and 4.5 g. (0.05 mole) of 70% nitric acid was added. The reaction mixture was heated to 50° and then allowed to stand overnight. Dilution with water gave 10 g. of Va, m.p. 83–84°, from which 7.5 g., m.p. 86–87°, was obtained by recrystallization from aqueous methanol.

2-Chloro-3-methyl-4-amino-6-*t*-butylphenol (VIa) from Va.—An acetic acid solution of 10 g. of Va was treated with small portions of zinc dust until colorless. After removal of excess zinc, the reaction mixture was made alkaline with ammonia containing a small amount of sodium sulfite to give 8.6 g. of VIa, m.p. 96–100°. Recrystallization from toluene–petroleum ether gave 6.0 g., m.p. 107–108°. Vb also was reduced using this procedure.

2-Bromo-3-methyl-4-amino-6-*t*-butylphenol (VIb) from IVb.—Four grams of cyclohexadieneone IVb was dissolved in 100 ml. of acetic acid plus 20 ml. of concentrated HCl. During cooling to prevent the temperature from going above 30°, small portions of zinc dust were added until the solution was colorless. After removal of excess zinc, the reaction solution was made alkaline with excess ammonia to give, after one petroleum ether recrystallization, 2.9 g., m.p. 99–100°. After recrystallization from petroleum ether, the melting point was 99.5–100°.

2,4-Dinitro-3-methyl-6-*t*-butylphenol (Vc). A. From 3-Methyl-6-*t*-butylphenol.—Below 50°, a solution of 32.8 g. (0.2 mole) of 3-methyl-6-*t*-butylphenol in 100 ml. of benzene was treated with 40.0 g. (0.45 mole) of 70% nitric acid diluted with 50 ml. of water. After 3 hr., the benzene layer was separated, washed and treated with a solution of 12 g. of sodium hydroxide in 100 ml. of water. Salt was added to assist the precipitation of the sodium salt of Vc which was washed with a saturated salt solution and petroleum ether. After recrystallization from salt water, acidification of an aqueous solution of the sodium salt gave Vc, which after recrystallization from aqueous acetic acid weighed 20.0 g., after recrystallization from petroleum ether, m.p. 99–100°; mixed m.p. with Vc from nitration of 3-methyl-4,6-di-*t*-butylphenol or Vc from decomposition of IVc showed no depression.

B. From Nitration of 3-Methyl-4,6-di-*t*-butylphenol.—Below 40°, 650 g. (4.2 moles) of 41% nitric acid was added to a solution of 440 g. (2.0 moles) of 3-methyl-4,6-di-*t*-butylphenol in an equal weight of benzene. After washing with water, the addition of petroleum ether to the benzene solution precipitated 275 g. of Vc, m.p. 95°. Recrystallization from hexane gave 152 g., m.p. 98–99°.

3-Methyl-4-nitro-6-*t*-butylphenol.—The procedure of Tchitchibabine[11] was used to prepare 3-methyl-6-*t*-butylphenyl acetate. Refluxing 180 g. of redistilled 3-methyl-6-*t*-butylphenol and 150 g. of acetic anhydride for 18 hr. followed by distillation produced 219 g., b.p. 139° (17 mm.).

To 60.0 ml. of acetic anhydride and a crystal of sodium nitrite held at 0 to −8°, 40 g. of fuming nitric acid (90%) and a solution of 60 g. of 3-methyl-6-*t*-butylphenyl acetate in 30 g. of acetic anhydride were added simultaneously over an hour period. The resulting reaction mixture was gradually heated to 12°, water was added, and the product was extracted with ether. The ether solution was extracted three times with 5% sodium hydroxide and then the ether was evaporated to give crude 3-methyl-4-nitro-6-*t*-butylphenyl acetate. This was refluxed 0.5 hr. with 80 ml. of 5% sodium hydroxide. The alkaline solution was treated with decolorizing carbon, and acidification precipitated the desired product, which was recrystallized from carbon tetrachloride; 24.2 g., m.p. 164–165°. For this compound Tchitchibabine[11] gives m.p. 165°.

