g. (67%) of residual sirup. Crystallization from petroleum ether gave colorless needles, m.p. 51–52°.

*Anal.* Calcd. for $C_{11}H_{14}Br_2O$: Br, 49.63; C, 41.02; H, 4.38; OH, 5.28. Found: Br, 48.8, 49.1; C, 41.09, 41.31; H, 4.53, 4.51; OH, 5.37, 5.27 ($Ac_2O$-Py). The infrared absorption spectrum in the region of the –OH band for this compound is given in Table I.

**Method B.**—A more convenient method for the preparation of IIIb consists in treating VII[6,8] in acetic acid with bromine. VII (20 g., 0.122 mole, b.p. 129–130° (20 mm.)) in 100 ml. of acetic acid was treated with 39.2 g. (0.245 mole) of bromine dropwise with swirling and cooling. The bromine was decolorized rapidly and hydrogen bromide was evolved. After standing several hours, the mixture was diluted to 500 ml. with cold water. A solid precipitated which was filtered with suction and crystallized from gasoline; white needles, m.p. 51.5–52.0°, were obtained. The yield of dry crude product melting at 48–50° was 38.2 g. (97.5%); mixed m.p. with preparation of method A 51–52°.

**Benzoate of IIIb.**—To 1.1 g. of IIIb dissolved in 10 ml. of pyridine was added 1.0 g. of benzoyl chloride. The mixture was heated at 70° overnight and then was cooled and poured into dilute sulfuric acid, from which was isolated 1.2 g. of white powder, m.p. 103–105°. This was recrystallized from alcohol giving colorless crystals, m.p. 105–106°.

*Anal.* Calcd. for $C_{18}H_{18}O_2Br_2$: Br, 37.51; mol. wt., 426.15. Found: Br, 37.60, 37.20; mol. wt., 410, 426.

**2,4,4-Tribromo-3-methyl-6-*t*-butyl-2,5-cyclohexadienone (Vb).**—To a solution of IIIb (32.2 g., 0.1 mole) in 100 ml. of cold glacial acetic acid was added 17.6 g. (0.11 mole) of bromine followed by refrigeration for 4 days. The frozen mixture was diluted with water and again chilled. A heavy reddish oil resulting was washed with dilute sodium sulfite solution and then with water. On chilling again in refrigerator overnight a crystalline product formed. This product, after crystallization from alcohol and again from *n*-hexane, gave lemon-yellow crystals, m.p. 129.5–130.5° dec., yield 6.3 g.

*Anal.* Calcd. for $C_{11}H_{13}OBr_3$: Br, 59.80. Found: Br, 59.86, 59.77.

**2-Bromo-3-methyl-6-*t*-butylquinone (VIIIb). Method A.**—A solution of 230 ml. of glacial acetic acid and 32.2 g. (0.1 mole) of IIIb was treated with a solution of 10 g. of sodium dichromate dihydrate in 25 ml. of water, in several portions with swirling. The solution was heated to 50° and allowed to stand several hours. After cooling, the solution was diluted with 100 ml. of water causing an orange solid to precipitate in nearly theoretical yield. The product, crystallized from petroleum ether and then from *n*-heptane, consisted of orange plates, m.p. 105–106°.

*Anal.* Calcd. for $C_{11}H_{13}BrO_2$: Br, 31.08. Found: Br, 31.10, 31.25.

**Method B.**—VIIIb may be obtained from IIIb by the method of Zincke and Wugk.[9] To 1.0 g. of IIIb dissolved in 10 ml. of glacial acetic acid was added 1 ml. of concentrated nitric acid. After standing one hour, water was added to incipient precipitation followed by cooling; bright yellow plates, m.p. 104–105°, precipitated; mixed m.p. with product from method A showed no depression.

**Infrared Measurements.**—It has been shown that the OH band of a given *ortho*-substituted phenol has nearly the same frequency in the melt and in concentrated $CCl_4$ solution. Therefore, all compounds were measured as concentrated solutions in $CCl_4$ except IIa which was examined as a super-cooled liquid. The sample thickness was 0.002 inch for all compounds. The infrared curves were corrected for the absorption due to the solvent. The infrared bands were measured with an automatic recording spectrometer having a large NaCl prism, designed and constructed in this Laboratory.

