Birch, Butler, and Siddall:

565. *Reactions of Cyclohexadienes. Part II.[1] Some Reactions of Adducts of Benzoquinones and 1-Methoxycyclohexadienes.*

By A. J. BIRCH, D. N. BUTLER, and J. B. SIDDALL.

Some 1-methoxycyclohexa-1,3-dienes readily form adducts with 1,4-benzo-quinones. The adducts undergo acid-catalysed ring-fission adjacent to the bridgehead methoxyl group, leading ultimately to a series of hydro-derivatives of dibenzofuran.

1-METHOXYCYCLOHEXA-1,4-DIENES are readily obtained from anisoles by reduction with an alkali metal and an alcohol in liquid ammonia.[2] The reaction has hitherto been chiefly used to convert the anisoles ultimately into unsaturated ketones by acidic hydrolysis of the enol-ether group,[2] as in the industrial production of 19-nor-steroids. Other potentially useful conversions of such dienes are under investigation and we report one of them.

The initial reduction products are 1-methoxycyclohexa-1,4-dienes, with unconjugated double bonds, but these can be brought into conjugation by the action of acids or bases under appropriate experimental conditions. One method involves the use of potassamide in liquid ammonia,[1,3] and if the compounds are soluble they are usually readily equilibrated, with the 1,3-diene predominating. Another method involves the use of potassium t-butoxide in dimethyl sulphoxide.[4]

The conjugated dienes undergo addition of dienophiles with outstanding ease. Some applications of the Alder–Rickert reaction[5] leading to methoxyphthalic acids have been reported.[6] Although the pure conjugated dienes are difficult to obtain, since the equilibrium mixture may contain up to 30% of the unconjugated isomer, the crude products often give fair to good yields of crystalline adduct with benzoquinone in boiling benzene. Any remaining unconjugated diene is oxidised to the aromatic compound with production of quinhydrone; in some cases the conjugated dienes themselves are aromatised appreciably.

The crude dienes containing (I; R = H) or (I; R = OMe)[1,3] give about 60% yield of adduct with benzoquinone. The spectra of the adducts ($\lambda_{max.}$ 220 mμ, $\nu_{max.}$ 1675 cm.$^{-1}$) agree with the expected enedione structure.[7] A broad maximum at about 370 mμ accounts for their yellow colour and is probably due to " space-conjugation " between the parallel double bonds, indicating *endo*-configurations, for which additional evidence is provided by photochemical ring-closures (see below).

The action of acids on the adducts causes carbon–carbon bond fission, which must be mechanistically dependent on the bridgehead methoxyl group since it does not occur in the absence of this group. The final product obtained by heating the adduct (II; R = H) with aqueous alcoholic acid is formulated as (VI; R = H) from its spectra and reactions; similarly, the adduct (II; R = OMe) produces a substance formulated as (V). Compound (VI; R = H) has $\nu_{max.}$ 1705 (isolated CO) and 3320 cm.$^{-1}$ (OH), and its ultraviolet spectrum ($\lambda_{max.}$ 231, 304 mμ) is similar to that of a quinol. Compound (V) has a similar carbonyl peak ($\nu_{max.}$ 1710 cm.$^{-1}$), and its ultraviolet spectrum ($\lambda_{max.}$ 254, 296 mμ) is similar to those of benzofuran derivatives. Both (V) and (VI; R = H), on dehydrogenation with palladium, give the same phenol (VII), m. p. 196—197°, whose derivatives and spectra agree with data in the literature.[8]

[1] Birch, Shoukry, and Stansfield, *J.*, 1961, 5376, is regarded as Part I.
[2] Birch, *Quart. Rev.*, 1950, **4**, 69; Birch and Smith, *Quart. Rev.*, 1958, **12**, 17; Birch, *J.*, 1944, 430; Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5360.
[3] Birch, *J.*, 1949, 1642; 1950, 1551.
[4] Schriesheim, Hofmann, and Rowe, *J. Amer. Chem. Soc.*, 1962, **84**, 3160; Birch, Graves, and Siddall, *J.*, 1963, 4234.
[5] Alder and Rickert, *Annalen*, 1936, **425**, 180; *Ber.*, 1937, **70**, 1354.
[6] Birch and Hextall, *Austral. J. Chem.*, 1955, **8**, 96.
[7] Mandelbaum, *J. Org. Chem.*, 1962, **27**, 2244.
[8] Schimmelschmitt, *Annalen*, 1949, **566**, 184.

Attempts were made to define intermediate stages in connection with the mechanism of the process.   Rearrangement of the adduct (II; R = OMe), which is much more facile than that of (II; R = H), was investigated under a variety of conditions.   Refluxing with aqueous methanol for a short time produces a substance, $C_{13}H_{12}O_3$, which is probably the furan (IV) from its spectra ($\lambda_{max.}$ 238sh and 325 mμ, $\nu_{max.}$ 1642 cm.$^{-1}$), the last band corresponding to an enol-ether double bond rather than to a carbonyl group.   As expected, further hydrolysis of (IV) with aqueous acid gives the ketone (V), and hydrogenation produces a dihydro-derivative which is unchanged by mild acid treatment and has a spectrum ($\lambda_{max.}$ 255 and 294 mμ) practically identical with that of (V).