2-Chloro-3-methyl-4-nitro-6-*t*-butylphenol (Va).—A solution of 0.5 g. of chlorine and 0.8 g. of 3-methyl-4-nitro-6-*t*-butylphenol in 220 ml. of carbon tetrachloride was allowed to stand overnight. Removal of the solvent gave crystals, m.p. 86–87°; recrystallized from aqueous methanol, m.p. 87.5–88.5; mixed m.p. with Va from decomposition of IVa, showed no depression.

2-Bromo-3-methyl-4-nitro-6-*t*-butylphenol (Vb).—A solution of 4.2 g. of 3-methyl-4-nitro-6-*t*-butylphenol and 1.6 g. of bromine in 520 ml. of carbon tetrachloride was allowed to stand overnight. Removal of solvent and recrystallization from methanol–water gave 4.1 g., m.p. 102–102.5°; mixed m.p. with Vb from decomposition of IVb was 102–102.5°.

2-Chloro-3,6-dimethyl-4-nitrophenol (IX).—A solution of 61.0 g. (0.5 mole) of 2,5-dimethylphenol in 300 ml. of benzene was treated with a solution of 50 g. of 70% nitric acid in an equal volume of water at 0–5°. The benzene layer was washed with water and with aqueous sodium acetate. After removal of solvent, the residue was steam distilled. Solution in aqueous acetic acid removed a resinous material and after solvent removal, the residue was taken up in alkali. Acidification of this solution gave a light yellow solid which was recrystallized from toluene–petroleum ether; 10 g., m.p. 117–119°. Auwers[14] gives a melting point of 121–123° for 2,5-dimethyl-4-nitrophenol.

A reaction mixture consisting of 3.3 g. of 2,5-dimethyl-4-nitrophenol, 3.2 g. of sulfuryl chloride and 400 ml. of carbon tetrachloride was allowed to stand overnight and then refluxed 2 hours. Cooling and addition of a small amount of petroleum ether precipitated impure starting material. Removal of the solvent was followed by recrystallization from toluene–petroleum ether, m.p. 118–119°. Mixed m.p. of IX with the product from 2-chloro-3,6-dimethyl-4-*t*-butylphenol, formed using the nitration procedure employed for IVa, was 118–119°.

Infrared Measurements.—The infrared bands were measured with an automatic recording spectrometer with a large NaCl prism, designed and constructed in this Laboratory. All compounds were measured as concentrated solutions in CCl_4, except IVc, which was measured in dioxane because of its insolubility in CCl_4. The infrared curves were corrected for the absorption due to the solvent. The sample thickness was 0.002 inch, except for IVc and Vc for which the thickness was 0.005 inch.

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Reactions of 3,4,6-Trialkylphenols. III. Oxidation Studies

BY HARRY E. ALBERT

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The oxidation of phenols has received considerable attention in the past investigations of the chemistry of this class of organic compounds. The large volume of literature on the formation of quinones by the oxidation of various phenolic compounds has been summarized recently.[1] This summary includes references to dimeric and polymeric compounds which have sometimes resulted from the oxidation of mononuclear phenolic compounds. As a general rule, the by-products obtained in quinone preparations are dark, insoluble amorphous materials, which undoubtedly result from coupling and polymerization. However, a few dimeric and trimeric compounds have been isolated and characterized.

During the past decade there has been increased interest in alkylated phenols, because of the commercial importance of a number of compounds of this class. However, much of the chemistry of these interesting compounds remains to be thor-

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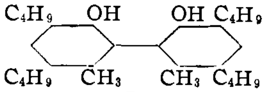
[1] R. Adams, "Organic Reactions," Vol. IV, John Miller & Sons., Inc., New York, N. Y., pp. 305–361.

oughly investigated. This paper summarizes the results of a number of oxidation experiments on highly alkylated phenols, results which would not be very well anticipated in view of the published literature on substituted phenolic compounds.

During the course of the nitration of 3-methyl-4,6-di-*t*-butylphenol, it was observed that a white crystalline compound separated from the reaction mixture as the addition of nitric acid proceeded. This compound was found to contain no nitrogen. It had a high melting point and was soluble in non-polar solvents, but relatively insoluble in polar solvents. Its lack of color and its infrared absorption spectrum concurred in eliminating the possibility that it had a quinoid structure. Carbon and hydrogen analyses, active hydrogen determination and molecular weight values were in good agreement with a hexaalkyldihydroxybiphenyl structure (I). Ultraviolet absorption curves for I and related compounds having different alkyl groups provided further substantiating evidence for the correctness of the assigned structure.



