670. *Oxidation of Alkoxy-phenols. Part V.* Some Examples of Cross-coupling*

By F. R. Hewgill and D. G. Hewitt

Oxidation of a mixture of 4-methoxy-2- and -3-t-butylphenols with potassium ferricyanide gives the dioxepin (II), while oxidation with silver oxide gives the hydroxydiphenyl ether (VIII). The structures of these compounds are proved by degradation and synthesis, respectively. Some new reactions of the two isomeric dioxepins (I) and (II) are discussed.

Few examples of intermolecular coupling in the oxidation of phenol mixtures are recorded, though there seems little reason why this should not occur if the components oxidise at similar rates.[1] Previously [2] an unusual oxidation product (I) of 4-methoxy-3-t-butylphenol was described. Interest in the novel structure of this material and in the mechanism of its formation has led us to examine the oxidation products of a mixture of 4-methoxy-2- and -3-t-butylphenols. The reasons for the choice of these two phenols were twofold. First, a mixture of the isomers (known as BHA) is one of the most extensively used anti-oxidants for addition to fat. Secondly, the oxidation product of 4-methoxy-2-t-butylphenol is dimeric [3] and the phenol apparently cannot form a dioxepin, thus ensuring that the mixture of products would be more readily separable.

Alkaline potassium ferricyanide oxidation of a 1 : 2 mixture of 4-methoxy-2- and -3-t-butylphenols gives as the major products 2,2′-dihydroxy-5,5′-dimethoxy-3,3′-di-t-butylbiphenyl, the known [2] dioxepin (I), and a third compound considered to be (II). The last product is of interest because of the incorporation of a 4-methoxy-2-t-butylphenol residue. This product is also obtained in *ca.* 50% yield by alkaline ferricyanide or silver oxide oxidation of a mixture of 2,2′-dihydroxy-5,5′-dimethoxy-4,4′-di-t-butylbiphenyl (III) and 4-methoxy-2-t-butylphenol. The nuclear magnetic resonance (n.m.r.) spectrum shows two similar (τ, 6·07) and one different (τ, 6·37) methoxyl, two similar t-butyl groups (τ, 8·59) and a third in a different environment (τ, 8·71), two pairs of aromatic protons (τ, 3·05, 3·06) and a pair of coupled vinylic protons (τ, 3·49, 4·80: $J = 3·0$ c./sec.). The infrared carbonyl absorption was compatible with an $\alpha\beta$-unsaturated ketone.

Chemical evidence for the structure of the dioxepin (II) is provided by hydrolysis in acetic acid in the presence of 2,4-dinitrophenylhydrazine to the dihydroxybiphenyl (III) and the azophenol (IV). The mechanism of hydrolysis in acetic acid has previously been discussed [2] in relation to (I).

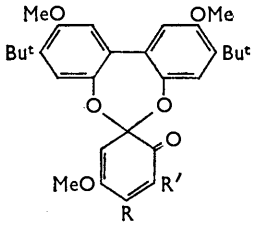
It is significant that hydrolysis of dioxepin (I) gave a mixture of azophenols [2] whereas dioxepin (II) under identical conditions gave only one. This is no doubt due to steric inhibition of nucleophilic attack at the carbonyl carbon atom of (II). This fact is further demonstrated by quantitative formation of the azophenol (IV) on treatment of the quinone

* Part IV, F. R. Hewgill and B. R. Kennedy, *J.*, 1965, 2921.

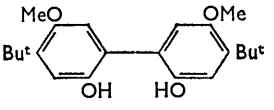
[1] C. G. Haynes, A. H. Turner, and W. A. Waters, *J.*, 1956, 2823.
[2] F. R. Hewgill, *J.*, 1962, 4987.
[3] J. Baltes and F. Volbert, *Fette und Seifen*, 1955, **57**, 660.

(VI) with 2,4-dinitrophenylhydrazine. In the unhindered isomeric quinone (VII) the directing influence of the methoxyl group becomes significant and a mixture,[2] in which the azophenol (V) predominates, results.

