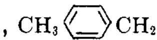
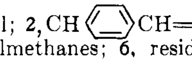
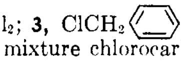
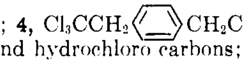
TABLE I

PRODUCTS OBTAINED *via* COAXIAL PYROLYSIS OF *p*-XYLENE AND CHLOROFORM AS A FUNCTION OF BLEND POINT

Pyrolysis conditions			Feed stock			Estimated amount *p*-Methylbenzyl				Products[a] isolated, g.				
T, °C.	*t*, sec.	P, mm.	*p*-Xylene, g.	Chloroform g.	Blend point[b]	produced,[c] g.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
1000	0.01	6.8	437	1251	14.5	44	18	0	0.5	1	15	17	—	—	[d]
1005	.009	4.2	525	1394	9.5	58	17	0	0	1.5	23	15	0.5	5	—
1000	.005	2.5	365	810	4.5	22	9.4	0	0	8.5	10	16	2	—	[e]
1000	.005	5.0	1491	2074	4.5	89	—	—	—	28	—	—	—	—	—
1000	.006	3.3	621	1266	4.5	43	—	—	—	15	—	—	—	—	—
1005	.01	4.8	356	836	2.5	41	19	0	0	5	21	41	1	—	—
1005	.007	4.7	1287	1847	1.5	109	—	—	—	1	—	—	—	—	—
1005	.01	3.7	401	1047	−0.5	46	18	19	0	0	18	36	—	—	—
1010	.006	3.3	453	1135	−10	36[f]	20	26	0	0	60	57	—	—	—

[a] **1,** ; **2,** ; **3,** ; **4,** ; **5,** mixture of 1,2-di-*p*-tolylethane and methylated diphenylmethanes; **6,** residue mixture chlorocarbons and hydrochloro carbons; **7,** C_2Cl_6; **8,** C_6Cl_6; and **9** miscellaneous products isolated and only partially characterized. [b] Measured in inches away from the end of the pyrolysis zone.[3] [c] Estimation based on calculated conversion of *p*-xylene to *p*-methylbenzyl radicals as a function of pyrolysis conditions.[6] [d] 0.5 g., m.p. 86–88°, b.p. = 145° at 3 mm., % C = 23.9. % Cl = 75.9; % H = 0.46; Infrared spectrum indicated that product might be a highly conjugated or aromatic compound. [e] 0.6 g., m.p. 111–113°, % C = 51.5; % H = 3.7; % Cl = 44.6; mol. wt. = 634. Infrared spectrum indicates the presence of *p*-xylene and CCl_3 groups. [f] Weight of products obtained far exceed that anticipated on the basis of earlier work relating conversion as a function of temperature and residence time (see *b* above). Indicates considerable interaction in the pyrolysis zone.

liquor by distillation at atmospheric pressure. The residue (20 g.), after separation of *p*-xylene (b.p. 138°), was a mixture of the usual low molecular weight products of *p*-xylene pyrolysis.[9] Elementary analysis indicated that this residue contained 0.3% chlorine.

β,β,β′,β′-Tetrachloro-*p*-divinylbenzene.—α,α′-Bistrichloromethyl-*p*-xylene (0.716 g.; 0.0021 mole) was dissolved in methanol (25 cc.). Sodium methoxide (1.5 g.) was added and the mixture was warmed on a steam bath for 0.5 hr. The reaction mixture was diluted with cold water (100 cc.) and the insoluble product was removed by filtration. The amount of chloride ion present in the aqueous mother liquor was determined by gravimetric analysis. The results showed that 0.0039 equivalent of chlorine (0.139 g.) was produced. Thus, about two moles of hydrogen chloride were eliminated per mole of starting material.

The product was recrystallized from a methanol water solution to yield the compound in the form of pearl-like platelets (m.p. 74–75°). The infrared spectrum (strong bands at 11.02, 11.44, 12.15, and 12.68 μ) is consistent with the anticipated structure of β,β,β′,β′-tetrachloro-*p*-divinylbenzene. The elemental analysis is consistent with the empirical formula for this compound.

Anal. Calcd. for $C_{10}H_6Cl_4$: C, 44.84; H, 2.42; Cl, 52.96. Found: C, 45.2; H, 2.02; Cl, 53.0.