**Infrared Interpretation.**—In all of the compounds, the C–H band was observed at about 3.39 $\mu$. The spectra of IIa, IIb and IIIa exhibit bands very close to 2.82 $\mu$, which is consistent with the structure of a phenolic OH adjacent to an *ortho* *t*-butyl group (Table I). The spectra of compounds IV and Va show no bands in the OH region. The bands observed in the spectra for IV and Va at 6.03 and 6.08 $\mu$, respectively, are believed to be due to conjugated ketone groups. Both benzoquinone and 2,5-di-*t*-butylquinone were found to have a band at 6.03 $\mu$, attributable to the conjugated carbonyl structure. This is further supported by the report of Rasmussen, Tunnicliff and Brattain[10] that the conjugation of a ketone group with a C=C group, as in acetophenone and isophorone, shifts the C=O band to the region of 5.90 to 6.00. The C=C band was observed in IIa, IIb, IIIb, IV and Va at 6.24, 6.25, 6.26, 6.29 and 6.21 $\mu$, respectively.

**Acknowledgment.**—The authors are deeply appreciative of the interest and helpful suggestions given by Dr. G. E. P. Smith, Jr. The assistance of Messrs. T. W. Osborne, J. Tighe and Mrs. Kay Piersol who did the analyses recorded here, of Dr. A. W. Scholl who determined the ultraviolet absorption spectra given, and of H. C. Ransaw who assisted with the infrared determinations, is gratefully acknowledged. The authors acknowledge and thank Drs. R. F. Dunbrook and F. W. Stavely for their interest, and the management of the Firestone Tire & Rubber Company for permission to publish this work.

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[8] A. E. Tchitchibabine, *Compt. rend.*, **198**, 1239 (1934).

[9] Th. Zincke and E. Wugk, *Ann.*, **363**, 296 (1908).

[10] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

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## Reactions of 3,4,6-Trialkylphenols. II. Nitric Acid Reaction Products and their Decomposition

BY HARRY E. ALBERT AND WILLIAM C. SEARS

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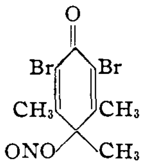
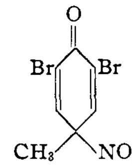
It has been shown, particularly by Auwers,[1-3] Fries[4-7] and Zincke,[8-10] that both in the naphthalene and benzene series, highly substituted phenolic compounds react with nitric acid to form quinoid compounds referred to as "chinetrols." These compounds were also obtained, but less readily,[6] when nitrous acid or nitrous oxide was used as the reagent. Although Auwers[3] in one of his later publications gave a nitrite ester structure (I) for such a reaction product from 2,6-dibromo-3,4,5-trimethylphenol and nitric acid, Fries[6] has shown a similar compound II not to have the nitrite ester group. All of the above-mentioned investigators have shown that one of the more common reactions of compounds having structures similar to II was the conversion to "chinols" where the nitro group is replaced by hydroxyl.



I



II

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[1] K. Auwers and H. Burrows, *Ber.*, **32**, 3034 (1899).

[2] K. Auwers, *ibid.*, **35**, 455 (1902).

[3] K. Auwers and K. Saurwein, *ibid.*, **55**, 2372 (1922).

[4] K. Fries and E. Hübner, *ibid.*, **39**, 435 (1906).

[5] K. Fries, *Ann.*, **389**, 305 (1912).

[6] K. Fries and G. Oehmke, *ibid.*, **462**, 1 (1928).

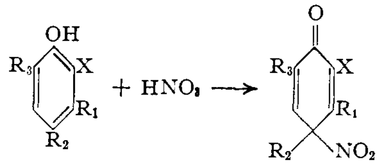
[7] K. Fries and A. Kuster, *ibid.*, **470**, 20 (1929).

[8] Th. Zincke, *ibid.*, **328**, 261 (1903).

[9] Th. Zincke and W. Emmerich, *ibid.*, **341**, 309 (1905).

