with stirring. The final mixture was refluxed for a similar period.

The indan-1-one (26.4 g., 0.20 mole) in ether (150 ml.) was added to the phenylmagnesium bromide solution over a half-hour period and the combined contents were refluxed for a second half-hour. The reaction mixture was poured into a stirred slush of iced water (400 g.) and ammonium chloride (3 g.). The ether layer was removed and the residual aqueous solution was extracted with three portions of ether (100 ml. each). The combined organic extracts were filtered through magnesium sulfate and the ether was removed *in vacuo*. The oily residue was distilled to give 34.5 g. (89.6%) of a yellow liquid, b.p. 118–119° (0.45 mm.), n_D^{20} 1.6320 [lit. value,[6] b.p. 200–201° (29 mm.), n_D^{24} 1.6313].

Anal. Calcd. for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.80; H, 6.27.

Ethyl 3-phenyl-1-indenylglyoxylate (II). A mixture of 3-phenylindene (9.61 g., 0.05 mole) and diethyloxalate (8.77 g., 0.06 mole) in dry ether (25 ml.) was added with stirring and under nitrogen to a sodium ethoxide solution, previously prepared from sodium (1.61 g., 0.07 g.-atom) and anhydrous ethanol. The solution was stirred for 3 hr. and was then poured into a chilled mixture of ether (100 ml.) and aqueous sulfuric acid (7%, 100 ml.) and was stirred for 0.5 hr. The ethereal layer was separated and the acidic solution was extracted again with ether (50 ml.). The combined ethereal extracts were washed with aqueous sodium bicarbonate, and water and were filtered through magnesium sulfate. The ether was stripped off and the residue was crystallized from benzene-petroleum ether to give 12.9 g. (88.3%) of orange needles, m.p. 104.0–104.5°. Infrared absorptions were at 2.91 and 5.91 μ.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.95; H, 5.41.

3-Phenylindenylglyoxylic acid (III). A solution of ethyl 3-phenyl-1-indenylglyoxylate (12.9 g., 0.044 mole) in ether (100 ml.) was stirred with aqueous sodium hydroxide (2%, 100 ml.) for 12 hr. The ether layer was discarded and the red basic solution was treated with a mixture of ether (100 ml.) and aqueous hydrochloric acid (5%, 100 ml.) and was stirred for 1 hr. The ethereal layer was removed and the acidic solution was extracted twice with ether (100-ml. portions). The combined ether extracts were washed twice with water, were filtered through magnesium sulfate and the ether was stripped off. The residue was crystallized from benzene to give 11.45 g. (98.4%) of reddish orange needles, m.p. 188–189° dec. Infrared absorptions at 2.86 and 5.97 μ.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.52; H, 4.75.

Attempted preparation of 3-phenylindene-1-carboxylic acid (IV). The glyoxylic ester (63 mg.) was added to a mixture of ammonium hydroxide (2 ml.), ethanol (2 ml.), water (10 ml.), and hydrogen peroxide (30%) (0.50 ml.), and the resulting solution was warmed on the steam bath for 1.5 hr. An additional portion of hydrogen peroxide (0.1 ml.) was added and the solution was heated for a final 0.5 hr. The cold solution was acidified with hydrochloric acid and was extracted with ether. The ethereal extract was washed with water, dried and was evaporated. The residue was identified as starting material by infrared comparison.

The glyoxylic acid (1.32 g.) was dissolved in aqueous sodium hydroxide solution (20 ml., 0.5*N*) and hydrogen peroxide (30%, 7.5 ml.) in water (10 ml.) and heated on the steam bath for 5 hr. The solution was neutralized with dilute sodium bicarbonate solution and extracted with ether to furnish a yellow oil (0.5 g.) whose infrared spectrum was identical with that of authentic 3-phenylindene.

2-Phenyl-3-hydroxyl-indan-2-one (VI). To a chilled suspension of hydrogen peroxide (90%, 0.82 ml., 0.03 mole) in methylene chloride (5 ml.) was added trifluoroacetic anhydride (5.08 ml., 0.036 mole) over a 10-min. period. The resulting solution was stirred further in the cold for 15 min. and was added to a stirred mixture of sodium carbonate (9.54 g., 0.09 mole), 3-phenylindene (3.85 g., 0.02 mole) and methylene chloride (30 ml.) over a half-hour period. The reaction was refluxed for an additional hour, the inorganic salts were filtered off, and the salt cake was triturated with fresh methylene chloride (30 ml.) and sucked dry. The combined organic extracts were evaporated to furnish an oily residue. A methylene chloride–petroleum ether (b.p. 60–68°) solution furnished 3.34 g. (80.1%, based on unrecovered starting material) of white crystals, m.p. 127.5–128.5°. Infrared-absorptions were at 2.85 and 5.70 μ. A sample of this compound was unaffected after 5 hr. by chromium trioxide-pyridine.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 79.99; H, 5.32.