The action of dry hydrogen chloride in ether on the adduct (II; R = OMe) produces an isomer, which, from its spectrum ($\lambda_{max.}$ 255 and 294 mμ), must contain the benzofuran nucleus.   It is probably (VIII), since the infrared spectrum has no band corresponding to
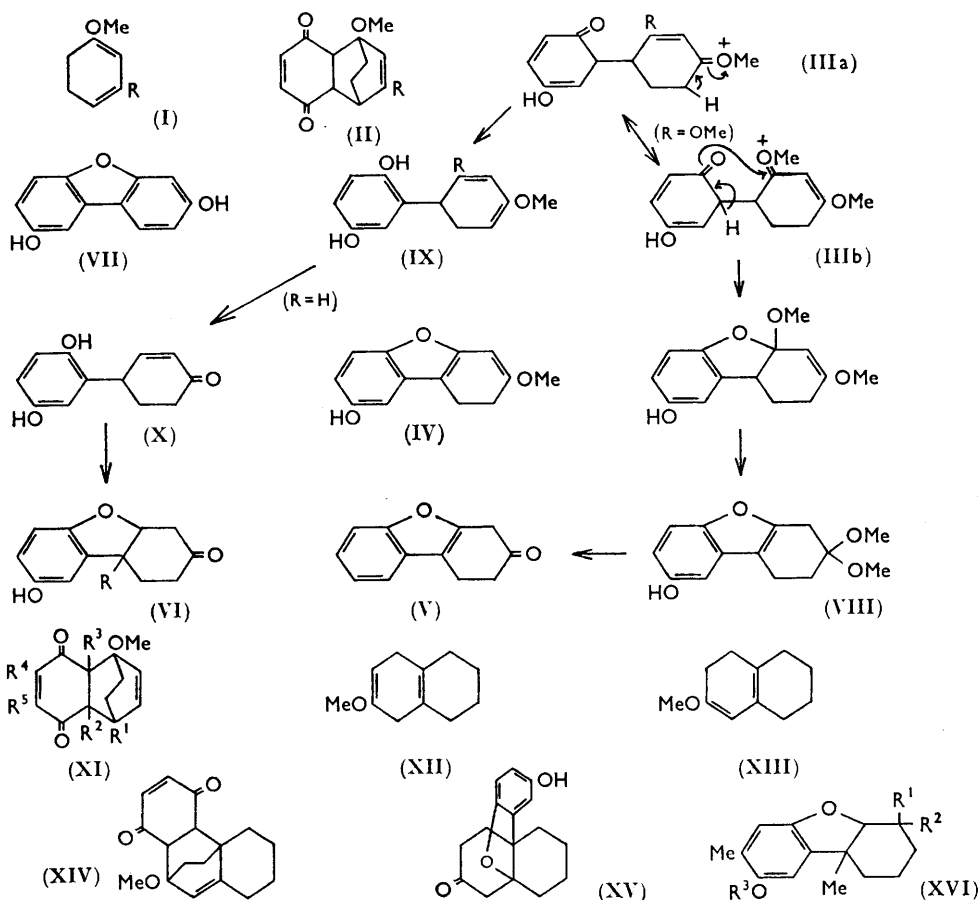
carbonyl or to a normal enol ether; several plausible routes could be suggested from the hypothetical intermediate (IX; R = OMe).   Compound (VIII) is also converted into (V) by aqueous acid.

The exact sequence is still not completely elucidated.   However, the intervention of an oxonium-carbonium intermediate is supported by the more ready rearrangement of (II; R = OMe) than of (II; R = H).   In the former case the intermediate cation would be stabilised by the extra methoxyl group by resonance involving (IIIa; R = OMe) and (IIIb).   Saturation of the double bonds in (II; R = H) also results in a compound which

cannot give a mesomeric cation as an intermediate, and in this case rearrangement does not occur with acid under the above conditions. The furan ring could be formed in several ways, either by direct cyclisation of (IIIb), as shown, or by ring-closure of an intermediate quinol of type (X). A quinol of this type (XXIII; $R^1 = R^2 = H$) has been made and found to ring-close spontaneously to the furan (XVI; $R^1 = R^2 = R^3 = H$). Aromatisation is not a driving force for the rearrangement, since this occurs readily, as noted below, in the case of the adduct (XI; $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = Me$) where aromatisation is blocked.

To provide information of use in synthesis, particularly of compounds containing angular methyl groups and quaternary carbon atoms, as well as to elucidate further points of mechanism, reactions of dienes and quinones substituted with methyl groups have been examined.

Benzoquinone and 1-methoxy-4-methylcyclohexa-1,3-diene give the adduct (XI; $R^1 = Me$, $R^2 = R^3 = R^4 = R^5 = H$) in about 60% yield. The structure of the adduct is supported by its spectra, notably an absorption maximum at 220 mμ. Treatment of the adduct with 0·03N-hydrochloric acid at room temperature gives the dibenzofuran (VI; R = Me) in high yield. The same product is formed by the action of toluene-*p*-sulphonic acid in benzene under reflux for 6 minutes, but after 1·5 min. the infrared absorption at 1640 cm.$^{-1}$ of the mixed product indicates the presence of some enol ether intermediate.

Another example of the production of a quaternary carbon atom involves the addition of benzoquinone to the hexahydronaphthalene (XIII), produced by conjugation of (XII). Since this work was carried out, the preparation of (XIII) by a similar method has been described, and a diene reaction carried out on it.[9] The present reaction gives the adduct (XIV) ($\lambda_{max.}$ 221 mμ) in rather poor yield. In general, the Diels–Alder reaction is reversible, and in the case of steric hindrance to addition, as here equilibrium clearly lies on the side of dissociation. Rearrangement of (XIV) gives (XV) ($\lambda_{max.}$ 232 and 304 mμ) the structure of which is supported by its spectra and by the formation of a 2,4-dinitrophenylhydrazone, a monoacetyl ester, and a monomethyl ether.

Addition of 2-methylbenzoquinone to 4-methyl-1-methoxycyclohexa-1,3-diene could give rise to two adducts (XI; $R^1 = R^4 = Me$, $R^2 = R^3 = R^5 = H$) and (XI; $R^1 = R^5 = Me$, $R^2 = R^3 = R^4 = H$), assuming that addition occurs in the usual way to the quinone double bond lacking the methyl group.[10] The reaction gives only one crystalline isomer, in 55% yield, the structure of which cannot be inferred directly from its spectra. The absorptions at $\lambda_{max.}$ 233 mμ (ε 10,000), $\nu_{max.}$ 1620, 1650, and 1655 cm.$^{-1}$, are characteristic of a methyl-substituted enedione system, and the proton magnetic resonance (p.m.r.) spectrum shows the presence of a methoxy-group, a quarternary methyl group, and a methyl group attached to a double-bonded carbon. Irradiation of the product gives a cage molecule, confirming the *cis-endo*-configuration, but the spectra of this do not permit distinction of the possible orientations.

