Cursory experiments showed that both N-(*p*-hydroxyphenyl)-*p*-quinoneimine-N-oxide and its anion are photosensitive and decompose at about the same rate when exposed to direct sunlight in a 1–1 mixture of benzene and methanol.

Wilmington, Del.

[Contribution from the Detroit Laboratories of the Ethyl Corporation]

Some Reactions of 2,6-Dialkylphenols[1]

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Several reactions of 2,6-diisopropylphenol and 2,6-di-*t*-butylphenol are reported. In all cases the diisopropylphenol underwent reaction in a normal manner. The di-*t*-butylphenol behaved in an anomalous manner in certain reactions, probably because of steric hindrance resulting from two *t*-butyl groups *ortho* to the hydroxyl group. Thus, benzoylation and cyanoethylation gave *para* products, and catalytic reduction stopped at the cyclohexanone stage. This paper describes some reactions of 2,6-diisopropyl- and 2,6-di-*t*-butylphenol with both normal and anomalous results being observed.

Catalytic reduction of 2,6-diisopropylphenol (DIP) proceeded as expected to give 2,6-diisopropylcyclohexanol. Phenylurethan derivatives of DIP and the cyclohexanol readily were prepared indicating the hydroxyl groups to be relatively unhindered. However, reduction of 2,6-di-*t*-butylphenol (DTB) ceased after uptake of two moles of hydrogen per mole of phenol to give the corresponding cyclohexanone. This cessation was also noted by Whitaker[2] in his work on 2,6-di-*t*-butyl-4-methylphenol. Distillation of the reduced DTB gave two stereoisomeric cyclohexanones (I and II) in yields of 80 and 20%, respectively. The configurations of I and II were established by lithium aluminum hydride reduction of I to two stereoisomeric cyclohexanols, III and IV. Since only the cyclohexanone in which the *t*-butyl groups are in a *cis* relationship can yield two isomers on reduction, the *cis* configuration has been assigned to I. Similar reduction of II, the *trans*-cyclohexanone, gave only one cyclohexanol (V). It was not possible to prepare hydroxyl or carbonyl derivatives of DTB, the cyclohexanones or the cyclohexanols by the usual methods.

Both DIP and DTB were oxidized readily by alcoholic ferric chloride and formed brilliantly colored 3,3′,5,5′-tetralkyldiphenoquinones which were reduced to the corresponding 4,4′-dihydroxydiphenyl compounds. The tetra-*t*-butyl derivatives have been reported previously by Jones.[3,4]

The phenols underwent a smooth conversion to Mannich products on treatment with formalin and dimethylamine in ethanol. The resulting N,N-dimethyl-3,5-dialkyl-4-hydroxybenzylamines were isolated in high yields.

The base-catalyzed condensation of DTB with aldehydes was investigated. Treatment of DTB with benzaldehyde in ethanolic sodium hydroxide gave bis-(3,5-di-*t*-butyl-4-hydroxyphenyl)-phenylmethane as the only product. However, use of formalin under similar conditions gave 3,5-di-*t*-butyl-4-hydroxybenzyl ethyl ether in addition to the expected 4,4′-methylene-bis-(2,6-di-*t*-butylphenol). The ether formed resulted from solvent participation in the reaction and the amount formed varied with reaction conditions and alcohol used. Use of stoichiometric base and low molecular weight primary alcohols, such as methanol or ethanol, increased the yield of the corresponding ether, whereas catalytic base and secondary alcohols such as isopropyl alcohol, gave exclusively the bis-methylene product in high yield.

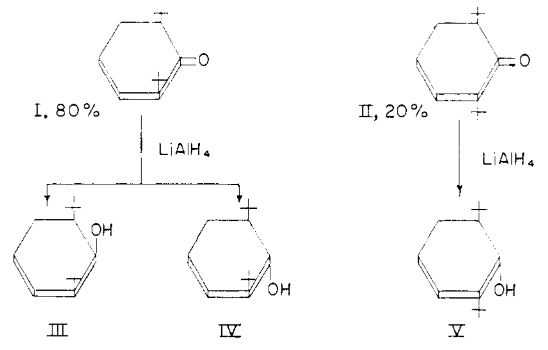

Fig. 1.

The anhydrous sodium salt of DTB was prepared through the reduced pressure evaporation of a methanol solution containing equivalent amounts of sodium methoxide and DTB. The powdery salt was decomposed rapidly by water to regenerate DTB and proved to be a reactive intermediate. Whereas DTB gave no derivative on treatment with phenyl isocyanate, its sodium salt gave a phenylurethan in 32% yield. The DTB was recovered on basic hydrolysis of the urethan.

The anhydrous sodium salt of DIP was prepared by direct reaction with sodium dispersion in toluene. The reaction was slow and hampered by the fact that the sodium salt as formed was insoluble in toluene and thus impaired stirring. The anhydrous salts of DTB and DIP were carboxylated under pressure to give the corresponding 3,5-dialkyl-4-hydroxybenzoic acids.

