*Tetrahedron* Vol. 27, pp. 1875 to 1883. Pergamon Press 1971. Printed in Great Britain

# REACTION OF *ORTHO* ALKENYL- AND ALKYLPHENOLS WITH 2,3-DICHLORO-5,6-DICYANOBENZOQUINONE (DDQ)

## SYNTHESES OF 2,2-DIALKYLCHROMENES

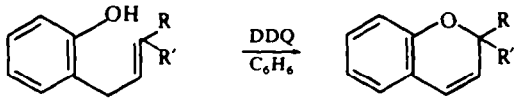
G. CARDILLO, R. CRICCHIO* and L. MERLINI†

Politecnico, Istituto di Chimica‡, 20133 Milano, Italy

(*Received in the UK* 20 *December* 1970; *Accepted for publication* 28 *December* 1970)

**Abstract**—The reaction of γ,γ-disubstituted ortho α,β-alkenyl, β,γ-alkenyl and alkylphenols with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in boiling $C_6H_6$ gave 2,2-dialkylchrom-3-enes. Lack of substitution at γ position usually inhibited the reaction. Thymol and 2,6-diisopropylphenol gave nuclear coupling products, whereas the spiropyran IV was obtained from 2-propenylphenol. The remarkable influence of the solvent on the products of the reaction is shown in the case of 2-isoamyl-5-heptylphenol. The possible mechanisms of the reaction are discussed.

OUR interest in the synthesis of natural chrom-3-enes led us recently to attempt[1,2] the cyclodehydrogenation of γ,γ-dialkylallylphenols with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in boiling $C_6H_6$, a reaction envisaged by Turner[3] and realized later by McCorkindale *et al.*[5]




I II

The successful results obtained by ourselves and others[6] induced us to investigate this reaction more deeply with the aim of extending its potentiality and obtaining mechanistic information. This was a more complex task than expected, we report here the first, preparative results.

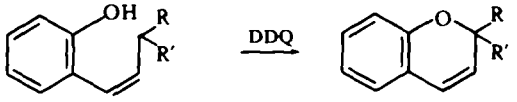
The obvious extension of the reaction to simpler *ortho* β,γ-alkenylphenols gave negative results. 2-but-2—enyl- (I, R = $CH_3$, R′ = H), 2-allyl- (I, R = R′ = H) and 2(1—phenyl-3′-allyl)-phenol, when reacted with 1-2 moles of DDQ in boiling $C_6H_6$ for many hrs remained unchanged. A trace of a compound (MW 222), most probably 4-phenylcoumarin, was obtained from the latter. On the other hand, a whole series of o-cinnamylphenols (I. R = $C_6H_5$, R′ = H) gave the corresponding flav-3-enes in good yield.[2] Substitution at γ carbon thus seems to play an important role in the reactivity of these phenols.

* Present address: Lepetit SpA, Milano.

† To whom enquiries should be addressed.

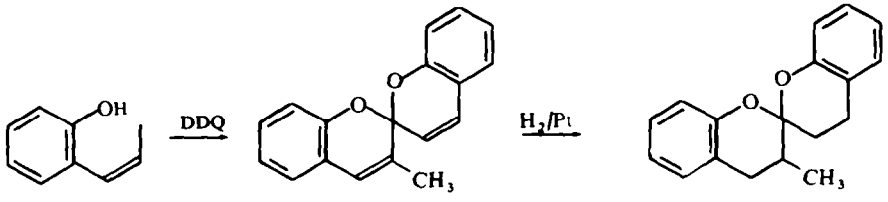
‡ Centro del C.N.R. per lo Studio delle Sostanze Organiche Naturali.

Another series which we investigated were *ortho* α,β-alkenylphenols. We expected attack of the quinone at the γ position, a vinylogous benzylic carbon.



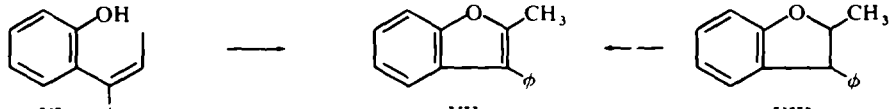

III

2-(3-methylbut-1-enyl)-phenol (III, R = R′ = Me) gave 2,2-dimethylchromene in 40–50% yield, as was expected*, but no reaction was given by 2-(but-1-enyl)-phenol (III, R = H, R′ = Me). However, 2-propenylphenol (III, R = R′ = H), treated with DDQ in $C_6H_6$ for 24 hr, gave a new dimeric compound. From the MS and NMR structure IV was inferred. Confirmation was by catalytic hydrogenation to V, and




