Szmant. Moreover, a plot of sulfonylphenol acidities[2] against σ reveals a relationship parallel to those reported here for the corresponding benzoic and acetic acids.

TABLE II

SUBSTITUENT EFFECTS ON THE ACIDITY OF PHENYLSULFONYLACETIC ACID

Substituent	σ (of Substituent)[a]	pK_a in 48% Aq. Ethanol[b]
4-NO_2	+0.778	3.29
3-NO_2	+0.710	3.45
H	0.000	3.66
4-CH_3	−0.170	3.72
4-OCH_3	−0.268	3.79
4-OH	−0.357	3.84

[a] Ref. *a* in Table I. [b] Ref. *b* in Table I.

Infrared studies of aryl sulfones[4] indicate that the S—O force constant also varies regularly with the σ of the substituent, resembling analogous observations with ketones.[5] As both this relationship and that describing the relative acidities within the three series of sulfone derivatives are valid in each case even at either extreme of substituent electronegativity, true variation in the character of the sulfone group, at least to the extent proposed by Szmant, is not evident.

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The Oxidation of Anisole and Diphenyl Ether with Trifluoroperoxyacetic Acid

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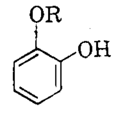
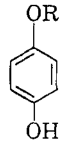
Received August 7, 1961

Friess[1] and co-workers studied the reactions of peroxybenzoic acid with the methyl ethers of di- and trihydric monocyclic phenols in chloroform solution. 1,4-Quinones were usually formed, in some cases with the loss of a methoxy group. More recently, the action of peroxyacetic acid[2] on a number of substituted di- and trimethoxybenzenes has been examined. Once again 1,4-quinones, formed by electrophilic 1,4-dihydroxylation and methoxy elimination, were usually the principal products obtained. With neither peroxy acid were the presumed primary products of oxidation, methoxyphenols, isolated. Less reactive monocyclic aryl ethers such as anisole[1–3] were reported to remain unchanged or to give water-soluble unidentified oils.

A recent publication[4] on the oxidation of aromatic hydrocarbons with trifluoroperoxyacetic acid prompts us to report some results of our own. Trifluoroperoxyacetic acid was found to oxidize anisole and diphenyl ether primarily by a process of electrophilic monohydroxylation. Moderate yields of phenols were obtained when an equimolar amount of peroxy acid was added slowly over several hours to a solution of the aryl ether in methylene chloride at 15–25°. Anisole (44% conversion) gave *o*-methoxyphenol (Ia) in 27% yield and *p*-methoxyphenol (IIa) in 7% yield. From diphenyl ether (44% conversion) *o*-phenoxyphenol (Ib) and *p*-phenoxyphenol (IIb) were obtained in 35% and 12% yields, respectively. In neither case were we able to isolate any of the corresponding meta isomer.



Ia. R = CH_3
b. R = C_6H_5



IIa. R = CH_3
b. R = C_6H_5

It was of interest that the phenols isolated from the oxidations of both anisole and diphenyl ether were predominantly the ortho isomers. The modest total yields (34–47%) were explained by noting that the phenols underwent further rapid oxidation, although no specific products were isolated. There was considerable doubt as to whether the observed ortho to para ratio (3:1) was due to a truly selective process or was merely the consequence of a rate of subsequent oxidation greater for the para isomer than for the ortho. In order to determine which of these alternatives was correct, an equimolar mixture of *o*-methoxyphenol and *p*-methoxyphenol was treated with a one-half molar quantity of trifluoroperoxyacetic acid. Analysis of the unchanged methoxyphenol showed that approximately twice as much para as ortho isomer had been consumed. The apparent selectivity of the hydroxylation of anisole can thus be accounted for to a large extent by the more rapid oxidation of *p*-methoxyphenol.

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EXPERIMENTAL

Oxidation of anisole. A solution of trifluoroperoxyacetic acid[5] (110 ml.; 2.1 *M*) in methylene chloride was added dropwise over a two-hour period to a stirred solution of anisole (21.6 g.; 0.2 mole) in 100 ml. of methylene chloride maintained at 15–20°. Stirring was continued at 25° for thirty minutes at which time 95% of the peroxy acid had been consumed. The mixture was diluted with methylene chloride and washed with a 10% sodium bicarbonate solution. After drying the solvent was removed by distillation. The residual liquid was distilled through a semimicro Vigreux column to give anisole, 12.0 g., b.p. 51–53° (20 mm.) and fraction 2, 4.0 g., b.p. 55–90° (3 mm.).

Analysis of fraction 2 by gas-liquid chromatography at 190° on a column packed with DC 710 on firebrick indicated the presence of three components. Comparison of the chromatogram with those of authentic specimens showed that the constituents were anisole (4%), *o*-methoxyphenol (73–77%), and *p*-methoxyphenol (18–23%).

