Oxidation of Alkoxyphenols. Part XI.[1] Further Observations on the Influence of an *o*-Methoxy-group

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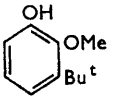
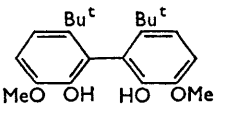
Ferricyanide oxidation of 3-t-butylguaiacol and of 4,6-di-t-butylguaiacol leads, respectively, to a polymer and a phenoxycyclohexadienone. Acid hydrolysis of the latter follows an unusual course. From 2-methoxy-1-naphthol a 1,1′-binaphtho-4,4′-quinone was obtained, and from 1-methoxy-2-naphthol a naphthyloxynaphthalenone. Ferric chloride oxidizes 3-methoxy-2-naphthol to a 1,1′-binaphthol. With lead tetra-acetate, 2-methoxy-1-naphthol gives 2-methoxy-1,4-naphthaquinone, 1-methoxy-2-naphthol gives 1-acetoxy-1-methoxy-1*H*-naphthalen-2-one, and with 3-methoxy-2-naphthol the chief products are the 1,1-diacetate and the 1,2-quinone. Frémy's salt oxidatively demethylates 4,6-di-t-butyl-guaiacol. No spiroketal trimers were obtained from these compounds, but co-oxidation of 2,2′-dihydroxy-3,3′-dimethoxy-5,5′-di-t-butylbiphenyl and 4-methoxy-2-t-butylphenol appears to give one.

In Part III [2] we reported that oxidation of 4-, 5-, and 6-t-butylguaiacols gave, respectively, a spiroketal, a polymer, and a 4,4′-biphenoquinone. We continued this comparison of the behaviour of *o*- and *p*-methoxyphenols on oxidation, with the determination of structural requirements for spiroketal formation in mind, and have now prepared and oxidised the remaining isomer, 3-t-butylguaiacol (I). This phenol was best obtained by nitration of 2-t-butylphenol followed by methylation, reduction, diazotization, and hydrolysis. Preparations involving Fries rearrangement of 2-t-butylphenyl acetate,[3] or benzoyl peroxide or lead tetra-acetate oxidation of 2-t-butylphenol were unsuccessful; mixtures of isomers were formed.

Oxidation of 3-t-butylguaiacol by alkaline ferricyanide or silver oxide led only to polymeric material. Thus, of the four t-butylguaiacols, only that with a substituent other than hydrogen at the 4-position gives a spiroketal. This result is in agreement with expectations based on the coupling constants of 2-methoxyphenoxy-radicals measured by Stone and Waters,[4] which show that the highest spin density in the ring is at carbon 4. Preferential oxidative coupling at this position should therefore occur, and if the 6-position, which has a relatively high spin density, is also available, as in 3- and 5-t-butylguaiacol, polymer formation is to be expected. The failure of 5-t-butylguaiacol to give a spiroketal may also be explained by the unfavourable steric requirement of the 6,6′-t-butyl groups in the prerequisite dimer (II).



(I)



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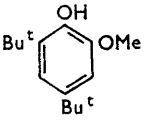

(III)

The oxidation of 4-methoxy-2,6-di-t-butylphenol has been examined in some detail by Cook [5] and Müller [6] and their co-workers; a red radical is produced which readily combines with oxygen to form a 4,4′-peroxide. Expecting similar behaviour we oxidized the isomeric 4,6-di-t-butylguaiacol (III) with alkaline ferricyanide. In light petroleum or benzene solution a green colour was produced, and evaporation left a yellow dimer containing no additional oxygen. The n.m.r. spectrum

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[1] Part X, F. R. Hewgill and D. G. Hewitt, *J. Chem. Soc.* (*C*), 1967, 726.

[2] F. R. Hewgill and B. S. Middleton, *J. Chem. Soc.*, 1965, 2914.

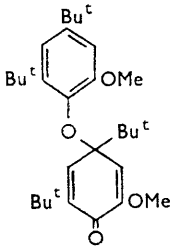
[3] Cf. S. S. Tiwari and B. N. Tewari, *J. Indian Chem. Soc.*, 1954, **31**, 79.

[4] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.

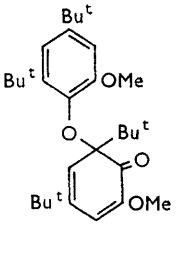
[5] C. D. Cook, D. A. Kuhn, and P. Fianu, *J. Amer. Chem. Soc.*, 1956, **78**, 2002.

[6] E. Müller and K. Ley, *Chem. Ber.*, 1955, **88**, 601.