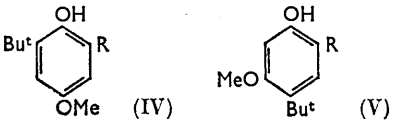
Silver oxide oxidation of a mixture of 4-methoxy-2- and -3-t-butylphenols differs significantly from ferricyanide oxidation. Considerably more polymer is formed and



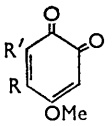
(I: R = Bu^t, R′ = H)
(II: R = H, R′ = Bu^t)



(III)



(IV) (V)
[R = N:NC$_6$H$_3$(NO$_2$)$_2$]

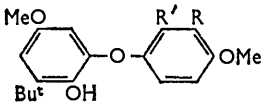


(VI: R = H, R′ = Bu^t)
(VII: R = Bu^t, R′ = H)

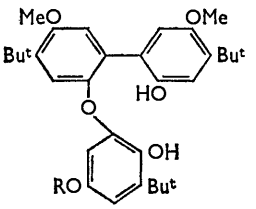
although the mixed dioxepin (II) is obtained in low yield, none of dioxepin (I) could be isolated. A third compound, believed to be the diphenyl ether (VIII), is now the major product. The latter is of interest in that it once again arises by cross-coupling of two different phenols.

The infrared spectrum of this diphenyl ether (VIII) shows only bonded hydroxyl absorption at 3550 cm.$^{-1}$ in agreement with a 2-hydroxydiphenyl ether system and excluding 5-hydroxylation, since an hydroxyl in the latter position would be expected to absorb at 3600 cm.$^{-1}$ as in the parent phenols. Further evidence for the bonded nature of the hydroxyl is provided by the slow rate of exchange with deuterium oxide (*ca.* half exchanged in five minutes). The n.m.r. spectrum does not distinguish between structures (VIII) and (IX). That structure (VIII) is correct has been demonstrated by condensation of 1-bromo-2,5-dimethoxy-3-t-butylbenzene with 4-methoxy-3-t-butylphenol, in *sym*-collidine using a cuprous oxide catalyst, to form the methyl ether of (VIII). Under these conditions, developed by Bacon and Hill [4] for the preparation of diphenyl ethers, 4-bromo-2-t-butylanisole failed to condense with 2,5-dimethoxy-3-t-butylphenol.

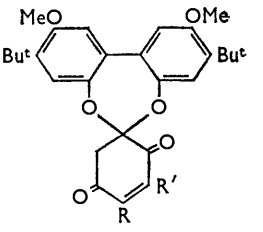
As expected,[2] hydrogenation of the dioxepin (II) gave a mixture containing the dihydroxybiphenyl (III) and an amorphous product, whose n.m.r. and infrared spectra are compatible with structure (X). Oxidation of this reduction product (X) with either silver oxide or alkaline ferricyanide gave blue solutions which very slowly faded to yellow, and from which the dioxepin (II) was isolated in good yield.



(VIII: R = Bu^t, R′ = H)
(IX: R = H, R′ = Bu^t)



(X: R = Me)
(XVI: R = H)



(XI: R = Bu^t, R′ = H)
(XII: R = H, R′ = Bu^t)

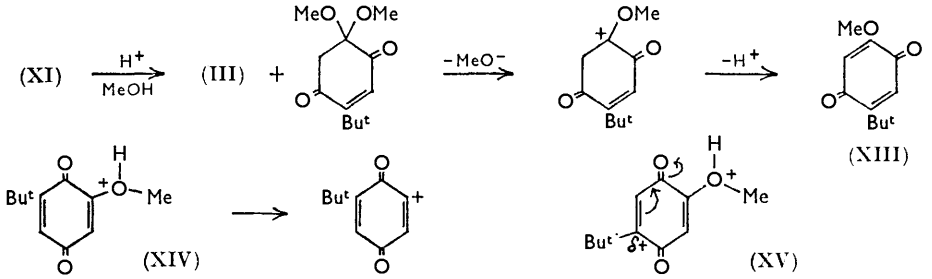
Hydrolysis of the dioxepins (I) and (II) with mineral acid catalysis follows an unexpected course and the products depend on the nature of the organic solvent. In aqueous acetone in the presence of hydrochloric acid, the cyclohexadienone methoxyl is

[4] R. G. R. Bacon and H. A. O. Hill, *J.*, 1964, 1108.

cleaved and the enediones (XI) and (XII), respectively, are formed. This reaction may be considered as hydrolysis of an enol ether, a reaction which is known to proceed readily. Each compound shows two distinct carbonyl absorptions in the infrared region, each compatible with an α-unsaturated γ-diketone system. The absence of hydroxyl from either the n.m.r. or infrared spectrum indicates that the compounds are entirely ketonic.