Several years after completion of this work, the assigned structure of this compound was also verified in the laboratories of the Minnesota Mining and Manufacturing Company by n.m.r. analysis (τ values: 2.46 for aromatic C–H and 3.18 for vinyl C–H[8]).

A sample of β,β,β′,β′-tetrachloro-*p*-divinylbenzene (1.5 g.) was oxidized at reflux temperature in 100 cc. of acetone saturated with potassium permanganate. The solvent was removed by evaporation. The manganese dioxide was dissolved in aqueous hydrochloric acid and the residue was leached with hot acetone. The acid residue (0.25 g.) was fused with phosphorus pentachloride (1 g.) and the melt was poured into methanol (5 cc.). The ester was precipitated by addition to excess water and then recrystallized from a water–methanol solution to yield dimethyl terephthalate in the form of long white needles (m.p. 138.5–139.0°); no depression with an authentic sample.

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(9) L. A. Errede and J. P. Cassidy, *J. Am. Chem. Soc.*, **82**, 3653 (1960).

Oxidation of Phenols with Cupric Salts

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Received October 3, 1962

Cupric salts of carboxylic acids oxidize phenols to produce products coupled at vacant *ortho* and *para* positions in a manner characteristic of single electron oxidizing agents. Disubstituted phenols (*ortho, para*) eliminate the possibility of direct polymer formation and are especially useful for the preparation of dimers.

The susceptibility of phenols to oxidation is well known. This characteristic has been a major obstacle in processes for the preparation of phenol itself by the direct oxidation of benzene with air. On the other hand, a number of more highly substituted phenols are of industrial importance as antioxidants because of their sensitivity to oxidizing agents and ability to terminate chain reactions. A considerable number of papers have appeared dealing with details of the mechanism of this reaction.[1]

A large number of oxidizing agents have been used with various phenols.[1b] The first step appears to involve the extraction of the phenolic hydrogen atom. The resulting phenoxy radical undergoes a complex series of reactions, the nature of which depends on the phenol itself, the oxidizing agent, and various conditions of reaction. Usually a mixture of products are formed with prominent yields of intractable resins.

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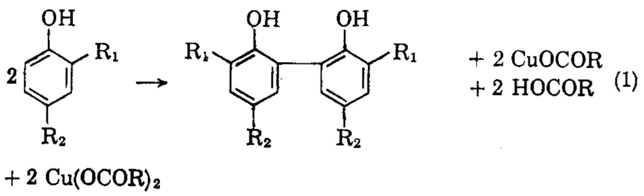
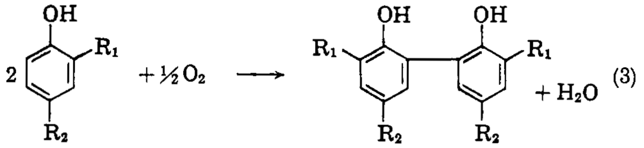
(1) For leading references see (a) V. K. Ingold, *Chem. Rev.*, **61**, 563 (1961); (b) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).

Identified products of the reaction may be broadly classified as phenolic dimers, trimers, and polymers or compounds resulting from a combination of the phenol and the oxidizing agent. The former are important when one electron oxidizing reagents are used.[2]

Cupric salts of carboxylic acids have been found to oxidize phenols in a manner characteristic of the single electron oxidizing agents to give products coupled at the vacant *ortho* or *para* positions. Disubstituted starting phenols eliminate the possibility of direct polymer formation and are especially useful for the preparation of dimers, equation 1. More highly oxidized products such as quinones generally are not produced.



$$2\,CuOCOR + 2\,HOCOR + \tfrac{1}{2}O_2 \longrightarrow 2\,Cu(OCOR)_2 + H_2O \qquad (2)$$

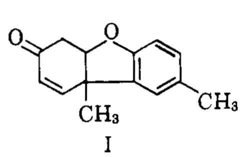


This method involves the combination of the cupric salt and molten phenol at a temperature of 120–225°. The phenol served as the solvent and was always present in excess. The temperature was usually rapidly increased after the combination of reactants. A dark blue-green solution was first formed and the characteristic copper salt color rapidly faded to give a yellow-amber solution. The reaction was complete in approximately five minutes. When the solution was allowed to cool (in a nitrogen atmosphere), the cuprous salt would frequently precipitate as brilliant white crystals. Virtually quantitative yields of the cuprous salt were usually produced.