IV V

by comparison with authentic samples of IV and V, prepared by condensation of methyl acetoacetate with salicylic aldehyde.[8] We have no clear explanation for this particular result. Recent reports[9] on the oxidation of propenylbenzene to cinnamaldehyde by DDQ might suggest that the corresponding aldehyde could be an intermediate. Further work is in progress to clarify this point, and to explore the potentiality of this reaction for the preparation of spiropyrans. From 2-(1-phenylpropenyl)-phenol (VI) 2-methyl-3-phenyl-benzofuran was obtained in 80% yield. The structure was confirmed by the preparation of the same compound by dehydrogenation with DDQ of 2-methyl-3-phenylcoumaran.[10]




VI VII VIII

Several examples of o-alkylphenols were then examined. 2-(3-Methylbutyl)-5-heptylphenol (IX, R = Me, R′ = n-$C_7H_{15}$), 2-(3-methylpentyl)-phenol (IX, R = Et, R′ = H) and 2,4-digeranyl-6-formylresorcinol (X) gave the corresponding chromenes in 50–60% yield. This double dehydrogenation appears to be useful as a new synthesis of 2,2-dialkylchromenes starting from readily accessible o-alkylphenols. Again in

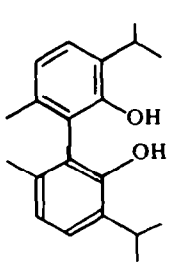
* A similar result was recently obtained by Dudley and Chiang on isolapachol.[7]

this series lack of substitution at $C_3$ in the side chain inhibited the reaction. 2-propyl (XI), 2-butyl (XII), 2-(1-methylpropyl) (XIII), 2-(1-phenylpropyl)-phenol (XIV) and 4-indanol (XV) gave practically no reaction in boiling $C_6H_6$. Only traces of a dimer

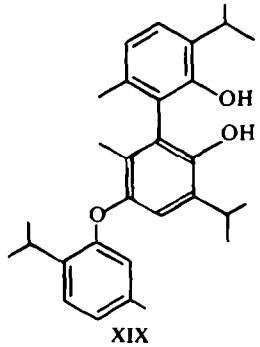
IX

with a molecular weight 2M–4 (a bis-quinone from p–p- coupling?) was obtained from XIII. Change of solvent to dioxane in the case of XI and XII and to MeOH for XIII did not improve the results.

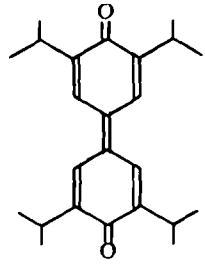
The striking influence of the substitution was furthermore revealed by the behaviour of thymol (XVI) and 2,6-diisopropyl-phenol (XVII). Thymol, depending on the phenol/DDQ molar ratio, gave the o–o coupling product XVIII and the trimer XIX. The structure of the latter was tentatively assigned on the basis of the MS, the presence of two acetylable hydroxyls and the NMR, even though a complete analysis of the aromatic protons pattern was not performed. The diphenoquinone XX[11] was obtained quantitatively from 2,6-diisopropylphenol, apparently through the p–p coupling product. Thus in these cases the classical nuclear coupling, usually obtained with one-electron oxidants, was the preferred reaction.



XVIII

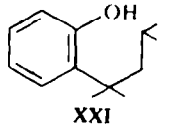


XIX

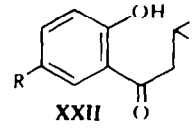


XX

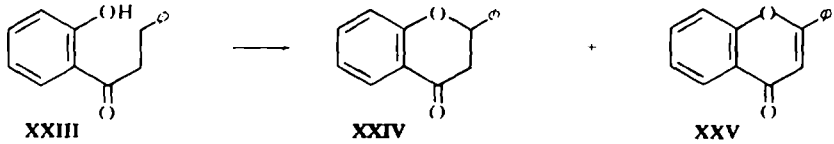
To obtain information on the reactivity of the γ position, the two phenols XXI and XXII (R = Me) were treated with DDQ in $C_6H_6$, but neither reacted. In MeOH, XXII (R = Me) gave the corresponding aldehyde (XXII, R = CHO), thus showing