I

In view of the above results it appeared worthwhile to determine whether a better yield of the hexaalkyldihydroxybiphenyl derivative could be obtained by the use of oxidizing agents other than nitric acid. Nitrous acid or hydrogen peroxide gave small yields of this oxidation product and oxidation in acetic acid solution using 2 equivalents of potassium dichromate and sulfuric acid at 50–55°, gave a good yield of the hexaalkyldihydroxybiphenyl. The excess oxidizing agent apparently was consumed in side reactions. One of these was demonstrated to be quinone formation by the isolation of 2-methyl-5-*t*-butylquinone from the reaction mixture after the principal product had been removed. In the formation of this quinone, the *t*-butyl group in the position *para* to the phenol group is removed.

When larger than double quantities of potassium dichromate were employed, a smaller yield resulted. Smaller yields were also obtained when chromic acid was used as the oxidizing agent in amounts equal to 1.0 to 1.4 times the theoretical quantity.

It was found also that 3,4-dimethyl-6-*t*-butylphenol, 3,4-dimethyl-6-*t*-octylphenol and 3,4-dimethyl-6-(α,α-dimethylbenzyl)-phenol gave hexaalkyldihydroxybiphenyl derivatives under similar conditions. A small yield of biphenyl derivative was obtained by the oxidation of 3-methyl-4-chloro-6-*t*-butylphenol. On the other hand, 2,5-dimethyl-4-*t*-butylphenol gave 2,5-dimethylquinone and a non-crystallizable oil was obtained by the oxidation of 3,4-dimethyl-6-*s*-butylphenol.

The effect of a substituent in the 2-position was studied in the oxidation of 2-chloro-3-methyl-4,6-di-*t*-butylphenol and 2-bromo-3-methyl-4,6-di-*t*-butylphenol using potassium dichromate and sulfuric acid in acetic acid solution. In each case the corresponding 2-halo-3-methyl-6-*t*-butylquinone was isolated, but no trace of the desired hexaalkyldihydroxybiphenyl derivative was obtained.

From the results of the above experiments it appears that for hexaalkyldihydroxybiphenyl formation from 3,4,6-trialkylphenols, the alkyl group in the 6-position must be tertiary. This requirement is evidence that steric hindrance of the phenolic hydroxyl group plays an important role in directing the course of the oxidation reaction. When the 2-position of 3,4,6-trialkylphenols is substituted, the oxidation reaction is directed primarily to quinone formation, and there is no evidence that the substituent in that position is removed to permit the formation of the hexaalkyldihydroxybiphenyl derivatives. Substitution of chlorine for a methyl group in a 3,4,6-trialkylphenol meeting the above requirement still permitted dihydroxybiphenyl formation, but a reduced yield was obtained.

Experimental

3,4-Dimethyl-6-*s*-butylphenol.—Seventy-four grams of 3,4-dimethylphenol plus 5 g. of 96% sulfuric acid catalyst were heated to 100°. Butene-1 was passed in at 100–110° for four hours. The catalyst was removed by washing and the product distilled. The desired phenol was found in the fraction taken at 144–150° at 20 mm., yield 38 g.

3,4-Dimethyl-6-*tt*-octylphenol.—Three hundred and sixty-six grams (3 moles) of 3,4-dimethylphenol and 560 g. (5 moles) of diisobutylene were treated with 50 g. of stannic chloride, the reaction temperature being allowed to rise to 70° during the addition. After heating 2 hours at 65–70°, the reaction mixture was washed while hot to remove the catalyst. After cooling and adding petroleum ether, 340 g. of product melting at 90.5° was obtained. A second crop of 175 g. (m.p. 88–89°) was obtained by cooling the filtrate. The first crop after recrystallization from petroleum ether gave m.p. 91.5°.

3,4-Dimethyl-6-(α,α-dimethylbenzyl)-phenol.—A mixture of 183 g. (1.5 moles) of 3,4-dimethylphenol and 230 g. (2 moles) of α-methylstyrene was treated with 30 g. of stannic chloride. The temperature rose rapidly to 70° and heating at 65–70° was continued for 1 hour. After the catalyst was removed by washing, vacuum distillation gave 185 g. of crude product, b.p. 178–190° at 10 mm.; recrystallized from petroleum ether, yield 140 g., m.p. 63–64°, raised to 64–65° by a second recrystallization.