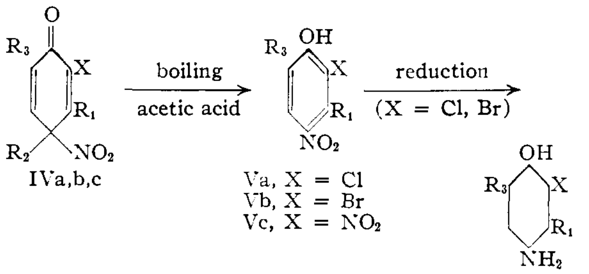
[10] Th. Zincke and M. Buff, *ibid.*, **341**, 318 (1905).

In the course of some nitration experiments in this Laboratory, designed to explain some anomalous results obtained in the nitration of 3-methyl-4,6-di-*t*-butylphenol, compounds which have been assigned structures similar to II have been isolated and characterized. It has been found that 2-substituted-3,4,6-trialkylphenols (III) react with nitric acid at relatively low temperatures (0–10°) to give compounds which are thought to be 2,3,4,-4,6-pentasubstituted-2,5-cyclohexadieneones (IV).



IIIa, IVa, X = Cl; $R_1 = CH_3$; $R_2 = R_3 = t\text{-}C_4H_9$
IIIb, IVb, X = Br; $R_1 = CH_3$; $R_2 = R_3 = t\text{-}C_4H_9$
IIIc, IVc, X = $NO_2$; $R_1 = CH_3$; $R_2 = R_3 = t\text{-}C_4H_9$
IIId, IVd, X = Cl; $R_1 = R_2 = CH_3$; $R_3 = t\text{-}C_4H_9$

When the alkyl group in the 4-position with respect to the oxygen containing carbon atom is *t*-butyl group, such as in 2-chloro-3-methyl-4-nitro-4,6-di-*t*-butyl-2,5-cyclohexadieneone (IVa), the cyclohexadieneone decomposes readily in acetic acid solution with the loss of this group to give a nitrophenol (Va), particularly in the presence of a small amount of sulfuric acid catalyst. If the *ortho* substituent is a halogen atom, then V can be reduced readily to give a stable aminophenol.



IVa,b,c

Va, X = Cl
Vb, X = Br
Vc, X = $NO_2$

VIa, X = Cl
VIb, X = Br

In the decomposition of 2-chloro-3-methyl-4-nitro-4,6-di-*t*-butyl-2,5-cyclohexadieneone (IVa), a quinone has been isolated as a by-product. The oxidation of 2-chloro-3-methyl-4,6-di-*t*-butylphenol (IIIa) has given this same quinone, which is without much question 2-chloro-3-methyl-6-*t*-butylquinone (VIII).

Using the regular decomposition procedure with IVd, which has a methyl group in the 4-position, no *p*-nitrophenol could be isolated. When acetic acid containing sodium acetate trihydrate was used in the same procedure, it was found that the nitro group had been replaced by an hydroxyl group to yield 2-chloro-3,4-dimethyl-4-hydroxy-6-*t*-butyl-3,-5-cyclohexadieneone (IVe).

In the series of reactions III → IV → V, it is very easy to obtain V without the isolation of the intermediate cyclohexadieneone (IV). The nitration of IIIa at about 50° gave a fairly good yield of Va. Also in the room temperature nitration of IIIc, which presumably is converted first to IVc, an appreciable amount of Vc was isolated.

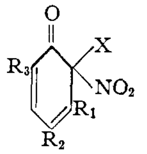
It was found that it is possible to reduce the cyclohexadieneone IVb directly to the aminophenol VIb with zinc and hydrochloric acid, thus avoiding the isolation of the nitrophenol intermediate Vb.