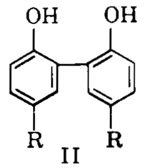
When air was bubbled through the solution, the cupric salt was regenerated, equation 2. This could be done at relatively low temperatures ($<140°$) where the cupric salt would accumulate or at the temperature of reaction itself. The net result under the latter conditions permitted the use of catalytic amounts of cupric salt, with air serving as the principal oxidizing agent, equation 3. In general, the use of oxygen at relatively high temperatures did not lead to the production of significant side reaction products when the substituents were large alkyl groups. However, the xylenols and cresols produced a somewhat larger amount of resinous material with oxygen, and phenol itself gave polymeric products exclusively. The cupric salt was considerably more specific than oxygen in its effect.

When phenol was oxidized with a cupric salt, in the absence of oxygen, a light amber oil was produced. Approximately one third of this product could be readily distilled and consisted primarily ($> 90\%$) of the *ortho–ortho* coupled dimer II (R = H). Small amounts of other products were present including 1–3% each of the *ortho–para* and *para–para* coupled dimers. The nonvolatile portion had an infrared spectrum very similar to that of phenol and was soluble in dilute aqueous base. The molecular weight could be varied by changing the relative amount of copper salt and phenol initially used. This material was presumed to be higher phenol polymers linked by carbon-carbon bonds at the *ortho* and *para* position of the ring.

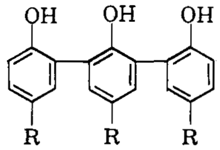
A very viscous crude oil was obtained from *p*-cresol. A small amount of crystalline neutral material was separated by extraction of the phenols with base, and was identified as Pummerer's ketone (I).[3] The base soluble phenolic oil, after acidification, was dissolved in hot isoöctane. On cooling, a viscous amber oil first appeared (~40%) followed by the expected crystalline dimer (II) and trimer (III) (~40%) (R = CH_3). The balance of the material was a pale yellow resinous glass. The structures of the phenol and cresol coupled products were verified by comparison of the infrared spectra or physical properties with authentic samples.



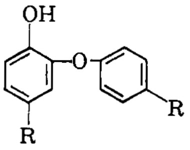
I



II



III



IV

The very small amount of neutral oil isolated, from the oxidation of *p*-*t*-butylphenol, did not have an infrared absorption band characteristic of the carbonyl group. It appeared to be a mixture of products with an average molecular weight of *ca.* five hundred.

The major portion of the crude reaction product (base soluble) was an amber glass. Treatment with pentane dissolved approximately 60% of the material leaving a crystalline white solid with an elemental analysis, molecular weight and infrared spectrum corresponding to that of the expected dimer II (R = *t*-C_4H_9). However, the possibility of an oxygen bridge between rings, as shown by IV (R = *t*-C_4H_9), cannot be eliminated with these data alone. The n.m.r. spectrum of this compound has been interpreted as shown in Table I. The relative amounts and types of ring hydrogen atoms are consistent only with the proposed dimer II, and eliminate the possibility of an ether bond.

The pentane soluble fraction could not be crystallized or purified. The amber glass which remained when the solvent was removed had an analysis and molecular weight consistent with that of the trimer III (R = *t*-C_4H_9). However, conclusive evidence for this structure is not available.

The disubstituted (*ortho* or *para*) phenols were coupled at the vacant activated positions to give dimers.

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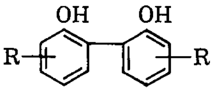
(2)(a) C. G. Haynes, A. H. Turner, and W. A. Waters, *J. Chem. Soc.*, 2823 (1945); (b) K. Bowden and C. H. Reece, *ibid.*, 2249 (1950); (c) R. G. R. Bacon and D. J. Munro, *ibid.*, 1339 (1960); (d) G. W. K. Cavill, E. R. Cole, P. T. Gilham, and D. J. McHugh, *ibid.*, 2785 (1954); (e) R. G. R. Bacon, R. Grune, and D. J. Munro, *ibid.*, 2275 (1954).

(3)(a) R. Pummerer, H. Puttfarchen, and P. Schopflochen, *Ber.*, **58**, 1808 (1925); (b) D. A. R. Barton, A. M. Deflorin, and O. E. Edwards, *J. Chem. Soc.*, 530 (1956).