XXI



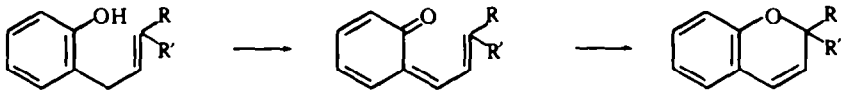
XXII



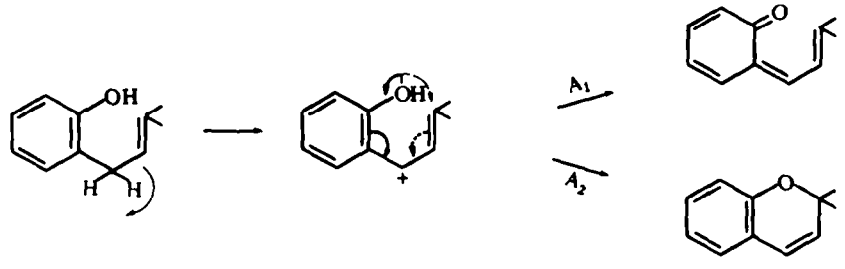
XXIII XXIV XXV

that the γ position was even more resistant to the oxidation than the aromatic Me. 2'-hydroxydihydrochalcone (XXIII), where the γ position is also benzylic, was attacked only in MeOH, to give, in low yield, a mixture of flavanone (XXIV) and flavone (XXV) the former most probably coming from the acid cyclization of the primary dehydrogenation product 2'-hydroxychalcone, and the latter from the dehydrogenation of XXIV itself.

Ollis ans Sutherland[4] and later Turner[3] suggested that the biogenesis of natural 2,2-dimethylchromenes from γ,γ-dimethylallylphenols could proceed through the formation of an o-quinonemethide, which can perform an electrocyclic ring closure to the chromene:



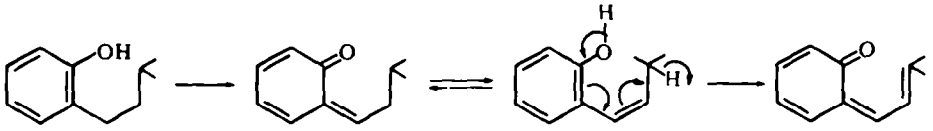

Evidence has recently accumulated on the close relationship between o-quinoneallides and chromenes. The existence of a thermal and photochemical equilibrium has been established,[12,13] and the intermediacy of quinoneallides in some syntheses of chromenes demonstrated[13–15] or shown to be probable.[16,17] Whether these quinones are formed in the reaction with DDQ and how they are formed, is still open to question.* The first step in the reaction seems to the formation of a charge-transfer complex between the strong electron acceptor DDQ and the donor phenol.[18] The colours form when DDQ is added to the donors and are ascribed to such a complex, which can breakdown afterwards with a two- or one-electron process, we observed this in many cases. In our preceeding paper,[1] where the dehydrogenation of γ,γ-dimethylallyphenols was reported, we indicated a scheme ($A_1$) that followed the suggestions of Turner[3] and was consistent with the two-stage ionic process proposed by Jackman, Braude and Linstead[19] for the dehydrogenation of hydroaromatic compounds and of allylic alcohols. The quinone can abstract a hydride ion from the



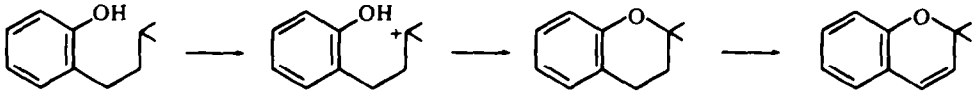

benzylic position, and loss of a proton gives the quinonemethide. The path indicated by dotted lines cannot be excluded, it has been proposed for this reaction and in the syntheses of chromenes involving the formation and ring closure of benzylic alcohols.[20]

* In some cases, however, such quinonemethides were isolated (see H. D. Becker, *J. Org. Chem.* **34**, 1211 (1969) and D. L. Coffen and P. E. Garrett, *Tetrahedron Letters* 2043 (1969).

It was the suggestion of this scheme that prompted us to try the reaction of DDQ with α,β-alkenylphenols, where the γ-H occupies a vinylogous position with respect to the benzylic one and should be easily abstracted, and also on o-alkylphenols, where the process can be repeated:



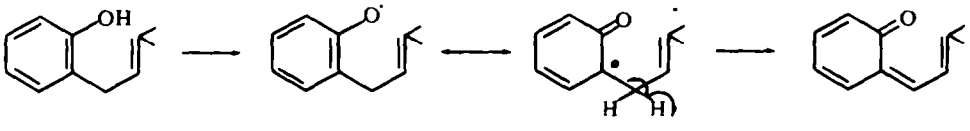
In o-propyl and o-butylphenol, where the abstraction of the γ-hydrogen would be less easy, because of the lesser stabilization of the secondary cation, at least the dehydrogenation of the chain to an α,β-unsaturated compound was expected. The failure of their reaction raised the question whether the first attack could be on the γ carbon, thus giving a chroman, which is then dehydrogenated to chromene:



(B)