In methanol more extensive degradation results, both dioxepins giving rise to the dihydroxybiphenyl (III). 2-Methoxy-5-t-butyl-*p*-benzoquinone (XIII) is also formed on hydrolysis of (I) in methanol, but no quinone has been isolated from the hydrolysis of the dioxepin (II), possibly because the expected quinone, 2-methoxy-6-t-butyl-*p*-benzoquinone, is unstable under the conditions of the reaction. The latter quinone is possibly degraded because the protonated intermediate (XIV) cannot be stabilised as effectively as the isomeric intermediate (XV). Polarisation as shown in structure (XV) tends to stabilise the oxonium ion through hydrogen-bonding with the carbonyl oxygen. This leaves a partial positive charge on a tertiary carbon atom bearing an electron-donating t-butyl group. However, in the case of structure (XIV) the corresponding partial charge would lie on a secondary carbon atom. Thus the intermediate (XIV) is less stable than (XV) and would be more prone to lose methanol to form a carbonium ion which could react further.

Hydrolysis of the enedione (XI) in methanol with hydrochloric acid also gives the dihydroxy-biphenyl (III) and the quinone (XIII). As well as providing confirmation of structure (XI), this also indicates the possible course of the degradation of the dioxepin (I) in methanol. It appears that the first step is formation of the enedione (XI), followed by further reaction as shown in the annexed Scheme. We recently reported transketalisation reactions of this type, but in the reverse direction.[5] Methoxyl group migration to form the quinone (XII) is untenable, since hydrolysis of (I) in ethanolic hydrochloric acid gives 2-ethoxy-5-t-butyl-*p*-benzoquinone.



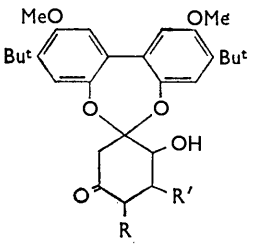
The structure of the enedione (XII) is established by hydrogenolysis to the trihydroxy-phenoxybiphenyl (XVI) which forms a triacetate and a pentamethyl ether, the latter identical to that derived from the trimethyl ether (X). Oxidation of the trihydroxy-compound (XVI) with silver oxide gives a product showing infrared absorption consistent with a 1,4-quinone. However, this product could not be purified since on heating in either methanol or light petroleum it rapidly, and almost quantitatively, rearranged to the enedione (XII).

In one hydrogenation of the enedione (XII) a second product was obtained in low yield. On the basis of the n.m.r. spectrum, which shows the presence of three t-butyl groups (τ, 8·58, 8·64, 8·93) and two similar methoxyls (τ, 6·03), and the infrared spectrum showing hydroxyl and carbonyl absorption, this compound is believed to be the hydroxy-ketone (XVII).

Subsequent reductions of the enedione (XII) gave only the trihydroxy-compound (XVI) and thus no further evidence has been obtained for structure (XVII). However, hydrogenation of the isomeric enedione (XI) gave no trihydroxy-compound but a

[5] F. R. Hewgill and D. G. Hewitt, *J.*, 1965, 1536.

quantitative yield of an hydroxy-ketone believed to be (XVIII). The n.m.r. spectrum of this compound (XVIII) shows two similar methoxyls (τ, 6·03), two similar t-butyl groups (τ, 8·58) and a third (τ, 8·93) apparently on a saturated carbon atom. Acetylation gave a monoacetate in which the acetate resonance showed abnormal shielding in the n.m.r. spectrum, appearing at τ, 8·29. Examination of models shows that this is only possible for the structure suggested, the acetate fuction being constrained in a position directly above one of the aromatic rings. Also in the spectrum of the acetate the two aromatic



(XVII: R = H, R' = Bu^t)
(XVIII: R = Bu^t, R' = H)

t-butyl groups are slightly separated (τ, 8·58, 8·62) presumably because of the relative proximity of the acetate group to one of them. That the dioxepin system remains intact during hydrogenation is demonstrated by the easy hydrolysis of the hydroxy-ketone (XVIII) to the dihydroxybiphenyl (III). It has not been possible to isolate the aliphatic residue of the third ring.

