authentic sample. The hot benzene filtrate was crystallized to isolate 11.0 g. of 4,4′-dinitrobibenzyl, m.p. 179–181°, mixed melting point undepressed with an authentic sample.

Oxidative coupling using cuprous chloride catalyst. A solution of 137 g. (1.00 mole) of *p*-nitrotoluene in 513 g. of 99.5% ethylenediamine and 87 g. of methanol was purged with nitrogen at room temperature, cooled to 9–11° and 5.0 g. of cuprous chloride added. The mixture was stirred under nitrogen for 10 min. and at the end of this period oxygen was passed through the mixture at 9–11° for 1 hr. The absorption of oxygen was 11.2 l. (about 0.5 mole). The temperature was then raised to 30–35° and the oxygen continued for an additional hour (absorption had virtually ceased). Water was added and the solid was filtered, washed with methanol, and dried. The yellow solid obtained (115 g., 85% yield) was treated with 3 l. of refluxing benzene. The insoluble material amounted to 22 g. (16% yield) of 4,4′-dinitrostilbene. After cooling 77 g. (57% yield) of 4,4′-dinitrobibenzyl, was obtained from the filtrate.

In order to achieve reproducible results, it was necessary to allow the cuprous chloride to react with the ethylenediamine solution of *p*-nitrotoluene in a nitrogen atmosphere for a short period of time before passing through the medium. Cupric salts were without effect in this reaction. The formation of small amounts of the cuprous salt of the *p*-nitrotoluene was apparently needed before the oxidative coupling could proceed.

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New Syntheses of Aryl Fluorides and Aryl Fluorosulfonates from Oxyfluorides of Sulfur

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Several aryl fluorides have been synthesized in an unusual displacement of a hydroxyl group by fluoride through the reaction of phenol or substituted phenols with sulfur oxytetrafluoride (SOF_4). Other reaction products were aryl fluorosulfonates, diaryl sulfates, hydrogen fluoride, and sulfuryl fluoride as summarized in Equations 1–3.

$$\mathrm{ArOH} + \mathrm{SOF_4} \longrightarrow \mathrm{ArF} + \mathrm{SO_2F_2} + \mathrm{HF} \qquad (1)$$

$$\mathrm{ArOH} + \mathrm{SO_2F_2} \longrightarrow \mathrm{ArOSO_2F} + \mathrm{HF} \qquad (2)$$

$$2\ \mathrm{ArOH} + \mathrm{SO_2F_2} \longrightarrow \mathrm{(ArO)_2SO_2} + 2\ \mathrm{HF} \qquad (3)$$

Fluorobenzene, *m*-chlorofluorobenzene, *m*-fluorotoluene, *p*-fluorotoluene, and methyl *m*-fluorobenzoate were prepared by this method. Conversions, methods of identification, and several physical properties of the products are summarized in Table I.

TABLE I

Products from Reaction of Phenols with Sulfur Oxytetrafluoride

Phenol	Conversion,^{a} Properties, and Methods of Characterization: ArF	ArOSO$_2$F	(ArO)$_2$SO$_2$
C_6H_5OH	30%^{b,c,d} B.p. 86° n_{D}^{25} 1.4624	15%^{e,f} B.p. 180° n_{D}^{25} 1.4628	30%^{b,g} B.p. 150° at 4 mm. n_{D}^{25} 1.5483
m-ClC_6H_4OH	20%^{e} B.p. 53° at 55 mm. n_{D}^{25} 1.4921	16%^{e,j} B.p. 46° at 2 mm. n_{D}^{25} 1.4879	
m-$CH_3C_6H_4OH$	20%^{d} B.p. 46° at 61 mm. n_{D}^{25} 1.4666	8%^{e} B.p. 46° at 1 mm. n_{D}^{25} 1.4658	12%^{e,k} M.p. 61°
p-$CH_3C_6H_4OH$	25%^{d} B.p. 55° at 90 mm. n_{D}^{25} 1.4673	15%^{e} B.p. 38–40 at 2 mm. n_{D}^{25} 1.4792	30%^{i,l} M.p. 58°
o-$CH_3O_2CC_6H_4OH$	12%^{h} B.p. 47° at 1 mm.	10%^{i} B.p. 82° at 1 mm.	