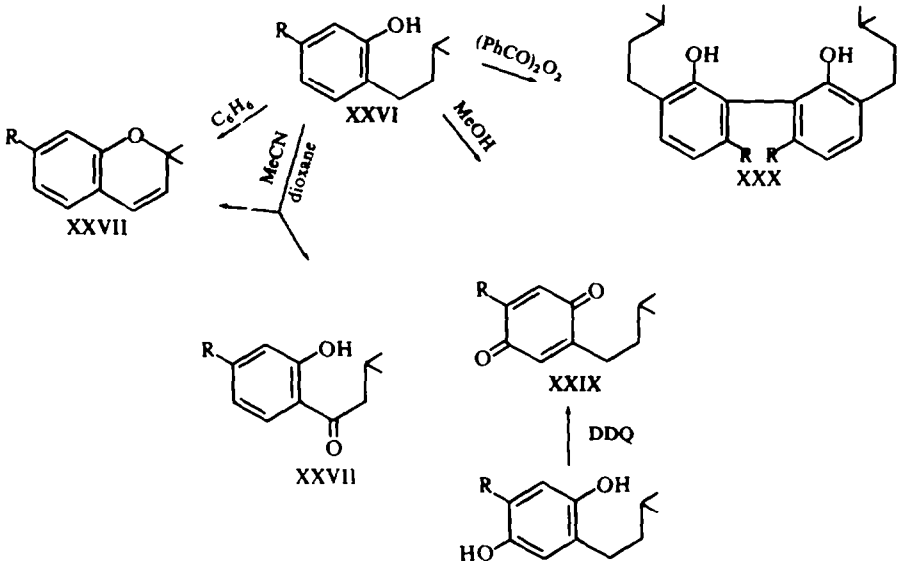
Against this hypothesis is the unreactivity of compounds XXI and XXII, and the rather variable nature of the dehydrogenation reaction of chromans. Even though we obtained good results in some instances,[1] flavan and 7-hydroxychroman, for example, are not dehydrogenated in boiling $C_6H_6$. Moreover, the results of the reaction with DDQ in MeCN, given below, seem to favour a primary attack on the benzylic hydrogen.

Another set of results has been produced by Becker,[22] whose studies on the contrary, point out the importance of the one-electron process in the oxidation of phenols with DDQ in MeOH, even though these results were obtained on phenols without ortho benzylic hydrogens. It must be remarked here that of the great deal of work so far dedicated to the oxidation of phenols, almost nothing was done on o-alkylphenols, most of the interest being devoted to nuclear coupling of hindered phenols.[13] Becker gave evidence (ESR and UV) for formation of phenoxy radicals, which can disproportionate to the starting phenol and to a *para* quinone-methide. If phenoxy radicals are formed as primary products in our reaction, two other mechanisms of formation of a quinone-methide can then be written, *via* disproportionation,[22,24] or *via* oxidation



of the radical by the quinone, as it was suggested by Strickson and Leigh for chromyl chloride oxidations (C).[25]

However the determinant solvent effect on the nature of the reaction products indicates that different mechanisms are possible in different solvents precluding generalizations. We have not yet systematically investigated the effect of a range of solvents on the reactivity of a series of phenols, but we report the striking example of 2-isoamyl-5-heptylphenol (XXVI), which gives the chromene XXVII with DDQ in $C_6H_6$, a mixture of XXVII and of 2-isopentanoyl-5-heptyl-phenol (XXVIII) in MeCN or dioxane, and 2-isoamyl-5-heptylquinone (XXIX) in MeOH aq. The




oxidation of XXVI with benzoyl peroxide in $C_6H_6$, a reagent known to act as a one-electron oxidant, gave only 10% of the o–o dimer XXX, i.e. a product of the usual radical nuclear coupling.

The complete dissimilarity between the behaviour of DDQ in $C_6H_6$ and MeOH would thus probably suggest that the ionic mechanism cannot be discarded at least in $C_6H_6$ solution. Becker[22c] has pointed out the importance of the polar solvent MeOH for the homolytic dissociation of the charge-transfer complex into radical ions.[26] It has also been noted that quinone oxidation is dependent on the nature of the substrate and can lead either to carbonium ions or to carbon radicals.[27]

Attempts to trap the quinonemethides by use of dienophiles as well as styrene or vinylether gave no results. No polystyrene was found, thus giving further evidence against the formation of radicals, which should initiate the polymerisation. It must be remarked that all our reactions were carried out in boiling $C_6H_6$, with no attempt to exclude air. Preliminary ESR measures in a static cell on a the reaction of XXVI with DDQ in $C_6H_6$ gave only a poorly resolved signal: however, the presence of DDQ as a reagent, which can give semi-quinone radicals with the corresponding hydroquinone, certainly complicates the use of such a method.

We are aware that our present results are far from giving a satisfactory answer to the problem of the reaction, but we hope at least to have illustrated the many points that are worthy of further investigation.