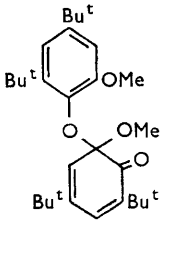
(carbon tetrachloride) of this dimer showed doublets at τ 3·06 and 3·38 (J = 2·2 c./sec.) and at 3·34 and 4·45 (J = 2·5 c./sec.) corresponding to four *meta*-coupled ring protons, two methoxy-groups (τ 6·54 and 6·55), and four t-butyl groups (τ 8·51, 8·66, 8·70, and 9·05). The similarity of the methoxyl chemical shifts, and the presence of one t-butyl resonance at high field are consistent with two (IVa and b) of the possible structures, but not with the third (IVc). Catalytic reduction, which gave only 4,6-di-t-butylguaiacol, supports the gross structure (IV). Structure (IVb), though it cannot



(IVa)



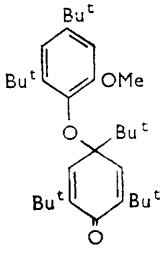
(IVb)



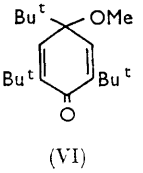
(IVc)

be excluded by the experimental evidence, is unlikely in view of Rieker's results,[7] which indicate that only phenols with an electron-withdrawing group in the *p*-position give rise to *o*-" quinol ethers."

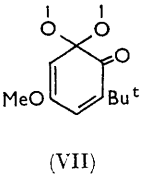
A most useful model in distinguishing between structures (IVa) and (IVc) by n.m.r. would have been compound (V). However, attempts to prepare this by oxidation of a mixture of 4,6-di-t-butylguaiacol and 2,4,6-tri-t-butylphenol, or by reaction of 4-bromo-2,4,6-tri-t-butylcyclohexadienone with the sodium salt of 4,6-di-t-butylguaiacol were unsuccessful. Similar difficulties have been observed [8] in the preparation of other hindered keto-ethers. In spite of this, other comparisons adequately support selection of structure (IVa). For compound (V) Matsuura [9] quotes chemical shifts of τ 8·77 (2Bu^t), 9·08 (1Bu^t), and 6·88 (OMe). The n.m.r. spectrum of bis-(1,3,5-tri-t-butylcyclohexa-2,5-dien-4-



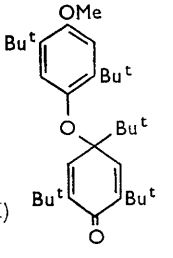
(V)



(VI)



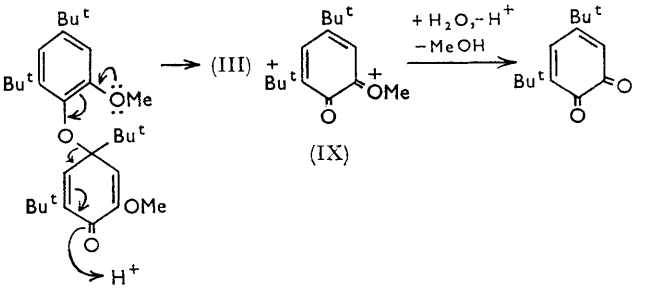
(VII)



(VIII)

one) peroxide (carbon tetrachloride) showed resonances at τ 8·73 (4Bu^t) and 9·14 (1Bu^t). Moreover, we have found [10,11] that a t-butyl group in compounds of the general structure (VII) has a chemical shift at no higher than τ 8·80, and this would be inconsistent with the assignment of structure (IVc).

Acid hydrolysis of the dimer below 50° gave 4,6-di-t-butylguaiacol, 3,5-di-t-butyl-1,2-benzoquinone, and presumably methanol, detected as formaldehyde by chromotropic acid after oxidation. The last two hydrolysis products are *prima facie* more consistent with structure (IVc), and in fact hydrolysis of aryloxy-dienones containing a t-butyl group on an sp^3 carbon as in compounds (V) and (VIII) leads to elimination of isobutene with production of a hydroxydiphenyl ether.[12,7] However, this generalisation appears to break down when *o*- or *p*-alkoxy-groups are present in the aromatic ring, as in the present case, and in other examples to be reported.[13] Here, the atypical reaction may be understood by acknowledging that electrons are more readily available from a methoxy- than from a t-butyl group, and the course of the reaction may be envisaged as in Scheme 1.



SCHEME 1

An alternative or subsidiary course involving protonation of the oxygen joining the rings would lead to the same result by way of a mesomeric form of the ion (IX). One cannot therefore decide between structures (IVa—c) on the basis of acid hydrolysis.* A similar situation obtains in the case of the trimer derived from 4-methoxy-2,5-di-t-butylphenol, and the claim made in Part IV [14] to thus distinguish between three possible isomers by acid hydrolysis is not valid. Other evidence presented there supports the structure given to the trimer.

