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 prominent peaks at m/e 315 (M – $C_6H_5C≡O$) and 105 (C_6H_5-$C≡O$). 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 – $C_6H_5C≡O$), 178 (perhaps $C_6H_5C≡CC_6H_5$), m/e 105 ($C_6H_5C≡O$). 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.

## 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]
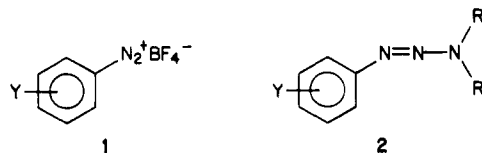
However, the major limitation of this last method is its incompatibility with the presence of an o-carbalkoxy group on the aromatic substrate.[5] Aryl p-tolylazo sulfones 4a–g are compounds related to aryldiazonium tetrafluoroborates and aryldialkyltriazenes. They are readily obtained through a metathesis 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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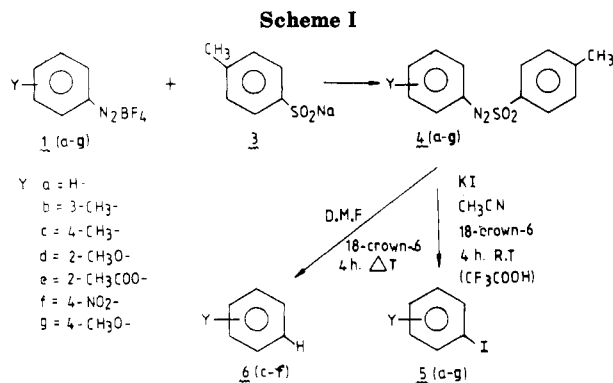
Scheme I

Y a = H-
b = 3-CH₃-
c = 4-CH₃-
d = 2-CH₃O-
e = 2-CH₃COO-
f = 4-NO₂-
g = 4-CH₃O-

Table I. Yields of Iododeazosulfonation and Reductive Deazosulfonation of Aryl Arylazo Sulfones 4a–g

starting material, 4	yields, % (isolated products)		
	5a–g		6a–g
	method A	method B	
a	60	64	
b	72	78	
c	80	84	63
d	61	67	88
e	52	74	90
f	56	61	84
g	43		

stability toward protic acids,[9] Lewis acids,[10] and bases.[11] Their chemical reactivity in dipolar additions[5] and toward toluene-*p*-sulfonyl iodide[12] have been studied.

Results and Discussion

We report here some results concerning the reactivity of aryl *p*-tolylazo sulfones toward the iodide anion.

The addition of potassium iodide at room temperature to a solution in acetonitrile of various aryl *p*-tolylazo sulfones (4a–g) and in the presence of a catalytic amount of 18-crown-6 ether[13] (method A) leads to the formation of the corresponding aryl iodides 5a–g with yields varying from 52% to 80% (Scheme I, Table I).

We have observed that the addition of at least 1 equiv of trifluoroacetic acid to the reaction mixture (method B) increased the yields of aryl iodides (Table I).

Furthermore, we have successfully performed the iodideazosulfonation reaction on a semi-micro scale (<0.500

g of 4e, method A, 1 h of reaction, 48%). This last result should allow us to use this reaction in the field of radiochemistry for labeling aromatic substrates with ¹²³I or ¹²⁵I. In this point of view, our method complements the triazene one. In any case it is superior to the tetrafluoroborate synthesis, which is not applicable for labeling chemistry.

Moreover, when the reaction is performed in refluxing acetonitrile in the presence of 18-crown-6 ether and iodide anions, a deazosulfonation reaction occurs simultaneously with the iodideazosulfonation one. The best procedure for this deamination reaction is refluxing a solution of 4a–g in dimethylformamide, in the presence of a catalytic amount of 18-crown-6 ether. The yields of isolated arenes are fairly good (Scheme I, Table I). This method affords a mild, neutral, reproducible and inexpensive alternative to the known procedures for the reductive deamination of aromatic primary amines,[14] without interaction with substituents. Work is now in progress to evaluate the reactivity of various aryl arylazo sulfones toward other nucleophiles used in labeling radiopharmaceuticals.

Experimental Section

General Methods. All the compounds cited in this paper are well-known. They have been fully characterized through melting point, ¹H NMR, MS, and thin-layer chromatography. Aryl arylazo sulfones 4a–g have been synthetized according to Ahern.[6]

Iododeazosulfonation. All the iodoarenes 5a–g were prepared by following the same procedure. We give here the typical procedure in the case of *o*-(methoxycarbonyl)iodobenzene (5e).

A mixture of 3.18 g (10 mmol) of 4e, 50 mg of 18-crown-6 ether, 1.66 g (10 mmol) of potassium iodide, and 60 mL of acetonitrile was stirred for 4 h at room temperature. The reaction mixture was poured into water (200 mL) and extracted with ether (3 × 100 mL). The mixed organic layers were dried (MgSO₄) and evaporated under reduced pressure. The residues were purified by column chromatography using a mixture of CHCl₃–C₆H₆ (15:85) as eluent.

Reductive Deazosulfonation. All the deaminations were conducted in the same way. We give here the experimental conditions in the case of 6e. A mixture of 3.18 g (10 mmol) of 4e, 50 mg of 18-crown-6 ether, and 60 mL of dimethylformamide was stirred for 4 h at refluxing temperature. The reaction mixture was then poured into water (200 mL) and extracted with ether (3 × 100 mL). The mixed organic layers were dried (MgSO₄) and evaporated under reduced pressure. The residues were purified by column chromatography using a mixture of CHCl₃–C₆H₆ (15:85) as eluent.

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