2-Chloro(bromo)-3-methyl-4,6-di-*t*-butylphenol.—See Part II.

Oxidation of 3,4,6-Trialkylphenols to Hexaalkyldihydroxybiphenyls. Oxidation of 3-Methyl-4,6-di-*t*-butylphenol.—One hundred and ten grams (0.5 mole) of 3-methyl-4,6-di-*t*-butylphenol (commercial grade recrystallized from petroleum ether) was dissolved in 500 ml. of acetic acid. A solution of 50 g. (0.17 mole equals 1.02 equivalents or twice the theoretical amount for biphenyl formation) of potassium dichromate in 300 ml. of water and 100 ml. of concentrated sulfuric acid was added to the above acetic acid solution at 50–55° during stirring. A solid light-colored product separated from the reaction mixture during the addition. The product was filtered and washed with methanol; yield 84.0 g., m.p. 232–235°; recrystallized from dioxane–methanol, yield 50.0 g., m.p. 239–240°.

Isolation of 2-Methyl-5-*t*-butylquinone from the Oxidation Products of 3-Methyl-4,6-di-*t*-butylphenol.—One hundred and ten grams (0.5 mole) of 3-methyl-4,6-di-*t*-butylphenol in one liter of acetic acid was treated with a solution of 50 g. (0.17 mole) of potassium dichromate in 200 ml. of water and 100 ml. of concentrated sulfuric acid at 50–55°. The hexaalkyldihydroxybiphenyl formed was filtered off and the filtrate was diluted with water. An orange oil separated and gradually solidified. This product was filtered and recrystallized from methanol; yield 5.2 g., m.p. 99–100°.

Formation of Benzoquinones by Oxidation of 3,4,6-Trialkylphenols. Oxidation of 2-Bromo-3-methyl-4,6-di-*t*-butylphenol.—Fifteen grams (0.05 mole) of 2-bromo-3-methyl-4,6-di-*t*-butylphenol was dissolved in 100 ml. of acetic acid. Five grams (0.017 mole) of potassium dichromate in 20 ml. of water plus 10 ml. of concentrated sulfuric acid was added at 25–30° during stirring. Water was added to the reaction mixture and after standing in a refrigerator several

TABLE I

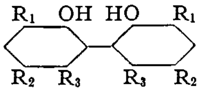
NEW 3,4,6-TRIALKYLPHENOLS AND DERIVATIVES

Compound	Yield, %	M.p. or b.p. (mm.), °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
3,4-Dimethyl-6-*tt*-octylphenol	74[a]	91.5	$C_{16}H_{24}O$	81.99	81.77[b]	11.18	11.30[b]
3,4-Dimethyl-6-(α,α-dimethylbenzyl)-phenol	38[c]	64–65[d]	$C_{17}H_{20}O$	84.96	84.86[b]	8.38	8.38
3,4-Dimethyl-6-*s*-butylphenol	35	144–150 (20)	$C_{12}H_{18}O$	80.85	80.70	10.17	10.24
2-Chloro-3-methyl-4,6-di-*t*-butylphenol	95[e]	53–54	$C_{12}H_{24}OCl$	13.91[g]	14.22[g]		
2-Bromo-3-methyl-4,6-di-*t*-butylphenol	64[f]	61.5–62	$C_{12}H_{24}OBr$	26.46[h]	26.62[h]		

[a] First crop from 366 g. (3 moles) of 3,4-dimethylphenol weighed 340 g. (m.p. 90.5°); second crop weighed 175 g. (m.p. 88–89°). [b] Average of two determinations. [c] Melting point of this product was 63–64°. [d] Crude product distilled at 178–190° at 10 mm. [e] Melting point of product was 48–49°. [f] Yield of purified product. [g] Chlorine, %. [h] Bromine, %.