## EXPERIMENTAL

UV spectra ($\lambda_{max}$ in nm) were measured in 95% EtOH soln, with a Beckman DK-2, NMR spectra (values in $\delta$, $J$ in Hz) with a Varian A-60 (TMS as internal standard), and MS with a Hitachi RMU6D instrument at 70 eV (80 uA), samples being directly introduced in the ion source at 250°.

All the phenols used as starting materials were commerically avallable or were prepared by known methods. The reactions with DDQ were usually performed on 200–250 mg of PhOH in 50 ml of dry $C_6H_6$. A DDQ/PhOH molar ratio of 1.1 was used for unsaturated phenols, that of 2.2 for alkylphenols. The mixture was refluxed 5–24 hr, and the reaction monitored by TLC. The reaction mixture was cooled, filtered when 2,3-dichloro-5,6-dicyanohydroquinone was pptd., evaporated and the residue extracted with hot $C_6H_{14}$ and, if necessary, with $C_6H_6$ or ether. The ext. was usually chromatographed through silica gel (Merck 0·05–0·20 mm) columns or on preparative Merck HF TLC plates. The purity of the products was checked by TLC and the identification depended on spectral analysis (NMR, MS and UV).

*β,γ-alkenylphenols*

2-(3-methylbut-2-enyl)-phenol (I, R = R′ = Me) when treated with DDQ according to the general procedure gave the known 2,2-dimethylchromene in 50% yield. 2-but-2-enylphenol and 2-allylphenol were recovered unchanged. 2-(1-phenylallyl)-phenol gave a trace of a compound with mass 222 (other peaks at 194 and 165 m/e), NMR ($CCl_4$): 6·22 (s, 1 H) and 7·2–7·4 (9 H), most probably 4-phenylcoumarin (lit.: 6·17 $\delta$).[28]

*α,β-alkenylphenols*

2-(3-*Methylbut*-1-*enyl*)-*phenol*. (III, R = R′ = Me) gave the known 2,2-dimethylchromene in 50% yield. 2-But-1′-enylphenol (III, R = H, R′ = Me) was recovered unchanged. 2-Propenylphenol (III, R = R′ = H) with 2 mole DDQ in boiling $C_6H_6$ for 24 hr gave, after chromatography with $C_6H_{14}$, 60% 3-methylspirodibenzopyran (IV), m.p. 80°, UV: 255, 296 ($\varepsilon$ = 19000, 3300), NMR ($CCl_4$): $CH_3$—C═CH— (1.93, d, $J$ = 1·5), 1 H (5·90, d, $J$ = 10), 10 H (6·4–7·2); mass: 262, 247, 160, 149, 146, 131, 121. Hydrogenation of 200 mg IV with 60 mg $PtO_2$ in 20 ml MeOH at room T gave, after filtn., evapn., and preparative TLC on silica gel with $C_6H_{14}/C_6H_6$ 1/1, V, as an oil, UV: 272, 279 ($\varepsilon$ = 3800, 3650); NMR ($CCl_4$): $CH_3$—CH (1·16, d, $J$ = 6·5), 7 H (1·8–3·3), 8 arom. H (6·5–7·1); MS: 266, 251, 159, 145, 131, 107). Both IV and V appeared identical on TLC and spectra with the samples prepared according to the literature.[8]

2-(1-*Phenylpropenyl*)-*phenol* (VI). 170 mg (VI) in 50 ml benzene with 200 mg DDQ for 24 hr, gave 130 mg (75%) of 2-methyl-3-phenylbenzofuran (VII), UV: 255, 278 sh, 286 ($\varepsilon$ = 14600, 5800, 3500); NMR ($CCl_4$): $CH_3$ (s, 2·47), 9 arom. H (7·0–7·5); MS: 208, 178, 165, 152, 131. The structure of VII was confirmed by its preparation from 2-methyl-3-phenylcoumaran in quantitative yield with DDQ in boiling $C_6H_6$.[29] 2-Propylphenol (XI, 400 mg) was recovered unchanged. When the reaction was performed in dioxane (100 ml) for 24 hr, a small amount of a compound with mass 270 (2M–2) was obtained after TLC on silica gel with $C_6H_{14}/C_6H_6$ 1/1. 2-Butylphenol (XII) and 2-(1-phenylpropyl)-phenol were recovered unchanged, from $C_6H_6$ or dioxane. 2-(1-Methylpropyl)-phenol gave only traces of a dimeric compound, with mass: 296, 267, 211. 2-(3-Methylpentyl)-phenol (IX, R = Et, R′ = H), prepared by Clemmensen reduction of 2′-hydroxy-(3′-methyl)-valerophenone, gave after preparative TLC with $C_6H_{14}/C_6H_6$ 1/1, 50% 2-methyl-2-ethylchromene, oil NMR($CCl_4$): $CH_3$—$CH_2$— (0·95, t, $J$ = 7, and 2 H at 1·5–1·8), $CH_3$—C—O (1·32, s), CH═CH (5.32, 6·28, $J$ = 10), 4 arom. H (6·5–7·0).