As pointed out by Müller *et al.*[15] the use of ultraviolet spectroscopy for distinguishing between 2,4- and 2,5-dienones bearing a phenoxy-substituent is of doubtful value, as it is hard to identify the K band unambiguously. Though the spectrum of compound (IV) (in ethanol), with $\lambda_{max.}$ 228, 283, and 302 mμ (log ε 4·32, 3·91, and 3·84), is similar to that of compound (VIII) (in methanol) [15] as it should be, we feel that the n.m.r. evidence is the

* In a recent publication, K. Dimroth, H. Perst, K. Schlömer, K. Worschech, and K.-H. Müller (*Chem. Ber.*, 1967, **100**, 629) claim that *p*-aryloxydienones exhibit a doublet in the i.r. carbonyl region, and *o*-derivatives only a singlet. Bands at 1690 and 1660 cm.$^{-1}$ in the spectrum of compound (IV) are thus further support for structure (IVa).

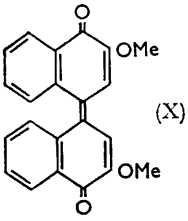
[7] A. Rieker, *Chem. Ber.*, 1965, **98**, 715.
[8] T. Matsuura and A. Nishinaga, *J. Org. Chem.*, 1962, **27**, 3072.
[9] T. Matsuura, *Bull. Chem. Soc. Japan*, 1964, **37**, 564.
[10] F. R. Hewgill, B. R. Kennedy, and D. Kilpin, *J. Chem. Soc.*, 1965, 2904.
[11] F. R. Hewgill and D. G. Hewitt, *J. Chem. Soc.*, 1965, 3660.
[12] T. Matsuura and H. J. Cahnmann, *J. Amer. Chem. Soc.*, 1960, **82**, 2055.
[13] C. J. R. Adderley and F. R. Hewgill, unpublished work.
[14] F. R. Hewgill and B. R. Kennedy, *J. Chem. Soc.*, 1965, 2921.
[15] (*a*) E. Müller, K. Ley, and G. Schlechte, *Chem. Ber.*, 1957, **90**, 2663; (*b*) cf. V. V. Ershov and A. A. Volod'kin, *Izvest. Akad. Nauk S.S.S.R., otdel. khim. Nauk*, 1963, 893, (*Chem. Abs.*, 1963, **59**, 7385).

most reliable criterion in distinguishing between these kinds of isomer.

The dimer (IVa) dissociates very readily to the 2-methoxy 4,6-di-t-butylphenoxy-radical; yellow solutions in light petroleum become green as the temperature is raised, and revert to yellow when cooled. Rast molecular weight determination gave a value of 239, which, compared with the required value of 471, shows complete dissociation at the melting point of camphor. Electron spin resonance (e.s.r.) measurements on the dimer showed a weak signal, $g = 2{\cdot}0042 \pm 0{\cdot}0001$, which indicates some dissociation in the solid state at room temperature.

As is the case with 4-methoxy-2,5-di-t-butylphenol,[16] oxidation of 4,6-di-t-butylguaiacol with Frémy's salt resulted in demethylation, to give 3,5-di-t-butyl-1,2-benzoquinone.

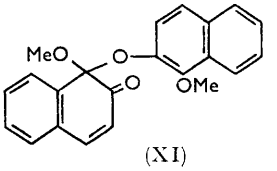
Examination of the effect of an *o*-methoxy-group on the oxidation of phenols was extended to the three isomeric *o*-methoxynaphthols. Although mixtures containing 2-methoxy-1-naphthol had been oxidised with lead dioxide and the binaphthoquinone (X) isolated,[17,18] oxidation of these compounds had not been further investigated until the recent observation of Brown, Lovie, and Thomson [19] that Frémy's salt oxidises 2-methoxy-1-naphthol to 2-methoxy-1,4-naphthaquinone and 1-methoxy-2-naphthol to 1,2-naphthaquinone, in agreement with our own findings.



(X)

Oxidation of 2-methoxy-1-naphthol with alkaline ferricyanide gave the quinone (X), which was reduced and methylated to give the corresponding dihydroxy- and tetramethoxy-compounds. An attempt to convert quinone (X) into a perylene quinone photolytically, as has been done for 3,3′-dimethyl-1,1′-binaphtho-4,4′-quinone,[20] was unsuccessful. Like Frémy's salt, lead tetra-acetate converts 2-methoxy-1-naphthol into 2-methoxy-1,4-naphthaquinone.

Previous preparations of 1-methoxy-2-naphthol [17,21,22] have given low yields, so we synthesized this compound by Friedel–Crafts acylation of 1-naphthol, followed by methylation, Baeyer-Villiger oxidation, and hydrolysis of the resulting acetate. Oxidation with alkaline ferricyanide gave the dimer (XI). The n.m.r. spectrum (deuteriochloroform) showed a complex absorption between τ 1·78 and 2·83 (10 H), two doublets at τ 3·13 (J = 8·9 c./sec., 1 aromatic H) and 3·78 (J = 10·4 c./sec. 1 vinylic H), and two methoxy-absorptions, at τ 6·02 and 6·43. Without spin-decoupling equipment the complementary low-field doublets could not be distinguished with certainty. The methoxy-signal at



