1493-13-6.

## A Convenient Synthesis of 2,3-Dihydrothiophene[1]

Nancy N. Sauer, Robert J. Angelici,* Y. C. Jason Huang, and Walter S. Trahanovsky*

*Ames Laboratory and the Department of Chemistry, Iowa State University, Ames, Iowa 50011*

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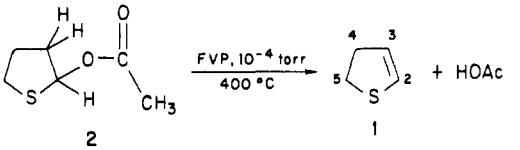
For the purpose of continuing studies of the mechanism of hydrodesulfurization of thiophene,[2] it became necessary to prepare 2,3-dihydrothiophene (**1**). This reactive vinyl thioether, which is proposed as a key intermediate in the hydrodesulfurization of thiophene,[3] is also of interest as a synthetic intermediate. The utility of vinyl thioethers in synthesis has been well-documented.[4] In addition, the chemistry of this reactive olefin is relatively unexplored.[5] Herein we report the preparation of 2,3-dihydrothiophene (**1**) in high yield by flash vacuum pyrolysis (FVP) of 2-(acetoxy)tetrahydrothiophene (**2**) at 400 °C.




2 1

Mixtures of 2,3- and 2,5-dihydrothiophene have been previously obtained by other methods,[6] including the Birch reduction of thiophene.[6a] The separation of these two isomers is complicated by the reactivity of the 2,3-dihydrothiophene which polymerizes upon heating and in the presence of acids.[6a] Small amounts of the 2,3-isomer were isolated from these mixtures by preparative gas chromatography.[7] Only 2,3-dihydrothiophene was obtained from preparative methods described by Sosnovsky.[8] The desired isomer was isolated in 20% yield by heating neat 2-(acetoxy)tetrahydrothiophene (**2**) at 130-150 °C for 1 h and in 60% yield by heating neat 2-(benzoyloxy)-tetrahydrothiophene at 100 °C for 2 h.[8] Extensive dimerization and polymerization of the dihydrothiophene were also reported under these conditions. This synthesis is made somewhat arduous by the purification of the rather unstable benzoyloxy derivative, which cannot be distilled under reduced pressure but must be purified chromatographically.[9]

FVP is a method which is ideally suited for the preparation of reactive molecules like 2,3-dihydrothiophene (**1**). Generally, thermal eliminations of molecules from compounds like **2** proceed readily under FVP conditions with the resulting unsaturated product being directly condensed at liquid nitrogen temperatures.[10]

### Results and Discussion

2-(Acetoxy)tetrahydrothiophene (**2**) was pyrolyzed at 400 °C and $10^{-4}$ torr (higher pressures can be used[11]). Products were collected in a cold trap at -196 °C. A $^1H$ NMR spectrum of the product mixture showed complete conversion of the starting acetate to 2,3-dihydrothiophene (**1**) and acetic acid. The acetic acid was readily removed by passing the product mixture slowly through a frit covered with solid $Na_2CO_3$. The 2,3-dihydrothiophene (**1**) may be

(1) Based on the work of N.N.S. in partial fulfillment of the requirements for the Ph.D. Degree at Iowa State University.

(2) (a) Lesch, D.; Richardson, J. W.; Angelici, R. J.; Jacobson, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (b) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569.

(3) (a) Zdrazil, M. *Collect. Czech. Chem. Commun.* **1975**, *40*, 3491. (b) Devanneaux, J.; Maurin, J. *J. Catal.* **1981**, *69*, 202.

(4) (a) Posner, G. H.; Brunelle, D. J. *J. Org. Chem.* **1973**, *38*, 2747. (b) Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 4474. (c) Cohen, L. A.; Steele, J. A. *J. Org. Chem.* **1966**, *31*, 2333.

(5) (a) Tietze, L. F.; Glüsenkamp, K. H.; Harms, K.; Remberg, G. *Tetrahedron Lett.* **1982**, *23*, 1147. (b) Gollnick, K.; Fries, S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 832. (c) Okuyama, T.; Nakada, M.; Toyoshima, K.; Fueno, T. *J. Org. Chem.* **1978**, *43*, 4546.

(6) (a) Birch, S. F.; McAllan, D. T. *J. Chem. Soc.* **1951**, 2556. (b) Gianturco, M. A.; Friedel, P.; Flanagan, V. *Tetrahedron Lett.* **1965**, *23*, 1847. (c) Johnson, P. Y.; Koza, E.; Kohrman, R. E. *J. Org. Chem.* **1973**, *38*, 2967.

(7) Durig, J. R.; Little, T. S.; Li, Y. S. *J. Chem. Phys.* **1982**, *76*, 3849.