Evidence that the nitro group in the nitrophenols V, resulting from the decomposition of the cyclohexadienones IV, is in the 4-position with respect to the phenol group was provided by independent syntheses. Nitration of 3-methyl-6-*t*-butylphenyl acetate,[11] prepared from 3-methyl-6-*t*-butylphenol, a compound of known structure,[12,13] gave the corresponding 4-nitro derivative, which was then hydrolyzed to give 3-methyl-4-nitro-6-*t*-butylphenol. Chlorination or bromination of the latter compound gave 2-chloro-3-methyl-4-nitro-6-*t*-butylphenol, respectively, which were shown by mixed melting points to be identical to the compounds Va and Vb obtained by decomposition of the cyclohexadieneones IVa and IVb. Also, nitration of 3-methyl-6-*t*-butylphenol produced 2,4-dinitro-3-methyl-6-*t*-butylphenol which was shown to be the same as Vc, from the cyclohexadieneone IVc, and identical to the dinitrophenol obtained when 3-methyl-4,6-di-*t*-butylphenol was nitrated at ordinary temperatures with an excess of nitric acid over that required for mononitration.

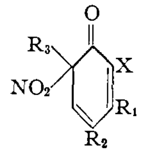
The nitration of 2-chloro-3,6-dimethyl-4-*t*-butylphenol (VIII) in acetic acid solution at 10° did not produce the expected cyclohexadieneone, but 2-chloro-3,6-dimethyl-4-nitrophenol (IX) was isolated. Under the conditions of the experiment, the cyclohexadieneone apparently was decomposed. The structure of IX was established by obtaining this compound by the sulfuryl chloride chlorination of 4-nitro-2,5-dimethylphenol, a known compound.[14] Here the *t*-butyl group in the 4-position of a 2,3,4,6-tetrasubstituted phenol was replaced by a nitro group using very mild conditions.

Still further evidence of the nitro group being in the 4-position in the nitrophenols V is provided by the already mentioned fact that IVd, having a methyl group in the 4-position, did not form a nitrophenol when decomposition conditions were used which readily gave a nitrophenol from cyclohexadieneones having a *t*-butyl group in the 4-position. The above experimental facts, together with the evidence from infrared absorption spectra, demonstrate conclusively that the nitrophenols obtained have the assigned structures V.

Possible cyclohexadieneone structures, in addition to IV, are X and XI, but both are thought to be unlikely because of the formation of a 4-nitro compound on decomposition. It is much more probable that the nitro group would remain at its initial ring position than for it to rearrange from the 2- or 6-position to the 4-position during the de-



X



XI

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[12] L. E. Forman and W. C. Sears, THIS JOURNAL, **76**, 4977 (1954).
[13] Koppers Co., Bulletin C-8-103, July 1, 1948.
[14] K. Auwers and F. Michaelis, *Ber.*, **47**, 1289 (1914).

TABLE I

2-SUBSTITUTED 3,4,6-TRIALKYLPHENOLS

| Compound, *t*-butylphenol | Yield of purified prod., % | B.p., °C. | M.p., °C. | Analyses, % | |
|---|---|---|---|---|---|
| | | | | Calcd. | Found |
| 2-Chloro-3-methyl-4,6-di- (IIIa) | 95[b] | 123–125 at 2 mm. | 53–54 | Cl 13.91 | 14.22 |
| 2-Bromo-3-methyl-4,6-di- (IIIb) | 64 | | 61.5–62 | Br 26.46 | 26.62[a] |
| 2-Nitro-3-methyl-4,6-di- (IIIc) | 62[c] | ............... | 83–84 | N 5.28 | 5.19[a] |
| 2-Chloro-3,6-dimethyl-4- | 75 | 122–124 at 2 mm. | | Cl 16.67 | 16.58 |
| 2-Chloro-3,4-dimethyl-6- | 79[d] | 129–133 at 10 mm. | | Cl 16.67 | 16.63 |

[a] Average of two determinations. [b] M.p. 48–49. [c] M.p. 80–81. [d] Redistilled product, b.p. 132–133° at 10 mm. was used.

