TABLE I

REACTIONS OF CARBON MONOXIDE WITH PHENOLS[a]

Phenol	Solvent	Catalyst	Catalyst concn[b]	Temp, °C	Product	Yield, %	Conversion, %[c]	Bp or mp, °C
o-Cresol	None	$Co_2(CO)_8$	0.0045	300	2(3H)-Benzofuranone	14	11	Bp 53–55 (0.08 mm)[d]
o-Cresol	None	$Co_2(CO)_8$	0.10	300	2(3H)-Benzofuranone	14	18	Bp 111–114 (8 mm)[e]
o-Cresol	None	Active Co[f]	0.024	300	2(3H)-Benzofuranone	22	17	Bp 140–150 (13 mm)[e]
2,6-Dimethylphenol	Benzene	$Co_2(CO)_8$	0.011	300	7-Methyl-2(3H)-benzofuranone	14	12	Mp 97.5–97.7[g]
2,4-Dimethylphenol	None	$Co_2(CO)_8$	0.0080	300	5-Methyl-2(3H)-benzofuranone	8	24	Mp 68.5–71.5[h]
o-Hydroxybenzyl alcohol	Dioxane	$Co_2(CO)_8$[i]	0.015	200	2(3H)-Benzofuranone	16		Bp 54–55 (0.1 mm)[e]

[a] At 910–1000-atm pressure of CO. [b] Mole of catalyst per mole of phenol. [c] Per cent starting material not recovered. [d] Infrared 5.5 μ (lactone carbonyl); $n^{25}D$ 1.552; lit. $n^{14}D$ 1.555, bp 245–249° [K. van Auwers, *Ber.* **52**, 129 (1919)]. Calcd for $C_8H_6O_2$: C, 71.63; H, 4.51; mol wt, 134. Found: C, 72.54; H, 5.34; mol wt, 135, 137. [e] Infrared identical with that of the analyzed product above. [f] Reduced sintered cobalt oxides. [g] Lit. 98° [O. Aubert, A. Augdahl, and E. Berner, *Acta Chem. Scand.*, **6**, 433 (1952)]; infrared 5. 5 μ (lactone carbonyl). [h] Lit. 74° (*ibid.*); infrared, 5.5 μ (lactone carbonyl). [i] Also Al_2O_3 (0.25 mol/mol of phenol).

Since the reaction involves loss of two hydrogen atoms from the substituted phenols, the probable intermediate is 6-methylene-2,4-cyclohexadien-1-one or o-quinone methide (**1**). This compound was postulated by Hultzch[2] as a dehydration intermediate from o-hydroxybenzyl alcohol which subsequently reacted as a diene analog with styrene. Gardner and coworkers[3] obtained **1** as an unstable intermediate by pyrolysis of o-methoxymethylphenol. Therefore, to obtain further evidence for the intermediacy of **1** in the carbonylation of o-cresol, o-hydroxybenzyl alcohol was allowed to react with carbon monoxide and dicobalt octacarbonyl in the presence of aluminum oxide as dehydrating agent. At 200° and 1000 atm, 2(3H)-benzofuranone (**2**) was indeed obtained as the only isolable product; at 300° only tar was found.

The optimum conditions for carbonylation of o-methylphenols were 300° and 900–1000-atm pressure of carbon monoxide. Even at these conditions yields were low because of tar formation. In some experiments, the diaryl ethers were isolated as side products. Attempts to increase yields by employing lower (170–180°) or higher (450–500°) temperatures and lower (175 atm) and higher (3000 atm) pressures were unsuccessful.

The best catalyst was dicobalt octacarbonyl, either preformed or prepared *in situ* from an active form of cobalt metal. The cobalt carbonyl probably functions as a dehydrogenation agent with formation of cobalt carbonyl hydride. The conversion into **2** was found to vary slightly with catalyst concentration (see Table I). No increase in yield resulted from use of a stoichiometric quantity of carbonyl at 175 atm and 250°, addition of oxidizing agents such as manganese dioxide, or addition of tertiary amines to counteract the acidity of the carbonyl hydride. Rhodium and ruthenium chlorides as catalysts at 300° and 900–1000 atm gave very small yields of **2**, but iron and nickel carbonyls gave none.

Experimental Section

The reactions, details of which are given in Table I, were carried out in 400-ml stainless steel shaker tubes for 9–16 hr. The products were isolated and purified by conventional methods.