TABLE I

N.M.R. SPECTRA[a]



Compound	Hydrogen							
	Hydroxyl		Aromatic			Aliphatic		
	P.p.m.	Ratio[b]	Ring position	P.p.m.	Ratio[b]	Ring position	P.p.m.	Ratio[b]
5,5′-*t*-$\mathrm{C_4H_9}$[c]	8.17	1	4·6	7.2[d]	2.1			
			3	6.1[d]	1			
3,3′-*t*-$\mathrm{C_4H_9}$-5,5′-$\mathrm{CH_3}$	5.16	1	4	7.09[e]	2.1	5-$\mathrm{CH_3}$	2.28	3.0
			6	6.81[e]		3-*t*-$\mathrm{C_4H_9}$	1.42	9.5
3,3′-*t*-$\mathrm{C_4H_9}$-5,5′,6,6′-$\mathrm{CH_3}$	4.75	1	4	7.05	1	5-$\mathrm{CH_3}$	2.24	3 0
						6-$\mathrm{CH_3}$	1 80	3 0
						3-*t*-$\mathrm{C_4H_9}$	1 35	9.6
3,3,′,5,5′-*t*-$\mathrm{C_4H_9}$	5.01	1	4	7.29[e]	2	3-*t*-$\mathrm{C_4H_9}$	1.27[f]	18.8
			6	7.02[e]		5-*t*-$\mathrm{C_4H_9}$	1.40[f]	
3,3′,5,5′-*t*-$\mathrm{C_5H_{11}}$	5.07	1	4	6.94[e]	2	3-*t*-$\mathrm{C_4H_9}$[f]	1.5–2.0[g]	3.8[g]
			6	7.18[e]		5-*t*-$\mathrm{C_4H_9}$	1.1–1.5[g]	13.5[g]
							0.5–0.9[g]	7.2[g]
3,3′,5,5′-*t*-$\mathrm{C_4H_9}$-6,6′-$\mathrm{CH_3}$	4.76	1	4	7.34	1	6-$\mathrm{CH_3}$	2.00	3.2
						t-$\mathrm{C_4H_9}$	1.42[h]	18.3
3,3′-*t*-$\mathrm{C_4H_9}$-5,5′-$\mathrm{CH_3}$-4,4′-OH[i]	4.64	1	2	7.09[j]	2	5-$\mathrm{CH_3}$	2.20	3.2
			6	7.24[j]		3-*t*-$\mathrm{C_4H_9}$	1.42	9.0

[a] Obtained with a Varian A-60 instrument utilizing $\mathrm{CDCl_3}$ as a solvent and tetramethylsilane as an internal reference. [b] Ratio of hydrogens normalized to smallest whole numbers as measured by integration of peak areas. [c] Acetone solvent. [d] Multiple peaks, midpoint of range reported. [e] Distinction not made for hydrogens at 4 and 6 positions. [f] Distinction not made for hydrogens at 3 and 5 positions. [g] Four peaks in 1.5–2.0 p.p.m. range, two large peaks in 1.1–1.5 range, 3 medium peaks in 0.5–0.9 range interpreted as methylene, methyl attached to *tert*-carbon and methyl attached to methylene carbon. [h] One single sharp peak. [i] 3,3′-Di-*t*-butyl-5,5′-dimethyl-4,4′-dihydroxydiphenyl. [j] Distinction not made between hydrogen at 2 and 6 position.

Yields were especially high with phenols containing large alkyl groups. The phenols were relatively insensitive to oxygen at the temperatures of reaction (150–180°) and catalytic amounts of cupric salt were conveniently regenerated with air, equation 2. The degree of conversion was controlled largely by the physical properties of the product. With 2,4-di-*t*-butylphenol, for example, the product was a solid at temperatures which exceeded that desired for reaction. The entire mass would solidify if conversions beyond 60–70°% were attempted. The individual compounds prepared by this reaction are listed in Table II.

The use of air for oxidizing phenols in this manner was reported previously by Hope, Pelton, and Long[4] who used alkali metal hydroxides as catalysts. The method appeared to be limited to 2,4-di-*t*-butylphenol and 2,4-di-*t*-amylphenol. The preparative value of this oxidative coupling reaction for disubstituted phenols was also recognized by Seubold, Rust, and Vaughan[5] who utilized a number of organic peroxides as oxidizing agents.