Experimental

Melting points were determined on a Kofler hot-stage apparatus. Infrared spectra were determined for carbon disulphide solutions on Perkin-Elmer Infracords, models 137 and 137G, and ultraviolet spectra for cyclohexane solutions on a Perkin-Elmer Spectrophotometer, model 137UV. Nuclear magnetic resonance spectra were determined on a Varian Associates A-60 spectrometer at 60 Mc./sec. for carbon tetrachloride solutions, using tetramethylsilane as an internal standard. Light petroleum had b. p. 56—60°. Alumina for chromatography had Activity II unless otherwise stated. Microanalyses were determined by the Australian Microanalytical Service, Melbourne.

Oxidation of 4-*Methoxy*-2- *and* -3-*t-butylphenol.*—(*a*) *In aqueous alkaline solution by ferricyanide.* A solution of potassium ferricyanide (3·3 g.) in water (50 ml.) and 10% aqueous potassium ferricyanide (100 ml.) was added dropwise to a stirred solution of 4-methoxy-2- (0·30 g.) and -3-t-butylphenol (0·60 g.) in benzene (50 ml.) under nitrogen. A transient blue colour appeared after each addition of ferricyanide. The benzene layer was separated, the aqueous layer extracted with benzene, and the combined benzene extracts washed with water, dried (Na_2SO_4), and evaporated to leave a yellow glass. Addition of light petroleum caused 2,2′-dihydroxy-5,5′-dimethoxy-3,3′-di-t-butylbiphenyl (20 mg.) to crystallise as prisms, m. p. and mixed m. p. with a sample prepared by ferricyanide oxidation of 4-methoxy-2-t-butylphenol, 230—230·5° (lit.,[3] 228°). The mother-liquors were adsorbed on alumina. Benzene–light petroleum (1 : 2) eluted 2,5′,10-*trimethoxy*-3,3′,9-*tri-t-butyldibenzo*[d,f]*dioxepin*-6-*spiro*-2′-*cyclohexa*-3′,5′-*dienone* (II) (0·25 g.) which crystallised from light petroleum as prisms, m. p. 213—215·5° (Found: C, 74·4; H, 8·0%; *M* (Rast), 522. $C_{33}H_{42}O_6$ requires C, 74·1; H, 7·9%; *M*, 535), $\lambda_{max.}$ 220, 260, 307, 340 (infl.) mμ (log ε 4·63, 4·22, 4·12, 3·34), $\nu_{max.}$ 1700 cm.$^{-1}$ (αβ-unsaturated ketone).

Benzene eluted 2,5′,10-trimethoxy-3,4′,9-tri-t-butyldibenzo[*d,f*]dioxepin-6-spiro-2′-cyclohexa-3′,5′-dienone (I) (50 mg.), m. p. alone and in admixture with an authentic sample,[2] 209—210° (from light petroleum).

More polar solvents eluted only non-crystalline material.

(*b*) *By silver oxide.* 4-Methoxy-2- (3 g.) and -3-t-butylphenol (6 g.) in ether (200 ml.) with a few drops of 10% aqueous sodium hydroxide were shaken with silver oxide (15 g.). After the original deep blue colour had faded to red-yellow the solution was filtered, dried (Na_2SO_4), and evaporated to give an orange glass which was adsorbed on alumina (Neutral, Activity III [6]). Elution with light petroleum gave a yellow solution which deposited colourless crystals (0·30 g.). Recrystallisation from light petroleum gave 2-*hydroxy*-4′,5-*dimethoxy*-3,3′-*di-t-butyldiphenyl*

[6] C. Djerassi, C. H. Robinson, and D. B. Thomas, *J. Amer. Chem. Soc.*, 1956, **78**, 5685.