TABLE II

2,4-DISUBSTITUTED-3,4,6-TRIALKYL-2,5-CYCLOHEXADIENEONES

| 2,5-Cyclohexadieneone | Yield, % | M.p., °C. | Empirical formula | Nitrogen, % | | Halogen, % | | Mol. wt. | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| 2-Chloro-3-methyl-4-nitro-4,6-di-*t*-butyl- (IVa) | 92[c] | 93[a] | $C_{15}H_{22}O_3NCl$ | 4.67 | 4.42 | 11.83 | 11.95[b] | 299.8 | 304[b] |
| 2-Bromo-3-methyl-4-nitro-4,6-di-*t*-butyl- (IVb) | 87.3[d] | 92–93[a] | $C_{15}H_{22}O_3NBr$ | 4.07 | 4.00[b] | 23.21 | 23.21[b] | 344.2 | 345[b] |
| 2,4-Dinitro-3-methyl-4,6-di-*t*-butyl- (IVc) | 59 | 90[a] | $C_{15}H_{22}O_5N_2$ | 9.03 | 8.95[b] | | | | |
| 2-Chloro-3,4-dimethyl-4-nitro-6-*t*-butyl- (IVd) | 88[f] | 93–94[a] | $C_{12}H_{16}O_3NCl$ | 5.44 | 5.22 | 13.76 | 13.38 | 257.7 | 268 |
| 2-Chloro-3,4-dimethyl-4-hydroxy-6-*t*-butyl- (IVe)[h] | 43[g] | 128–129 | $C_{12}H_{17}O_2Cl$ | | | 15.50 | 15.17[b] | 228.7 | 253[b] |

[a] These compounds melt with decomposition. [b] Average of two determinations. [c] M.p. 89° dec. [d] M.p. 86° dec. [e] M.p. 86.5° dec. [g] Yield purified material. [h] Calcd.: C, 63.01; H, 7.49. Found: C, 63.21[b]; H, 7.66.[b]

TABLE III

2,3,4,6-TETRASUBSTITUTED PHENOLS

| Compound | Yield, % | M.p., °C. | Empirical formula | Nitrogen, % | | Halogen, % | | Mol. wt. | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| 2-Chloro-3-methyl-4-nitro-6-*t*-butylphenol (Va) | 94[a]<br>83[b] | 87 | $C_{11}H_{14}O_3NCl$ | 5.75 | 5.77 | 14.55 | 14.69[c] | 243.5 | 225[c] |
| 2-Chloro-3-methyl-4-amino-6-*t*-butylphenol (VIa) | 68[d] | 111–112 | $C_{11}H_{16}ONCl$ | 6.56 | 6.34 | 16.34 | 16.69[c] | 213.5 | 204 |
| 2-Bromo-3-methyl-4-nitro-6-*t*-butylphenol (Vb) | 69[e] | 105.5–102 | $C_{11}H_{14}ONBr$ | 4.88 | 4.74 | 27.83 | 27.71[c] | 288 | 268[c] |
| 2-Bromo-3-methyl-4-amino-6-*t*-butylphenol (VIb) | 83[f]<br>96[g] | 99.5–100 | $C_{11}H_{16}ONBr$ | 5.45 | 5.18 | 31.08 | 30.55[c] | 258 | 243[c] |
| 2,4-Dinitro-3-methyl-6-*t*-butylphenol (VIb) | 39[h] 82[i]<br>54[k] | 99–99.5[e] | $C_{11}H_{14}O_5N_2$ | 11.02 | 10.89 | | | | |
| 2-Chloro-3,6-dimethyl-4-nitrophenol (IX) | 38[m] | 118–119 | $C_8H_6O_3N_3Cl$ | 6.95 | 6.78[c] | 17.59 | 17.68[c] | | |

[a] Yield of purified material obtained from corresponding cyclohexadieneone. [b] Yield (m.p. 83–84°) obtained directly from 2-chloro-3-methyl-4,6-di-*t*-butylphenol. [c] Average of two separate determinations. [d] M.p. 107–108°. [e] First crop from 45 g. of cyclohexadieneone: 18 g., m.p. 99–101°; second crop, 8 g., m.p. 98.9°. [f] Yield (m.p. 88–91°) obtained by reduction of corresponding nitrophenol. [g] Yield (m.p. 99–100°) obtained by reduction of corresponding cyclohexadieneone. [h] Yield of purified product from nitration of 3-methyl-6-*t*-butylphenol. [i] Yield (m.p. 98–99°) obtained by decomposition of cyclohexadieneone. [k] Yield (m.p. 92°) from nitration of 3-methyl-4,6-di-*t*-butylphenol. [m] Yield (m.p. 114°) from nitration of 2-chloro-3,6-dimethyl-4-*t*-butylphenol.