The n.m.r. spectra of a number of new dimers, prepared from phenols with one vacant *ortho* position, are shown in Table I. The types and ratios of the various hydrogen atoms are consistent with the structures proposed and eliminate the possibility of an oxygen link between rings of the type shown by compound IV.

Cupric *o*-toluate was used as the oxidizing agent most frequently because of its excellent solubility. The benzoate and acetate were also convenient reagents. The latter was not suitable for direct regeneration with air, however, because the free acetic acid distilled from the reaction mixture.

In order to determine whether oxidative coupling would occur with phenols containing alkoxy substituents, 2-*t*-butyl-4-ethoxyphenol was prepared. Compounds of this type have been reported to possess outstanding qualities as food antioxidants.[6] Although a considerable number of these compounds were listed,[6] no physical properties or specific methods of synthesis were reported. *p*-Ethoxyphenol was alkylated with isobutylene to give a mono-*t*-butyl derivative which melted at 96–97°. It was identified as 2-*t*-butyl-4-ethoxyphenol, on the basis of the value of the hydroxyl stretching frequency in the infrared region at concentrations low enough to prevent intermolecular association. It had a strong band at 3618 cm.$^{-1}$ and a weak band at 3652 cm.$^{-1}$. *p*-Ethoxyphenol had a single strong band at 3623 cm.$^{-1}$. The amount and direction of the shift and the location and appearance of a second weaker band is characteristic of an *ortho*-substituted *t*-butyl group in phenols.[7] A smaller amount of dibutylated product (m.p. = 102–103°) was isolated which had a strong band at 3617.5 cm.$^{-1}$ and a weak band at 3652 cm.$^{-1}$. The virtual identity of absorption frequencies with that of the monobutylated product could only allow this to be 2,5-di-*t*-butyl-4-ethoxyphenol.

A dimer of 2-*t*-butyl-4-ethoxyphenol was formed, which was difficult to purify. At present, it is not possible to conclusively verify the structure.

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(4) J. H. F. Hope, F. L. Pelton, and M. W. Long, Jr., U.S. Patent 2,885,444 (1959).

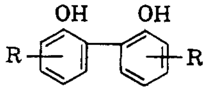
(5) F. H. Seubold, Jr., F. F. Rust, and W. E. Vaughan, U. S. Patent 2,890,282 (1959).

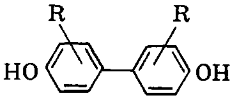
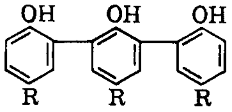
(6) (a) J. A. Chenicek and R. H. Rosenwald, U.S. Patent 2,442,457 (June 1, 1948); (b) R. H. Rosenwald, U.S. Patent 2,666,709 (January 19, 1954); (c) R. H. Rosenwald, U.S. Patent 2,679,459 (May 25, 1954); (d) J. A. Chenicek, U.S. Patent 2,690,396 (September 28, 1954); (e) R. H. Rosenwald and J. A. Chenicek, *J. Am. Oil Chemists' Soc.*, **28**, 185 (1951); *Chem. Abstr.*, **45**, 6766 (1951).

(7) K. U. Ingold and D. R. Taylor, *Can. J. Chem.*, **39**, 471 (1961).