ether (VIII) as needles, m. p. 116—117° (Found: C, 73·7; H, 8·3. $C_{22}H_{30}O_4$ requires C, 73·7; H, 8·4%), $\nu_{max.}$ 3550 cm.$^{-1}$ (bonded OH), τ, 8·58, 8·64 (Bu^t), 6·16, 6·37 (OMe), 3·47, 3·78 (doublets J = 3·0 c./sec., ArH) and a clearly defined AB_2 system. With acetic anhydride–pyridine the product gave an *acetate* as needles, m. p. 84—86° (from aqueous methanol) (Found: C, 71·7; H, 8·1. $C_{24}H_{32}O_5$ requires C, 72·0; H, 8·1%), $\nu_{max.}$ 1775 cm.$^{-1}$ (acetate). τ, 7·80 (acetate). Methylation gave 2,4′,5-*trimethoxy*-3,3′-*di-t-butyldiphenyl ether* as prisms, m. p. 66·5—68° (from methanol) (Found: C, 74·3; H, 8·7. $C_{23}H_{32}O_4$ requires C, 74·2; H, 8·7%), whose infrared spectrum showed no OH absorption.

Adsorption of the residue (6·5 g.) from the mother-liquors from the hydroxydiphenyl ether on alumina, followed by elution with light petroleum, gave 2,5′,10-trimethoxy-3,3′,9-tri-t-butyldibenzo[d,f]dioxepin-6-spiro-2′-cyclohexa-3′,5′-dienone (II) (0·20 g.), m. p. and mixed m. p. 213—215·5°.

Oxidation of 2,2′-*Dihydroxy*-5,5′-*dimethoxy*-4,4′-*di-t-butylbiphenyl* (III) *and* 4-*Methoxy*-2-*t-butylphenol*.—A mixture of the dihydroxybiphenyl (38·4 mg.) and the phenol (18·8 mg.) in benzene (10 ml.) was shaken with potassium ferricyanide (220 mg.) in water (5 ml.) and 5% aqueous sodium hydroxide (6 ml.) for 15 min. After 1·5 hr. the benzene layer was separated, washed with water, and dried (Na_2SO_4). Evaporation left a red gum which after adsorption on alumina and elution with benzene–light petroleum (1 : 2) gave the dioxepin (II) (30 mg.), m. p. and mixed m. p. 213—215·5°.

A similar result was obtained on oxidation of an ether solution of the two phenols with silver oxide.

Hydrolysis of the Dioxepin (II) *with Acetic Acid in the Presence of* 2,4-*Dinitrophenylhydrazine*.—The dioxepin (300 mg.) and 2,4-dinitrophenylhydrazine (260 mg.) were heated at 100° in acetic acid (50 ml.) for 0·5 hr. The red solution was then poured into water and extracted with ether. The ether extract was washed with sodium hydrogen carbonate solution, water, dried (Na_2SO_4), evaporated and the residue dissolved in benzene–light petroleum (1 : 1) and adsorbed on alumina. Benzene eluted a little yellow material followed by a purple band (50 mg.) which gave a crimson solution from which 2-(2,4-*dinitrophenylazo*)-4-*methoxy*-6-*t-butylphenol* (IV) was obtained as dark red rectangular plates, m. p. 242—243° (Found: C, 54·8; H, 5·0; N, 14·8. $C_{17}H_{18}N_4O_6$ requires C, 54·5; H, 4·9; N, 15·0%). Further elution with benzene gave 2,2′-dihydroxy-5,5′-dimethoxy-4,4′-di-t-butylbiphenyl (III), m. p. 168—169°, undepressed in admixture with an authentic sample.[2]

4-Methoxy-6-t-butyl-1,2-benzoquinone [7] (VI) (1·36 g.) on treatment with 2,4-dinitrophenylhydrazine (1·4 g.) as described above gave the same azophenol (2·6 g., 100%), m. p. and mixed m. p. 242—243°. This product was also obtained by treatment of 4-methoxy-2-t-butylphenol with diazotised 2,4-dinitroaniline.