Cyanoethylation of DIP and DTB was carried out and found to yield different types of products. Treatment of DIP with acrylonitrile in the presence of the sodium salt gave the normal aryloxy product, *β*-(2,6-diisopropylphenoxy)-propionitrile. However, under similar conditions DTB cyano-

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[1] Presented before the Division of Organic Chemistry, 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 11–16, 1955.

[2] A. C. Whitaker, This Journal, **69**, 2414–2415 (1947).

[3] D. G. Jones, British Patent 686,261, January 21, 1953; *C. A.*, **48**, 4593 (1954).

[4] D. G. Jones, British Patent 687,293, February 11, 1953; *C. A.*, **48**, 3385 (1954).

ethylated in the *p*-position to give β-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionitrile (VI) as the only product in 13% yield. The structure of the latter material was established by hydrolysis of VI to the corresponding propionic acid VII which was independently synthesized as shown in Fig. 2.

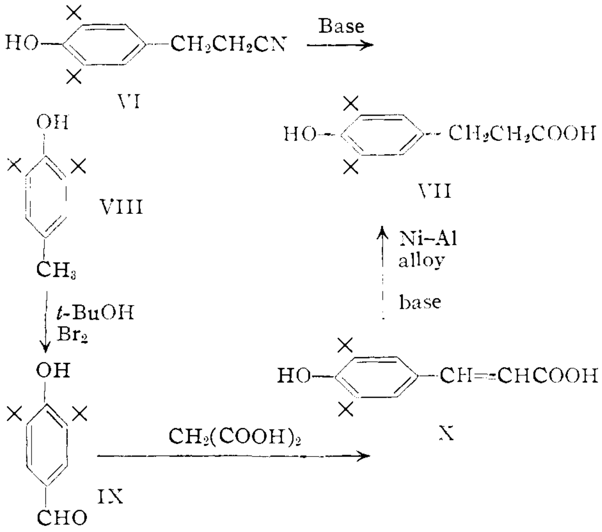

Fig. 2.

It is interesting to note that 2-*t*-butyl-6-isopropylphenol cyanoethylates in the normal manner to give a low yield of the aryloxy derivative. Thus, the difference of one methyl group on the α-carbon of one substituent exerts a critical steric effect on the point of cyanoethylation.

When the sodium salt of DIP was allowed to react with benzoyl chloride, the phenol ester, 2,6-diisopropylphenyl benzoate, was isolated in 65% yield. However, similar treatment of DTB gave an anomalous result with the formation of two products, white 4-benzoyl-2,6-di-*t*-butylphenol (XI) and the brilliant yellow enolbenzoate XII. Although these products were isolated from separate runs, it is probable that XI is the precursor of XII.

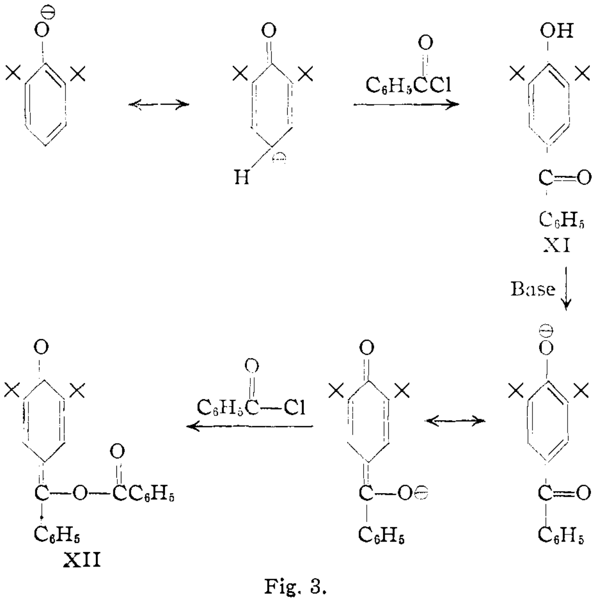

Fig. 3.

The infrared spectrum of XI is consistent with the proposed structure showing a highly hindered hydroxyl band at 2.73μ and a conjugated carbonyl at 6.05μ. The spectrum of XII shows a highly conjugated carbonyl at 6.2μ similar to that observed in the spectra of the highly colored tetraalkyldiphenoquinones described above. This band was attributed to the dienone structure of XII. A second carbonyl appeared at 5.7μ and was attributed to the enolbenzoate ester linkage. No free hydroxyl bands were present.

Catalytic reduction of XII proceeded at a very fast rate at atmospheric pressure to give three products, α-(3,5-di-*t*-butyl-4-hydroxylphenyl)-benzylbenzoate (XIII), 4-benzyl-2,6-di-*t*-butylphenol (XIV) and benzoic acid. The latter two products were presumed to have arisen through hydrogenolysis of XIII. The infrared spectrum of XIII, which was isolated as a white solid, showed destruction of the dienone system with the formation of a hindered hydroxyl at 2.7μ. The benzoate carbonyl was still present at 5.7μ. The structure of XIV was ascertained by comparison with an authentic sample obtained by alkylation of 4-benzylphenol.[5] As expected, the basic hydrolysis of XII gave XI and benzoic acid.

