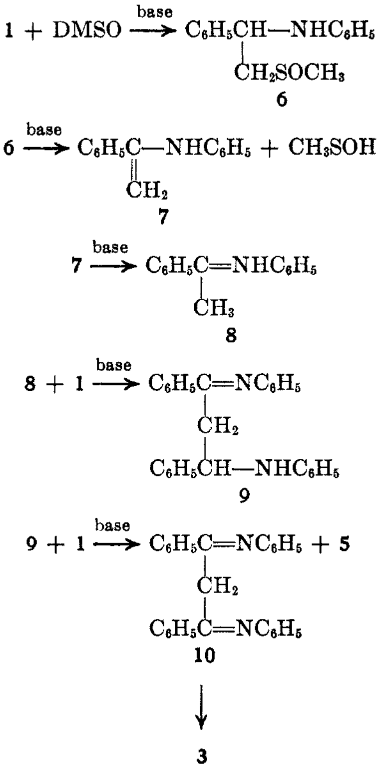
TABLE I

BASE-CATALYZED REACTIONS OF BENZALDEHYDE ANIL (1)

Run	1, mmol	DMSO$_2$, mmol	Azobenzene, mmol	Acetophenone anil, mmol	Potassium *t*-butoxide, mmol	DMF, ml	Reaction time, min	Yield of 3, %
1	10	10			20	15	15	27
2	20	10			30	25	15	34
3	10	5			20	15	10	34
4	10	5	8		20	15	30	60
5	10	10	5		20	15	10	59
6	20			5	20	15	10	74
7	20			5	30	25	20	74
8	10			5	10	15	15	64

SCHEME I



$$1 + \mathrm{DMSO} \xrightarrow{\text{base}} \underset{\mathbf{6}}{\mathrm{C_6H_5\underset{\displaystyle CH_2SOCH_3}{\underset{|}{C}}H{-}NHC_6H_5}}$$

$$6 \xrightarrow{\text{base}} \underset{\mathbf{7}}{\mathrm{C_6H_5\underset{\displaystyle CH_2}{\underset{\|}{C}}{-}NHC_6H_5}} + \mathrm{CH_3SOH}$$

$$7 \xrightarrow{\text{base}} \underset{\mathbf{8}}{\mathrm{C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NHC_6H_5}}$$

$$8 + 1 \xrightarrow{\text{base}} \underset{\mathbf{9}}{\mathrm{C_6H_5\underset{\displaystyle C_6H_5\underset{|}{C}H{-}NHC_6H_5}{\underset{|}{\underset{\displaystyle CH_2}{\underset{|}{C}}}}{=}NC_6H_5}}$$

$$9 + 1 \xrightarrow{\text{base}} \underset{\mathbf{10}}{\mathrm{C_6H_5\underset{\displaystyle C_6H_5\underset{|}{C}{=}NC_6H_5}{\underset{|}{\underset{\displaystyle CH_2}{\underset{|}{C}}}}{=}NC_6H_5}} + 5$$

$$\mathbf{10} \longrightarrow \mathbf{3}$$

Experimental Section

All base-catalyzed condensation reactions summarized in Table I were carried out under nitrogen agitation in freshly distilled dry DMF. Benzaldehyde anil was prepared from benzaldehyde and aniline. Potassium *t*-butoxide was purchased from MSA Research Corp. Acetophenone anil was prepared from acetophenone dimethylacetal and aniline.[9] Dimethyl sulfone was commercial grade material. N-Phenylbenzylamine was prepared from benzyl chloride and aniline.[10] The nmr spectrum of 3 was recorded on a 100-Mc Varian spectrometer, using deuteriochloroform as solvent. The uv spectra were obtained with a Cary recording spectrophotometer, Model 14.

The experiments described below are standard procedures for the experiments listed in Table I.

Base-Catalyzed Reaction of Benzaldehyde Anil with Dimethyl Sulfone.—Potassium *t*-butoxide (2.24 g, 20 mmol) was added to a solution of benzaldehyde anil (1.81 g, 10 mmol) and DMSO$_2$ (470 mg, 5 mmol) in DMF (15 ml) agitated by a stream of nitrogen. After 15 min, the deep red reaction mixture was diluted with methanol (50 ml) and a few milliliters of water to give a yellow crystalline precipitate. It was removed by filtration, washed with methanol, and dried to give 640 mg (34%) of **3**: mp 213° (lit.[1] mp 213–214°) (recrystallization from a chloroform–methanol mixture did not raise the melting point); nmr spectrum (in δ), 5.4 (1, singlet), 6.6–7.6 (20, multiplet), 13.1 (1, broad singlet, exchangeable by D$_2$O).