2-(1,1,3-*Trimethylbutyl*)-*phenol* (XXI). This was prepared by alkylation of NaOPh (from 6·9 g PhOH and 1·8 g Na) in 100 ml dry $C_6H_6$ with 1,3-dimethyl-1-bromopentane (13 g). Stirring 18 hr, refluxing 18 hr, addn. of EtOH, washing with 5% NaOH, evapn. and chromatography through silica gel with hexane gave 900 mg pure XXI, oil, MS: 192, 135, 121, 107, 91; NMR ($CCl_4$): $Me_2CH$ (0·70, d, $J$ = 6 and 1 H at ca. 1·3), 2 Me – C (1·33, s), $CH_2$ (d, 1·77, $J$ = 5), 1 OH (4·60) and 4 H (6·3–7·2). Further elution gave 2 g 4-(1,1,3-trimethylbutyl)-phenol, oil, NMR ($CCl_4$): $Me_2CH$ (0·70, d, $J$ = 6) and 1 H at ca. 1·25), $Me_2C$ (1·25, s), $CH_2$ (d, 1·5), 4 H ($A_2B_2$, 6·6–7·2), 1 OH (6·20). Reaction of XXI with DDQ gave only traces of a dimer, with MS: 380, 323, 267, 192, 135, 107.

2,4-*Dihydroxy*-3,5-*di*(*tetrahydrogeranyl*)-*benzaldehyde* (X). This was prepared by catalytic hydrogenation of 2,4-dihydroxy-3,5-digeranylbenzaldehyde,[30] when reacted (120 mg) with DDQ gave 17 mg of 2-methyl-2-(4-methylpentyl)-6-formyl-7-hydroxy-8-tetrahydrogeranylchromene, isolated after TLC with $C_6H_6/C_6H_{14}$ 1/1, NMR ($CCl_4$): 31 H (0·8–1·8), Me—C—O (1·38, s), Aryl—$CH_2$— (2 H, 2·3–2·7), CH═CH (5·43, 6·27, $J$ = 10), $H_5$ (6·87, s), OH (11·60).

*2,6,2',6'-Tetraisopropyldiphenoquinone.* 2,6-Diisopropylphenol (500 mg) with 630 mg DDQ in boiling $C_6H_6$ for 3 hr gave, after preparative TLC with $C_6H_{14}/C_6H_6$ 1/1, 200 mg 2,6,2',6'-tetraisopropyldiphenoquinone (XX[11]), UV 421 (ε 68000), MS: 354, 339, 324, 309, 296, 281, 267; NMR ($CCl_4$): 4 $Me_2CH$ (1·22, d, $J$ = 6·5) and quintuplet 3·20, $J$ = 6·5), 4 H (s, 7·55). When thymol was reacted with DDQ in molar ratio 1/1 for 4 hr in $C_6H_6$, the chromatography of the reaction product through silica gel with $C_6H_{14}/C_6H_6$ afforded as a main product 3,3'-diisopropyl-6,6'-dimethyl-2,2'-dihydroxydiphenyl (XVIII), viscous oil, UV 282 (ε 5100), MS: 298, 283, 241, 223, 213, 134; NMR ($CCl_4$): 2 $Me_2CH$ (d, 1·25 and quintuplet 3·27, $J$ = 6·5), 2 Aryl—$CH_3$ (1·93, s), 4 arom. H (2 identical AB systems, 6·77 and 7·12, $J$ = 7·5), 2 OH (4·67). When the molar ratio DDQ/thymol was 0·66, the main product isolated by chromatography was the trimer XIX, viscous oil, UV 282 (ε 7500), mass 446, NMR ($CCl_4$): 18 H (3 $Me_2CH$ at 1·1–1·4), 3 Aryl—$CH_3$ (1·83, 2·00, 2·22), 3 CH—$Me_2$ (quintuplet, 3·27, $J$ = 6·5), 2 OH (4·55 and 4·68), 6 arom. H (6·2–7·3). Acetylation of XIX with $Ac_2O$ in pyridine gave a diacetate, m.p. 117–118°. (Found: C, 76·95; H, 7·98. Calc. for $C_{34}H_{42}O_3$: C, 76·80; H, 7·99), MS: 530, 488, 446; NMR ($CCl_4$): 18 H (1·1–1·4), 2 MeCO + 3 Aryl—Me (1·67, 1·80, 1·83, 2·01, 2·22), 3 CH—$Me_2$ (quintuplets, 2·88, 2·93; 3·35), 6 arom. H (6·2–7·2).