Acid-catalysed rearrangement of the adduct gives a phenol whose p.m.r. spectrum in dioxan shows one OH resonance, confirmed by addition of deuterium oxide, and a singlet at 3·50τ corresponding to two aromatic protons with identical chemical shifts. Rearrangement of the adduct (XI; $R^1 = R^5 = Me$, $R^2 = R^3 = R^4 = H$) would give a phenol having two *meta* aromatic protons, whereas the other isomer would give the phenol (XVI; $R^1 = R^2 = R^3 = H$) in which they are *para*; the identical chemical shift makes it impossible to distinguish between the two. However, the methyl ether (XVI; $R^1 = R^2 = H$, $R^3 = Me$) shows two singlets (1 H each) at 3·35 and 3·40τ in deuterochloroform solution. Since the protons have non-identical chemical shifts but do not couple they must have a *para* orientation, confirming structure (XVI; $R^1 = R^2 = R^3 = H$) for the phenol and hence (XI; $R^1 = R^4 = Me$, $R^2 = R^3 = R^5 = H$) for the original adduct. This orientation

[9] Othman and Rogers, *Tetrahedron Letters*, 1963, 1339.
[10] Ansell, Nash, and Wilson, *J.*, 1963, 3012.

supports the conclusions of Ansell, Nash, and Wilson,[10] regarding the effect of substitution in such additions.

In order to examine the rearrangement of a system where aromatisation is blocked by a quaternary carbon atom, 2,5-dimethylbenzoquinone was caused to react with 1-methoxy-cyclohexa-1,3-diene. The addition is slow and reversible, and the mixture of two products, separable by chromatography, in approximately equal proportions probably results from the thermodynamic control. The products are (XI; $R^1 = R^2 = R^4 = H$, $R^3 = R^5 = Me$) ($\lambda_{max.}$ 230 mμ, $\nu_{max.}$ 1635 and 1660 cm.$^{-1}$) and (XI; $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = Me$) ($\lambda_{max.}$ 234 mμ, $\nu_{max.}$ 1660 and 1670 cm.$^{-1}$). The structure of the latter is confirmed by a single proton resonance at 7·07τ (MeO·C·CH·C:O). The former structure is best confirmed by smooth rearrangement to a compound with the properties expected for the furan (XVII). Irradiation by sunlight of the adduct (XI; $R^1 = R^2 = R^4 = H$, $R^3 = R^5 = Me$) in the solid state gives an isomer which, from its spectra and properties, is (XVIII; $R = Me$, $R' = H$) (see below).

Rearrangement of the adduct (XI; $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = Me$) with acid gives different products according to the conditions. With 0·03N-hydrochloric acid in ethanol a substance, $C_{14}H_{16}O_3$, probably (XX) is obtained ($\lambda_{max.}$ 226 mμ, $\nu_{max.}$ 1605, 1675, 1705, and 1717sh cm.$^{-1}$). The absorptions must be due to the presence of an $\alpha\beta$-unsaturated carbonyl and two saturated carbonyl groups in six-membered rings. The p.m.r. spectrum confirms the presence of two protons attached to a double-bonded carbon and of tertiary and quaternary methyl groups. Hydrogenation gives a dihydro-derivative ($\nu_{max.}$ 1705 cm.$^{-1}$), lacking the $\alpha\beta$-unsaturated ketone. Sodium methoxide gives poor yields of cyclo-hex-2-enone and 2,5-dimethylbenzoquinone as the only recognisable products. They are explicable as products of reverse Michael reactions.
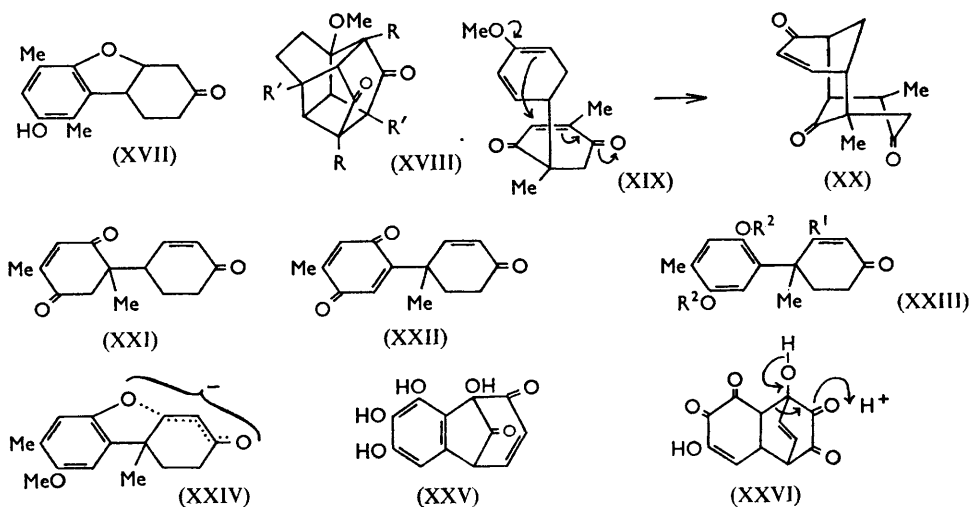
The unusual Michael reaction involved in the formation of (XX) may proceed through an intermediate enol ether (XIX), as shown. In support of this idea is the fact that the action of N-hydrochloric acid in ethanol on the adduct (XI; $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = Me$) gives, as the only isolable product, a substance, $C_{14}H_{16}O_3$, which is obtained as a by-product in the first reaction. It appears to be (XXI) since there is evidence of two $\alpha\beta$-unsaturated ketone systems [$\lambda_{max.}$ 235 mμ (ε 18,000), $\nu_{max.}$ 1620, 1675, and 1695 cm.$^{-1}$]. It is not converted into (XX) by further action of acid, and cannot, therefore, be an intermediate.

Projected synthetic work required the opening of the heterocyclic ring to give an $\alpha\beta$-unsaturated ketone. One successful method is to oxidise the phenol, *e.g.*, (XVI;

$R^1 = R^2 = R^3 = H$), with ferric chloride to give the quinone, *e.g.*, (XXII), in good yield. Reduction of (XXII) gives evidence from spectra of the intermediate production of the corresponding quinol, but only regenerated (XVI; $R^1 = R^2 = R^3 = H$) can be isolated.