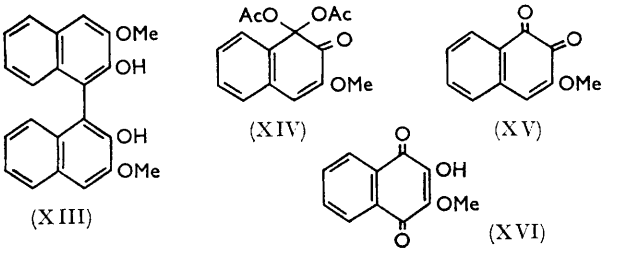
(XI) (XII)

τ 6·43 is consistent with the group's situation on a quaternary carbon. Reactions used to confirm this structure involved hydrogenation to the parent naphthol, and hydrolysis in acetic acid to give 1-methoxy-2-naphthol, methanol, and, in the presence of *o*-phenylenediamine, benzo[α]phenazine. 1,2-Naphthaquinone itself and 1-methoxy-2-naphthol were obtained after spontaneous decomposition of the dienone.

Oxidation of 1-methoxy-2-naphthol with lead tetra-acetate gave a product too unstable for analysis, but its n.m.r. spectrum (deuteriochloroform), showing a doublet of doublets at τ 2·63 and 3·82 (J = 10·4 c./sec., 2 vinylic H), a complex signal τ 2·38—2·67 (4 aromatic H), a methoxy-signal at τ 6·54, and an acetoxy-signal at τ 7·88, left little doubt that the compound was the naphthalenone (XII). Hydrogenolysis gave 1-methoxy-2-naphthol, and sublimation 1,2-naphthaquinone.

With these oxidants, 1,8-dimethoxy-6-methyl-2-naphthol gave only the corresponding *o*-quinone.[19]

Oxidation of 3-methoxy-2-naphthol with alkaline ferricyanide or silver oxide gave products which we could not purify, and which are probably polymeric. With ferric chloride the binaphthol (XIII) was obtained. Its structure was confirmed by demethylation to the known [23] 2,2′,3,3′-tetrahydroxybinaphthyl.



(XIII) (XIV) (XV) (XVI)

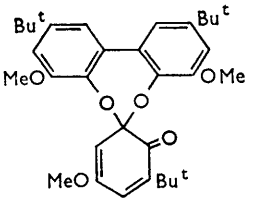
With lead tetra-acetate three products, (XIV), (XV), and (XVI), were obtained from 3-methoxy-2-naphthol. The n.m.r. spectrum (deuteriochloroform) of the first (XIV) showed four aromatic protons (τ 2·38—2·92), a vinylic proton (τ 3·55), a methoxy-group (τ 6·14), and a *gem*-diacetoxy-group (τ 7·96). The position of the latter was confirmed by hydrolysis with acetic acid to 3-methoxy-1,2-naphthaquinone. This, the second oxidation product, and 2-methoxy-1,4-naphthaquinone,

[16] E. Müller, H. Kaufmann, and A. Rieker, *Annalen*, 1964, **671**, 61.
[17] A. Bezdzik and P. Friedlander, *Monatsh.*, 1909, **30**, 271.
[18] H. Cassebaum and W. Langenbeck, *Chem. Ber.*, 1957, **90**, 339.
[19] A. G. Brown, J. C. Lovie, and R. H. Thomson, *J. Chem. Soc.*, 1965, 2355.
[20] B. R. Brown and A. H. Todd, *J. Chem. Soc.*, 1963, 5564.
[21] T. Bisanz, *Roczniki Chem.*, 1956, **30**, 111.
[22] K. H. Bell and H. Deuwell, *Austral. J. Chem.*, 1963, **16**, 101.
[23] H. W. Wanzlick, M. Lehmann-Herchler, and S. Mohrmann, *Chem. Ber.*, 1957, **90**, 2521.

isolated from the reaction with 2-methoxy-1-naphthol, are probably both artifacts produced by hydrolysis of the corresponding *gem*-diacetates, a reaction which we have previously shown to be especially easy for alkoxydienones.[10] The third product (XVI) almost certainly arises by aerial oxidation of 3-methoxy,1,2-naphthaquinone. Cooke and Owen [24] have shown that this reaction occurs very readily in alkaline solution.

These results show that the dominant factor in the behaviour of these naphthols on oxidation is the familiar directing effect associated with α- and β-naphthol. Thus, in the absence of e.s.r. measurements, spin densities in the naphthyloxy-radicals are probably of similar relative magnitude to the frontier electron densities calculated by Fukui and his co-workers.[25]

3-Methoxy-2-naphthol, which might reasonably have been expected to couple to give a spiroketal trimer on oxidation, may preferentially be converted to 2,8′-ethers of the type reported [26] for β-naphthol, though we were unable to purify the oxidation products. In an attempt to intercept this process we oxidized a mixture of 2,2′-dihydroxy-3,3′-dimethoxy-1,1′-binaphthyl and 4-t-butylguaiacol, hoping to obtain a mixed spiroketal. However, the only product isolated was the spiroketal [2] derived from 4-t-butylguaiacol itself. Too large a discrepancy in the rates of oxidation of the reactants may account for this failure. On the other hand, though the product could not be crystallised, oxidation of a mixture of 2,2′-dihydroxy-3,3′-dimethoxy-5,5′-di-t-butylbiphenyl and 4-methoxy-2-t-butylphenol with ferricyanide appears from the n.m.r. spectrum to have given the mixed spiroketal (XVII).