In a typical example, o-cresol (200 ml) and dicobalt octacarbonyl (3 g) were shaken in a 400-ml stainless steel tube with carbon monoxide at 300° and 1,000 atm for 9.5 hr during which the pressure drop was 95 atm. The product was filtered and distilled under reduced pressure to give o-cresol (178 ml); a fraction with bp 72–80° (1 mm), 4.1 g, $n^{25}D$ 1.5522; and a fraction with bp 110–140° (0.1 mm), 1.5 g, $n^{25}D$ 1.5697. The middle fraction was refractionated to give **2** at 53–55° (0.08 mm); the high-boiling fraction partly crystallized to give di-o-tolyl ether, mp 92° after recrystallization from petroleum ether.

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.14; H, 6.74.

In addition to the evidence given in Table I for the structure of **2**, further proof of structure was obtained by conversion of **2** into three solid derivatives whose melting points agreed with those reported in the literature. Saponification of **2** with dilute alkali gave o-hydroxyphenylacetic acid; reactions of **2** with ammonium hydroxide and hydrazine hydrate gave o-hydroxyphenylacetamide and o-hydroxyphenylacethydrazide.

Registry No.—**2**, 553-86-6; carbon monoxide, 630-08-0; 7-methyl-2(3H)-benzofuranone, 4385-36-8; 5-methyl-2(3H)-benzofuranone, 21823-22-3; di-o-tolyl ether, 4731-34-4; o-cresol, 95-48-7; 2,6-dimethylphenol, 576-26-1; 2,4-dimethylphenol, 105-67-9; o-hydroxybenzyl alcohol, 90-01-7.

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[2] K. Hultzch, *Chem. Ber.*, **74**, 898 (1941).

[3] P. D. Gardner, H. Sarrafizadeh R., and R. L. Brandon, *J. Amer. Chem. Soc.*, **81**, 5515 (1959); S. B. Cavitt, H. Sarrafizadeh R., and P. D. Gardner, *J. Org. Chem.*, **27**, 1211 (1962).

Cyclization of Diphenyl Sulfone-2-carboxylic Acids to Thiaxanthone 5,5-Dioxides

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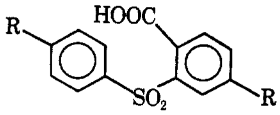
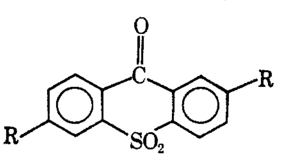
Received March 19, 1969

Cyclization of o-carboxydiphenyl sulfones (**1**), including derivatives with electron-withdrawing groups such as a *m*-nitro group, occurs readily in concentrated sulfuric acid or thionyl chloride.[3–5] However, o-car-



1, R = H
3, R = COOH



2, R = H
4, R = COOH

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[2] Taken in part from the graduate research by P. Gauvin in the Department of Chemistry, Boston College.

[3] W. S. Weedon and H. W. Doughty, *Amer. Chem. J.*, **33**, 396 (1905).

[4] D. A. Shirley, E. A. Lehto, C. W. Holley, and H. A. Smith, *J. Org. Chem.*, **22**, 1073 (1957).

[5] C. V. T. Campbell, D. A. Ferguson, and J. D. Loudon, *J. Chem. Soc.*, **111**, 747 (1941).

boxy sulfones containing *para*-deactivating groups are reported not to undergo ring closure.[6]

We have now found that diphenyl sulfone-2,4′,5-tricarboxylic acid (**3**), although inert to cyclization with sulfuric acid at 160 or 200° as expected,[6] is smoothly converted into thiaxanthone 5,5-dioxide-2,7-dicarboxylic acid (**4**) on heating in polyphosphoric acid. The yield of **4** in the PPA cyclization increased with increasing temperature. Reaction for 0.5 hr at 250, 275, and 290° gave **4** in yields of 10, 40, and 85%, respectively. It was then found that reaction of **3** in concentrated H_2SO_4 at 270° gave **4** in 85% yield. An acid medium was essential; heating **3** in Dowtherm at 260° or in a melt at 300° produced no thiaxanthone.

For qualitative comparison, diphenyl sulfone-2-carboxylic acid[7] and 4′-methyldiphenyl sulfone-2-carboxylic acid[8] were readily cyclized, as expected, by heating in PPA for 0.5 hr at 210°. The known products[9] of these sulfones, thiaxanthone 5,5-dioxide and 2-methylthiaxanthone 5,5-dioxide, respectively, were obtained in 97% yield.

Experimental Section[10]

2,4′,5-Trimethyldiphenyl Sulfone.—The Friedel-Crafts procedure (80°, 4 hr) starting with 100 g (0.526 mol) of *p*-toluenesulfonyl chloride, 150 g (1.41 mol) of *p*-xylene, and 133.3 g (1 mol) of aluminum chloride gave 203 g (78%) of the title compound after crystallization of the crude reaction product from aqueous methanol, mp 106–107°, lit.[11] mp 109°.