Fractional distillation of fraction 2 through a micro spinning band column at 4 mm. pressure yielded *o*-methoxyphenol, b.p. 53–55°, and *p*-methoxyphenol, b.p. 85–87°. The latter isomer was recrystallized from methylene chloride-hexane to give white plates, m.p. and mixed m.p. 53–54°.

Anal. Calcd. for $C_7H_8O_2$: C, 67.7; H, 6.48; phenolic acidity, 0.805 eq./100 g. Found for *o*-methoxyphenol: C, 67.5; H, 6.51; phenolic acidity, 0.80 eq./100 g. Found for *p*-methoxyphenol: C, 67.6; H, 6.53; phenolic acidity, 0.81 eq./100 g.

Oxidation of diphenyl ether. Trifluoroperoxyacetic acid in methylene chloride (110 ml. of 2.1 *M* solution) was added dropwise over a ninety-minute period to a stirred solution of diphenyl ether (34.4 g., 0.2 mole) in 120 ml. of methylene chloride at 20–25°. Fifteen minutes after the addition was complete 95% of the peroxy acid had been consumed. The dark brown mixture was washed with 10% sodium bicarbonate, dried, and the methylene chloride removed under vacuum. Unreacted diphenyl ether, 19.0 g.; b.p. 102–104° (7 mm.), was recovered by distillation through a Vigreux column.

The residual solid was fractionally sublimed at 60–80° and 0.5 mm. pressure. Each fraction was analyzed by gas-liquid chromatography at 200° on a column packed with DC-11 on firebrick at a helium flow-rate at 60 ml./min. Comparison of each chromatogram with those of authentic samples showed that the total sublimate (8.1 g.) contained *o*-phenoxyphenol (5.7 g.), *p*-phenoxyphenol (1.9 g.), and diphenyl ether (0.5 g.).

The first few fractions of sublimate were triturated with cold *n*-hexane and filtered. The insoluble crystalline material was recrystallized from *n*-hexane to give white needles melting at 103–104°. The melting point was undepressed on admixture with an authentic sample of *o*-phenoxyphenol.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.5; H, 5.42; phenolic acidity, 0.537 eq./100 g. Found: C, 77.8; H, 5.48; phenolic acidity, 0.525 eq./100 g.

The last few fractions melted at 77–81° and were recrystallized from *n*-hexane to give white plates melting at 82–83°. The melting point was undepressed on admixture with an authentic sample of *p*-phenoxyphenol.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.5; H, 5.42; phenolic acidity, 0.537 eq./100 g. Found: C, 77.9; H, 5.35; phenolic acidity, 0.54 eq./100 g.

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The Decarbonylation of α-Anilino-α,α-diphenylacetic Acid by *p*-Toluenesulfonyl Chloride and Pyridine

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Received August 28, 1961

We have observed a novel decarbonylation of α-anilino-α,α-diphenylacetic acid (I), by the action of *p*-toluenesulfonyl chloride and pyridine, leading to the formation of benzophenone anil (II). The by-products (carbon monoxide and pyridinium *p*-toluenesulfonate) suggest that the reaction proceeds by formation of an unusual mixed anhydride, followed by a base-catalyzed elimination.

The reaction was discovered during an attempt to prepare the *N*-*p*-toluenesulfonyl derivative of the amino acid I. The acid was recovered unchanged after treatment with *p*-toluenesulfonyl chloride and aqueous sodium hydroxide (even under forcing conditions), but reacted smoothly when anhydrous pyridine was employed as the base. However, the reaction products were those described above; none of the expected tosyl derivative was isolated.

The base-catalyzed decomposition of α-(arylsulfonamido)carboxylic acids and acid chlorides has been reported previously by Wiley and his coworkers.[1-3] In the case of the free acids the decomposition products were aldehydes, disulfides, and carbon dioxide[2]; the acid chlorides gave aldehydes, sulfonamides, and carbon monoxide.[3] A cyclic mechanism was suggested to account for these transformations.[1]

The formal analogy between these observations and our results led us to postulate that the *N*-toluenesulfonyl derivative was formed first and subsequently underwent a rapid decomposition to the anil, carbon dioxide, and *p*-toluenesulfinic acid (as the pyridinium salt). However, the gaseous by-products of the reaction gave no precipitate when passed through aqueous barium hydroxide and, in fact, proved to be exclusively carbon monoxide as determined by infrared methods. In addition, the solid by-product was identified as pyridinium *p*-toluenesulfonate by comparison of the *S*-benzylthiuronium salt with an authentic sample. As sulfinic acids are relatively stable in the salt form,[4] it is unlikely that pyridinium *p*-toluenesulfonate could have arisen from previously formed *p*-toluenesulfinate.

These results suggest that the present reaction pursues a different course from that of the simpler

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