(8) Sosnovsky, G. *Tetrahedron* **1962**, *18*, 903.

(9) Sosnovsky, G. *Tetrahedron* **1962**, *18*, 15.

(10) (a) Wiersum, U. E. *Recl.: J. R. Neth. Chem. Soc.* **1982**, *101*, 317. (b) Wiersum, U. E. *Recl.: J. R. Neth. Chem. Soc.* **1982**, *101*, 365.

(11) Similar product purity and yield were obtained by using an ordinary vacuum pump with pressures of ca. 0.1 torr.

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obtained as a neat liquid by this method. A solution of 1 can be obtained by distillation of $CS_2$ into the cold trap after the pyrolysis is complete. Presumably, other inert solvents such as $CHCl_3$, $CH_2Cl_2$, and hexane would also work. The acetic acid is removed by passing the solution of 1 through the frit covered with $Na_2CO_3$. Freshly prepared 1 is stored under nitrogen in a dry ice/isopropyl alcohol bath.[12] Slow decomposition is observed for samples stored at room temperature.

2,3-Dihydrothiophene obtained by this preparation was characterized by its mass and $^1H$ and $^{13}C$ NMR spectra. In the mass spectrum, the molecular ion peak is observed at $m/e$ 86, and the base peak is at $m/e$ 85, in agreement with a previously reported spectrum.[6c] The $^1H$ NMR spectrum of this compound was reported earlier.[13] The chemical shifts we observed closely match those reported earlier as do the coupling constants seen for the olefinic resonances. However, for the $H_4$ protons only an average of the two coupling constants to $H_2$ and $H_3$ was observed. No apparent second-order splitting of the methylene protons was seen as reported by Korver et al.[13b] The $^{13}C$ NMR spectrum of 1 has not been reported. The resonances which were observed are very close to those reported for the olefinic carbons in thiophene, 126 and 124 ppm (neat), and for the methylene carbons in tetrahydrothiophene, 31.7 and 31.2 ppm.[14]

## Experimental Section

The experimental procedure and apparatus for the gas-phase pyrolysis have been previously described.[15] NMR spectra were obtained on a Nicolet 300-MHz or Bruker WM 300-MHz spectrometer. Chemical shifts are reported in ppm from the internal standard, tetramethylsilane. Electron ionization mass spectra (EIMS) were obtained on a Finnigan 4000 spectrometer. Reagent grade solvents and chemicals were used without further purification.

Tetramethylene sulfoxide was prepared as described previously[16] in 90% yield (bp 105–107 °C (15 torr)). 2-(Acetoxy)-tetrahydrothiophene (2) was prepared by the method of Horner and Kaiser[17] in 84% yield (bp 96 °C (12 torr)): mass spectrum (70 eV), $m/e$ (relative intensity) 146.1 (6.2, $M^+$), 103.1 (8.5), 86.1 (31.1), 85.1 (10.0), 60.1 (9.6), 58.1 (10.0), 45.1 (16.6), 43.1 (100.0).

**2,3-Dihydrothiophene (1)** was prepared by pyrolysis of 2. Freshly distilled 2-(acetoxy)tetrahydrothiophene (5.00 g, 34.0 mmol) was placed in the sample compartment of the pyrolysis unit which was covered by a jacketed heating mantle to keep the sample at approximately 60 °C during the pyrolysis. The oven temperature was maintained at 400 °C, and the pressure was lowered to ca. $10^{-4}$ torr.[11] Products were collected in a U-shaped trap immersed in liquid nitrogen. After 2 h the pyrolysis was complete, and 20 mL of $CS_2$ was distilled into the trap if desired. Nitrogen was let into the system, and the trap was disconnected and capped under nitrogen flow. The trap was removed from the liquid nitrogen bath, and the product melted. The resulting liquid was transferred by syringe to a medium schlenk frit covered with 2.7 g (26 mmol, 1.5 equiv) of $Na_2CO_3$ under nitrogen. The solution was allowed to sit on the frit until no further evolution of $CO_2$ gas was observed (ca. 5 min) and then was filtered into a storage flask. If $CS_2$ was added earlier, then the frit was washed 3 times with 5-mL portions of $CS_2$, and the solution and washings were stored in a dry ice/isopropyl alcohol bath. The yield of the neat liquid product was 2.53 g (86%): $^1H$ NMR ($CDCl_3$) $\delta$ 6.14 (dt, 1 H, $J_{2-3}$ = 5.93 Hz, $J_{2-4}$ = 2.18 Hz, $H_2$), 5.59 (dt, 1 H, $J_{2-3}$ = 5.93 Hz, $J_{3-4}$ = 2.75 Hz, $H_3$), 3.21 (t, 2 H's, $J_{4-5}$ = 8.72 Hz, $H_5$), and 2.74 (tt, 2 H's, $J_{4-5}$ = 8.72 Hz, $J$ = 2.46 Hz, $H_4$); $^{13}C$(H) NMR ($CDCl_3$) $\delta$ 126.1 ($C_2$), 122.0 ($C_3$), 32.3 ($C_5$), and 35.1 ($C_4$); EIMS (70 eV), $m/e$ (relative intensity) 86.1 (62.0, $M^+$), 85.1 (100), 71.7 (7.0), 60.1 (4.0), 59.1 (5.3), 58.0 (11.0), 57.0 (6.1), 50.1 (7.3), 46.0 (4.6), 45.0 (41.5), 43.1 (22.9), 41.1 (6.2), 39 (15.6).