(XVII)

EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained with a Varian A 60 spectrometer at 60 Mc./sec. with tetramethylsilane as internal reference. Infrared and ultraviolet spectra were obtained with Perkin-Elmer 137 G and 137 UV instruments. Light petroleum had b. p. 55—60°.

3-t-Butylguaiacol.—2-t-Butylphenol (43·7 g.) in acetic acid (33 ml.) was added during 90 min. to a stirred mixture of nitric acid (32·5 ml.; 70%) and acetic acid (105 ml.) at −15°. The mixture was stirred for a further 2 hr. at this temperature, poured into water, and extracted with ether. The extract was washed with sodium hydrogen carbonate and water, the ether was removed, and the residue was steam-distilled. The distillate (4 l.) was extracted with ether; the extract was dried and distilled to give *2-nitro-6-t-butylphenol* (23 g.) as a yellow oil, b. p. 80°/0·5 mm. (Found: C, 61·6; H, 6·7; N, 7·3. $C_{10}H_{13}NO_3$ requires C, 61·5; H, 6·7; N, 7·2%), $\nu_{max.}$ (CS_2) 737 cm.$^{-1}$.

Treatment with dimethyl sulphate in acetone over anhydrous potassium carbonate gave *2-methoxy-3-t-butylnitrobenzene* as an orange oil, b. p. 92°/0·25 mm. (Found: C, 63·6; H, 7·3; N, 6·6. $C_{11}H_{15}NO_3$ requires C, 63·1; H, 7·2; N, 6·7%). Hydrogenation in ethanol over palladium–charcoal gave *2-methoxy-3-t-butylaniline*, a yellow oil, b. p. 64°/0·1 mm. (Found: C, 74·2; H, 9·5; N, 7·8. $C_{11}H_{17}NO$ requires C, 73·7; H, 9·6; N, 7·8%).

This amine (4 g.) was diazotized in aqueous sulphuric acid, and the diazonium salt was added dropwise to boiling sulphuric acid (100 ml.; 50%) and sodium sulphate (50 g.). The product, continuously removed by distillation, was extracted from the distillate with ether; the extract was washed with sodium hydrogen carbonate then water, and dried. The solvent was removed and the residue chromatographed on silicic acid; elution with light petroleum–ether (19 : 1) gave *3-t-butylguaiacol* (0·8 g.) as plates, m. p. 97·5° (from light petroleum) (Found: C, 73·3; H, 8·9. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%).

Oxidation of 3-t-Butylguaiacol.—A solution of 3-t-butylguaiacol (174 mg.) in ether (50 ml.) was shaken for 15 min. with a solution of potassium ferricyanide (0·80 g.) in aqueous sodium hydroxide (25 ml.: 2%). The ether was separated, washed with water, dried, and evaporated to leave a green-brown glass. Chromatography on alumina did not reveal any inhomogeneity. Molecular weight (Rast) was 791. The n.m.r. spectrum showed a variety of t-butyl, methoxy- and aromatic protons, but no vinylic protons. With sodium acetate in place of sodium hydroxide no oxidation occurred. Oxidation with silver oxide in ether gave a similar result to that with ferricyanide in sodium hydroxide.

Ferricyanide Oxidation of 4,6-Di-t-butylguaiacol.—4,6-Di-t-butylguaiacol (2·1 g.) in light petroleum (40 ml.) was shaken for 30 min. with potassium ferricyanide (6·0 g.) and sodium hydroxide (1·5 g.) in water (50 ml.). The green petroleum layer was separated, washed with water, dried, and evaporated to give *2-methoxy-4-(2-methoxy-4,6-di-t-butylphenoxy)-4,6-di-t-butylcyclohexa-2,5-dienone* (IVa) (1·96 g.) as yellow needles, m. p. 133·5—136° (from light petroleum) (Found: C, 76·6; H, 9·7. $C_{30}H_{46}O_4$ requires C, 76·6; H, 9·8%), $\nu_{max.}$ (Nujol) 1690 and 1660 cm.$^{-1}$; ($CHCl_3$) 1695 and 1665 cm.$^{-1}$. The use of benzene as solvent in the oxidation gave an identical result. No peroxide could be isolated when the oxidation was carried out in oxygen as described by Cook *et al.*,[5] and n.m.r. spectroscopy indicated that the product was a complex mixture.

Reactions of the Dienone (IVa).—Hydrogenation in ethanol over palladium–charcoal required 1·13 mol. of hydrogen, and gave 4,6-di-t-butylguaiacol.