Synthesis of 2,4′,5-*trimethoxy*-3,3′-*di-t-butyldiphenyl Ether*.—Bromine (8·9 g.) in acetic acid (150 ml.) was added dropwise during 1 hr. to a stirred solution of 4-methoxy-2-t-butylphenol (10 g.) in acetic acid (200 ml.). Stirring was continued for 20 min. while a stream of air was blown over the solution. The solution was then poured into water and the product (14 g.) extracted with ether. Methylation with dimethyl sulphate (10 g.) and anhydrous potassium carbonate (11 g.) in refluxing acetone gave 1-*bromo*-2,5-*dimethoxy*-3-*t-butylbenzene* (10 g.) as a pale yellow oil after distillation at 106°/0·95 mm., n_D^{22} 1·5389 (Found: C, 53·0; H, 6·4; Br, 29·0. $C_{12}H_{17}BrO_2$ requires C, 52·8; H, 6·3; Br, 29·3%).

The bromo-compound (0·545 g.) and 4-methoxy-3-t-butylphenol (0·433 g., 1·2 mol.) were heated for 63 hr. with cuprous oxide (0·33 g.) in refluxing *sym*-collidine (50 ml.). The mixture was cooled, poured into concentrated hydrochloric acid (100 ml.), and extracted with ether. The ether solution was washed with concentrated hydrochloric acid, water, and sodium hydroxide solution, dried (Na_2SO_4), and evaporated. The residue (0·716 g.) was adsorbed on alumina. Light petroleum eluted 1-bromo-2,5-dimethoxy-3-t-butylbenzene (60 mg.). Benzene–light petroleum (1 : 2) eluted 2,4′,5-trimethoxy-3,3′-di-t-butyldiphenyl ether (460 mg.), m. p. and mixed m. p. 66·5—68° (from methanol), having identical infrared and n.m.r. spectra to those of the methyl ether of (VIII) described previously.

Hydrogenation of the Dioxepin (II).—The dioxepin (22·6 mg.) in ethanol over 10% palladium on charcoal absorbed 1·05 ml. of hydrogen at 17° and 799 mm. (*i.e.*, 1·10 mol.). Evaporation of the filtered solution gave a glass. The product (250 mg.) from a larger scale hydrogenation

[7] F. R. Hewgill, B. R. Kennedy, and D. Kilpin, *J.*, 1965, 2904.

was dissolved in light petroleum and the solution washed several times with 10% sodium hydroxide solution and water, dried (Na_2SO_4), and evaporated to give 2-*hydroxy*-2′-(2-*hydroxy*-5-*methoxy*-3-*t*-*butylphenoxy*)-5,5′-*dimethoxy*-4,4′-*di*-*t*-*butylbiphenyl* (X) as a glass (Found: C, 74·0; H, 8·6. $C_{33}H_{44}O_6$ requires C, 73·9; H, 8·3%), $\nu_{max.}$ 3550 (bonded OH), shoulder at 3600 cm.$^{-1}$ (weak free OH). With acetic anhydride–pyridine the product gave a *diacetate* as a glass after chromatography on alumina (Found: C, 71·7; H, 8·1. $C_{37}H_{48}O_8$ requires C, 71·6; H, 7·8%). Treatment with dimethyl sulphate and potassium carbonate in refluxing acetone during 48 hr. gave 2,5,5′-*trimethoxy*-2′-(2,5-*dimethoxy*-3-*t*-*butylphenoxy*)-4,4′-*di*-*t*-*butylbiphenyl* as prisms, m. p. 166·5—167·5° (from benzene–methanol) (Found: C, 74·7; H, 8·7. $C_{35}H_{48}O_6$ requires C, 74·4; H, 8·6%). The infrared spectrum showed no OH absorption.

Acidification of the alkaline washings of the hydrogenated solution gave 2,2′-dihydroxy-5,5′-dimethoxy-4,4′-di-t-butylbiphenyl (33 mg.), m. p. and mixed m. p. 168—169°.

Oxidation of the Reduction Product.—The amorphous reduction product (10 mg.) in ether (5 ml.) was shaken with silver oxide (40 mg.) until the original deep blue colour had faded to yellow (*ca.* 4 hr.). Evaporation of the filtered solution gave the dioxepin (II) (8 mg.), m. p. and mixed m. p. 212—214°.

A similar result was obtained by potassium ferricyanide oxidation.