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(12) Solutions stored in this manner were found to be quite stable for periods of 2–3 weeks.

(13) (a) Abraham, R. J.; Parry, K.; Thomas, W. A. *J. Chem. Soc. B* **1971**, 446. (b) Korver, P. K.; Van Der Haak, P. J.; Steinberg, H.; DeBoer, Th. J. *Recl.: J. R. Neth. Chem. Soc.* **1965**, *84*, 129.

(14) Silverstein, R. M.; Bassler, G. C.; Morril, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; pp 262 and 266.

(15) Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. *J. Org. Chem.* **1971**, *36*, 3575.

(16) Tarbell, D. S.; Weaver, C. *J. Am. Chem. Soc.* **1941**, *63*, 2939.

(17) Horner, L.; Kaiser, P. *Justus. Liebigs Ann. Chem.* **1959**, *626*, 19.

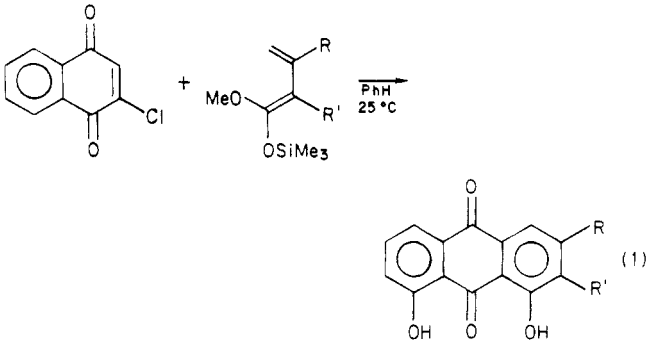
# Diels–Alder Reactions of Quinone Sulfoxides

George A. Kraus* and Soon Hyung Woo

*Department of Chemistry, Iowa State University, Ames, Iowa 50011*

*Received June 14, 1985*

The Diels–Alder reaction has often been used to construct polycyclic quinones from either benzoquinones or naphthoquinones.[1] This strategy has led to elegant syntheses of certain anthracyclines and also many other acetate-derived compounds. Several researchers, most notably Gesson and Brassard, have determined that the presence of a chlorine or bromine atom on the starting quinone framework permits the ready assemblage of the polycyclic quinone[2] (eq 1). The regeneration of the




(1)

quinone moiety is facilitated by the elimination of the HCl or HBr. Recently, Rapoport has reported improved yields of certain anthraquinones by the simple expedient of delaying the dehydrohalogenation step.[3] A limitation of the haloquinone strategy is that the requisite haloquinone may not be easily synthesized, especially if the halogen group must be introduced late in the synthetic sequence. This is particularly difficult if an alkene or amine is present. We report herein that sulfinyl quinones represent convenient alternatives to haloquinones. With appropriate selection of reaction conditions, sulfoxide elimination regenerates the quinone unit during the Diels–Alder reaction. Moreover, with quinones such as juglone, either the 2- or 3-sulfinyl quinones can be obtained.[4]

(1) Desimoni, G. "Natural Products Synthesis"; American Chemical Society: Washington, DC 1983; ACS Monogr. No. 180.

(2) Echavarren, A.; Prados, P.; Farina, F. *Tetrahedron* **1984**, *40*, 4561. McNamara, J. M.; Kishi, Y. *Tetrahedron* **1984**, *40*, 4685. Gesson, J.-P.; Jacquesy, J.-C.; Renoux, B. *Tetrahedron* **1984**, *40*, 4743. Bauman, J. G.; Barber, R. B.; Gless, R. D.; Rapoport, H. *Tetrahedron Lett.* **1980**, *21*, 4777. Guay, V.; Brassard, P. *J. Org. Chem.* **1984**, *49*, 1853.

(3) Bauman, J. G.; Hawley, R. C.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 1569.

0022-3263/86/1951-0114$01.50/0 