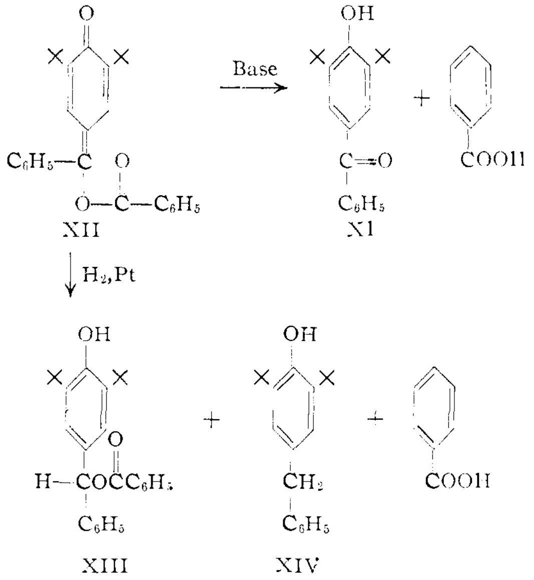

Fig. 4.

The reductions, cyanoethylations and acylations described above graphically illustrate the steric effect of the two *o*-*t*-butyl groups in DTB on the course of these reactions since DIP showed no anomalous behavior. However, it is obvious that the hydroxyl of DTB is not completely inaccessible since a phenylurethan was obtained from the sodium salt of DTB.

Experimental[6]

Reduction of 2,6-Diisopropylphenol.—The hydrogenation bomb was charged with 100 g. (0.56 mole) of 2,6-diisopropylphenol[7] and 7 g. of nickel catalyst obtained from Uni-

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(5) G. H. Stillson and D. W. Sawyer, U. S. Patent 2,248,831, July 8, 1941; *C. A.*, **35**, 7176 (1941).

(6) All melting points and boiling points are uncorrected.

(7) A. J. Kolka, J. P. Napolitano and G. G. Ecke, *J. Org. Chem.*, **21**, 712 (1956).

versal Oil Products Co. Reduction was effected at 200° using hydrogen pressures of from 34 to 102 atm. The pressure drop corresponded to approximately three moles of hydrogen per mole of the phenol. The product was filtered and fractionated without attempting to separate the stereoisomers; b.p. 130.5–131.2° (30 mm.), $n^{20}\mathrm{D}$ 1.4639. The infrared spectrum indicated the presence of a hydroxyl group and the absence of a carbonyl group.

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.19; H, 13.43. Found: C, 78.0; H, 13.2.

Reaction with phenyl isocyanate yielded the phenylurethan, m.p. 98–100°.

Anal. Calcd. for $C_{19}H_{29}NO_2$: C, 75.20; H, 9.62. Found: C, 75.0; H, 9.72.

Phenylurethan of 2,6-Diisopropylphenol.—Phenyl isocyanate reacted directly with the phenol in the presence of a trace of pyridine to yield the derivative which was recrystallized from petroleum ether; m.p. 148–150°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.74; H, 7.79. Found: C, 76.8; H, 7.84.

Reduction of 2,6-Di-*t*-butylphenol.—Hydrogenation of 150 g. (0.73 mole) of the phenol using 7.5 g. of UOP nickel catalyst was effected at 195° and 34–68 atm. Hydrogen absorption came to an abrupt halt after a pressure drop corresponding approximately to the reaction of two moles of hydrogen per mole of the phenol. Fractionation of the product through a column having about 40 theoretical plates yielded the two stereoisomers of 2,6-di-*t*-butylcyclohexanone: low boiling isomer (m.p. 35–36°, b.p. 135° (35 mm.), 120 g., 80% yield); high boiling isomer (m.p. 2–7°, b.p. 142–146° (30 mm.), 30 g., 20% yield). The infrared spectra of the isomers revealed the presence of a carbonyl and the absence of a hydroxyl group. Attempts to prepare 2,4-dinitrophenylhydrazones were unsuccessful.

Anal. Calcd. for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found (low boiling isomer): C, 80.1; H, 12.6 (high boiling isomer): C, 80.2; H, 12.1.

Reduction of Low Boiling Isomer of 2,6-Di-*t*-butylcyclohexanone.—A solution of 60.6 g. (0.29 mole) of this isomer in 50 ml. of ether was added to a solution of 5.18 g. (100% excess) of lithium aluminum hydride in 500 ml. of ether. The product was hydrolyzed with water, treated with 5% hydrochloric acid and the organic layer separated. Fractionation yielded two stereoisomers of 2,6-di-*t*-butylcyclohexanol in approximately equal amounts.

The low boiling isomer (b.p. 147° (32 mm.)) after recrystallization from isoöctane melted at 84–85°, and the higher boiling isomer (b.p. 149–152° (32 mm.)) melted at 22–23° without recrystallization. The infrared spectra of the isomers showed the presence of hydroxyl and the absence of carbonyl groups. Attempts to prepare phenylurethan derivatives by reaction with phenyl isocyanate were unsuccessful.

