(10 × 75 mm), which were soaked twice in distilled water and then oven dried. Two indentations were made in the ampules, the lower one to allow a wire to grip the tube when it was in the oil bath and the higher one to permit easy sealing after charging. Kinetic runs were performed by standard procedures with 10 or 11 × ca. 0.45 mL solutions prepared in a 5-mL volumetric flask containing the ester (16.3 mg). After the kinetic run, ampules were not opened until immediately before the HPLC analysis (also the opened ampules were resealed temporarily with Teflon tape).

**High-Performance Liquid Chromatography.** The HPLC equipment was a Waters Solvent Metering Pump (M45), a Cecil double-beam UV detector (flow cell volume 8 μL), and an Hewlett Packard electronic integrator (HP3090A), assembled with a Rheodyne 20 μL loop injection valve and operated as described elsewhere.[14] The chromatography column (15 cm × 1/4 in.) was packed with 5 μm SPERISORB ODS (Phase Separations) and had $N > 8000$ plates. Results were obtained by eluting with methanol/water (90% v/v) at 25 °C; flow rate = 1 mL/min; $\lambda = 280$ nm; absorbance range = 1.0. Injections of 1.80 ± 0.02 μL were made with a Hamilton 10 μL syringe (701 SNR), manipulated according to the manufacturers instructions for chromatographic applications. Each chromatographic separation took <3 min, the acid being eluted just before the various peaks associated with the elution of HFIP. Additives (buffers or salts) had little effect on the chromatography; tetraethylammonium tetrafluoroborate appeared to cause broadening of the acid peak and 2,6-di-*tert*-butylpyridine eluted as a separate peak of longer retention time (4.3 min). The runs (Table I) show the order in which the experiments were carried out, and the column was not used for any other purpose in the meantime.

Best values of peak areas were obtained by averaging three to five reliable values, after inspection of the HPLC trace to ensure that the "tick marks" of the electronic integrator were correctly positioned and after excluding data for a small number (ca. 1 in 20) of unreliable injections. Typically nine or ten quenched reaction mixtures in approximately equal increments of extent of reaction were analyzed in each kinetic run. The rate constants were obtained with the aid of the LSKIN computer program.[15]

**Acknowledgment.** We are grateful for financial support from SERC (Grant GR/C/12739). G.E.G. is grateful to the Council of the University of Adelaide for the granting of Study Leave (during 1984), which allowed part of the work reported here to be carried out.

**Registry No.** I, 52890-21-8.

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(14) Bentley, T. W.; Freeman, A. E. *J. Chem. Soc., Perkin Trans. 2*, **1984**, 1115.

(15) DeTar, D. F. In "Computer Programs for Chemistry"; DeTar, D. F., Ed.; W. A. Benjamin: New York, 1968; Vol. I, pp 126–173.

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# Ozonation of Phenyl-Substituted Thiophenes

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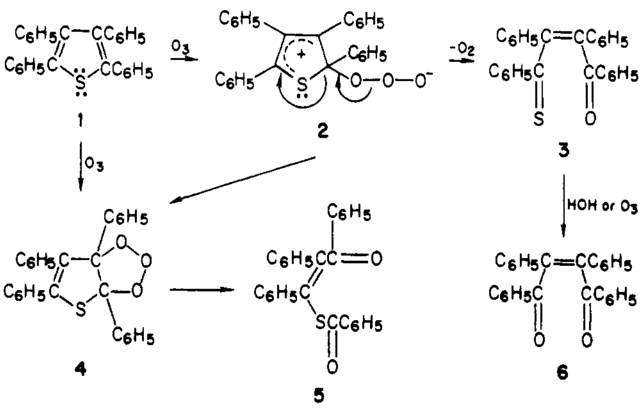
Much study has been given to the ozonation of substituted furans,[1] the most fruitful results coming from 2,5-diarylfurans[1-3] and 2,3,4,5-tetraphenylfuran.[1,4,5] When equimolar quantities of ozone and furan were employed, *cis*-butenediones were obtained as minor products in yields of 3–35%, depending on the aryl substituents, solvent, and temperature.[1] Along with this type of product, which results from electrophilic ozone attack at position 2 of the furan ring followed by loss of oxygen and 1,2-bond cleavage, products derived from 2,3-bond attack and cleavage were obtained.[1]