TABLE II

PHENOL DIMERS AND TRIMERS



R	Formula	M.p., °C	T_{max}, °C	Analysis or lit. m.p.	Mol. wt. Th	Mol. wt. Found
5,5′-CH_3	$C_{14}H_{14}O_2$	152–154	190	M.p. 154°[a]		
5,5′-t-C_4H_9	$C_{20}H_{26}O_2$	207–208	190	F C 81.05, H 8.91 Th C 80.49, H 8.78	298	288
3,3′,5,5′-CH_3	$C_{16}H_{18}O_2$	133–134	175	M.p. 137–138[b] M.p. 133–134[c]	. . .	. . .
3,3′-t-C_4H_9-5,5′-CH_3	$C_{22}H_{30}O_2$	Glass	180	F C 80.84, H 8.69 Th C 80.93, H 9.26	326	312
3,3′-t-C_4H_9-5,5′,6,6′-CH_3	$C_{24}H_{34}O_2$	165–166	190	F C 81.24, H 9.41 Th C 81.31, H 9.67	355	347
3,3′,5,5′-t-C_4H_9	$C_{28}H_{42}O_2$	200–202	180	F C 81.10, H 9.97 Th C 81.90, H 10.31	411	402
3,3′,5,5′-t-C_5H_{11}	$C_{30}H_{46}O_2$	Oil[d]	195	F C 82.07, H 10.63 Th C 82.34, H 10.79	439	426
3,3′-t-C_4H_9-5,5′-OC_2H_5 (tentative)	$C_{24}H_{34}O_4$	91–95	195	F C 74.75, H 8.67 Th C 74.58, H 8.87	386	363
3,3′,5,5′-t-C_4H_9-6,6′-CH_3	$C_{30}H_{46}O_2$	246–249	220	F C 81.83, H 10.03 Th C 82.13, H 10.57	. . .	. . .
3,3′-CH_3-5,5′-t-C_4H_9	$C_{22}H_{30}O_2$	Glass	170	F C 80.77, H 9.09 Th C 80.93, H 9.26	326	338
						
2,2′,6,6′-CH_3	$C_{16}H_{18}O_2$	221–223	185	M.p. 220–221[e]	. . .	. . .
2,2′-CH_3-6,6′-t-C_4H_9	$C_{22}H_{30}O_2$	185–186	170	F C 80.85, H 9.04 Th C 80.93, H 9.26	326	317
						
CH_3	$C_{21}H_{20}O_3$	193–195	190	M.p. 197[f]	. . .	. . .
-t-C_4H_9 (tentative)	$C_{30}H_{38}O_3$	Glass	190	F C 80.73, H 9.25 Th C 80.68, H 8.58	446	446

[a] See ref. 3b. [b] See ref. 8. [c] See ref. 3d. [d] n^{22}_D 1.5250. [e] See ref. 9. [f] See ref. 2b.

Experimental

The reactor was constructed of Pyrex tubing, 1 × 15 in., with an inverted bell shaped upper section approximately 3 × 6 in. A top was connected to the reactor with a ground glass seal and was fitted with two ball joint openings for a removable thermowell and gas inlet tube, both of which extended to the bottom of the reactor. An opening near the top led to a condenser followed by a Dry Ice trap. Nitrogen or air was used for agitation. Heating was achieved electrically with resistance tape. The temperature could be increased approximately 15° per min.

The solid cupric salt was added to the molten phenol at a temperature of 120°. The slurry was rapidly heated to give a characteristic blue-green solution at 140–165°. The color faded rapidly at 165–190°, as the cupric salt was reduced to give a clear yellow or amber solution. On cooling, brilliant white crystals of the cuprous salt frequently appeared. Air or oxygen could be bubbled through the mixture at this point to increase the conversion.

The reaction mixture was cooled and treated with a two- to threefold excess of ether. The cuprous salt precipitated, and was separated by filtration. A very small amount of the copper salt was reoxidized on exposure to air, to give the ether filtrate a blue-green color.

The ether solution was extracted with 10–20 ml. of 5% aqueous hydrochloric acid to decompose and remove the copper salt. The light yellow to amber ether solution was then extracted with excess saturated bicarbonate solution to remove the free carboxylic acid. The latter could be recovered by acidification of the aqueous phase. No attempt was made to recover acid which remained in the aqueous solution saturated with ether.

With phenols containing methyl or hydrogen in the *ortho* position, an extraction was frequently made with 5% aqueous sodium hydroxide solution at this point to separate the phenolic material from any neutral compounds. The latter were isolated by evaporation of the solvent. The aqueous phase was subsequently acidified and the phenols extracted with an organic solvent such as ether or methylene chloride.

Frequently, the product could be obtained by crystallization after reducing the volume of ether solvent followed by dilution with pentane. The recovery was more efficient, however, if the ether solvent and starting phenol were removed by a low pressure distillation from a Vigreux–Claisen flask. The nonvolatile residue was then treated with various solvents to purify the products by crystallization.