1-Phenyl-2-bromo-indan-1-ol (VII). In a 1-l. three-neck flask equipped with stirrer, thermometer, and dropping funnel was placed water (150 ml.), Tide (0.70 g.), and 3-phenylindene (4.81 g., 0.025 mole). After warming to 80° and complete emulsification had occurred, a saturated solution of bromine in aqueous sodium bromide (bromine, 4.0 g., sodium bromide, 10.0 g., water, 150 ml.) was added dropwise over 0.5 hr. Since the reaction solution had not turned a permanent yellow, an additional small quantity of brominating solution was added to the flask.

After stirring for 4 hr., the solution was decanted and the residual yellow gum was stirred with fresh, cold water for a further similar period. The gum was collected and dried, wt. 5.5 g., and was triturated with petroleum ether to furnish 2.1 g. (50.0%, based on unrecovered starting material) of white needles, m.p. 131.0–132.0. Infrared absorption was at 2.95 μ.

Anal. Calcd. for $C_{15}H_{13}BrO$: C, 62.28; H, 4.53; Br, 27.65. Found: C, 62.53; H, 4.61; Br, 27.28.

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Oxidation of *p*-Nitrotoluene to 4,4′-Dinitrobibenzyl and 4,4′-Dinitrostilbene

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The preparation of 4,4′-dinitrobibenzyl by the oxidative coupling of *p*-nitrotoluene has been described by House[1] and was based on the method of Green *et al.*[2] In this method the solid *p*-nitrotoluene was added to a methanolic potassium hydroxide solution and air was passed through the mixture for 8 hours to form 4,4′-dinitrobibenzyl. The kinetics of the oxidation have been studied in methanolic potassium hydroxide[3] and in a solution of potassium *t*-butoxide in *t*-butyl alcohol.[4] In the

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latter system significant amounts of by-product p-nitrobenzoic acid were formed, especially when oxygen was present at a pressure of one atmosphere or greater.

Now it has been found that excellent yields and rapid reaction rates result when certain amines or ethers are employed with methanolic potassium hydroxide as the medium for the reaction with oxygen at atmospheric pressure. Even methanolic sodium hydroxide was effectively used with ethylenediamine; 88% yield was obtained in a two-hour reaction period at 10°. These reaction conditions were also employed to oxidize 4,4′-dinitrobenzyl to 4,4′-dinitrostilbene. Thus these amines and ethers which are accelerators for the oxidation probably aid in formation (and solubilization) of the intermediates in the ion-radical mechanism recently proposed by Russell and Moye.[4]

The coupling of p-nitrotoluene with oxygen gas in 33% methanolic potassium hydroxide is accelerated by the addition of either pyridine, ethylenediamine, dioxane, or the diethyl ether of diethylene glycol; on the other hand the addition of either 2 - methyl - 5 - ethylpyridine, triethylamine, monoethyl ether of diethylene glycol, ethylene glycol, or methanol had little or no effect on the oxidation rate. Under otherwise optimum conditions, our results show that at higher temperatures (30–50°), the oxidation proceeds to give larger amounts of 4,4′-dinitrostilbene and an insoluble, infusible polymer. The structure of the latter has not been investigated by the authors, but it may be similar to the polyamide reportedly obtained by the reaction of p-nitrotoluene with sodium hydroxide.[5]

The oxidative coupling of o-nitrotoluene with air in a suspension of alcohol-free potassium ethoxide in ether has been reported to give 2,2′-dinitrobibenzyl in 25–30% yield.[6] This oxidation proceeded in our hands at 5–10° in methanolic potassium hydroxide-ethylenediamine medium with oxygen to form 2,2′-dinitrobibenzyl in 36% yield. However, several attempts to couple oxidatively 2,4-dinitrotoluene using either ethylenediamine or pyridine with methanolic potassium hydroxide were unsuccessful. Although oxygen was absorbed slowly, no precipitate formed after the crude reaction mixture was diluted with water. Acidification of the solution precipitated an amorphous material melting above 385°. These results are similar to those observed by Green and Baddiley,[7] who found it necessary to employ iodine as the oxidizing agent for the coupling of 2,4-dinitrotoluene.