[a] Calculated from amount of phenol used in the reaction of equimolar mixtures of phenol and sulfur oxytetrafluoride. [b] Comparison with listed boiling point. [c] Comparison with listed freezing point and refractive index. [d] Correspondence of infrared absorption with reported absorption for the corresponding compound. [e] Correspondence of infrared absorption with expected absorption for postulated functionalities. [f] Comparison of NMR fluorine resonance, b.p., f.p., and refractive index with product from reaction of phenol and sulfuryl chloride fluoride. [g] Hydrolysis to phenol. [h] Hydrolysis to *o*-fluorobenzoic acid. [i] NMR fluorine resonance. [j] Anal. Calcd. for $C_6H_4ClSO_3F$: C, 34.22; H, 1.91. Found: C, 34.69; H, 2 00. [k] Anal. Calcd. for $C_{14}H_{14}SO_4$: C, 60.41; H, 5.07. Found: C, 60.08; H, 5.03. [l] Anal. Calcd. for $C_{14}H_{14}SO_4$: C, 60.41; H, 5.07. Found: C, 60.48; H, 5.08.

Formation of aryl fluorosulfonates in this reaction system suggested an improved synthesis of these esters by reaction of phenols with sulfuryl chloride (Equation 4).

$$\mathrm{ArOH} + \mathrm{ClSO_2F} \xrightarrow{\text{pyridine}} \mathrm{ArOSO_2F} + \mathrm{HCl} \qquad (4)$$

This reaction is similar to the synthesis of monoaryl sulfates from chlorosulfonic acid and phenols.[1] Sulfuryl chloride fluoride is conveniently obtained from sodium fluoride and sulfuryl chloride.[2] This new synthesis of fluorosulfonic acid esters using sulfuryl chloride fluoride is more convenient and gives higher yields than the usual synthetic method involving pyrolysis of fluorosulfonic acid salts of aryl diazonium compounds.[3]

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EXPERIMENTAL

The following procedures are typical for the synthesis of aryl fluorides and of aryl fluorosulfonates from phenols.

Reaction of phenol with sulfur oxytetrafluoride. A stainless steel-lined autoclave of 400-ml. capacity was charged with phenol (24 g., 0.25 mole) and evacuated. Sulfur oxytetrafluoride[4] (31 g., 0.25 mole) was introduced, and the reaction mixture was shaken and heated at 150° for 9 hr. The gaseous product (27 g.), principally sulfuryl fluoride, distilled at −49° to −44°. The remainder comprised 27 g. of black, fuming liquid. After washing with aqueous 5% sodium hydroxide and with water, 22 g. of liquid was left. Upon distillation this liquid gave 7 g. (0.07 mole) of fluorobenzene, b.p. 85–87°, f.p. −40°, $n_D^{25.5}$ 1.4624 and 7 g. (0.04 mole) of phenyl fluorosulfonate, b.p. 175–180°, f.p. −21, $n_D^{25.5}$ 1.4628. Fraction 1 was further identified as fluorobenzene by comparison of its infrared absorption with an authentic sample. Fraction 2 had infrared absorption peaks at 3.25 μ, corresponding to $=$CH; at 6.25 μ, 6.3 μ, and 6.7 μ, corresponding to aromatic $-C=C-$; and at 12.3 μ, suggesting an S—F bond.

Anal. of Fraction 2. Calcd. for $C_6H_5SO_3F$: C, 40.91; H, 2.86. Found: C, 41.11; H, 3.06.

The distillation residue weighed 8 g. It was combined with residues of similar experiments, and the composite was distilled to give a fluorine-free distillate (b.p. 145–150°/5 mm., n_D^{25} 1.5483), which was hydrolyzed by hot aqueous sodium hydroxide to phenol and sulfate ion.