TABLE II

HEXASUBSTITUTED DIHYDROXYBIPHENYLS OBTAINED BY OXIDATION OF 3,4,6-TRISUBSTITUTED PHENOLS



Compound	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. wt. Calcd.	Mol. wt. Found	Act. H per molecule (Zerewitinoff) Calcd.	Act. H per molecule (Zerewitinoff) Found
$R_1 = R_2 = t\text{-}C_4H_9$ $R_3 = CH_3$	76[a]	241–242	$C_{30}H_{46}O_2$	82.13	81.94	10.57	10.82	438.7	423	2	1.79[b]
$R_1 = t\text{-}C_4H_9$ $R_2 = R_3 = CH_3$	76[c]	160.5–161.5	$C_{24}H_{34}O$	81.31	81.16[b]	9.67	9.78[b]	354.5	346[b]	2	1.82[b]
R_1 = *tt*-Octyl $R_2 = R_3 = CH_3$	89[d]	122–123	$C_{32}H_{50}O_2$	82.35	81.98	10.80	11.12	466.7	430	2	1.79[b]
R_1 = (α,α-dimethylbenzyl) $R_2 = R_3 = CH_3$	50[e]	205–207	$C_{34}H_{38}O_2$	85.31	85.15	8.00	7.95	475.6	441	2	1.74[b]
$R_1 = CH_3$; R_2 = Cl R_3 = *t*-Butyl	23[f]	149–151	$C_{22}H_{28}O_2Cl_2$[g]	66.80	66.84[b]	7.09	7.14[b]	395	287[b]		

[a] At this yield, m.p. 232–235°. [b] Average of two determinations. [c] At this yield, m.p. 140–142°. [d] At this yield, m.p. 106°. [e] Essentially pure product. [f] At this yield, m.p. 137–142°. [g] Calcd.: Cl, 18.0. Found: Cl, 17.7.

TABLE III

OXIDATION OF HIGHLY SUBSTITUTED PHENOLS TO QUINONES

Phenolic cmpd. oxidized	Product, -quinone	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. weight Calcd.	Mol. weight Found
4-*t*-Butyl-2,5-dimethylphenol	2,5-Dimethyl-	21[a]	126–127[b]	$C_8H_8O_2$	70.57	70.66	5.92	6.18		
2-Bromo-3-methyl-4,6-di-*t*-butylphenol	2-Bromo-3-methyl-6-butyl-	24[c]	103.5–105	$C_{11}H_{13}O_2Br$[d]	51.38	51.43	5.09	5.34	257.2	257
2-Chloro-3-methyl-4,6-di-*t*-butylphenol	2-Chloro-3-methyl-6-*t*-butyl-	18	93.5–94	$C_{11}H_{13}O_2Cl$[e]	62.12	62.44	6.16	6.24	212.6	214
3-Methyl-4,6-di-*t*-butylphenol	2-Methyl-5-*t*-butyl-	22[f]	99–100[g]	$C_{11}H_{14}O_2$	74.13	74.00	7.92	8.19		

[a] At this yield, m.p. 121.5–122°. [b] R. Nietzke, *Ann.*, **215**, 168 (1882), reports 125°; L. I. Smith, J. W. Opie, S. Wawzonek and W. W. Prichard, *J. Org. Chem.*, **4**, 318 (1939), report 123.5–125°; L. I. Smith and J. W. Opie, *ibid.*, **6**, 427 (1941), report 123–125°. [c] Yield of purified product. [d] Calcd.: Br, 31.1. Found: Br, 31.7. [e] Calcd.: Cl, 16.67. Found: Cl, 16.89. [f] Based on 3-methyl-4,6-di-*t*-butylphenol not converted to dihydroxybiphenyl. [g] M. Battegay and P. Haeffely, *Bull. soc. chim.*, [4] **35**, 988 (1924), report 95°; O. A. Zeide and B. M. Dubinin, *J. Gen. Chem. U.S.S.R.*, **2**, 455 (1932); *C. A.*, **27**, 961 (1933), report 96°.

hours, orange-red crystals were obtained which were filtered and dried. The gummy solid (weight 13.2 g.) was recrystallized from petroleum ether to give 3.2 g. of yellow-orange crystals, m.p. 102–104°; recrystallized from methanol, yield 3.1 g., m.p. 103.5–105°.

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Some New Amino Alkylphenols

BY HARRY E. ALBERT

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Although a considerable number of alkylaminophenols in which the alkyl group is attached to nitrogen have been reported in the literature, relatively few amino alkylphenols having the alkyl group attached to the benzene ring have been de-