***p*-Cresol.**—One hundred grams of cupric *o*-toluate was added to 120 g. of *p*-cresol at 120°. The heavy slurry was stirred with nitrogen and rapidly heated to 190° in 5 min. and immediately cooled. Sixty-one grams of cuprous *o*-toluate, 34 g. of toluic acid, 82 g. of *p*-cresol, 25 g. of high boiling product, and 1.5 g. of neutral oil were isolated. The neutral oil slowly solidified to a waxy solid and was spread on a porous plate and then recrystallized from hexane to give 1 g. of fluffy white needles, m.p. 123.5–124°, identified as Pummerer's ketone (I), (lit.,[4] m.p. 124°).

The high boiling oil was dissolved in boiling isoöctane and allowed to cool slowly. A viscous oil was deposited slowly. The liquid was decanted and allowed to cool further. After two or

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(8) E. Bamberger, *Ber.* **40**, 1926 (1907).

(9) K. Auwers and V. Markovits, *ibid.*, **38**, 234 (1905).

three transfers, the solution, near room temperature, was allowed to stand overnight. A crystalline solid appeared. Slow crystallization was essential to avoid deposition of oils. Several crops of crystals were obtained by reduction of this solvent volume and eventually dilution with hexane. Infrared scans indicated the presence of two major solid products. The first to appear (5 g., crude m.p. 125–140°) was recrystallized from carbon tetrachloride to give a white solid, melting at 193–195°, identified as the trimer (lit.,[3a] m.p. 197°). The second solid product (5 g.) was recrystallized from isoöctane to give a white granular solid, m.p. 150–152°, identified as the dimer (lit.,[3a] m.p. 154°). Approximately 8 g. of a light yellow glass remained when the remaining solvent was evaporated.

p-t-**Butylphenol.**—One hundred and fifty grams of *p-t*-butylphenol, m.p. 99–100°, and 100 g. of cupric *o*-toluate were combined and heated to 190° and worked up in a similar manner. Fifty-eight grams of cuprous *o*-toluate, 37 g. of *o*-toluic acid, 34 g. of nonvolatile product, 112 g. of starting phenol, and 3 g. of neutral compounds were isolated. The nonvolatile product was an amber glass which was crushed and treated with pentane. A cotton-like white crystalline solid remained (12 g.) which was recrystallized from isoöctane, m.p. 207–208, identified as dimer II (R = *t*-Bu). The pentane soluble portion could not be crystallized. The solvent was pumped off leaving a pale amber glass, which could not be positively identified as trimer III, (R = *t*-Bu).

2,4-Dimethylphenol.—A mixture of 150 g. of 2,4-dimethylphenol (Eastman White Label) and 75 g. of cupric benzoate were heated to 170° in 5 min. in a nitrogen atmosphere. The resulting yellow solution gave 45.2 g. of cuprous benzoate, 28.6 g. of benzoic acid, 120 g. of starting material and 29 g. of nonvolatile crude product. The latter was recrystallized from a large volume of pentane. An oily impurity was present with the dimer: first crop, 7 g., m.p. 100–115°; second crop, 11 g., m.p. 120–127°; third crop, 4 g., m.p. 132–134°; final residue 5 g. of oily solid.

2,6-Dimethylphenol.—A mixture of 100 g. of 2,6-dimethylphenol, m.p. 44–45°, and 50 g. of cupric benzoate were combined and rapidly heated to 175° in a nitrogen atmosphere. The yellow solution gave 30.7 g. of cuprous benzoate and 17 g. of benzoic acid. The ether solution was evaporated and the residue treated with pentane. A pale yellow solid, m.p. 219–223° (13.5 g.) was recovered by filtration. The yellow color could not be removed by recrystallization from various common organic solvents. This color was finally removed by treatment with hydrogen in methanol solution using a palladium on charcoal catalyst to give a white solid dimer, m.p. 221–223°.

2,4-Di-*t*-butylphenol.—A solution of 170 g. of 2,4-di-*t*-butylphenol, m.p. 48°, and 35 g. of cupric *o*-toluate was heated to 170 ± 5° for 150 min. with air bubbling through at the rate of 800 ml./min. Ninety-seven grams of crude dimer was isolated, m.p. 190–200°. The recovered starting material contained an orange impurity which was not isolated. Recrystallization from pentane gave granular white crystals of dimer, m.p. 200–202° (lit.,[5a] m.p. 193–195).