2-(3-Methylbutyl)-5-heptylphenol (XXVI[31]) was treated as follows: (*A*) 1 g XXVI and 1·1 g DDQ in 100 ml $C_6H_6$ were refluxed 2 days. Working up as usual gave 40% 2,2-dimethyl-7-heptylchromene (XXVII) as an oil. (Found: C, 83·27; H, 10·01. Calc. for $C_{16}H_{22}O$: C, 83·43; H, 9·63), MS: 258, 243, 229, 171, 158; NMR ($CCl_4$): 13 H (0·8–1·4), 2 $CH_3$—C—O (1·38, s), Aryl—$CH_2$ (2·3–2·6), CH=CH (5·41 and 6·20, $J$ = 10), 3 arom. H (6·4–6·9). (*B*) 250 mg XXVI and 550 mg DDQ in 20 ml $CH_3CN$ were refluxed 24 hr. Evaporated up with petrolether, and prep. TLC of the ext. on silica gel with $C_6H_{14}/C_6H_6$ 1/1 gave 5 mg of the chromene XXVII, and 20 mg of 2-(3-methylbutanoyl)-5-heptylphenol (XXVIII), UV: 262, 325 (ε 15700, 4800), MS: 276, 261, 234, 219, 205, 192, 177, 150, 134, identical on TLC and spectra with an authentic sample.[31] (*C*) 500 mg XXVI and 900 mg DDQ were dissolved in 33 ml MeOH and 8 ml $H_2O$ and left 15 hr at room T. Filtn., evapn., and chromatography through silica gel with hexane gave 200 mg of 2-(3-methylbutyl)-5-heptylbenzoquinone (XXIX[32]), IR = 6·1 (nujol), MS: 276, 259, 220, 193, 177, 163, 149, 136, 123; NMR ($CCl_4$): $Me_2CH$ (0·93, d, $J$ = 6·5), 18 H (0·9–1·7), Aryl—$CH_2$ (4 H, 2·2–2·5), 2 H (6·45). The same compound was readily obtained from the corresponding hydroquinone[32] and DDQ at room T in EtOH, thus confirming the identification. (*D*) 250 mg XXVI and 210 mg benzoylperoxide in 30 ml dry $C_6H_6$ were refluxed 24 h. The mixture was taken up with aq. $NaHCO_3$, the org. layer was evapd., and the residue chromatographed on preparative silica gel plate with $C_6H_{14}/C_6H_6$ 1/1 to give 40 mg 3,3'-di-(3-methylbutyl)-6,6'-diheptyl-2,2'-dihydroxydiphenyl (XXX), MS: 522, 465, 423; NMR ($CCl_4$): large absorption between 0·8–2·8, 1 OH (4·55), 2 AB systems at 6·78 and 7·08, $J$ = 7·5.

*2-(3-Methylbutanoyl)-4-methylphenol* (XXII, R = Me). This did not react with DDQ in $C_6H_6$. The reaction of 150 mg XXII (R = Me) with 180 mg DDQ in 3 ml MeOH at reflux gave, after preparative TLC with $C_6H_{12}$/AcOEt 4/1, 60 mg of 2-(3-methylbutanoyl)-4-formylphenol (XXII, R = CHO), MS: 206, 191, 177, 173, 164, 149, 122; NMR ($CDCl_3$): $Me_2CH$ (1·04, d, $J$ = 6·5 and 1 H, m, 1·8–2·3), —$CH_2$—CH (2·93, d, $J$ = 6·5), 3 arom. H ($H_6$, 7·07; $H_5$, 7·92; $H_3$, 8·27; $J_{3,5}$ = 2; $J_{5,6}$ = 8), CHO (9·82) 1 OH (13·05).

*2'-Hydroxydihydrochalcone* (XXIII). This did not react with DDQ in $C_6H_6$, but when 90 mg XXIII were treated with 100 mg DDQ in 5 ml MeOH at reflux for 2 days, a mixture of flavanone (XXIV) and flavone (XXV) was obtained.

*Acknowledgement*—We thank Dr. A. Gamba, University of Milano, for the ESR experiment.