Anal. Calcd. for $C_{14}H_{28}O$: C, 79.17; H, 13.29. Found (low boiling isomer): C, 79.2; H, 13.3; (high boiling isomer): C, 78.8; H, 13.2.

Reduction of High Boiling Isomer of 2,6-Di-*t*-butylcyclohexanone.—Reduction of 9.5 g. (0.045 mole) of this compound was effected with 2.00 g. of lithium aluminum hydride dissolved in 150 ml. of ether. Distillation gave a 2.7-g. heart cut (b.p. 147–149° (30 mm.)). The infrared spectrum showed the presence of a hydroxyl and the absence of a carbonyl group.

Anal. Calcd. for $C_{14}H_{28}O$: C, 79.17; H, 13.29. Found: C, 79.5; H, 13.3.

3,3′.5,5′-Tetraalkyldiphenoquinones.—A mixture of 10 g. (0.056 mole) of 2,6-diisopropylphenol and 500 ml. of water was heated to reflux and emulsified by vigorous stirring. A solution of 20 g. (0.074 mole) of ferric chloride hexahydrate in 50 ml. of water was added dropwise over a 0.5 hr. period and the refluxing mixture heated and stirred for 5 hr. After cooling, the organic material was removed by ether extraction. The ether extract was dried over sodium sulfate and evaporated. The residue was recrystallized twice from ethanol to yield 4.0 g. (40%) of 3,3′,5,5′-tetraisopropyldiphenoquinone as brilliant purple plates, m.p. 196–198°.

Anal. Calcd. for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 81.6; H, 9.22.

By the same procedure 2,6-di-*t*-butylphenol was converted to 3,3′,5,5′-tetra-*t*-butyldiphenoquinone in 35% yield, m.p. 245° (lit.[3] 245°).

3,3′,5,5′-Tetraalkyl-4,4′-dihydroxybiphenyl.—A solution of 25 g. (0.071 mole) of 3,3′,5,5′-tetraisopropyldiphenoquinone in 500 ml. of acetic acid was heated to reflux and zinc dust added in small portions until the solution became colorless. The hot solution was filtered to remove excess zinc and the filtrate poured into one liter of cold water. The solid was removed by filtration and recrystallized from ethanol–water to give 19 g. (76%) of 3,3′,5,5′-tetraisopropyl-4,4′-dihydroxybiphenyl as white needles, m.p. 109–109.5°.

Anal. Calcd. for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 80.9; H, 9.25.

Similar treatment of the 3,3′,5,5′-tetra-*t*-butyldiphenoquinone gave a 93% yield of 3,3′,5,5′-tetra-*t*-butyl-4,4′-dihydroxybiphenyl, m.p. 184–185° (lit.[4] 178°).

N,N-Dimethyl-3,5-diisopropyl-4-hydroxybenzylamine.—To a solution of 89 g. (0.5 mole) of 2,6-diisopropylphenol in 500 ml. of ethanol was slowly added at room temperature 248 g. (1.38 moles of dimethylamine) of 25% aqueous dimethylamine solution. The reaction mixture was then cooled to 0° and 75 g. (0.93 mole of CH_2O) of 37% formalin solution added dropwise over a 30-minute period. On completion of the addition, the flask contents were brought to room temperature and stirred for 1 hr. After refluxing an additional 3 hr., the reaction mass was poured into 2 liters of cold water. The precipitate was filtered, washed with water and dried to give 114 g. of crude N,N-dimethyl-3,5-diisopropyl-4-hydroxybenzylamine, m.p. 85–87°. A small portion was crystallized from petroleum ether, m.p. 87–88°.

Anal. Calcd. for $C_{15}H_{25}NO$: C, 76.54; H, 10.70; N, 5.95. Found: C, 77.00; H, 10.60; N, 5.89.

N,N-Dimethyl-3,5-di-*t*-butyl-4-hydroxybenzylamine.—Treating 103 g. (0.5 mole) of 2,6-di-*t*-butylphenol as above gave 129 g. (98%) of crude product, m.p. 90–92°. Crystallization from petroleum ether gave white prisms, m.p. 92–93.5°.

Anal. Calcd. for $C_{17}H_{29}NO$: C, 77.51; H, 11.10. Found: C, 77.60; H, 11.00.

2,6-Di-*t*-butylphenol and Benzaldehyde.—A mixture of 66 g. (1.0 mole based on 85% min. assay) of potassium hydroxide and 206 g. (1.0 mole) of 2,6-di-*t*-butylphenol was dissolved in 350 ml. of ethanol. While maintaining a continuous nitrogen sweep over the system, a total of 106 g. (1.0 mole) of benzaldehyde was added slowly to the green solution. Toward the end of the addition, solids began to appear in the flask. The mixture was stirred overnight and the solids filtered off. Crystallization of this material gave 132 g. (53%) of bis-(3,5-di-*t*-butyl-4-hydroxyphenyl)-phenylmethane, m.p. 161–163°.

Anal. Calcd. for $C_{35}H_{48}O_2$: C, 83.95; H, 9.66. Found: C, 83.80; H, 9.60.