Another method appeared to be treatment with base leading to removal of a proton α to the carbonyl group, which should be followed by charge transfer to form the phenoxide anion. Reaction of the furan (XVI; $R^1 = R^2 = H$, $R^3 = Me$) with an excess of methyl iodide and potassium t-butoxide for 15 minutes at room temperature gives a mixture, separable by chromatography, of (XXIII; $R^1 = R^2 = Me$) (83%) and (XVI; $R^1 = R^2 = R^3 = Me$) (15%), the structures being assigned on the basis of the spectra, notably the p.m.r. spectra. In order to see whether this unexpected result is due to slow equilibration of the enolate anion with the phenoxide anion, the phenol (XVI; $R^1 = R^2 = H$, $R^3 = Me$) was equilibrated for 6 hours with potassium t-butoxide (1 mole) under nitrogen and treated with methyl iodide; the experiment was repeated using 2 moles of the base. In the former case starting material (68%) was recovered and evidence obtained of the production of (XVI; $R^1 = R^3 = Me$, $R^2 = H$) (25%) and of (XXIII; $R^1 = H$, $R^2 = Me$) (4%). In the latter case, (XVI; $R^1 = R^2 = R^3 = Me$) (9%), (XXIII; $R^1 = R^2 = Me$) (55%), and (XXIII; $R^1 = H$, $R^2 = Me$) (11%) were obtained, as indicated by spectra after partial separation. It is not clear whether these results indicate that an equilibrium exists between the enolate anion and the phenoxide anion, which is in favour of the former until one *C*-methyl group has been introduced, or whether the anion is the mesomeric one shown in (XXIV), where the addition of the first methyl cation occurs most rapidly at the carbon centre rather than one of the oxygen centres, and of the second methyl cation on the phenoxide oxygen rather than on carbon.

All of the adducts are sensitive to light, producing cage compounds readily in solution or in the solid state in daylight.* This confirms the expected *cis-endo*-configuration. In two cases the photo-isomers were examined. When left in daylight for some days, the adduct (XI; $R^1 = R^2 = R^4 = H$, $R^3 = R^5 = Me$) gives a colourless isomer (XVIII; $R = Me$, $R' = H$), $\nu_{max.}$ 1728 and 1750 cm.$^{-1}$, with only end-absorption in the ultraviolet. The p.m.r. spectrum of this compound supports the proposed structure; there are no protons attached to double-bonded carbon, and two singlets at 8·79 and 8·87τ, corresponding to two quaternary methyl groups. The methoxy-group at 6·92τ is more diamagnetically shielded by the β-carbonyl group than in the adducts themselves (6·5—6·65τ). The colourless compound (XVIII; $R = H$, $R' = Me$) from (XI; $R^1 = R^4 = Me$, $R^2 = R^5 = H$) showed similar lack of unsaturation and the presence of two quaternary methyl groups.

There are indications in the literature that the type of bond-fission described above may be a general one, as expected on a theoretical basis. Eugster and Bosshard [12] treated furan with acetylquinone and isolated not the normal Diels–Alder product but the product resulting from this type of rearrangement with bond-fission. They noted the possibility of a two-step process, but apparently favoured a direct substitution. The acid-catalysed regeneration of 2,6-dimethylpyrone from its photo-dimer [13] probably involves a series of such bond-fissions.

Bentley and Ball [14] observed similar acid-catalysed fissions, although under more drastic conditions, with some adducts from thebaine.

The rearrangements also have a bearing on the production of the agreed [15,16] intermediate (XXV) in purpurogallin formation. Horner and his co-workers [16] recently proposed the direct formation of this intermediate by " dipolar addition " of two molecules

---

* Such photo-isomerisations to cage compounds have been shown to be general for quinone adducts to cyclic dienes.[11]

[11] Cookson, Crundwell, and Hudec, *Chem. and Ind.*, 1958, 1003.
[12] Eugster and Bosshard, *Helv. Chim. Acta*, 1963, **46**, 815.
[13] Yates and Jorgenson, *J. Amer. Chem. Soc.*, 1958, **80**, 6150.
[14] Bentley and Ball, *J. Org. Chem.*, 1958, **23**, 1720.
[15] Dewar, *Chem. and Ind.*, 1951, **12**, 28; Salfeld, *Angew. Chem.*, 1957, **69**, 723.
[16] Horner, Weber, and Dürckheimer, *Chem. Ber.*, 1961, **94**, 2881.

of hydroxy-1,2-benzoquinone, in contrast to earlier views [15] which suggested initial form-ation of the normal Diels–Alder adduct (XXVI) and rearrangement. An extension of the above mechanisms suggests the possibility of the rearrangement of (XXVI) to (XXV), involving the electronic shifts shown; purpurogallin formation is known to occur most efficiently in slightly acid solution.

The synthetic importance of the reaction, which can be extended to addenda other than quinones, is that it permits for the first time the use of a Diels–Alder reaction with a cyclic diene to produce products without a bridge. Further applications will be published shortly.

EXPERIMENTAL

Infrared spectra of all products were examined but are not always discussed. Light petroleum had b. p. 40—60°. Ultraviolet spectra were examined in ethanol.

Addition of Benzoquinone to 1-*Methoxycyclohexa-1,3-diene.*—To a stirred solution of potass-amide (from potassium, 0·95 g.) in dry ammonia (400 c.c.) under nitrogen, was added 2,5-di-hydroanisole (1-methoxycyclohexa-1,4-diene) (17·4 g.) in ether (20 c.c.). After 25 min., methanol (5 c.c.) was slowly added, followed by water, and the product extracted with pentane. The solvent was removed under reduced pressure, to leave a mixed product (16 g.), shown by gas chromatography on a silicone column to contain 72—76% of 1-methoxycyclohexa-1,3-diene, 17—20% of starting material, and 7% of 1-methoxycyclohexene, which was present in the starting material. The ultraviolet spectrum [$\lambda_{max.}$ 268 mμ (ε 4900)] was unchanged after distill-ation of the mixture, b. p. 43°/12 mm. The value ε 6520 was estimated for the pure conjugated diene from that of a mixture containing 74·5% by gas chromatography.