Anal. Calcd for $C_{27}H_{22}N_2$: C, 86.60; H, 5.92; N, 7.48; mol wt, 374.46. Found: C, 86.60; H, 6.00; N, 7.40; *m/e*, 374.

Base-Catalyzed Reaction of Acetophenone Anil with Benzaldehyde Anil.—Potassium *t*-butoxide (2.24 g, 20 mmol) was added to a solution of benzaldehyde anil (3.62 g, 20 mmol) and acetophenone anil (0.975 g, 5 mmol) in DMF (15 ml) agitated by a stream of nitrogen. After 10 min, the dark red reaction mixture was diluted with methanol (50 ml) and a few milliliters of water to give 1.38 g (74%) of **3**, mp 213°. The mixture melting point with the material obtained in the experiment described above was not depressed.

Acid-Catalyzed Hydrolysis of 3.—A solution of **3** (1 g) in methanol (75 ml) containing concentrated hydrochloric acid (11 ml) was refluxed for 31 hr. Vpc analysis indicated by that time complete consumption of **3**. Partial evaporation of solvent gave 510 mg (85%) of dibenzoylmethane, mp 78–79°. The mixture melting point with authentic dibenzoylmethane was not depressed. The ir spectrum was identical with that of authentic material.

Registry No.—1, 538-51-2; 3, 19919-86-9; DMSO, 67-68-5; DMSO$_2$, 67-71-0.

---

[9] E. Knövenagel, *Ber.*, **55**, 1929 (1922).

[10] "Organic Syntheses, Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1932, p 97.

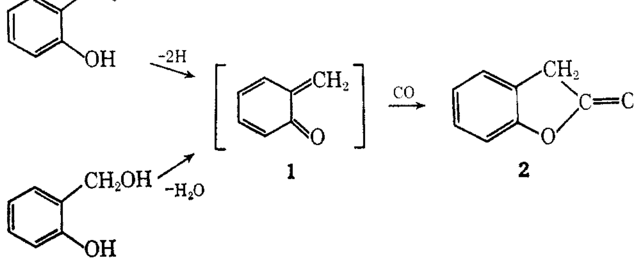
Reactions of Carbon Monoxide with *o*-Methyl- and *o*-Hydroxymethylphenols

HOWARD E. HOLMQUIST

Central Research Department,
E. I. du Pont de Nemours and Company,
Experimental Station, Wilmington, Delaware 19898

Received May 19, 1969

A previous publication from this laboratory[1] reported that the reaction of carbon monoxide with *o*-toluenethiol in the presence of dicobalt octacarbonyl at high temperature and pressure gave S-*o*-tolyl thio-*o*-toluate. The analogous reaction with *o*-cresol would give *o*-tolyl *o*-toluate. We have now found, however, that under the same conditions, *o*-cresol is converted into 2(3H)-benzofuranone (**2**). Similarly, 2,4- and 2,6-dimethylphenol are converted into 5- and 7-methyl-2(3H)-benzofuranone.



---

[1] H. E. Holmquist and J. E. Carnahan, *J. Org. Chem.*, **25**, 2240 (1960).

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.

---

[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).

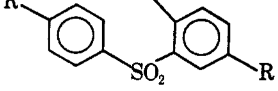
Cyclization of Diphenyl Sulfone-2-carboxylic Acids to Thiaxanthone 5,5-Dioxides

O. FRANCIS BENNETT[1] AND PAUL GAUVIN[2]

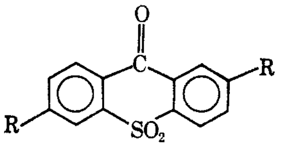
Department of Chemistry, Boston College, Chestnut Hill, Massachusetts and Eastern Laboratories, E. I. du Pont de Nemours and Company, Inc., Gibbstown, New Jersey

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

---

[1] To whom correspondence should be addressed: Department of Chemistry, Boston College.

[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).