A solution of the dienone (534 mg.) in acetic acid (10 ml.) was diluted with water (25 ml.) after 10 min. and distilled briefly. The distillate (5 ml.) was oxidised with permanganate, and then gave a positive test for formaldehyde with chromotropic acid. Similar tests on the dienone and its other hydrolysis products were negative. The residue was diluted and extracted with ether, and the extract was washed with sodium hydrogen carbonate, then water. Distillation gave 4,6-di-t-butylguaiacol. Similar hydrolysis of another

[24] R. G. Cooke and W. R. Owen, *Austral. J. Chem.*, 1962, **15**, 486.

[25] K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, 1952, **20**, 722; K. Fukui, T. Yonezawa, C. Nayata, and H. Shingu, *ibid.*, 1954, **22**, 1433.

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portion of dienone (without heat), followed by ether extraction, gave a product, which, on crystallisation from light petroleum afforded 3,5-di-t-butyl-1,2-benzoquinone (48 mg.).

Oxidation of 4,6-*Di-t-butylguaiacol with Frémy's Salt.*—A solution of 4,6-di-t-butylguaiacol (511 mg.) in acetone (50 ml.) was shaken with Frémy's salt (6·0 g.) in aqueous potassium dihydrogen phosphate (640 ml.; M/90) for 25 min. Extraction with chloroform gave 3,5-di-t-butyl-1,2-benzoquinone (50 mg.), m. p. 115—116° (from light petroleum) (lit.,[27] m. p. 113—114°). Infrared and ultraviolet spectra were identical with those reported.[28]

Attempted Preparation of 2,4,6-*Tri-t-butyl*-4-(2-*methoxy*-4,6-*di-t-butylphenoxy*)*cyclohexa*-2,5-*dienone* (with C. M. Turle).—(*a*) An equimolar mixture of 2,4,6-tri-t-butylphenol and 4,6-di-t-butylguaiacol was oxidised with manganese dioxide under nitrogen as described by Becker.[29] The only isolable product was bis-(1,3,5-tri-t-butylcyclohexa-2,5-dien-4-one) peroxide, m. p. 144—146° (lit.,[30] 148—149°).

(*b*) Equimolar quantities of sodium 2-methoxy-4,6-di-t-butylphenolate and 4-bromo-2,4,6-tri-t-butylcyclohexa-2,5-dienone were heated under reflux in dry dioxan under nitrogen for 3 hr.[15a] Though the solution became blue and sodium bromide precipitated, only 4,6-di-t-butylguaiacol and 2,4,6-tri-t-butylphenol could be isolated.

2-*Methoxy*-1-*naphthol.*—Lead tetra-acetate (65 g.) and 2-methoxynaphthalene (21 g.) were stirred in acetic acid (250 ml.) at 50° for 91 hr. Dilution with water, extraction with ether, and sublimation of the extract to remove 2-methoxynaphthalene, followed by distillation, gave 2-methoxy-1-naphthyl acetate (11·2 g.), b. p. 120°/0·2 mm., m. p. 70—72° (from methanol) (lit.,[31] 69·5—70·5°). When heated slowly the material changed from prisms to cubes at *ca.* 150° and had m. p. 185°.

Hydrolysis of the acetate in methanolic sulphuric acid gave 2-methoxy-1-naphthol as needles, m. p. 54—55° (from light petroleum) (lit.,[32] 53·5—54·5°), $\lambda_{max.}$ (EtOH) 237, 293sh., 302, and 331 mμ (log ε, 4·70, 3·62, 3·63, and 3·46). Thin-layer chromatography on silica gel eluted with benzene showed only one spot (R_F 0·49), while 1-methoxy-2-naphthol had R_F 0·24. The benzoate had m. p. 106·5—107° (lit.,[32] 104—105°).

Oxidation of 2-*Methoxy*-1-*naphthol.*—(a) *By alkaline ferricyanide.*—A solution of 2-methoxy-1-naphthol (0·9 g.) in ether (50 ml.) was shaken briefly with potassium ferricyanide (5 g.) and sodium hydroxide (1·3 g.) in water (50 ml.). The precipitate gave 3,3′-dimethoxy-1,1′-binaphtho-4,4′-quinone (51 mg.), m. p. 270—271° (lit.,[18] 240—245°), $\nu_{max.}$ ($CHCl_3$) 1625 and 1585 cm.$^{-1}$, $\lambda_{max.}$ ($CHCl_3$) 342 and 544 mμ (log ε 3·94 and 4·55), τ ($CDCl_3$) 6·12 (OMe) (Found: C, 76·3; H, 4·8; OMe, 17·2. Calc. for $C_{22}H_{16}O_4$: C, 76·7; H, 4·7; OMe, 18%).

Hydrogenation in acetic acid over palladium–charcoal required 1·02 mol. of hydrogen. Reduction with sulphur dioxide gave 4,4′dihydroxy-3,3′-dimethoxy-1,1′-binaphthyl, m. p. 260—261° (lit.,[18] 259—260°). Methylation with dimethyl sulphate gave 3,4,3′,4′-tetramethoxy-1,1′-binaphthyl, m. p. 151—152° (lit.,[18] 146°).