A solution of the mixture (16 g.) and resublimed benzoquinone (16 g.) in benzene (150 c.c.) was boiled under reflux for 1·4 hr. After cooling, quinhydrone (3 g.) was removed by filtration and the solution filtered through alumina (Spence H) to remove quinhydrone and some benzo-quinone. The fitrate was concentrated to 60 c.c. and light petroleum (40 c.c.) added. 1,4,4a,8a-*Tetrahydro-1-methoxy-1,4-ethanonaphthalene-5,8-dione* (II; R = H) (19 g.) crystallised as yellow needles, m. p. 114—116°, $\lambda_{max.}$ 221 mμ (ε 11,700), $\nu_{max.}$ 1610 and 1675 cm.$^{-1}$ (Found: C, 71·4; H, 6·3. $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·5%).

1,2,3,4,4a,9b-*Hexahydro-8-hydroxy-3-oxodibenzofuran.*—The above adduct (II; R = H) (5 g.) in ethanol (100 c.c.) and 10N-hydrochloric acid (0·1 c.c.), was left for 30 hr. in the dark. After concentration under reduced pressure to 30 c.c., water (100 c.c.) and ether (40 c.c.) were added, and extraction of the product completed with ether. After washing with potassium hydrogen carbonate solution, a colourless gum was obtained which crystallised from ethyl acetate–light petroleum. The resulting *dibenzofuran* (VI; R = H) (4·6 g.) had m. p. 142—144·5°, $\lambda_{max.}$ 231 and 304 mμ (ε 4900 and 4400), $\nu_{max.}$ (in Nujol) 1695 and 3280 cm.$^{-1}$ (Found: C, 70·95; H, 5·85. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%).

A mixture of this phenol (240 mg.) and palladium–charcoal (30%; 300 mg.) was heated at 280° for 20 min. and sublimed at 10^{-2} mm., to give 2,7-dihydroxybenzofuran (VII) (31 mg.), m. p. 193—197° (from benzene–methanol), undepressed by the specimen below; the diacetate had m. p. 163—165°.

Addition of Benzoquinone to 1,3-*Dimethoxycyclohexa-1,3-diene.*—The crude 1,3-diene (11 g.), obtained from the 1,4-diene as above, and benzoquinone (6 g.) were refluxed in benzene (250 c.c.) for 3 hr. and worked up as above. 1,4,4a,8a-*Tetrahydro-1,3-dimethoxy-1,4-ethanonaphthalene* 5,8-*dione* (II; R = Me) (9 g.) formed yellow needles, m. p. 123—125°, $\lambda_{max.}$ 221 mμ (ε 11,500) (Found: C, 68·0; H, 6·7. $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·5%).

Rearrangement with acid, as above, gave 1,2,3,4-*tetrahydro-8-hydroxy-3-oxodibenzofuran* (V), m. p. 228—230°, $\lambda_{max.}$ 254 and 296 mμ (ε 12,500 and 4850), $\nu_{max.}$ (in CCl$_4$) 3520 and 1730 cm.$^{-1}$ (Found: C, 71·05; H, 5·0. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%). Dehydrogenation as above gave 2,7-dihydroxybenzofuran, m. p. 195—197° (diacetate, m. p. 164—165°; dimethyl ether, m. p. 110—112°).

The above adduct (II; R = OMe) (730 mg.) was refluxed with methanol–water (50%; 12 c.c.) until the yellow colour faded (10 min.). On cooling, pale pink needles (437 mg.) separated, m. p. 150—165°. This material was sublimed at 0·1 mm., to give 8,9-*dihydro-2-hydroxy-7-methoxydibenzofuran* (IV), m. p. 164—166° (from benzene–light petroleum), $\lambda_{max.}$ 238sh and 325 mμ (ε 8620 and 17,800), $\nu_{max.}$ (in Nujol) 3520 and 1642 cm.$^{-1}$ (Found: C, 72·0; H, 5·65. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%).

The last compound (IV) (157 mg.), with methanol (5 c.c.) and N-hydrochloric acid (5 c.c.), gave the above ketone (V), m. p. 228—230°.

The dihydro-compound (IV) (208 mg.) was hydrogenated in ethanol (30 c.c.) with palladium–charcoal (5%), just over 1 mole of hydrogen being absorbed, to give 6,7,8,9-*tetrahydro-2-hydroxy-7-methoxydibenzofuran* (197 mg.), m. p. 122—123° (from benzene–light petroleum), $\lambda_{max.}$ 255 and 294 mμ (ε 11,000 and 5580), $\nu_{max.}$ 3400 cm.$^{-1}$.

The above adduct (II; R = OMe) (1·52 g.), in dry methanol (50 c.c.) and dry benzene (20 c.c.), was cooled to 0°, and dry hydrogen chloride passed in until the yellow colour disappeared. The residue, after evaporation of the solvent under reduced pressure, was chromatographed in benzene on deactivated alumina. The eluate crystallised from benzene to give 6,7,8,9-*tetrahydro-2-hydroxy-7,7-dimethoxydibenzofuran* (VIII), m. p. 138—140°, $\lambda_{max.}$ 225 and 294 mμ (ε 10,800 and 5820), $\nu_{max.}$ (in Nujol) 3310 cm.$^{-1}$ (Found: C, 67·9; H, 6·65. $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·5%). A portion of the product gave the ketone, m. p. 228—230°, on brief heating with aqueous methanolic hydrochloric acid.

Addition of Benzoquinone to 1-Methoxy-4-methylcyclohexa-1,3-diene.—The reduction of *p*-tolyl methyl ether gave the 2,5-dihydro-derivative, shown by gas chromatography to contain 6—8% of the tetrahydro-derivative. Conjugated as above, the product was shown by gas chromatography to contain 81% of 1-methoxy-4-methylcyclohexa-1,3-diene after 45 min. Reaction of this mixture (26·2 g.) with benzoquinone (26 g.) in boiling benzene (200 c.c.) for 6 hr., and working up as above, gave 1,4,4a,8a-*tetrahydro-1-methoxy-4-methyl-1,4-ethanonaphthalene-5,8-dione* (XI; R^1 = Me, $R^2 = R^3 = R^4 = R^5$ = H) (24·6 g.), m. p. 64—67°, $\lambda_{max.}$ 221 mμ (ε 11,000), $\nu_{max.}$ 1630, 1665, and 1670 cm.$^{-1}$ (Found: C, 72·65; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). Rearrangement with methanolic hydrochloric acid as described above gave 1,2,3,4,4a,9b-*hexahydro-8-hydroxy-9a-methyl-3-oxodibenzofuran* (VI; R = Me), m. p. 125—127·5° (from acetone–light petroleum), $\lambda_{max.}$ 230 and 303 mμ (ε 4360 and 4300), $\nu_{max.}$ (in Nujol) 1610, 1690, and 3290 cm.$^{-1}$ (Found: C, 71·75; H, 6·6. $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·5%). This hydroxy-ketone, refluxed in acetone over potassium carbonate with methyl sulphate for 12 hr., gave the *methyl ether*, m. p. 97—99·5°, $\nu_{max.}$ 1715 cm.$^{-1}$ (Found: C, 72·2; H, 6·8. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). The p.m.r. spectrum had resonances at 8·52τ (quaternary Me) and three aromatic CH at 3·31τ; it was otherwise identical with that of the product (below) from the adduct involving methylbenzoquinone.