The oxidative coupling of p-nitrotoluene has been achieved in ethylenediamine alone with cuprous chloride. Cupric salts did not catalyze the reaction, which is somewhat surprising in view of the results of Kharasch and Sosnovsky,[8] who found that either cupric or cuprous salts were effective catalysts for the oxidative coupling of diphenylacetonitrile to tetraphenylsuccinonitrile in basic media. This technique has been employed extensively for the oxidative coupling of acetylenes.[9]

EXPERIMENTAL

Alkaline oxidative coupling using oxygen gas. The following procedure can be regarded as typical of the techniques employed during the course of this work. The experiments using a variety of solvents have been published recently.[10]

A solution of 137 g. (1.00 mole) of p-nitrotoluene in 400 g. of 85% ethylenediamine was added over a 1-hr. period to 500 g. of a 20% solution of sodium hydroxide in methanol. Oxygen was passed through the mixture at 7–10° at a rate fast enough to maintain a slight excess. The oxygen absorption was determined by measurement of the volume introduced through a flow meter and the volume of blow-off through a wet meter. After an additional hour of agitation, the absorption of oxygen had virtually ceased and 800 ml. of water was added. A total of 10.4 l. (0.43 mole) of oxygen was absorbed. The resulting solid was filtered, washed with methanol and dried. The yellow solid obtained (120 g., 88% yield) was treated with 3 l. of refluxing benzene. There was 7 g. (5% yield) of material which did not dissolve in hot benzene and was mainly *trans*-4,4′-dinitrostilbene, m.p. 240–280° (reported[11] m.p. 288–291°). A total of 102 g. (75% yield) of 4,4′-dinitrobibenzyl, m.p. 178–180° (reported[12] m.p. 180.5°) was obtained from the benzene filtrate.

Alkaline oxidative coupling in the absence of oxygen gas. A solution of 400 g. of 85% ethylenediamine and 500 g. of 20% sodium hydroxide in methanol was stirred at 10° while nitrogen was passed through to remove air. While the nitrogen feed was maintained, 137 g. (1.00 mole) of p-nitrotoluene was added all at once and the stirring was continued for 2 hr. at 10°. Ice water (800 ml.) was added and the crude product was filtered and dried to obtain 122 g., m.p. 120–162°. Recrystallization from 2 l. of methanol gave 68 g. (50%) of 4,4′-dinitrobibenzyl, no depression with a mixed melting point. Both 4,4′-dinitrobibenzyl (1 g.) and p-nitrotoluene (26 g.) were crystallized from the methanol filtrate. However, no other compounds could be separated from the complex mixture.

Oxidation of 4,4′-dinitrobibenzyl to 4,4′-dinitrostilbene. A mixture of 800 g. of 85% ethylenediamine, 125 g. of 20% solution of sodium hydroxide in methanol and 27 g. of 4,4′-dinitrobibenzyl (0.1 mole) was stirred at 10° while excess oxygen was passed through the mixture for 3.2 hr. The dark green mixture was diluted with 800 ml. of ice water and filtered. The resulting precipitate was washed well with water and then methanol. After drying, the greenish yellow solid (24.5 g.) had a m.p. of 202–265°. It was digested in 500 ml. of boiling benzene and filtered hot to obtain 12.5 g. of slightly impure 4,4′-dinitrostilbene. The latter was crystallized from nitrobenzene to obtain 11.3 g. (44% yield) of deep yellow 4,4′-dinitrostilbene, m.p. 293–295°. The infrared spectrum was identical to that of an

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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.

$$ArOH + SOF_4 \longrightarrow ArF + SO_2F_2 + HF \quad (1)$$

$$ArOH + SO_2F_2 \longrightarrow ArOSO_2F + HF \quad (2)$$

$$2\ ArOH + SO_2F_2 \longrightarrow (ArO)_2SO_2 + 2\ HF \quad (3)$$

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	$ArOSO_2F$	$(ArO)_2SO_2$
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-$CH_3C_5H_4OH$	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).

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

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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