composition. The use by Auwers, Fries and Zincke of a *p*-quinoid structure II in the benzene series, the formation of a quinone VII from the decomposition of a cyclohexadieneone IVa and the aforementioned behavior of IVd on decomposition constitute further evidence for assigning structure IV to the cyclohexadieneones described in this paper.

### Infrared Interpretation

In all compounds the C–H band was observed at about 3.39 μ. Buswell, Dietz and Rodebush[15] reported that a broad O–H band in *o*-nitrophenol was observed at about 3.05 μ due to chelation. Evidently, the band at about 2.99 μ in IIIc (Table IVa) corresponds to the one above in *o*-nitrophenol. Similarly, the band at 3.04 μ in Vc (Table IVg) is indicative of a phenol with an *o*-nitro group.

The fact that the spectra of the nitration products shown in Table IVb, c, d exhibited no bands in the O–H region indicated that these compounds were not phenols. The bands observed at 5.96, 5.97 and 5.98 μ in IVa (Table IVb), IVb (Table IVc) and IVc (Table IVd), respectively, are believed to be due to the ketone groups.[12] The C=C bands of these three compounds were found at 6.23, 6.25 and 6.17 cm.$^{-1}$, respectively.

Upon decomposition, the cyclohexadieneone compounds reverted to phenols as indicated by the reappearance of the O–H band at 2.83, 2.83 and 3.04 μ in Table IVe, f, g, respectively. Simultaneously, the previously observed ketone bands vanished, but the C=C bands remained. The fact that the

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[15] A. M. Buswell, V. Dietz and W. H. Rodebush, *J. Chem. Phys.*, **5**, 501 (1937).

TABLE IV

a. 2-Nitro-3-methyl-4,6-di-*t*-butylphenol

| $\lambda$, $\mu$ | $\nu$, cm.$^{-1}$ | *I* (% transmission) |
|---|---|---|
| 2.99 | 3345 | 72 |
| 3.36 | 2976 | 21 |
| 6.26 | 1597 | 69 |
| 6.36 | 1572 | 32 |
| 6.56 | 1524 | 12 |
| 6.78 | 1475 | 18 |
| 6.90 | 1449 | 27 (sh) |
| 6.96 | 1437 | 46 |

b. 2-Chloro-3-methyl-4-nitro-4,6-di-*t*-butyl-2,5-cyclohexadieneone (IVa)

| | | |
|---|---|---|
| 3.40 | 2941 | 24 |
| 5.96 | 1678 | 12 |
| 6.23 | 1605 | 32 |
| 6.42 | 1558 | 19 |
| 6.60 | 1515 | 67 (sh) |
| 6.78 | 1475 | 24 |
| 6.95 | 1439 | 48 (sh) |

c. 2-Bromo-3-methyl-4-nitro-4,6-di-*t*-butyl-2,5-cyclohexadieneone (IVb)

| | | |
|---|---|---|
| 3.36 | 2976 | 25 |
| 5.97 | 1675 | 13 |
| 6.25 | 1603 | 32 |
| 6.42 | 1558 | 11 |
| 6.68 | 1497 | 40 |
| 6.80 | 1471 | 25 |
| 6.95 | 1439 | 48 (sh) |

d. 2,4-Dinitro-3-methyl-4,6-di-*t*-butyl-2,5-cyclohexadieneone (IVc)

| | | |
|---|---|---|
| 3.38 | 2958 | 21 |
| 5.98 | 1675 | 17 |
| 6.17 | 1621 | 46 |
| 6.47 | 1596 | 14 |

e. 2-Chloro-3-methyl-4-nitro-6-*t*-butylphenol (Va)