In addition, 23.1 g. of sodium benzoate was isolated.

2,6-Di-*t*-butylphenol and Formaldehyde, Run I.—To a solution of 66 g. (1.0 mole based on 85% min. assay) of potassium hydroxide in 400 ml. of absolute ethanol was added 206 g. (1.0 mole) of 2,6-di-*t*-butylphenol with stirring. With the reaction mixture at room temperature, a total of 82.4 g. (1.0 mole of CH_2O) of 37% formalin solution was then added in a dropwise manner over a 15-minute period. The reaction temperature rose to 45° and a white precipitate began to appear. The stirred mixture was cooled to 3°, filtered and the solid was washed with cold absolute ethanol until the washings were water-white. The red filtrate and combined washings were evaporated to a volume of 500 ml., yielding a second crop of crystals. The total weight of crystalline 4,4′-methylene-bis-(2,6-di-*t*-butylphenol) obtained in this fashion was 124.5 g. (53%). The solid was washed with hot water containing a trace of hydrochloric acid and recrystallized from ethanol to give needles, m.p. 153–155°.

Anal. Calcd. for $C_{29}H_{44}O_2$: C. 82.2; H. 10.4. Found: C, 81.8; H, 10.5.

The combined filtrate from above was acidified with 90 ml. of concentrated hydrochloric acid. Addition of a large volume of water gave a separate organic phase, which was extracted with ether. After drying the organic phase and removing the solvent, the residue was distilled through a Vigreux column to give 64 g. (24%) of 3,5-di-*t*-butyl-4-hydroxybenzyl ethyl ether as a viscous yellow oil, b.p. 162–163° (11 mm.). The oil solidified on scratching and after two recrystallizations from low boiling petroleum ether gave white needles, m.p. 38–38.5°.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.4; H, 10.7. Found: C, 77.8; H, 10.8.

2,6-Di-*t*-butylphenol and Formaldehyde, Run II.—Employing an isopropyl alcohol solvent (400 ml.) containing only 6.6 g. (0.1 mole based on 85% min. assay) of potassium hydroxide, 206 g. (1.0 mole) of 2,6-di-*t*-butylphenol was treated with 41.2 g. (0.5 mole of CH_2O) of 37% formalin solution. After stirring at 40–45° for 3 hr., the mixture was cooled, filtered and washed as in the previous experiment to give an 89% yield of 4,4'-methylene-bis-(2,6-di-*t*-butylphenol), m.p. 153–154°.

Sodium 2,6-Di-*t*-butylphenoxide.—A solution of 2.3 g. (0.1 mole) of sodium in 125 ml. of methanol was treated with stirring with 20.7 g. (0.1 mole) of 2,6-di-*t*-butylphenol. A vacuum was applied to the system and the alcohol evaporated while the flask contents were stirred and heated to 80°. Continued stirring and heating gave the product as a fine light green powder. The last trace of methanol was removed by gently flaming with a bunsen burner.

The free phenol may be regenerated from the sodium salt by the addition of water. Thus when 125 ml. of water was added to the above product, a light green oil separated which was extracted from the aqueous caustic phase with ether. After drying over sodium sulfate, distillation gave an 85% recovery of 2,6-di-*t*-butylphenol, m.p. 35–36°, b.p. 70° (0.5 mm.).

Phenylurethan of 2,6-Di-*t*-butylphenol.—To a slurry of 0.25 mole of sodium 2,6-di-*t*-butylphenoxide in 300 ml. of toluene was added 30 g. (0.25 mole) of phenyl isocyanate. Cooling was applied to maintain the reaction mixture at 40°. Upon completion of the addition the mixture was stirred for 2 hr. at 50° and then let stand overnight. Hydrolysis with 150 ml. of water yielded 18 g. of insoluble product. The organic layer of the filtrate was separated, dried over sodium sulfate and partially evaporated to give an additional 6 g. of product bringing the total yield to 24 g. (32%). Recrystallization from ethanol gave white needles, m.p. 187–188°.

Anal. Calcd. for $C_{21}H_{27}NO_2$: C, 77.50; H, 8.36. Found: C, 77.5; H, 8.23.

Distillation of filtrate residues gave 27.6 g. of liquid distillate, b.p. 68–76° (0.5 mm.), from which 15.1 g. (29% recovery) of 2,6-di-*t*-butylphenol was crystallized. The distillation residue (5.7 g.) was identified as 3,3',5,5'-tetra-*t*-butyldiphenoquinone (m.p. 238–242°).

The fact that the derivative was the phenylurethan and not 3,5-di-*t*-butyl-4-hydroxybenzanilide was demonstrated by hydrolysis. A solution of 10 g. (0.038 mole) of the derivative, 8 g. (0.2 mole) of sodium hydroxide, 40 ml. of ethanol and 20 ml. of water was refluxed for 5 hr. The mixture was poured into 500 ml. of water and the product extracted with ether. The ether extract was washed with dilute hydrochloric acid, dried over magnesium sulfate, evaporated and the residual liquid distilled to give 3.2 g. (40%) of 2,6-di-*t*-butylphenol, b.p. 66–68° (0.4 mm., m.p. 34–36°). Acidification of the water solution gave rapid evolution of a gas presumed to be carbon dioxide.