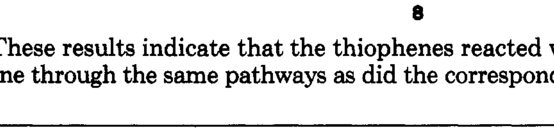
Scheme I



The ozonation of substituted pyrroles has also been given considerable study.[1] Again, the most instructive results were those from an aryl-substituted pyrrole, namely, 2,3,4,5-tetraphenylpyrrole; unfortunately, the work is reported only in the dissertation[6] and review[1] literature. The results were more complex than those from the ozonation of aryl-substituted furans, but it appears that all products can be explained by an initial electrophilic ozone attack rather than an initial bond attack.[1]

The only reported ozonations of a thiophene, before the present work, was with thiophene itself.[1] Because of the instructive studies with aryl-substituted furans and pyrroles, ozonations were performed with 2,5-diphenyl- and 2,3,4,5-tetraphenylthiophene (**1**). When the latter was treated with an equimolar amount of ozone at 0 °C, only 40% of the thiophene reacted; at −78 °C, only 20% of the thiophene reacted (Scheme I). From the 0 °C reaction the products, after a workup involving ethanol and in percentage yields based on unrecovered thiophene, were 1,2,3,4-tetraphenyl-2-butene-1,4-dione (**6**, 61%), thio ester **5** (20%), ethyl benzoate (7%), and benzoic acid (7%). The benozate and benzoic acid yields are based on an expected 2 mol of each from 1 mol of the thiophene, since approximately 2 mol of ozone per mol of thiophene actually reacted. No sulfone of **1** was detected; ozonation of the known sulfone[7] was very sluggish and yielded none of the products obtained from **1**. From the −78 °C ozonation of **1**, **6** was detected by TLC.

Ozonation of 2,5-diphenylthiophene (**7**) at 0 °C with 1 molar equiv of ozone resulted in a 46% recovery of **7** and yields of 18% and 48% of 1,4-diphenyl-2-butene-1,4-dione (**8**) and benzoic acid, respectively, as the only isolable products (yields again based on unrecovered **7** and an expected 2 mol of benzoic acid per mol of **7** reacting).



These results indicate that the thiophenes reacted with ozone through the same pathways as did the corresponding

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(1) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1982; Vol. II, Chapter 6.

(2) White, H. M.; Colomb, H. O., Jr.; Bailey, P. S. *J. Org. Chem.* **1965**, *30*, 481.

(3) Bailey, P. S.; White, H. M.; Colomb, H. O., Jr. *J. Org. Chem.* **1965**, *30*, 487.

(4) Lutz, R. E.; Welstead, W. J., Jr.; Bass, R. G.; Dale, J. I. *J. Org. Chem.* **1962**, *27*, 1111.

(5) Welstead, W. J., Jr. Ph. D. Dissertation, University of Virginia, Charolottesville, 1962.

(6) Taylor, C. R., Jr. Ph.D. Dissertation, University of Virginia, Charlottesville, 1962.

(7) Hinsberg, O. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 1611.

furans. The mechanisms, by analogy to those proposed for the corresponding furans,[1] are outlined in Scheme I. The degree of electrophilic ozone attack with tetraphenylthiophene (at least 61%, depending on the source of ethyl benzoate and benzoic acid, which could arise from either **5** or **6**) was much greater than that with tetraphenylfuran (35%). The isolated yields of products from initial electrophilic attack of ozone on tetraphenylpyrrole were approximately the same as from **1**, but no products from initial bond attack were apparent.[1,6] It is surprising that no attack on either **1** or **7** to yield a sulfone appears to have occurred.