| | | |
|---|---|---|
| 2.83 | 3534 | 33 |
| 3.34 | 2994 | 23 |
| 6.20 | 1613 | 43 |
| 6.40 | 1563 | 36 |
| 6.55 | 1527 | 15 |
| 6.73 | 1486 | 31 |
| 6.85 | 1460 | 41 |
| 6.93 | 1443 | 33 |

f. 2-Bromo-3-methyl-4-nitro-6-*t*-butylphenol (Vb)

| $\lambda$, $\mu$ | $\nu$, cm.$^{-1}$ | *I* (% transmission) |
|---|---|---|
| 2.83 | 3534 | 59 |
| 3.37 | 2967 | 45 |
| 6.22 | 1608 | 57 |
| 6.42 | 1558 | 49 |
| 6.55 | 1527 | 14 |
| 6.79 | 1473 | 53 |
| 6.92 | 1445 | 50 |

g. 2,4-Dinitro-3-methyl-6-*t*-butylphenol (Vc)

| | | |
|---|---|---|
| 3.04 | 3311 | 61 |
| 3.39 | 2950 | 29 |
| 6.22 | 1608 | 21 |
| 6.34 | 1577 | 12 |
| 6.42 | 1558 | 14 |
| 6.47 | 1596 | 12 |
| 6.55 | 1527 | 9 |
| 6.80 | 1471 | 21 |
| 6.96 | 1437 | 10 |

h. 2-Chloro-3-methyl-4-amino-6-*t*-butylphenol (VIa)

| | | |
|---|---|---|
| 2.78 | 3597 | 57 |
| 2.92 | 3425 | 66 |
| 3.38 | 2958 | 22 |
| 6.19 | 1616 | 31 |
| 6.35 | 1575 | 41 |
| 6.56 | 1524 | 79 |
| 6.71 | 1490 | 22 |
| 6.92 | 1445 | 33 |

j. 2-Bromo-3-methyl-4-amino-6-*t*-butylphenol (VIb)

| | | |
|---|---|---|
| 2.82 | 3546 | 63 |
| 2.93 | 3413 | 76 |
| 3.39 | 2950 | 37 |
| 6.19 | 1616 | 44 |
| 6.38 | 1567 | 47 |
| 6.73 | 1486 | 29 |
| 6.92 | 1445 | 43 |

O–H band was not broadened by chelation indicated that the nitro group was not *ortho* to the hydroxyl group.

Upon reduction, the nitro groups in Va and Vb were converted to amino groups as indicated[16] by the new N–H bands at 2.92 and 2.93 $\mu$ for VIa (Table IVh) and VIb (Table IV), respectively. The corresponding O–H and C–H and C=C bands remained about the same.

## Experimental

**Preparation of a 2-Chloro-3,4,6-trialkylphenol, 2-Chloro-3-methyl-4,6-di-*t*-butylphenol** (IIIa).—A solution of 138 g. (0.63 mole) of purified 3-methyl-4,6-di-*t*-butylphenol in 400 ml. of $CCl_4$ was treated with 85 g. (0.63 mole) of sulfuryl chloride at 0–5° for 3 hours. Evaporation of the solvent gave 153.6 g., m.p. 48–49°. This product was purified by crystallization from petroleum ether, m.p. 53–54°. A similar method was used for IIId.

**2-Bromo-3-methyl-4,6-di-*t*-butylphenol** (IIIb).—Eighty grams (0.5 mole) of bromine in 400 ml. of $CCl_4$ was added to 110 g. (0.5 mole) of 3-methyl-4,6-di-*t*-butylphenol at 0–5°. The residue obtained after removal of HBr and solvent was recrystallized from methanol-water. The yield was 95 g. (64%), m.p. 61.5–62°.

**2-Nitro-3-methyl-4,6-di-*t*-butylphenol** (IIIc).—A solution of 330 g. of 3-methyl-4,6-di-*t*-butylphenol in 300 ml. of benzene was treated at 5–10° for 2 hours with a solution prepared by mixing 142 g. of 70% nitric acid with 150 ml. of water. Evaporation of the benzene solution gave a brown crystalline solid (345 g.). This was precipitated as the sodium salt in aqueous methanol solution by the addition of sodium hydroxide and then sodium chloride. The sodium salt was dissolved in acetic acid and the free nitro compound (m.p. 80–81°, 246 g.) precipitated by the addition of water. Recrystallization from petroleum ether and methanol-water raised the m.p. to 83–84°.