(b) *By lead tetra-acetate.* A solution of 2-methoxy-1-naphthol (316 mg.) and lead tetra-acetate (1·9 g.) in chloroform (22 ml.) and acetic acid (2 ml.) was set aside overnight. Dilution with water, extraction with chloroform (the extract was washed with sodium hydrogen carbonate, then water), and crystallisation from benzene–light petroleum gave 2-methoxy-1,4-naphthaquinone (197 mg.).

1-*Methoxy*-2-*naphthol.*—A solution of peracetic acid (21·3 g.) and sodium acetate (5·4 g.) in acetic acid (260 ml.) was added during 1 hr. to a stirred solution of 2-acetyl-1-methoxynaphthalene (33·6 g.) in acetic acid (40 ml.) at 41°. The solution was stirred for a further 14 hr. at this temperature, cooled, and treated with an excess of aqueous sodium bisulphite. Extraction with chloroform gave 1-methoxy-2-naphthyl acetate (18·8 g.), m. p. 92—93° (from ethanol) (lit.,[21] 91—92°). Hydrolysis as for 2-methoxy-1-naphthyl acetate gave 1-methoxy-2-naphthol, m. p. 92·5—93° (lit.,[2] 92°), τ ($CDCl_3$) 6·04 (OMe).

Oxidation of 1-*Methoxy*-2-*naphthol.*—(a) *By alkaline ferricyanide.* A solution of 1-methoxy-2-naphthol (2·95 g.) in ether (75 ml.) was shaken for 30 min. with potassium ferricyanide (14·0 g.) and sodium hydroxide (3·5 g.) in water (150 ml.). Separation and concentration of the ether gave 1-*methoxy*-1-(1-*methoxy*-2-*naphthyloxy*)-1H-*naphthalen*-2-*one* (0·62 g.) as yellow prisms, m. p. 135—137° [Found: C, 75·9; H, 5·4%); *M* (f.p. depression of cyclohexane), 340. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%; *M*, 346] $\nu_{max.}$ (CS_2) 1680 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 234, 284, 295, and 324 mμ (log ε, 4·84, 3·90, 3·91, and 3·98).

Hydrogenation of the naphthalenone in ethanol required 1·04 mol. of hydrogen and gave 1-methoxy-2-naphthol.

A sample of the naphthalenone (2·75 g.), kept at room temperature for 5 weeks, was chromatographed on alumina. Elution with benzene gave unchanged naphthalenone (0·58 g.) and 1-methoxy-2-naphthol (0·52 g.). Sublimation of the naphthalenone gave 1,2-naphthaquinone.

The naphthalenone was heated in acetic acid for 10 min. and gave methanol (detected as described earlier) and 1-methoxy-2-naphthol. A solution of the naphthalenone and *o*-phenylenediamine in acetic acid, set aside for 6 days, gave benzo[*a*]phenazine, m. p. and mixed m. p. 141—141·5°.

(b) *By lead tetra-acetate.* A solution of 1-methoxy-2-naphthol (405 mg.) and lead tetra-acetate (2·2 g.) in chloroform (22 ml.) and acetic acid (2 ml.) was set aside for 12 hr. The solution was washed with water and the chloroform layer and further chloroform extracts were washed with sodium hydrogen carbonate, then water. Evaporation gave yellow needles (522 mg.), which gave 1-*acetoxy*-1-*methoxy*-1H-*naphthalen*-2-*one* as yellow prisms, m. p. 101—102° (from ether) $\lambda_{max.}$ (EtOH) 233infl, 241, and 319 mμ (log ε 4·26, 4·27, and 3·94), $\nu_{max.}$ (CS_2) 1750 and 1685 cm.$^{-1}$. Spontaneous decomposition was evident after 3 hr., and the material was not analysed.

Hydrogenation of this acetate in ethanol over palladium–charcoal required 1·08 mol. of hydrogen, and gave 1-methoxy-2-naphthol. After 12 hr. at 100° the acetate had sublimed to give 1,2-naphthaquinone.

Oxidation of 3-*Methoxy*-2-*naphthol.*—(a) *By alkaline ferricyanide.* With various concentrations of sodium hydroxide and various reaction times only intractable tars were obtained.

(b) *By silver oxide.* A solution of 3-methoxy-2-naphthol

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(2 g.) in chloroform (20 ml.) was shaken for 50 hr. with silver oxide (3 g.) After filtration and chromatography of the filtrate on alumina, a golden-brown glass was obtained, *M* (f.p. depression of benzene), 480.