An attempt to prepare the phenylurethan of 2,6-di-*t*-butylphenol by reaction of the free phenol with phenyl isocyanate was unsuccessful.

Carboxylation of Sodium 2,6-Diisopropylphenoxide.—A sodium dispersion was prepared using 11.5 g. (0.5 mole) of sodium and 500 ml. of toluene. The dispersion was maintained at 60 to 65° while 89 g. (0.5 mole) of 2,6-diisopropylphenol was added. After completion of the addition the mixture was refluxed for 2 hr., cooled and transferred to a two-liter steel autoclave. Carboxylation was effected by heating for 15 hr. at 260° under 28–30 atm. of carbon dioxide pressure. After cooling to 60°, the excess carbon dioxide was vented and the contents of the autoclave treated with 200 ml. of water. The aqueous phase was separated and acidified with 50 ml. of 12 *N* hydrochloric acid. The precipitated 3,5-diisopropyl-4-hydroxybenzoic acid was removed and vacuum-dried (48 g., 43% theory, m.p. 139–141°). A 10-g. portion was recrystallized from benzene to yield white needles, m.p. 141°. The material had an allotropic crystalline form, m.p. 146°.

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.28; H, 8.10; neut. equiv., 222. Found: C, 70.1; H, 7.97; neut. equiv., 216.

Carboxylation of Sodium 2,6-Di-*t*-butylphenoxide.—A slurry of the sodium salt of 2,6-di-*t*-butylphenol in toluene was prepared by allowing 309 g. (1.5 moles) of 2,6-di-*t*-butylphenol to react with 81 g. (1.5 moles) of sodium methoxide in 2.5 liters of toluene at reflux (methanol was continuously removed as the azeotrope). The slurry thickened as the alcohol was removed. When all of the methanol had been removed as evidenced by the temperature of the refluxing vapors, the mixture was cooled and transferred to a one-gallon autoclave. Carboxylation was carried out over a 13-hr. period at 160° under a maximum carbon dioxide pressure of 50 atm. After cooling, the autoclave was discharged and the reaction mass extracted with dilute aqueous sodium bicarbonate. The aqueous phase was then acidified with concentrated hydrochloric acid to give the solid 3,5-di-*t*-butyl-4-hydroxybenzoic acid which, when dry, weighed 82 g. (22%). Recrystallization from benzene gave white crystals, m.p. 218–219°.

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 72.0; H, 8.85. Found: C, 72.1; H, 8.89.

Cyanoethylation of 2,6-Diisopropylphenol.—The sodium salt of 2,6-diisopropylphenol was prepared from 17.8 g. (0.1 mole) of phenol, 2.3 g. (0.1 gram atom) of sodium and 150 ml. of methanol as previously described. To the dry salt was added with stirring 26.7 g. (0.15 mole) of 2,6-diisopropylphenol followed by 125 ml. of acrylonitrile. The mixture was heated at 50° for 2 hr., allowed to cool and poured into 500 ml. of cold water. The mixture was then extracted with ether, the ether extract was dried over magnesium sulfate and evaporated to give a reddish-brown solid. Crystallization from isoöctane gave 12 g. (20%) of crude β-(2,6-diisopropylphenoxy)-propionitrile, m.p. 93–96°. A small portion of this material was recrystallized from ethanol to give white needles, m.p. 94.5–96°.

Anal. Calcd. for $C_{15}H_{21}NO$: C, 77.9; H, 9.15. Found: C, 78.0; H, 9.07.

The infrared spectrum substantiated the presence of the ether linkage and the absence of the hydroxyl.

Cyanoethylation of 2,6-Di-*t*-butylphenol.—Sodium 2,6-di-*t*-butylphenoxide (0.1 mole) was prepared from 20.7 g. (0.1 mole) of 2,6-di-*t*-butylphenol and 2.3 g. (0.1 gram atom) of sodium by the method described previously. After adding 185 g. (0.9 mole) of 2,6-di-*t*-butylphenol, the mixture was heated with stirring to 55°. A total of 212 g. (4.0 moles) of freshly distilled acrylonitrile was added in a dropwise manner over a 1-hr. period. The reaction mixture was slowly heated to reflux at 85°, whereupon the reaction mass became homogeneous and a deep green color developed. After 1 hr. of stirring at reflux, the reaction mass was a thick slurry due to precipitation of a light brown amorphous solid. After transferring the slurry to a larger flask and adding 212 g. (4.0 moles) of acrylonitrile, the mixture was refluxed an additional 6 hr. The cooled mixture was poured into one liter of cold water, mixed well and filtered to give 130 g. of the amorphous solid which could not be crystallized and was sparingly soluble in organic solvents. The organic portion of the filtrate was separated, dried over magnesium sulfate, evaporated and the resulting oil crystallized from petroleum ether to give 35 g. (13%) of β-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionitrile, m.p. 111–113°.