## REFERENCES


1 G. Cardillo, R. Cricchio and L. Merlini, *Tetrahedron* **24**, 4825 (1969).
2 G. Cardillo, R. Cricchio and L. Merlini, *Tetrahedron Letters* 907 (1969).
3 A. B. Turner, *Quart. Rev.* **18**, 347 (1964).
4 W. D. Ollis and I. O. Sutherland, *Recent Developments in the Chemistry of Natural Phenolic Compounds*, Pergamon Press, London, p.84 (1961).
5 I. R. Campbell, C. H. Calzadilla and N. J. McCorkindale, *Tetrahedron Letters* 5107 (1966).
6 R. Mechoulam, B. Yagnitinsky and Y. Gaoni, *J. Am. Chem. Soc.* **90**, 2418 (1968); F. Piozzi, P. Venturella and A. Bellino, *Gazz. Chim. Ital.* **99**, 711 (1969); S. Nozoe and K. T. Suzuki, *Tetrahedron Letters* 2457 (1969).
7 K. H. Dudley and R. W. Chiang, *J. Org. Chem.* **34**, 120 (1969).

[8] A. Löwenstein and W. Katz, *Ber. Dtsch. Chem. Ges.* **59**, 1377 (1926).
[9] I. H. Sadler and J. A. G. Stewart, *Chem. Comm.* 773 (1969); F. E. Lutz and E. F. Kiefer, *Tetrahedron Letters* 4851 (1970).
[10] P. M. Brown and R. H. Thomson, *J. Chem. Soc.* (C) 1184 (1969).
[11] C. Walling and R. B. Hodgdon, *J. Am. Chem. Soc.* **80**, 228 (1958).
[12] J. Kolc and R. S. Becker, *J. Phys. Chem.* **71**, 4045 (1967).
[13] R. Hug, H. J. Hansen and H. Schmid, *Chimia* **23**, 108 (1969).
[14] E. E. Schweizer, D. M. Crouse and D. L. Dalrymple, *Chem. Comm.* 354 (1969).
[15] J. Zsindely and H. Schmid, *Helv. Chim. Acta* **51**, 1510 (1968).
[16] G. Cardillo, L. Merlini and S. Servi, *Ann. Chim. Rome* **60**, 564 (1970).
[17] H. Heaney and J. M. Jablonski, *Chem. Comm.* 1139 (1968); P. W. Hutchinson and J. A. Tomlinson, *Tetrahedron Letters* 5027 (1968).
[18] W. Brown, A. B. Turner and A. S. Wood, *Chem. Comm.* 876 (1969) and refs. quoted.
[19] L. Jackman, in *Advances in Organic Chemistry: Methods and Results*, Vol. II, Interscience, New York 1960, p. 329; see also D. Walker and J. D. Hiebert, *Chem. Rev.* **67**, 153 (1967); J. W. A. Findlay and A. B. Turner, *Chem. and Ind.* 158 (1970); J. Ackrell and J. A. Edwards, *Ibid.* 1202 (1970) and refs. quoted.
[20] L. Crombie and coworkers, *Chem. Comm.* 970 (1969) and preceding papers; V. V. Kane and R. K. Razdan, *Tetrahedron Letters* 591 (1969); G. Cardillo, R. Cricchio, L. Merlini and G. Nasini, *Gazz. Chim. Ital.* **99**, 612 (1969).
[21] D. R. Beck et al. *J. Am. Chem. Soc.* **90**, 4706 (1968).
[22] [a] H. D. Becker, *J. Org. Chem.* **30**, 982 (1965); [b] *Ibid.* **34**, 1198 (1969); [c] *Ibid.* **34**, 1203 (1969).
[23] H. Musso, in *Oxidative Coupling of Phenola*, W. I. Taylor and A. R. Battersby ed., Arnold and Dekker, London 1967, p. 2.
[24] R. H. Bauer and G. M. Coppinger, *Tetrahedron* **19**, 1201 (1963).
[25] J. A. Strickson and M. Leigh, *Ibid.* **24**, 5145 (1968).
[26] P. H. Emslie, R. Foster and T. J. Thomson, *Rec. Trav. Chim.* **83**, 1311 (1964); K. M. C. Davis and M. C. R. Symons, *J. Chem. Soc.* 2079 (1965).
[27] D. H. Reid, M. Fraser, B. B. Molloy, H. A. S. Payne and R. G. Sutherland, *Tetrahedron Letters* 530 (1961).
[28] U. K. Pandit and I. P. Dirk, *Tetrahedron Letters* 891 (1963).
[29] L. Claisen and E. Tietze, *Ber. Dtsch. Chem. Ges* **58**, 275 (1925).
[30] G. Cardillo, R. Cricchio, L. Merlini and G. Nasini, *Gazz. Chim. Ital.* **99**, 308 (1969).
[31] C. Cardani, G. Casnati, F. Piozzi and B. Cavalleri, *Ibid.* **88**, 487 (1958).
[32] C. Cardani and G. Casnati, *Rend. Ist. Lombardo Sci. Lett.* **91**, 130 (1957).