Hydrolysis of the Dioxepins by Mineral Acid.—(*a*) *In acetone.* 2,5′,10-Trimethoxy-3,3′,9-tri-t-butyldibenzo[*d*,*f*]dioxepin-6-spiro-2′-cyclohexa-3′,5′-dienone (II) (109 mg.) was allowed to stand for 24 hr. at room temperature in acetone (25 ml.) containing 10% hydrochloric acid (5 ml.). The orange solution was then concentrated to 10 ml., poured into water, and extracted with ether. Evaporation of the dried (Na_2SO_4) ether solution gave 2,10-*dimethoxy*-3,3′,9-*tri*-*t*-*butyldibenzo*[d,f]*dioxepin*-6-*spiro*-1′-*cyclohexa*-3′-*ene*-2′,5′-*dione* (XII) as small cream plates, m. p. 224—225° (from light petroleum) (Found: C, 73·5; H, 7·7. $C_{32}H_{40}O_6$ requires C, 73·8; H, 7·7%), $\lambda_{max.}$ 218, 233(sh), 258 (infl.), 303 mμ (log ε 4·58, 4·47, 4·23, 4·04), $\nu_{max.}$ 1700, 1730 cm.$^{-1}$ (α-unsaturated γ-diketone). τ 3·20 (vinylic H), 6·67 (–CO–CH_2–).

The isomeric dioxepin (I) (112 mg.) under the same conditions gave 2,10-*dimethoxy*-3,4′,9-*tri*-*t*-*butyldibenzo*[d,f]*dioxepin*-6-*spiro*-1′-*cyclohexa*-3′-*ene*-2′,5′-*dione* (XI) (90 mg.) as pale yellow prisms (from methanol), which changed to squat prisms at 200—203° and had m. p. 208—211° (Found: C, 73·7; H, 7·9%), $\lambda_{max.}$ 218, 233(sh), 259 (infl.), 303 mμ (log ε 4·55, 4·44, 4·20, 4·01), $\nu_{max.}$ 1700, 1720 cm.$^{-1}$ τ 3·44, 6·80.

(*b*) *In methanol.* Dioxepin (I) (3·4 g.) was heated for 3 hr. in refluxing methanol (300 ml.) containing 20% hydrochloric acid (50 ml.). The mixture was concentrated to 200 ml., poured into water, and extracted with ether. The product was adsorbed on alumina. Benzene–light petroleum (1 : 2) eluted a brown solution which deposited yellow crystals of 2-methoxy-5-t-butyl-*p*-benzoquinone (XIII) (0·20 g.), m. p. and mixed m. p. with an authentic sample,[7] 162—163°, after concentration and addition of light petroleum to the eluate. Methanol eluted 2,2′-dihydroxy-5,5′-dimethoxy-4,4′-di-t-butylbiphenyl (III) (0·92 g.), m. p. and mixed m. p. 169—170°.

Under the same conditions, the dione (II) gave only the dihydroxybiphenyl (III). No quinone could be isolated.

2,10-Dimethoxy-3,4′,9-tri-t-butyldibenzo[*d*,*f*]dioxepin-6-spiro-1′-cyclohexa-3′-ene-2′,5′-dione (XI) (140 mg.) was treated with methanolic hydrochloric acid as described above and gave 2-methoxy-5-t-butyl-*p*-benzoquinone (XIII) (10 mg.) and the dihydroxybiphenyl (III) (75 mg.).

(*c*) *In ethanol.* Using the procedure described in (b), but with ethanol as solvent, (I) (0·7 g.) gave 2,2′-dihydroxy-5,5′-dimethoxy-4,4′-di-t-butylbiphenyl (0·2 g.) and 2-ethoxy-5-t-butyl-*p*-benzoquinone (0·1 g.), m. p. 153—154°, undepressed on admixture with an authentic sample.[7]

Stability of 2-*Methoxy*-6-*t*-*butyl*-p-*benzoquinone.*—The quinone[7] (107 mg.) was heated for 3 hr. in refluxing methanol (25 ml.) containing 20% hydrochloric acid (5 ml.). Dilution with water followed by extraction with ether gave an orange crystalline solid, m. p. 94—125°, $\nu_{max.}$ 3400 (bonded OH), 1655 cm.$^{-1}$ (bonded C=O). There was no absorption attributable to methoxyl groups. Repeated crystallisation raised the m. p. but did not substantially improve the purity. The product was adsorbed on alumina. Benzene eluted unchanged quinone (10 mg.), m. p. and mixed m. p. 84—86°. Acetic acid eluted strongly adsorbed material which failed to crystallise.