Anal. Calcd. for $C_{17}H_{25}NO$: C, 78.70; H, 9.72. Found: C, 78.80; H, 9.78.

Hydrolysis of β-(3,5-Di-*t*-butyl-4-hydroxyphenyl)-propionitrile.—A mixture of 3.0 g. (0.012 mole) of β-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionitrile, 4.6 g. (0.2 mole) of sodium hydroxide, 25 ml. of ethanol and 6 ml. of water was heated to reflux and after ten minutes began to evolve ammonia. After refluxing overnight the solution was cooled and poured into 100 ml. of cold water. Acidification with dilute hydrochloric acid gave a cream colored solid which was filtered off and crystallized from aqueous ethanol to give 3 g. (93%) of β-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionic acid as white needles, m.p. 172–173°.

Anal. Calcd. for $C_{17}H_{26}O_3$: C, 73.4; H, 9.41. Found: C, 73.6; H, 9.52.

3,5-Di-*t*-butyl-4-hydroxybenzaldehyde.—Following a procedure similar to that described by Campbell,[8] 64 g. (0.4 mole) of bromine was added with stirring to 22.3 g. (0.1 mole) of 2,6-di-*t*-butyl-4-methylphenol in 300 ml. of *t*-butyl

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(8) T. W. Campbell and G. M. Coppinger, This Journal, 74, 1469 (1952).

alcohol at 25°. The temperature rose to 67°. The mixture then began to cool, and the reaction was assumed complete when the addition of several ml. of bromine raised the temperature only a degree. After an hour of stirring, the mixture was cooled to 20° and the crystalline product filtered off. This material was washed with 10% sodium thiosulfate solution, with distilled water and then dried in a vacuum desiccator. The total yield of 3,5-di-*t*-butyl-4-hydroxybenzaldehyde was 21.5 g. (91%), m.p. 189°. Campbell reports m.p. 189°.

3,5-Di-*t*-butyl-4-hydroxycinnamic Acid.—The aldehyde was condensed with malonic acid by the method of Robinson.[9] A mixture of 15.1 g. (0.06 mole) of 3,5-di-*t*-butyl-4-hydroxybenzaldehyde, 20 g. (0.19 mole) of malonic acid, 55 ml. of pyridine and 2 ml. of piperidine was heated for 1.5 hr. on a steam-bath. The cooled reaction mixture was then poured with rapid stirring into 30 ml. of 12 *N* hydrochloric acid and 50 g. of crushed ice. The gummy yellow precipitate which formed became granular after 1 hr. of stirring. After filtration and washing with water, the solid was crystallized from a benzene–isoöctane mixture giving 9.5 g. (54%) of 3,5-di-*t*-butyl-4-hydroxycinnamic acid, m.p. 218°. The infrared spectrum of the material supported the expected structure.

Anal. Calcd. for $C_{17}H_{24}O_3$: C, 73.9; H, 8.74. Found: C, 74.4; H, 8.75.

Reduction of 3,5-Di-*t*-butyl-4-hydroxycinnamic Acid.—According to the method outlined by Papa,[10] a solution of 5 g. (0.02 mole) of 2,6-di-*t*-butyl-4-hydroxycinnamic acid in 150 ml. of 1% aqueous sodium hydroxide was heated to 90°. While the mixture was held at this temperature, 15 g. of Raney nickel–aluminum alloy was added in small portions with stirring. The mixture was then stirred for 1 hr. at 90° and an additional 5 g. of the alloy together with 25 ml. of 1% sodium hydroxide was added. The hot solution was filtered and the residue washed thoroughly with water. The clear filtrate was poured into dilute hydrochloric acid and the white solid filtered off to give 3.5 g. (70%) of crude β-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionic acid. Recrystallization of a portion of this material from aqueous ethanol gave needles, m.p. 171–173°. The mixed melting point of this material and that obtained from the hydrolysis of β-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionitrile was 172–174°. The infrared spectra of the two acids were identical.

Cyanoethylation of 2-Isopropyl-6-*t*-butylphenol.—The sodium salt (0.26 mole) of 2-isopropyl-6-*t*-butylphenol was prepared in a manner similar to that described above. To the flask containing the dry salt was then added an additional 20 g. (0.1 mole) of 2-isopropyl-6-*t*-butylphenol and the resulting slurry heated to 40°. Over a 1-hr. period, 100 ml. of freshly distilled acrylonitrile was added in a dropwise manner. The mixture was then stirred for 5 hr.

The reaction mixture was poured into 250 ml. of water, the organic portion extracted with ether, the ether layer dried over magnesium sulfate and evaporated. The remaining oil was distilled to give 16.9 g. (85% recovery) of the starting phenol, b.p. 105–110° (9 mm.). Distillation was continued at a lower pressure to give 1.7 g. (6%) of β-(2-isopropyl-6-*t*-butylphenoxy)-propionitrile, b.p. 111–115° (0.3 mm.), m.p. 59–60.5°.

Anal. Calcd. for $C_{16}H_{23}NO$: C, 78.30; H, 9.45. Found: C, 78.10; H, 9.31.