These results were summarized in an earlier review.[1] Although some further studies might be useful, none from this laboratory are anticipated.

## Experimental Section

**2,3,4,5-Tetraphenylthiophene** was synthesized from 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one and sulfur by the method of Dilthey et al.[8] It was purified by sublimation (mp 187–188 °C). Into a solution of 5.71 g (14.7 mmol) of the thiophene in 180 mL of dichloromethane cooled to 0 °C was passed 14.7 mmol of ozone (only 10.4 mmol of ozone reacted, with the rest going into the iodide trap). Evaporation of the reddish brown reaction solution provided 6.4 g of a yellowish solid which, upon slow crystallization from ethanol, yielded, first, 3 g of unreacted starting material; further evaporation and crystallization yielded two fractions: 1 g of a whitish powder and 2.2 g of a dark semisolid residue. Each was chromatographed over silica gel, eluting with a 1:1 benzene–hexane followed by pure benzene. From each a small amount of additional starting material was obtained. Further eluting of the column bearing the whitish powder gave, after repeated crystallization from ethanol and cyclohexene, a 20% yield (based on unrecovered **1**) of thio ester **5** melting at 164–165 °C.

Anal. Calcd. for $C_{28}H_{20}SO_2$ (**5**): C, 79.97; H, 4.79; S, 7.63. Found: C, 79.99; H, 5.09; S, 7.78.

The mass spectrum showed a parent peak at *m/e* 420 and prominant peaks at *m/e* 315 ($M - C_6H_5C{\equiv}O$) and 105 ($C_6H_5C{\equiv}O$). The IR spectrum showed an ester carbonyl peak at 1667 $cm^{-1}$.

From chromatography of the dark semisolid residue (above) was obtained a small amount of recovered **1**, ethyl benzoate (7% yield based on an expected 2 mol per mol of **1** reacting), 1,2,3,4-tetraphenyl-2-butene-1,4-dione (**6**, mp 215–217 °C after repeated recrystallization from ethanol, 61% yield based on unrecovered **1**), and benzoic acid (mp 107–114 °C, identified by IR, 7% yield based on an expected 2 mol per mol of unrecovered **1**).

An IR spectrum of the dione showed a carbonyl peak at 1653 $cm^{-1}$ and the mass spectrum showed a parent peak at *m/e* 388 and prominent peaks at *m/e* 283 ($M - C_6H_5C{\equiv}O$), 178 (perhaps $C_6H_5C{\equiv}CC_6H_5$), *m/e* 105 ($C_6H_5C{\equiv}O$). Lutz and Boykin[9] reported a melting point of 213–215 °C.

Further evidence for the thio ester structure of **5** was obtained by refluxing an anhydrous methanol solution of **5** and sodium methoxide. The oily product, obtained by acidification of the reaction mixture with dilute hydrochloric acid, extraction with ether, and evaporation of the ether extract, appeared to be a mixture of methyl benzoate and the mercaptan arising from alcoholysis of **5**: IR bands at 2564 (S—H), 1724 (ester carbonyl), 1653 (keto carbonyl), 1603 (C=C), 1282, and 1111 $cm^{-1}$ (ester C—O—C).

**2,5-Diphenylthiophene (7)** was synthesized by the method of Böhme et al.[10] from 1,4-diphenylbutane-1,4-dione and phosphorus pentasulfide (mp 157–158 °C). Treatment of a solution of 3.54 g (15 mmol) of the thiophene in 150 mL of dichloromethane with 15 mmol of ozone at 0 °C gave, after workup similar to that with tetraphenylthiophene, a 45% recovery of **7**, an 18% yield of *cis*-1,4-diphenyl-2-butene-1,4-dione (**8**, mp 130–132 °C), and a 48% yield of benzoic acid (mp 124–125 °C); yields are based on unrecovered **7** and an expected 2 mol of benzoic acid per mol of **7**. The remaining product was a black tar.

