Pergamon

Tetrahedron Letters, Vol. 35, No. 24, pp. 4175-4176, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)00849-3

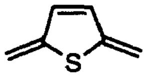
Reaction of 2,5-Dimethylene-2,5-dihydrothiophene with Triplet Oxygen

Chin-Shui Huang, Chun-Chieh Peng and Chin-Hsing Chou*

Department of Chemistry, National Sun Yat-Sen University,
Kaohsiung, Taiwan, 80424, China

Abstract: 2,5-Dimethylene-2,5-dihydrothiophene (1), prepared by the pyrolysis of 5-methylthenyl benzoate (3), has been detected by low-temperature NMR spectroscopy. 1 reacts with triplet oxygen to form a cyclic bisperoxide 6. Upon heating, 6 decomposes to give 2,5-bis(hydroxymethyl)thiophene (7), 2-formyl-5-hydroxymethylthiophene (8) and 2,5-diformylthiophene (9) in a ratio of 1:2:1, respectively.

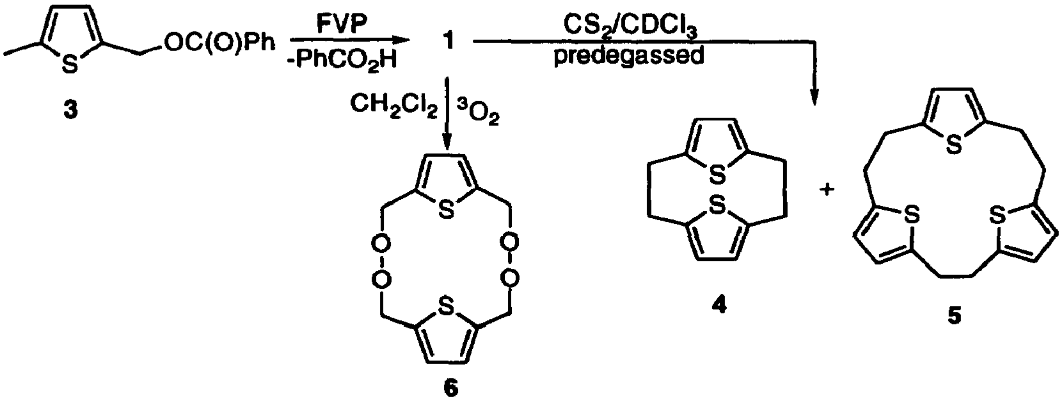
The reactive 2,5-dimethylene-2,5-dihydrothiophene (1), a thiophene analogue of *p*-quinodimethane (2),[1-10] has been prepared both in solution[5,9] and by pyrolysis,[11] and its UV and IR spectral data have been reported by matrix isolation technique.[11] Compound 1, once generated, undergoes di- and trimerization reactions to give a cyclic dimer and a cyclic trimer. In this communication we report the detection of 1 by low-temperature NMR and the result of the reaction of 1 with triplet oxygen.



1

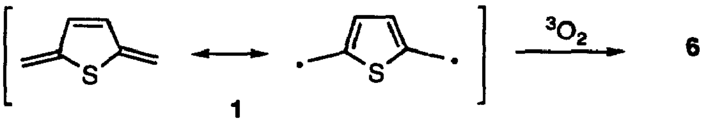
2

1 was prepared by the flash vacuum pyrolysis (FVP) of 5-methylthenyl benzoate (3) at 600 °C and ca. 10^{-2} torr by the procedure that has been previously described.[12] ^{1}H and ^{13}C NMR spectra of the product mixture collected in predegassed 1:1 mixture of $CDCl_3/CS_2$ at -75 °C indicated that 1 was the primary pyrolysis product of 3 in 90% yield.[13] When the product mixture was warmed to room temperature, 1 was converted to cyclic dimer (4, 5%) and trimer (5, 30%)[14] along with substantial amounts of polymers. A similar result was obtained when 1 was collected in predegassed CH_2Cl_2. However, when 1 was collected in CH_2Cl_2 without preclusion of oxygen, the major product formed was a cyclic bisperoxide 6 (45%) along with small amounts of 4 (trace) and 5 (3%).