2,6-Diisopropylphenol and Benzoyl Chloride.—A total of 2.3 g. (0.1 gram atom) of sodium was dispersed in 300 ml. of dry dioxane at 101° under a nitrogen atmosphere. After cooling the dispersion to 60°, a solution of 17.5 g. (0.1 mole) of 2,6-diisopropylphenol in 30 ml. of dioxane was added dropwise over a 30-minute period. A slow evolution of hydrogen occurred. The stirred mixture finally was heated to 100° and after 20 minutes no further hydrogen evolution was observed. The green solution was cooled to 58° and 14 g. (0.1 mole) of benzoyl chloride was added over a 5-minute interval. The precipitation of sodium chloride at this point was accompanied by a temperature rise to 64°. After standing overnight, the inorganic solid was filtered off and the filtrate was evaporated under reduced pressure. The residue remaining was taken up in ether, washed with aqueous sodium hydroxide and the organic phase dried and evaporated. The resultant oil readily crystallized from aqueous ethanol to give 18.4 g. (65%) of 2,6-diisopropylphenyl benzoate, m.p. 70–72°.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 80.81; H, 7.9. Found: C, 80.90; H, 8.2.

2,6-Di-*t*-butylphenol and Benzoyl Chloride.—Using the sodium alkoxide technique described previously, 0.25 mole of sodium 2,6-di-*t*-butylphenoxide was prepared. To the dry salt was added 300 ml. of dry dioxane and the resulting slurry was heated to 60°. A total of 33 g. (0.25 mole) of benzoyl chloride in 25 ml. of dioxane was added rapidly to the stirred mixture. The reaction mixture rose to 80° and a yellow color developed. The mixture was allowed to cool to 25° with stirring, poured into cold water, and the resulting mixture was extracted with ether. After drying the organic phase over magnesium sulfate, the ether was removed at reduced pressure and the oily residue was crystallized from ligroin to give 18.7 g. (24%) of 2,6-di-*t*-butyl-4-benzoylphenol, m.p. 124–126°.

Anal. Calcd. for $C_{21}H_{22}O_2$: C, 81.25; H, 8.44. Found: C, 81.20; H, 8.53.

When the above procedure was modified by pouring the reaction mixture into cold water as soon as the temperature had dropped to 70° rather than 25°, a total of 20 g. (40% based on acid chloride) of the yellow enolbenzoate XII was obtained. Recrystallization from isoöctane gave yellow needles, m.p. 164–166°.

Anal. Calcd. for $C_{28}H_{31}O_3$: C, 81.13; H, 7.30. Found: C, 80.80; H, 7.26.

Catalytic Reduction of XII.—The reduction was conducted in a glass micro-hydrogenation apparatus designed to operate at atmospheric pressure and room temperature. The system was first charged with 0.25 g. of platinum oxide and 15 ml. of dry ethyl acetate. Hydrogen was then admitted to the system and the catalyst was reduced. When hydrogen absorption had ceased, a solution of 10 g. (0.02 mole) of XII in 50 ml. of ethyl acetate was introduced into the apparatus. The hydrogenation was started, and after 2.5 hr. at 29° and 1 atmosphere, 1100 ml. of hydrogen had been absorbed. The reduction was stopped, the catalyst filtered off and the ethyl acetate evaporated at reduced pressure. The residue was taken up in ether and washed with 5% aqueous sodium hydroxide. Acidification of the aqueous phase gave 1.0 g. (35%) of benzoic acid, m.p. 120–121°, mixed m.p. with an authentic sample gave no depression. The organic phase was evaporated and the residue crystallized from petroleum ether to give 4.5 g. (45%) of α-(3,5-di-*t*-butyl-4-hydroxyphenyl)-benzyl benzoate (XIII), m.p. 147–150°.

Anal. Calcd. for $C_{28}H_{32}O_3$: C, 80.73; H, 7.74. Found: C, 81.10; H, 7.93.

The petroleum ether filtrate was evaporated to give a yellow oil which resisted all attempts to crystallize. The oil was chromatographed over alumina *via* petroleum ether to give 2.0 g. (30%) of 2,6-di-*t*-butyl-4-benzylphenol, m.p. 59–60.5°. A mixed melting point with an authentic sample of the benzylphenol prepared according to the procedure of Stillson[5] was undepressed and the infrared curves were identical.

Basic Hydrolysis of XIII.—A solution of 3.0 g. (0.073 mole) of XIII and 3 g. (0.045 mole based on 85% min. assay) of potassium hydroxide in 40 ml. of ethanol and 20 ml. of water was refluxed for 30 minutes. The solution was then poured into cold water and saturated with carbon dioxide to give a white solid. Filtration gave 2.22 g. (90%) of 2,6-di-*t*-butyl-4-benzoylphenol, m.p. 125–126°, identical with the material isolated from the reaction of benzoyl chloride and 2,6-di-*t*-butylphenol. Acidification and evaporation of the filtrate gave benzoic acid in 80% yield, m.p. 119–121°.

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