Reaction of phenols with sulfuryl chloride fluoride. A solution of 20 g. (0.2 mole) of phenol in 80 ml. of pyridine was stirred in a flask fitted with a condenser cooled by solid carbon dioxide. The mixture was chilled to 0°, and 30 g. of sulfuryl chloride fluoride (0.28 mole) was introduced. The mixture was slowly warmed and held at 40° for 1 hr. It was then poured into iced hydrochloric acid, and the product was extracted with ether. The ethereal extract was washed with water, then with dilute aqueous sodium hydroxide and again, with water. Phenyl fluorosulfonate (30 g., 0.17 mole) was recovered by distillation.

In a similar procedure *p*-methoxyphenol was converted (45%) to *p*-methoxyphenyl fluorosulfonate (b.p. 75° at 2 mm., n_D^{25} 1.4798).

Anal. Calcd. for $C_7H_7O_4SF$: C, 40.77; H, 3.42; S, 15.55. Found: C, 41.06; H, 3.40; S, 15.41.

Similarly, *p*-chlorophenol gave *p*-chlorophenyl fluorosulfonate (50%) (b.p. 61° at 2 mm., n_D^{25} 1.4872).

Anal. Calcd. for $C_6H_4O_3SClF$: S, 15.22; Cl, 16.84; F, 9.02. Found: S, 15.03; Cl, 17.16; F, 9.39.

Infrared absorption spectra were consistent with the proposed formulas.

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Preparation of Some Arylalkenes

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In connection with nitration studies of alkenes, the necessity arose for the preparation of a number of arylalkenes. The precursors for most of the arylalkenes were readily dehydrated tertiary arylcarbinols; however, the methods for the dehydration of many of these alcohols which have been described in the literature were found to be time-consuming.[1]

By using warm 20% sulfuric acid–acetic acid (by volume) it was observed that the crude alcohols could be converted within thirty seconds to the corresponding alkenes in over-all yields generally exceeding 70% (based on the carbonyl compound used in the preparation).[2]

This method, as described, does not appear to be applicable to the dehydration of purely aliphatic tertiary alcohols or secondary arylcarbinols, since 1-methylcyclohexene and *trans*-stilbene were prepared in yields of only 20 to 30% from the corresponding tertiary and secondary alcohols respectively.

EXPERIMENTAL

General procedure. In each instance preparation of the carbinol was carried out by adding the carbonyl-containing reagent (Table I) to approximately 10% excess of appropriate Grignard reagent (generally 0.3–0.5 mole scale). The reaction mixture was then poured into cold ammonium chloride solution with stirring and the carbinol extracted with additional ether. The extract was washed with water, dried for a short period over sodium sulfate, and the ether was evaporated under reduced pressure on the steam bath. The resulting crude alcohol melt, while still warm, was treated with freshly prepared (warm) 20% (by volume) sulfuric acid–acetic acid (200 ml./mole of alcohol). The resulting mixture was swirled for 15–30 sec. (two phases separated immediately) and poured into ether–water (600 ml. of ether–1 l. of water per mole of alcohol). The ether was washed with water and dilute potassium bicarbonate, dried over calcium chloride, and evaporated under reduced pressure. The crude arylalkene residue was purified by vacuum distillation. On occasions where the crude alcohol did not melt on the steam bath, the solid was swirled with the sulfuric acid–acetic acid reagent until the solid phase had expired, and for several minutes thereafter. For those solid alkenes where purification by distillation was impracticable (see Table I), the acid dehydration mixture was poured into cold water containing excess sodium acetate. The solid was filtered, washed free of acetic acid, and recrystallized from methanol.

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[1] Refluxing aqueous sulfuric acid has been widely employed to effect dehydration of tertiary arylcarbinols. See: (a) C. F. H. Allen and S. Converse, *Org. Syntheses*, **Coll. Vol. I**, 266 (1941). (b) H. Adkins and W. Zartman, *Org. Syntheses*, **Coll. Vol. I**, 606 (1943).

[2] Acetic acid–sulfuric acid has been used by a number of previous investigators for dehydrations. The present method resembles most nearly that of R. Lagrave, *Ann. Chim.* (10), **8**, 386 (1927).