(c) *By ferric chloride.* Aqueous ferric chloride (5·6 g.) was added during 20 min. to a stirred suspension of 3-methoxy-2-naphthol (3·48 g.) in boiling water. Continuous extraction with chloroform and crystallisation from the same solvent gave 2,2′-*dihydroxy*-3,3′*dimethoxy*-1,1′-*binaphthyl* (243 mg.) as prisms, m. p. 255·5—256·5° [Found: C, 76·0; H, 5·3; OMe, 16·8%; *M* (Rast), 351. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2; OMe, 17·9%; *M*, 346], $\lambda_{max.}$ (EtOH) 235, 277infl., 286, 297, 313, and 327 mμ (log ε 5·08, 3·96, 4·01, 3·99, 3·77, and 3·84), $\nu_{max.}$ ($CHCl_3$) 3565 cm.$^{-1}$, τ ($CDCl_3$) 5·89 (OMe).

A solution of the binaphthyl (236 mg.) in acetic acid (15 ml.) and hydrobromic acid (10 ml.) was boiled under reflux for 6 hr. Evaporation of the solvent under reduced pressure and crystallisation of the residue from tetrahydrofuran gave 2,2′,3,3′-tetrahydroxy-1,1′-binaphthyl (91 mg.), infrared spectrum identical with that of an authentic sample.[23] Acetylation gave the tetra-acetate, m. p. and mixed m. p. 188°.

(c) *By lead tetra-acetate.* A solution of 3-methoxy-2-naphthol (2·0 g.) and lead tetra-acetate (10·7 g.) in chloroform (110 ml.) and acetic acid (10 ml.) was set aside for 17 hr. The solution was washed with water and sodium hydrogen carbonate; removal of the solvent left a red solid (2·66 g.). Recrystallisation from methanol gave a mixture of yellow cubes and red needles, and further recrystallisation from methanol, then acetone, gave 1,1-*diacetoxy*-3-*methoxy*-1H-*naphthalen*-2-*one* (384 mg.) as yellow cubes, m. p. 222·5—223° [Found: C, 62·5; H, 5·0%; *M* (Rast), 255. $C_{15}H_{14}O_6$ requires C, 62·1; H, 4·9%; *M*, 290], $\nu_{max.}$ ($CHCl_3$) 1760, 1705, and 1635 cm.$^{-1}$, $\lambda_{max.}$ (EtOH) 234 and 357 mμ (log ε 4·22 and 3·77). Hydrolysis of this material by boiling acetic acid gave 3-methoxy-1,2-naphthaquinone, m. p. 180—185°, infrared spectrum identical with that of an authentic sample.

The red needles were manually separated and gave 3-methoxy-1,2-naphthaquinone, m. p. 184—189° (from methanol) (lit.,[27] 185—186°). The infrared spectrum was identical with that of a sample prepared by the method of Teuber and Götz.[33]

Acidification of the original sodium hydrogen carbonate washings and extraction with ether gave material which was chromatographed on alumina. Elution with chloroform gave 2-hydroxy-3-methoxy-1,4-naphthaquinone, m. p. and mixed m. p. with material prepared by the method of Cooke and Owen [24] 152—153° (from ether–light petroleum).

Co-oxidation of 2,2′-*Dihydroxy*-3,3′-*dimethoxy*-1,1′-*binaphthyl and* 2-*Methoxy*-4-*t*-*butylphenol.*—A solution of the binaphthol (343 mg.) and the phenol (769 mg.) in benzene (50 ml.) was shaken for 30 min. with a solution of potassium ferricyanide (1·3 g.) and sodium hydroxide (1·3 g.) in water (50 ml.). After separation of the benzene layer and removal of the solvent, the residue was chromatographed on alumina. Elution with benzene–chloroform (4 : 1) gave 3′,4,8-trimethoxy-2,5′,10-tri-t-butyldibenzo[*d,f*][1,3]dioxepin-6-spiro-1′-cyclohexa-3′,5′-dien-2′-one, m. p. and mixed m. p.[2] 226—227°, as the only identifiable product.

Co-oxidation of 2,2′-*Dihydroxy*-3,3′-*dimethoxy*-5,5′-*di*-*t*-*butylbiphenyl and* 4-*Methoxy*-2-*t*-*butylphenol.*—A solution of the dihydroxybiphenyl (580 mg.) and the phenol (1·04 g.) in ether (50 ml.) was similarly treated. Elution with light petroleum–benzene (2 : 1) gave an orange glass (180 mg.), unchanged after extraction with aqueous sodium hydroxide and further chromatography, τ ($CDCl_3$) 2·85, 3·02 (doublets, J = 2·0 c./sec., 4 aromatic H), 3·36, 4·65 (doublets, J = 2·5 c./sec., 2 C:C*H*·C), 6·19 (2 OMe), 6·27 (OMe), 8·59 (2 Bu^t), and 8·71 (Bu^t), suggesting that the product was 4,5′,8-*trimethoxy*-2,3′,10-*tri*-*t*-*butyldibenzo*[d,f][1,3]*dioxepin*-6-*spiro*-2′-*cyclohexa*-3′-5′-*dienone*.

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