Addition of 2,5-Dimethylbenzoquinone to 1-Methoxycyclohexa-1,3-diene.—1-Methoxycyclohexa-1,3-diene (16·5 g.) (73% purity by gas chromatography) and 2,5-dimethylbenzoquinone (14·5 g.) were refluxed in benzene (200 c.c.) for 15 hr. in the dark. The initial red colour faded only slowly. Chromatography in benzene–light petroleum (50%) on alumina (Spence O) and initial elution with benzene–light petroleum (50—75%) gave unreacted quinone, followed, in pure benzene, by a pale yellow gum which crystallised on trituration with ether and gave 1,4,4a,8a-*tetrahydro-1-methoxy-4a,7-dimethyl-1,4-ethanonaphthalene-5,8-dione* (XI; $R^1 = R^3 = R^5$ = H, $R^2 = R^4$ = Me) (1·29 g.), m. p. 119—121°, $\lambda_{max.}$ 233·5 mμ (ε 7600), $\nu_{max.}$ 1628, 1655, and 1665 cm.$^{-1}$ (Found: C, 72·7; H, 7·2%; *M*, 210. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%; *M*, 246). The p.m.r. spectrum had a singlet at 7·07τ, permitting assignment of structure.

Further elution of the column with ether in benzene (10—30%) gave 1,4,4a,8a-*tetrahydro-1-methoxy-6,8a-dimethyl-1,4-ethanonaphthalene-5,8-dione* (XI; $R^1 = R^2 = R^4$ = H, $R^3 = R^5$ = Me) (0·827 g.), m. p. 119—122° depressed by the last compound, $\lambda_{max.}$ 233 and 330—370 mμ (ε 7600 and 330), $\nu_{max.}$ 1630 and 1660 cm.$^{-1}$ (Found: C, 73·35; H, 7·25. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%). The structure was assigned on the basis of a doublet at 7·35τ (*J* = 2·5 c./sec.) assigned to the ring-junction proton (C-4a) coupled with the bridgehead proton (C-4). This adduct rearranged with acid under the usual conditions, to give 1,2,3,4,4a,9b-*hexahydro-8-hydroxy-6,9-dimethyl-3-oxodibenzofuran* (XVII), m. p. 179—182°, $\lambda_{max.}$ 231 and 305 mμ (ε 4980 and 4540), $\nu_{max.}$ 1705 and 3280 cm.$^{-1}$ (Found: C, 71·9; H, 6·65. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). The p.m.r. spectrum showed one OH at 3·66τ removed by the addition of deuterium oxide, and one aromatic proton at 3·10τ. The same adduct, on standing in daylight for several days, became colourless. Crystallisation from benzene–light petroleum gave a *cage molecule* (XVIII), m. p. 145°, $\nu_{max.}$ 1728 and 1750 cm.$^{-1}$ (Found: C, 73·0; H, 7·2; OMe, 12·8%; *M*, 260. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4; OMe, 12·6%; *M*, 246). The ultraviolet spectrum showed only end-absorption, $\lambda_{max.}$ 207 mμ (ε 1600).

Rearrangement of the 6,8a-dimethyl isomer (XI; $R^1 = R^3 = R^5$ = H, $R^2 = R^4$ = Me) (200 mg.) in 0·03N-hydrochloric acid in ethanol (20 c.c.) for 30 hr. in the dark gave colourless

crystals (130 mg.), m. p. 205—206·5°. This trione, probably (XX), had $\lambda_{max.}$ 226 and 288 mµ (ε 9100 and 130), $\nu_{max.}$ (in Nujol) 1600, 1662, 1695, and 1710 cm.$^{-1}$, $\nu_{max.}$ (in CHCl₃) 1675, 1707, and 1717 cm.$^{-1}$, and resonances at τ 2·84 (1 H, 2 doublets corresponding to $R \cdot CH_X \cdot CH_B \vdots CH_A \cdot COR'$), 3·97 (1 H, 2 doublets corresponding to $R \cdot CH_X \cdot CH_B \vdots CH_A \cdot COR'$; J_{AB} 10 c./sec., J_{BX} 6·5 c./sec., J_{AX} 1·5 c./sec.), 6·8—7·4 (6 H, multiple, allylic H, or α to carbonyl), 7·85 (2 H, 2 triplets, $CH \cdot CH_2 \cdot CH$), 8·75 (3 H, doublet, tertiary $CH \cdot CH_3$), and 8·83 (3 H, singlet, quaternary $C \cdot CH_3$). It gave a *dihydro-derivative*, m. p. 160—164°, $\nu_{max.}$ 1705 cm.$^{-1}$ (Found: C, 71·5; H, 7·8. $C_{14}H_{18}O_3$ requires C, 71·8; N, 7·0%). Only end-absorption was noted in the ultraviolet spectrum.

Chromatography of the mother-liquors from the above triketone on alumina (Spence H) (30 mg.) gave, on elution with benzene, a yellow *trione*, probably (XXI) (20 mg.), m. p. 138—144°, $\lambda_{max.}$ 231—233, 288, and 320 mµ (ε 17,000, 130, and 320), $\nu_{max.}$ 1620, 1630sh, 1662sh, 1670, and 1685 cm.$^{-1}$ (Found: C, 71·8; H, 6·95. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). Hydrogenation over palladium–charcoal (10%) gave a colourless *tetrahydro-derivative*, $\nu_{max.}$ 1705 and 1710 cm.$^{-1}$ (Found: C, 71·3; H, 8·2. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%).