2-*t*-Butyl-4,5-dimethylphenol.—A mixture of 100 g. of 2-*t*-butyl-4,5-dimethylphenol m.p. 43–46° and 75 g. of cupric *o*-toluate were combined and rapidly heated to 190° in a nitrogen atmosphere. The lemon yellow solution gave 44.9 g. of cuprous benzoate, 28.1 g. of toluic acid, 54 g. of starting phenol, and 38.5 g. of nonvolatile crude. The latter gave a white granular solid, m.p. 165–166°, after one recrystallization from pentane.

2-*t*-Butyl-4-methylphenol.—A mixture of 100 g. of 2-*t*-butyl-4-methylphenol, m.p. 52–53° and 50 g. of cupric benzoate were heated to 180° in 5 min. The yellow solution gave 29.4 g. of cuprous benzoate, 17 g. of benzoic acid, 70 g. of recovered starting material, and 26 g. of nonvolatile product. The latter was a glass which would not crystallize and was identified as dimer.

2,4-Di-*t*-butyl-5-methylphenol.—A mixture of 45 g. of 2,4-di-*t*-butyl-5-methylphenol, m.p. 62–63°, and 50 g. of cupric *o*-toluate were combined and brought to a temperature of 220° in 25 min. in a nitrogen atmosphere. The viscous dark amber solution gave 28.5 g. of cuprous *o*-toluate and 19 g. of toluic acid. The ether solution was reduced in volume and cooled to give 19 g. of dimer, m.p. 244–248°. Recrystallization from hexane increased the melting point to 246–249°.

2-*t*-Butyl-6-methylphenol.—A solution of 132 g. of 2-*t*-butyl-6-methylphenol (obtained from Ethyl Corporation) and 50 g. of cupric *o*-toluate was heated to 160° and air bubbled through the liquid for 90 min. at a rate of 800 ml./min. Nitrogen was turned on and the temperature raised to 180° and immediately cooled. The dark red-amber solution gave 29.4 g. of cuprous *o*-toluate, 19 g. of toluic acid, 64 g. of starting phenol, and 67 g. of nonvolatile product. Recrystallization of the latter from hexane gave coarse tan crystals, m.p. 185–186°. The trace of color could be removed by treatment with zinc in acetic acid.

2-*t*-Butyl-4-ethoxyphenol.—One hundred grams of *p*-ethoxyphenol, m.p. 66°, was dissolved in 300 ml. of benzene at 30°. After the addition of 6 g. of concentrated sulfuric acid catalyst, 40.5 g. of isobutylene was bubbled into the liquid solution over a 2.5-hr. period, keeping the temperature in the 25–35° range. The solution was extracted with water and then with 750 ml. of 5% sodium hydroxide solution in many portions. Acidifications of the latter gave 25 g. of starting material. The benzene solution was dried and the solvent removed to give 92 g. of viscous amber oil which was vacuum distilled from a Vigreux-Claisen flask. The first fraction, a bright orange oil, b.p. 113–118°/2 mm., 23.6 g., was recrystallized from hexane to give white needles, m.p. 96–97°, identified as 2-*t*-butyl-4-ethoxyphenol.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.31; H, 8.95.

The second fraction, b.p. 118–122°/2 mm., 42 g., could not be purified by recrystallization from hexane. The third fraction, a pale yellow oil, b.p. 122°/2 mm., 16 g., and flask residue, 6.2 g., were recrystallized from hexane to give glistening white needles, m.p. 102–103°, identified as 2,5-di-*t*-butyl-4-ethoxyphenol.

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.44; H, 10.22.

The second fraction and residues from the hexane recrystallizations were then dissolved in hot moist methanol. A much better separation of the mono- and dibutylated product was possible with this solvent.

A mixture of 24.5 g. of 2-*t*-butyl-4-ethoxyphenol, m.p. 93–96°, and 21 g. of cupric *o*-toluate was heated to 195° in a period of 5 min. The dark yellow-amber solution gave 13.1 g. of cuprous *o*-toluate, 8 g. of *o*-toluic acid, 13.5 g. of starting phenol, and 10 g. of nonvolatile, heavy viscous red-brown oil. Recrystallization from hexane and pentane gave a white, granular solid, m.p. 91–95°.

Acknowledgment.—The author is indebted to Dr. A. W. Baker for assistance with the interpretation of the infrared and n.m.r. spectra and to Mrs. Veda M. Brink for assistance with the experimental work.