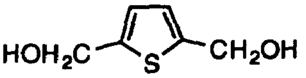
When oxygen was bubbled through the solution of **1** in CH_2Cl_2 at -78 °C and allowed to warm to room temperature, **6** increased to 83%. This shows that atmospheric triplet oxygen was responsible for the oxidation of **1** to **6**. Based on the poor solubility of **6** in ether, **6** can be purified by washing it with ether and redissolving it in either CH_2Cl_2 or $CHCl_3$. The structure of **6** was determined from its ^1H and ^{13}C NMR spectral data[15] and CIMS spectral data, by using CH_4 as a reactant gas, in which a $[M+1]^+$ peak at 285 was observed.[15] Further evidence for the formation of **6** was obtained by reducing **6** with $LiAlH_4$ in THF, from which 2,5-bis(hydroxymethyl)thiophene (**7**) was formed as the sole product.

p-Quinodimethane (**2**) is known to behave chemically as a diradical[4] and react with triplet oxygen to give poly-*p*-quinodimethane peroxide.[3] It is plausible that a diradical form of **1** may be involved in the reaction of **1** with oxygen.

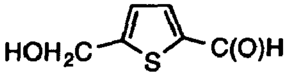


1

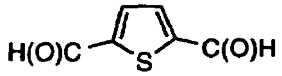
Furthermore, when the solution of **6** in CH_2Cl_2 was kept at room temperature for more than two weeks, **6** decomposed to give a quantitative yield of **7**, 2-formyl-5-hydroxymethylthiophene (**8**) and 2,5-diformylthiophene (**9**) in a ratio of 1:2:1, respectively.



7



8



9

References and Notes

1. Szwarc, M. *Nature,* **1947,** *160,* 403.
2. Errede, L. A.; Landrum, B. F. *J. Am. Chem. Soc.* **1957,** *79,* 4852.
3. Errede, L. A.; Hopwood, S. L. Jr. *J Am. Chem. Soc.* **1957,** *79,* 6507.
4. Errede, L. A.; Hoyt, J. M. *J. Am. Chem. Soc.* **1960,** *82,* 436.
5. Winberg, H. E.; Fawceett, F. S.; Mochl, W. E.; Theobald, C. W. *J. Am. Chem. Soc.* **1960,** *82,* 1428.
6. Errede, L. A.; Gregorian, R. S.; Hovt, J. M. *J. Am. Chem. Soc.* **1960,** *82,* 5218.
7. Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970,** *92,* 1436.
8. Kaupp, G. *Angew. Chem. Int. Ed. Engl.* **1976,** *15,* 442.
9. Ito, Y.; Mityata, S.; Nakatsuka, M.; Saegusa, T. *J. Org. Chem.* **1981,** *46,* 1043.
10. Yamashita, Y.; Kobayashi, Y.; Miyashi, T. *Angew. Chem. Int. Ed. Engl.* **1989,** *28,* 1052.
11. Munzel, N.; Kesper, K.; Schweig, A.; Specht, H. *Tetrahedron Lett.* **1988,** *29,* 6239.
12. Chou, C. H.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1986,** *108,* 4138.
13. **1**: ^1H NMR (1:1 $CS_2/CDCl_3$, -75 °C) δ 6.46 (s, 2H), 5.19 (s, 2H), 4.96 (s, 2H); ^{13}C NMR (1:1 $CS_2/CDCl_3$, -75 °C) δ 149.02, 134.99, 104.06.
14. ^1H NMR and mass spectral data of **4** and **5** are identical to that of the authentic samples.[9] **4**: ^{13}C NMR ($CDCl_3$) δ 151.18, 126.80, 32.12. **5**: ^{13}C NMR ($CDCl_3$) δ 140.30, 124.31, 31.17.
15. **6**: ^1H NMR ($CDCl_3$) δ 6.91 (s, 4H), 5.03 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 139.46, 127.91, 71.17; CH_4-CIMS m/z (rel. int.) 285 (1, M^++1), 143 (100, $M^+/2$ +1), 127 (38).

(*Received in China* 3 *January* 1994; *accepted* 30 *January* 1994)