**Preparation of Cyclohexadieneones, 2-Chloro-3-methyl-4-nitro-4,6-di-*t*-butyl-2,5-cyclohexadieneone** (IVa).—At 10°, a solution of 33 g. of 70% nitric acid in 100 ml. of acetic acid was added to an acetic acid (700 ml.) solution of 76.4 g. of IIIa. After one hour, ice was added to precipitate the product weighing 83 g. (93%), m.p. 89.5° dec. A petroleum ether crystallization gave light cream-colored crystals, m.p. 93° dec. A similar procedure was used for IVb, IVc and IVd.

**Cyclohexadieneone Decomposition, Conversion of IVa to 2-Chloro-3-methyl-4-nitro-6-*t*-butylphenol (Va) and 2-Chloro-3-methyl-6-*t*-butylquinone** (VII).—A solution of the cyclohexadieneone (57 g.) in 400 ml. of acetic acid containing 1 ml. of concentrated sulfuric acid was heated to boiling, treated with decolorizing carbon and filtered. Dilution with water gave a crude yield of 41.1 g. of IVa. A petroleum ether solution of this was extracted with 1% sodium hydroxide and the sodium salt of Va was precipitated by the addition of sodium chloride. This was dissolved in acetic acid and the free nitrophenol precipitated by water, yield 21 g., m.p. 84–86°.

Evaporation of the alkali-extracted petroleum ether solution gave 14 g. of an oily solid which was recrystallized twice from petroleum ether to give 2.2 g. of yellow crystals, m.p. 93–94°; after recrystallization from methanol m.p. 93.5–95°; mixed m.p. with 2-chloro-3-methyl-6-*t*-butylquinone, 93.5–94.5°.

Cyclohexadieneone decomposition in a more dilute solution produced the nitrophenol in a higher state of purity with little quinone formation. Ten grams of IVa in 200 ml. of acetic acid containing 0.5 ml. of concentrated sulfuric acid was heated to boiling. Cooling and dilution with water gave 7.6 g. (94%) of light yellow Va, m.p. 87°. The decomposition of IVb and IVc was carried out in a similar manner.

**2-Chloro-3-methyl-6-*t*-butylquinone.**—At room temperature, a solution of 10 g. (0.034 mole) of potassium dichromate in 40 ml. of water plus 20 ml. of concentrated sulfuric acid was added to 200 ml. of acetic acid containing 25 g. (0.098 mole) of IIIa. Dilution with water gave a precipitate (222 g.) which after recrystallizations from petroleum ether and methanol weighed 3.8 g., yellow crystals, m.p. 93.5–94.5°. Oxidation of IIIb also was accomplished using this procedure.

*Anal.* Calcd. for $C_{11}H_{13}O_2Cl$: C, 62.12; H, 6.16; Cl, 16.67; mol. wt., 212. Found: C, 62.44; H, 6.24; Cl, 16.89; mol. wt., 214.

**2-Chloro-3,4-dimethyl-4-hydroxy-6-*t*-butyl-3,5-cyclohexadieneone** (IVe).—A solution of 7 g. (0.033 mole) of IVd and 7 g. of sodium acetate trihydrate in 200 ml. of acetic acid was heated to boiling, cooled and diluted with water. The resulting solid was recrystallized three times from aqueous methanol; 2.7 g., m.p. 128–128.5°. This same product was obtained by heating an ethanol solution of IVd to boiling or by heating to boiling a solution of 2.6 g. of IVd in a dioxane solution containing 2.6 g. of sodium benzoate.

**Formation of Va by Nitration of IIIa.**—A solution of 12.6 g. (0.05 mole) of IIIa in 400 ml. of water was cooled to 10°

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[16] V. Z. Williams, *Rev. Sci. Instruments*, **19**, 135 (1948).

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

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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.