The isomeric quinone (XIII) after treatment under the same conditions was recovered quantitatively.

Reduction of the Hydrolysis Products.—Hydrogenation of 2,10-dimethoxy-3,3′,9-tri-t-butyldibenzo[*d*,*f*]dioxepin-6-spiro-1′-cyclohexa-3′-ene-2′,5′-dione (XII) (150 mg.) in ethanol over 10%

palladium on charcoal gave a glass which was adsorbed on alumina. Benzene eluted *2′-hydroxy-2,10-dimethoxy-3,3′,9-tri-t-butyldibenzo*[d,f]*dioxepin-6-spiro-1′-cyclohexan-5′-one* (XVII) (20 mg.), as colourless prisms, m. p. 235—237° (from benzene–light petroleum) (Found: C, 73·7; H, 8·8. $C_{32}H_{44}O_6$ requires C, 73·3; H, 8·5%), $\nu_{max.}$ 3580 (OH), 1730 cm.$^{-1}$ (C=O). Benzene–chloroform (1 : 1) eluted *2-hydroxy-(2,5-dihydroxy-3-t-butylphenoxy)-5,5′-dimethoxy-4,4′-di-t-butylbiphenyl* (XVI) (100 mg.), which crystallised as rectangular plates, m. p. 187·5—188·5° (from benzene–light petroleum) (Found: C, 73·7; H, 8·2. $C_{32}H_{42}O_6$ requires C, 73·5; H, 8·1%), $\nu_{max.}$ 3550 (bonded OH), 3595 cm.$^{-1}$ (weak free OH). Acetylation gave a *triacetate* as plates, m. p. 184—185·5° (from benzene–light petroleum) (Found: C, 70·3; H, 7·4. $C_{38}H_{48}O_9$ requires C, 70·3; H, 7·5%), $\nu_{max.}$ 1770 cm.$^{-1}$ (acetate). Methylation gave a pentamethyl ether, identical with the pentamethyl ether, m. p. 166·5—167·5°, described previously.

The trihydroxyphenoxybiphenyl (XVI) (100 mg.) in ether (10 ml.) was shaken with silver oxide (200 mg.) for 5 min. The yellow solution was filtered and evaporated to give an orange glass, $\nu_{max.}$ 3570 (weak free OH), 3500 (bonded OH), 1680, 1650 cm.$^{-1}$ (quinone C=O). This product could not be further purified, since heating in solvents caused quantitative rearrangement to the less soluble ene-dione (XII), m. p. and mixed m. p. 224—225°.

On subsequent hydrogenations of (XII), only the trihydroxyphenoxybiphenyl was obtained.

Hydrogenation of the isomeric dioxepin (XI) (100 mg.) gave *2′-hydroxy-2,10-dimethoxy-3,4′,9-tri-t-butyldibenzo*[d,f]*dioxepin-6-spiro-1′-cyclohexan-5′-one* (XVIII) (95 mg.) which crystallised as needles, m. p. 138—140° (from aqueous methanol) (Found: C, 72·8; H, 8·3. $C_{32}H_{44}O_6$ requires C, 73·3; H, 85%), $\nu_{max.}$ 3600, 1725 cm.$^{-1}$. Acetylation gave an *acetate* as needles, m. p. 194—196° (from light petroleum) (Found: C, 72·4; H, 8·2. $C_{34}H_{36}O_7$ requires C, 72·1; H, 8·2%), $\nu_{max.}$ 1725 (C=O), 1750 cm.$^{-1}$ (aliphatic acetate). The cyclohexanone (XVIII) (120 mg.) was heated in refluxing methanol (50 ml.) containing 20% hydrochloric acid (5 ml.) for 30 min. Dilution with water and extraction with ether gave 2,2′-dihydroxy-5,5′-dimethoxy-4,4′-di-t-butylbiphenyl (III) (70 mg.), m. p. and mixed m. p. 169—170°.

We thank General Motors-Holdens Pty. Ltd. for a Post-graduate Research Fellowship to D. G. H.

School of Chemistry, University of Western Australia,
Nedlands, Western Australia. [*Received, December 14th,* 1964.]