Diphenyl Sulfone-2,4′,5-tricarboxylic Acid (3).—Following the reported procedure for the oxidation of 2,5-dimethyldiphenyl sulfone,[12] aqueous nitric acid (580 ml, 35%) oxidation of 2,4′,5-trimethyldiphenyl sulfone (198 g) in a stainless steel pressure vessel afforded crude **3**. Purification of this product was achieved in 48% yield by crystallization from acetic acid, mp 336–339° dec.

Anal. Calcd for $C_{15}H_{10}O_8S$: C, 51.40; H, 2.87; S, 9.15; neut equiv, 116.8. Found: C, 51.10; H, 3.30; S, 9.30; neut equiv, 117.8.

Treatment of **3** with ethereal diazomethane gave 2,4′,5-tricarbomethoxydiphenyl sulfone (88%), mp 139.6–140.5°, from aqueous methanol.

Anal. Calcd for $C_{18}H_{16}O_8S$: C, 55.10; H, 4.11; sapon equiv, 130.8. Found: C, 55.10; H, 4.20; sapon equiv, 129.0.

Cyclization of 3 into Thiaxanthone 5,5-Dioxide-2,7-dicarboxylic Acid (4).—In a typical reaction, 10.0 g (0.0286 mol) of **3** was added to 150 ml of polyphosphoric acid (Victor Chemical Co.). The stirred reactants were heated in a dry atmosphere at 290° for 0.5 hr, and the cooled reaction mixture was poured into 2 l. of distilled water and allowed to digest overnight. The solid was collected by suction filtration, washed thoroughly with cold water, and extracted five times with 150-ml portions of hot methanol. The light tan solid residue was dried at 110° (2 hr) to give 8.10 g (85%) of pure **4**, mp 426–429° dec.

Anal. Calcd for $C_{15}H_8O_7S$: C, 54.22; H, 2.42; S, 9.64; neut equiv, 166.1. Found: C, 53.90; H, 2.61; S, 9.70; neut equiv, 166.1.

Dimethyl and Didecyl Esters of 4.—Normal esterification of **4** could not be achieved due to its extreme insolubility. However, treatment of **4** with ethereal diazomethane gave the diester, dimethyl thiaxanthone 5,5-dioxide-2,7-dicarboxylate, mp 200–201°, from methanol. In addition, reaction of **4** with thionyl chloride followed by treatment with excess methanol afforded the dimethyl ester.

Anal. Calcd for $C_{17}H_{12}O_7S$: C, 56.66; H, 3.36. Found: C, 56.80; H, 3.62.

Similar reaction of **4** with thionyl chloride followed by treatment with excess *n*-decanol gave the corresponding didecyl ester mp 80–81°, from aqueous methanol.

Anal. Calcd for $C_{35}H_{48}O_7S$: C, 68.79; H, 7.90. Found: C, 68.90; H, 8.20.

Using conventional methods,[13] attempts to prepare 2,4-DNP derivatives of **4**, and its two esters, were not successful. Closely related systems, *e.g.* xanthone,[14] also fail to give a 2,4-DNP derivative.

Dimethylformamide (DMF) Adduct of 4.—When **4** was dissolved in boiling DMF, the cooled solution afforded a yellow solid adduct with composition **4·2DMF**. The theoretical amount of DMF was lost when this adduct was heated at 170°, and pure white **4** was recovered.

Anal. Calcd for $C_{21}H_{22}N_2O_9S$: C, 52.71; H, 4.64; neut equiv, 239.2. Found: C, 53.23; H, 4.88; neut equiv, 239.0.

Registry No.—**3**, 21615-52-1; trimethyl ester of **3**, 21615-53-2; **4**, 21615-54-3; dimethyl ester of **4**, 21615-55-4; didecyl ester of **4**, 21615-56-5; DMF adduct of **4**, 21615-57-6.

Acknowledgment.—We wish to thank Mr. Rudolph Goetz for the cyclization results found for diphenyl sulfone-2-carboxylic acid and for 4′-methyldiphenyl sulfone-2-carboxylic acid.

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The Structures of the Photodimers of 9-Nitroanthracene, 9-Aminoanthracene, and 9-Anthryl Isocyanate[1]

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Received May 5, 1969

The photodimers of 9-substituted anthracenes have posed a vexing problem in structure. Chemical methods have proved quite satisfactory for interrelating dimers[2] but have been less useful for distinguishing between the head-to-head and head-to-tail orientations. Among the physical methods which have been employed in the study of these structures, the use of dipole moments has been the most successful in distinguishing head-to-head (2) from head-to-tail (1) structures.[3–5] Our interest in the photochemistry of 9-nitroanthracene[6] and sodium 9-anthroate[7] prompted us to undertake a study of the structure of the photodimer of 9-nitroanthracene.[8]

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