Further elution of the column with ether–methanol (5%) gave an impure phenol, m. p. 148—159°, $\nu_{max.}$ (in Nujol) 1160, 1170, 1182, 1700, and 3380 cm.$^{-1}$.

Reaction of 1-Methoxy-4-methylcyclohexa-1,3-diene with 2-Methylbenzoquinone.—The crude 1,3-diene (above) (29·5 g.) was treated with 2-methylbenzoquinone (25 g.) as for benzoquinone. Chromatography of the product on alumina (Spence H) in benzene gave 1,4,4a,8a-*tetrahydro-1-methoxy-4,7-dimethyl-1,4-ethanonaphthalene-5,8-dione* (XI; $R^1 = R^4 = Me$, $R^2 = R^3 = R^5 = H$) (26 g.), prisms, m. p. 85—88° (from ether–light petroleum), $\lambda_{max.}$ 223 and 350 mµ (ε 10,000 and 320), $\nu_{max.}$ 1620, 1650, and 1665 cm.$^{-1}$ (Found: C, 73·3; H, 7·5. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%). The p.m.r. spectrum showed resonances at τ 3·51 (1 H, quartet, J 1·5 c./sec.), 3·95 (1 H, doublet), and 4·15 (1 H, doublet) (AB system, Δ 17 c./sec., J 8·5 c./sec.), 6·58 (3 H), 6·67 (1 H), 7·23 (1 H) (Δ 36 c./sec., J 8·5 c./sec.), 8·09 (3 H, doublet, J 1·5 c./sec.), 7·75—8·9 (4 H, multiplet), and 8·76 (3 H).

A solution of the adduct (6 mg.) in deuterochloroform (0·4 c.c.) was irradiated in a Pyrex p.m.r. tube with a tungsten lamp until the yellow colour disappeared. On re-scanning the spectrum the original olefinic proton resonances had completely disappeared. Two quaternary methyl groups were present (8·74 and 9·20τ), and a methoxy-group (6·88τ). The *cage molecule* (XVIII; $R = H$, $R' = Me$), m. p. 136—139°, had no selective ultraviolet absorption, $\nu_{max.}$ 1060, 1082, 1105, 1750, and 1767 cm.$^{-1}$ (Found: C, 73·1; H, 7·3. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%).

Under the usual acidic conditions, the initial adduct (19·2 g.) gave 1,2,3,4,4a,9b-*hexahydro-8-hydroxy-7,9b-dimethyl-3-oxodibenzofuran* (XVI; $R^1 = R^2 = R^3 = H$), m. p. 162—164·5°, $\lambda_{max.}$ 231 and 303 mµ (ε 4500 and 4250), $\nu_{max.}$ 1710 and 3390 cm.$^{-1}$ (Found: C, 72·0; H, 6·9. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). Methylation of this phenol with methyl sulphate and potassium carbonate in acetone gave the *methyl ether* (XVI; $R^3 = Me$, $R^1 = R^2 = H$), m. p. 120—123, $\nu_{max.}$ 1720 cm.$^{-1}$ (Found: C, 73·35; H, 7·4. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%). Acetylation with acetic anhydride and pyridine gave the *acetyl derivative*, m. p. 136·5—139°, $\nu_{max.}$ 1500, 1710, and 1750 cm.$^{-1}$ (Found: C, 70·4; H, 6·8. $C_{16}H_{18}O_4$ requires C, 70·05; H, 6·6%).

The above phenol (500 mg.) in methanol (25 c.c.) was titrated with a solution of hydrated ferric nitrate (2·0 g.) in methanol. Addition of water, extraction, and chromatography on Florisil in benzene–ether (40%) gave 5-*methyl*-2-(1-*methyl*-4-*oxocyclohex*-2-*enyl*)*benzoquinone* (XXII), orange plates (405 mg.), m. p. 103—105·5°, $\lambda_{max.}$ 257 mµ (ε 18,000), $\nu_{max.}$ 1657 and 1685 cm.$^{-1}$ (Found: C, 73·1; H, 6·6. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%). This quinone, on hydrogenation in ethanol over palladium–charcoal (5%), rapidly took up two molar equivalents of hydrogen. Immediately afterwards, the ultraviolet spectrum showed $\lambda_{max.}$ 225 and 295 mµ (ε 14,700 and 3350). After 5 hr. this had altered to 232 and 305 mµ (ε 4500 and 4350), identical with that of the dibenzofuran (XVI; $R^1 = R^2 = R^3 = H$) which was isolated and was identical with that reported above.

Methylation of the Dibenzofuran (XVI; $R^1 = R^2 = H$, $R^3 = Me$).—(*a*) A solution of the furan (500 mg.) in methyl iodide (5 c.c.) was added rapidly to a solution of potassium (400 mg.) in t-butyl alcohol (10 c.c.) and stirred for 10 min. under nitrogen. Water was added and the product isolated with ether. Chromatography on alumina (Spence O) (100 g.) gave, on elution with ether in light petroleum (4%), a gum (415 mg.), $\lambda_{max.}$ 230·5 and 293 mµ (ε 14,500 and 4380),

$\nu_{max.}$ 1510 and 1677 cm.$^{-1}$. Significant resonances in the p.m.r. spectrum at τ 3·31 (1 H, singlet, aromatic), 3·36 (1 H, singlet, aromatic), and 3·28 (1 H, quartet, J 1·5 c./sec., CO·CH:C·CH$_3$), together with other expected peaks, prove it to be the arylcyclohexenone (XXIII; R^1 = R^2 = Me).

Further elution of the column with 6—8% ether–light petroleum gave 1,2,3,4,4a,9b-*hexahydro-8-methoxy-4,4,7,9b-tetramethyl-3-oxodibenzofuran* (XVI, R^1 = R^2 = R^3 = Me) (75 mg.), prisms, m. p. 136·5—138° (from light petroleum–ether), $\lambda_{max.}$ 231 and 304 mμ (ε 4950 and 4700), $\nu_{max.}$ 1720 cm.$^{-1}$ (Found: C, 74·6; H, 8·2. C$_{17}$H$_{22}$O$_3$ requires C, 74·4; H, 7·7%). The structure was confirmed by the p.m.r. spectrum with bands at 8·69 and 8·75τ due to new quaternary methyl groups.