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**Registry No.** **1**, 1884-68-0; **5**, 95798-63-3; **6**, 7510-34-1; **7**, 1445-78-9; **8**, 959-27-3; 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one, 479-33-4; sulfur, 7704-34-9; ethyl benzoate, 93-89-0; benzoic acid, 65-85-0; 1,4-diphenylbutane-1,4-dione, 495-71-6; phosphorus pentasulfide, 1314-80-3; ozone, 10028-15-6; dichloromethane, 75-09-2.

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[8] Dilthey, W.; Schommer, W.; Höschen, W.; Dierichs, H. *Ber. Dtsch. Chem. Ges.* **1935**, *B68*, 1159.

[9] Lutz, R. E.; Boykin, D. W., Jr. *J. Org. Chem.* **1967**, *32*, 1179.

[10] Böhme, H.; Pfeifer, H.; Schneider, E. *Ber. Dtsch. Chem. Ges.* **1942**, *B75*, 900.

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# Aryl Arylazo Sulfone Chemistry. 1. Synthesis of Arenes and Iodoarenes

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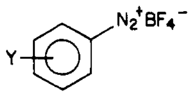
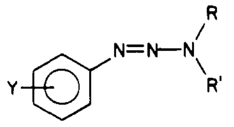
The Sandmeyer reaction between an aryldiazonium salt and the iodide anion is one of the most widely used methods for the introduction of an iodine atom into an aromatic substrate.[2] However, this method suffers from numerous competitive side reactions and modified methods have been introduced.

Due to their convenient and safe preparation, aryldiazonium tetrafluoroborates **1** have been used recently by several workers[3] to synthetize aryl iodides. Simultaneously, it has been observed that the iodide anion can substitute the dialkyltriazene moiety of various 1-aryl-3,3-dialkyltriazenes **2**, leading to the corresponding aryl iodides.[4]


1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However, the major limitation of this last method is its incompatibility with the presence of an *o*-carbalkoxy group on the aromatic substrate.[5] Aryl *p*-tolylazo sulfones **4a–g** are compounds related to aryldiazonium tetrafluoroborates and aryldialkyltriazenes. They are readily obtained through a metathesis reaction between sodium *p*-toluenesulfinate (**3**) and aryldiazonium tetrafluoroborates **2a–g** using dichloromethane as solvent[6] (Scheme I).

Aryl arylazo sulfones have been studied in terms of their thermal[7] and photochemical[8] behavior as well as their

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[2] Roedig, A. In Houben-Weyl "Methoden der Organischen Chemie", 4th ed.; Georg Thieme: Stuttgart, **1960**; p 517.

[3] (a) Karzeniowski, S. H.; Gokel, G. W. *Tetrahedron Lett.* **1977**, 3519. (b) Citterio, A.; Arnoldi, A. *Synth. Commun.* **1981**, *11*, 639.

[4] (a) Foster, N. I.; Heindel, N. D.; Burns, H. D.; Murh, W. *Synthesis* **1980**, 572. (b) Ku, H.; Barrio, J. R. *J. Org. Chem.* **1981**, *46*, 5239. (c) Satyamurthy, N.; Barrio, J. R. *J. Org. Chem.* **1983**, *48*, 4394.

[5] Leblanc, R. J.; Vaughan, K. *Can. J. Chem.* **1972**, *50*, 2544.

[6] Ahern, M. F.; Leopold, A.; Beadle, J. R.; Gokel, G. W. *J. Am. Chem. Soc.* **1982**, *104*, 548.

[7] (a) Rosenthal, A. J.; Overberger, C. G. *J. Am. Chem. Soc.* **1960**, *82*, 108. (b) Kice, J.-L.; Gabrielsem, R. S. *J. Org. Chem.* **1970**, *35*, 1004 and 1010. (c) Yoshida, M.; Futura, N.; Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2356.