(*b*) A solution of the furan (1·0 g.) in t-butyl alcohol (20 c.c.) containing potassium (160 mg.) was equilibrated under nitrogen for 6 hr. An excess of methyl iodide (5 c.c.) was added during 5 min. and the products extracted with ether, after addition of water. Starting material (430 mg.) crystallised from ether–light petroleum. Chromatography of the mother-liquors (562 mg.) on alumina (Spence O) (150 g.) gave, on elution with ether in light petroleum (2—4%), a colourless gum (40 mg.), $\lambda_{max.}$ 221 and 293 mμ (ε 15,200 and 4400), $\nu_{max.}$ 1675 cm.$^{-1}$. The p.m.r. spectrum showed it to be the arylcyclohexenone (XXIII; R^1 = H, R^2 = Me); τ 3·04 (1 H, doublet, J 11 c./sec., CO·C*H*·CH·C·CH$_3$), 3·94 (1 H, doublet, J 11 c./sec., CO·CH·C*H*·C·CH$_3$) 3·31 and 3·36 (2 H, singlets, aromatic), 6·22 and 6·30 (3 H, singlets, aromatic OMe), 7·85 (3 H, singlet, aromatic CMe), 8·50 (3 H, singlet, quaternary CMe), and 7·3—8·3 (4H, multiplet, CO·CH$_2$·CH$_2$·C).

Further elution of the column with 8% ether–light petroleum gave a mixture (502 mg.) of the ketone (XVI; R^1 = R^3 = Me, R^2 = H) and starting material (XVI, R' = R^2 = R^3 = H) in approximately 1 : 1 ratio, from the p.m.r. spectrum.

(*c*) Methylation as under (*b*) was carried out using two molar equivalents of potassium. The product was chromatographed on a long column of alumina (Spence O; 200 g.); elution with ether–light petroleum gave a mixture of the two ring-opened products (XXIII; R^1 = H, R^2 = Me) (11%) and (XXIII; R^1 = R^2 = Me) (55%), followed by a mixture of starting material (25%) and the trimethyl compound (XVI; R^1 = R^2 = R^3 = Me) (9%). The ratios of products were obtained by examining p.m.r. resonance spectra in CDCl$_3$; (XVI; R^1 = R^2 = H, R^3 = Me) τ 3·35 (1 H, singlet, aromatic CH), 3·40 (1 H, singlet, aomatic CH *para* to first), 5·30 (1 H, triplet, CH$_2$·C*H*OAr), 6·20 (3 H, singlet, aromatic OMe), 7·24 (2 H, triplet, CO·C*H$_2$*·CHOAr), 7·82 (3 H, triplet, aromatic Me), 7·5—8·4 (4 H, multiplet, CO·CH$_2$·CH$_2$·CMe), and 8·52 (3 H, singlet, quaternary Me).

The spectrum of the trimethyl compound was identical with the above except for bands at τ 3·69 (1 H, singlet, C·C*H*OAr), 8·52 (3 H, singlet, quaternary Me), and 8·69 and 8·75 (6 H, 2 singlets, new quaternary Me), and the band at 7·24 above (2H, triplet, CO·C*H$_2$*·CHOAr) was missing. Other relevant spectra are noted above.

Addition of Benzoquinone to 3,4,5,6,7,8-Hexahydro-2-methoxynaphthalene (XIII).—1,4,5,6,7,8-Hexahydro-2-methoxynaphthalene (XII) (14·4 g.) in ether (15 c.c.) was added to potassamide (from potassium, 0·3 g.) in ammonia (300 c.c.). After 65 min., ethanol (5 c.c.) was added, the ammonia evaporated to about 150 c.c., and water (200 c.c.) added. Distillation of the product gave an oil, b. p. 118—121°/13 mm., shown by gas chromatography on a silicone column to contain 15% of starting material, and by ultraviolet absorption, $\lambda_{max.}$ 274 mμ (ε 5400), to contain about 80% of the conjugated diene (XIII) (Calc. ε ~6750 for the pure diene).

A solution of the foregoing mixture (13·1 g.) and benzoquinone (15 g.) in benzene (200 c.c.) was boiled under reflux for 17 hr., cooled, and filtered through alumina (Spence H) after filtration. Evaporation gave an orange oil (18·4 g.), a portion of which (1 g.) was chromatographed on alumina (Spence O) in benzene–light petroleum. The initial eluate contained chiefly 5,6,7,8-tetrahydro-2-methoxynaphthalene, followed by benzoquinone. Further elution with ether in benzene (10%) gave what appeared to be the expected adduct (57 mg.), m. p. 92—99° (decomp.). This decomposed into the initial components on attempted crystallisation, but its structure is supported by spectra ($\lambda_{max.}$ 221 and 350 mμ (ε 9800 and 320), $\nu_{max.}$ 1630 and 1665 cm.$^{-1}$). Chromatography of the bulk of the material gave crude adduct (1·02 g.) a portion of which (670 mg.) rearranged with acid under the usual conditions to give the *phenol* (XV) (670 mg.), m. p. 169—172° (from ethyl acetate–light petroleum), $\lambda_{max.}$ 231 and 303 mμ (ε 5090 and 4580), $\nu_{max.}$ (in Nujol) 1608, 1692, and 3210 cm.$^{-1}$ (Found: C, 74·5; H, 7·2. C$_{16}$H$_{18}$O$_3$ requires C, 74·4; H, 7·0%). Methylation with diazomethane under the usual conditions gave the *methyl ether*,

Birch, Butler, and Siddall.

prisms, m. p. 140—143° (from benzene–light petroleum), $\nu_{max.}$ 1710 cm.$^{-1}$ (Found: C, 74·95; H, 7·25. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·4%). Acetylation with acetic anhydride in pyridine gave the *acetyl derivative*, m. p. 87—89° from ether–light petroleum (Found: C, 72·3; H, 6·4. $C_{18}H_{20}O_4$ requires C, 72·0; H, 6·7%). The phenol gave a 2,4-*dinitrophenylhydrazone* in rather poor yield, m. p. 230—260° (decomp.), $\lambda_{max.}$ 361 mμ (Found: C, 60·65; H, 5·0. $C_{22}H_{22}N_4O_6$ requires C, 60·3; H, 5·1%).

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER.