Spirans. Part 13.[1] The Synthesis and Orientation of Spirans related to Abel's Ketone (Naphtho[2,1-*b*]furan-2(1*H*)-spiro-1'(2'*H*)-naphthalen-2'-one)

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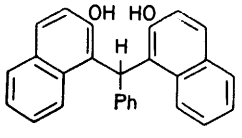
The aryl substituent in stereoisomers (2) and (3) of 1-phenylnaphtho[2,1-*b*]furan-2(1*H*)-spiro-1'(2'*H*)-naphthalen-2'-one are subject to hindered rotation by an energy barrier of *ca.* 15 kcal mol^{-1}. If the phenyl substituent carries an *ortho* substituent, however, rotation is prevented at temperatures up to 60 °C (the highest examined): only one rotamer is obtainable (the other is too crowded) and it has the *ortho*-substituent cisoid with respect to the triarylmethine proton.

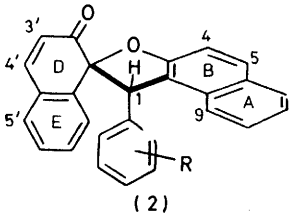
The temperature-variable broadening of the signals from the protons of the aryl substituent serves to identify these in the ^{1}H n.m.r. spectra. Some other resonances can be regularly identified by combinations of coupling constants, double-irradiation experiments, and shifts induced by using benzene instead of trichloromethane as solvent, but the only one of value for determining the configuration at the triarylmethine centre is that already known, *i.e.* the upfield shift in the resonance of the vinylic (3') proton caused by the aryl substituent when this lies immediately below it. A less precise but more general test of configuration is afforded by the mutual shielding of the aryl substituent and ring E when these are in adjacent planes.

Methods of preparation are given for several related spirans, especially those containing the spiro-1'(4'*H*)-naphthalen-4'-one nucleus, and n.m.r. methods used to establish the configurations.

In the preceding paper [1] we reported that some oxidising agents cyclise the dinaphthol (1) specifically to one or other of the (racemic) stereoisomeric spirans (2a) and (3a), the configuration of the product being determined

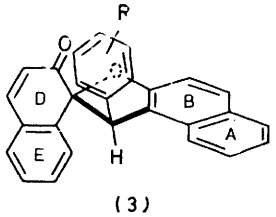


(1)



(2)

a H
b 2—OMe
c 3—OMe
d 4—OMe
e 2—F
f 3—F
g 4—F
h 3,4—$(OMe)_2$
i 3,4,5—$(OMe)_3$
j 4—Pr^i
k 3—NO_2



(3)

by steric compressions in the transition states. After cyclisation is complete the spiran can relax into a less hindered configuration (with the furanoid oxygen atom pseudoequatorial). Even so, enough steric compression remains to hamper the free rotation of the μ-aryl substituent.

Near 25 °C the ^{1}H n.m.r. spectrum of either stereoisomer (2a) or (3a) consists of a series of sharp lines together with some very broad ones that sharpen as the temperature is raised or lowered. The process is most easily monitored by means of the methoxy-signals in the μ-3-methoxyphenyl analogues (2c) and (3c); in either, the methoxy-group gives a single sharp band at higher temperatures that broadens and then splits into two bands as the temperatures falls (Figure). In contrast, a μ-4-methoxy-group as in (2d) and (3d) always gives a single sharp band because it lies on the axis of rotation which therefore does not affect it. In confirmation, 3,4-dimethoxy- and 3,4,5-trimethoxy-analogues each afford a sharp band for one methoxy-group, the bands for the other(s) being broad and temperature-variable. For isomer (2c) the coalescence temperature is 30 °C, with ν_A δ 3.39 and ν_B 3.63 (at 220 MHz); these figures yield an activation energy of *ca.* 15.0 kcal mol^{-1}. For isomer (3c) the corresponding figures, 23, 3.50 and 3.78, yield the slightly lower activation energy 14.5 kcal mol^{-1}. The trimethoxy-spirans behave nearly identically, an important point that confirms the evidence from models that the methoxy-groups are too distant to contribute to the hindrance and therefore to the activation energy. The hindrance therefore depends upon the collisions experienced by the *ortho* hydrogen atoms; conversely, these protons experience marked diamagnetic shielding by the naphthalene nuclei and, therefore, at middling temperatures, appear as a broad hump at *ca.* δ 6.8, a field well above that of any of the other benzenoid protons in the μ-4-aryl group or in ring E.

Rotation of the μ-aryl substituent is prevented at temperatures up to 60 °C (the highest examined) by a fluorine atom or any larger substituent in the *ortho*-position. The aryl group is now constrained to lie in a plane more or less perpendicular to the AB plane in either series and it follows that its two *ortho*-positions are different and non-interchangeable.

In practice we have observed only one in each pair of rotamers. The isolated compounds are all assigned the conformation (4) with the substituent R cisoid to the methine proton. Not only is this arrangement much less

compressed than the alternative, but also it is required by the substantial downfield shift suffered the methine proton resonance whatever the nature of the *ortho*-substituent (Table 1).

The fixed conformation of *ortho*-substituted μ-phenyl

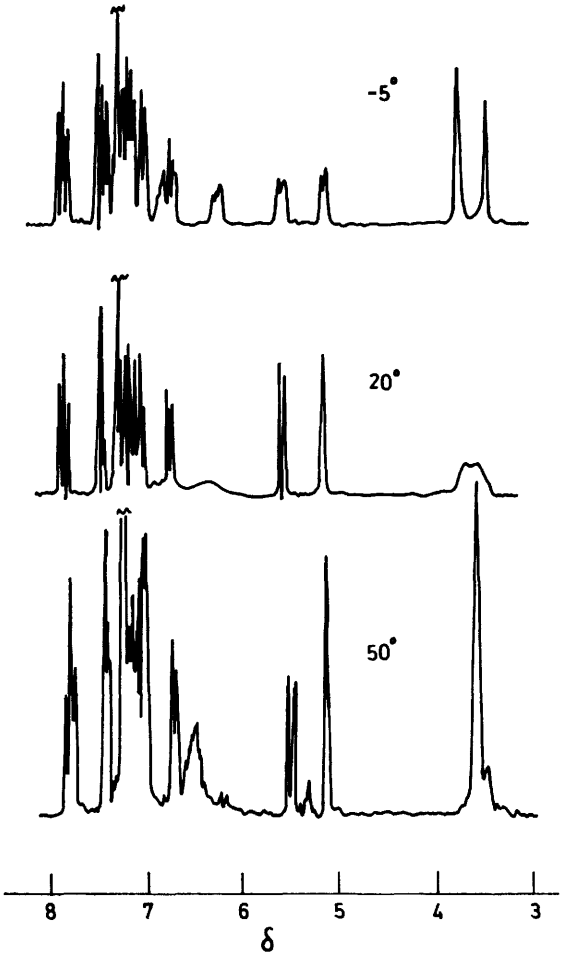
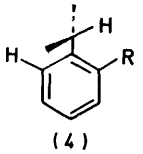


FIGURE ^{1}H N.m.r. curves for the methoxyspiran (3c) at 220 MHz in $CDCl_3$ at various temperatures

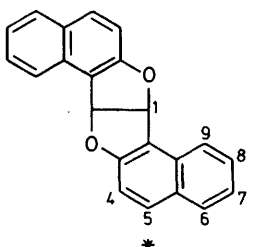
spirans allows a check on certain other points. As explained previously,[1] spirans of series (2) are easily distinguished from those of series (3) by the marked diamagnetic shift induced in the resonance of the vinylic proton at the 3′-position when the μ-aryl group lies below it. Since an *ortho*-substituent hardly affects the size of this shift we conclude that even when there is no such *ortho*-substituent the aryl group either tends to



(4)

remain in the plane perpendicular to the AB system or to librate about it. Thus signals from the μ-aryl protons are broadened (since they exchange their environments) while all other signals remain sharp (since it does not matter which side of the μ-aryl group is presented to them). The exception should be the *para*-proton of the aryl group. This is on the axis and presumably always gives a sharp resonance although it can be identified only when a *meta*-substituent moves it upfield or downfield into a clear region of the spectrum as with spirans (2c) and (2k) (Table 1).

Certain other signals could be assigned regularly. The α-protons of naphthalene systems normally resonate at somewhat lower fields than the β-protons or benzene protons as a class,[2] hence three protons (positions 5, 6, and 9) of rings A and B should resonate near δ 7.8 as happens in the naphthofuran derivative [3] (5) (Table 2).



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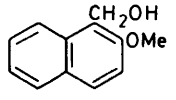

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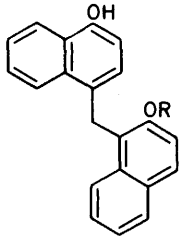
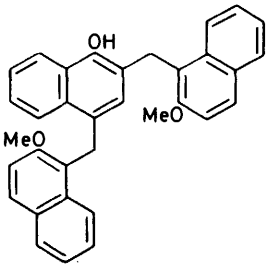


(7) a ; R = Me
b ; R = H



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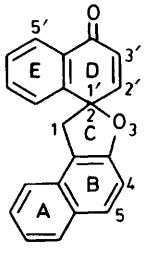

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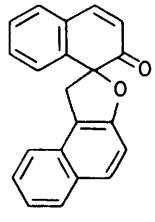


(10)

*Comparative numbering for use on Table 2 only

But in the spirans only two protons give signals at low fields; one band must have been shifted upfield into a region confused by many other signals. Of the two remaining signals, one is always a simple doublet part of an AB spin system (J 8.5 Hz). The other part is near 7.4 and often overlaid by other bands so double irradi-

ation was employed to identify it in spirans (2b), (2i), and (3i). This AB system may be broadened a little by long-range couplings but in no case could *meta* or any other splitting be detected by increased resolution or by double irradiation; hence it can be assigned to the protons at position 5 (δ 7.8) and 4 (7.4) as in Table 1. show that the 4-proton will be the most affected, the 6-proton the least, in accordance with the results.

The only other resonances that could be assigned throughout both series originated from the vinylic 3′- and 4′-protons and formed an AB system with J 10 Hz. As mentioned above, the 3′-proton allows the relative

TABLE 1

^{1}H N.m.r. assignments for spirans of series (2) and (3) [a]

	Spiran (2) R =	Ring Protons 1	4	5	6	3′	4′	μ-4	OMe μ-4	OMe μ-3(5)
a	H	5.35	7.46	7.86	7.83	6.22	7.32	?		
b	2-OMe	5.85	7.45	7.88	7.81	6.16	7.38		3.44	
c	3-OMe	5.31	7.41	7.81	7.76	6116	7.30	6.49	3.44	
d	4-OMe	5.33	7.46	7.68	7.83	6.22	7.02		3.58	
e	2-F	5.76	7.43	7.88	7.83	6.19	7.37	?		
f	3-F	5.37	?	?	?	6.27	?	?		
g	4-F	5.39	7.49	7.90	7.86	6.26	7.37			
h	3,4-$(OMe)_2$	5.32	7.45	7.86	7.82	6.24	?		3.68	3.35 br
i	3,4,5-$(OMe)_3$	5.30	7.46	7.87	7.82	6.24	7.35		3.64	3.45 br
j	4-Pr^i [c]	5.36	7.49	7.91	7.85	6.27	7.37			
k	3-NO_2	5.48	7.54	7.96	7.84	6.33	?	7.89		
	Spiran (3) R =									
a	H	5.24	7.52	7.92	7.87	5.56	7.21	?		
b	2-OMe	5.83	7.41	7.82	7.78	5.43	7.12		3.59	
c	3-OMe	5.12	7.45	7.87	7.77	5.50	7.10	6.75	3.56	
d	4-OMe	5.12	7.43	7.85	7.78	5.49	7.09		3.65	
e	2-F	5.63	7.45	7.87	7.82	5.52	?	?		
f	3-F	5.17	7.46	7.93	7.88	5.61	6.98	?		
g	4-F	5.19	7.50	7.90	7.81	5.55	7.28			
h	3,4-$(OMe)_2$	5.19	7.48	7.91	7.85	5.59	7.14		3.83	3.7 br
i	3,4,5-$(OMe)_3$	5.13	7.37	7.89	7.84	5.58	7.10		3.82	3.6 br
j	4-Pr^i [d]	5.18	7.47	7.87	7.82	5.50	7.12			
k	3-NO_2	5.26	7.51	7.95	8.08	5.53	?	8.10		

[a] At 220 MHz and/or 100 MHz in $CDCl_3$ at 28 °C with $SiMe_4$ as internal reference. A query (?) indicates a band that should be present but could not be identified. For splittings see text. [b] Broad; sharp at 50 °C. [c] Also 1.03 (3 H, d) and 2.66 (1 H, septet, J 7 Hz). [d] Also 1.16 (3 H, d) and 2.82 (1 H, septet, J 7 Hz).

The second resonance near 7.8 almost always exhibits a minor splitting of about 2 Hz in accordance with an assignment to the proton at position 6. All three protons at positions 4, 5, and 6 resonate at fields rather lower than their counterparts in the model naphthofuran (5); though at some distance, they are subject to slight deshielding by each of three structural units, *i.e.* ring E, the carbonyl group, and the μ-aryl group, and models configuration to be determined easily because it strongly reflects any shielding caused by an adjacent μ-aryl group. The 4′-proton is less affected and in any case it is hard to pick out its doublet from other bands in the same region, near δ 7.2, and decoupling methods were employed for spirans (2b), (2i), (3j), (3i), and (10). In other cases assignment was assisted by the use of benzene as solvent to induce upfield shifts which are small for vinylic

TABLE 2

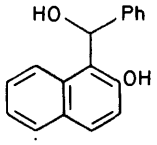
^{1}H N.m.r. assignments for reference compound (5) and various types of spiran [a]

Compound	Proton position 1	4	5	6	7	8	9	2′	3′	4′	5′	μ-Ph 2,6
(5)	6.78	7.01 [b]	7.69 [b]	7.72 [c]	7.26 [d]	7.50 [d]	8.00					
(9)	3.47 [e] 3.89 [e]	?	7.84 [f]	7.71 [g]	?	?	?	6.64 [h]	6.42 [h]		8.09 [i]	
(10)	3.54 [e] 4.07 [e]	7.32 [f]	7.86 [f]	7.82 [g]	?	?	?		6.35 [h]	7.44 [h]		
(13a)	5.28	?	7.89 [f]	7.89 [g]	?	?	?	6.65 [h]	5.97 [h]		8.17 [i]	6.87 [j]
(13b)	5.31	?	7.92 [f]	7.89 [g]	?	?	?	7.11			8.20 [i]	6.85 [j]
(14)	5.12	7.28 [f]	7.77 [f]	~7.75 [g]	?	?	?		5.75 [h]	6.24 [h]	7.96 [ik]	6.80 [j]

[a] Usually at 100 MHz and for solutions in $CDCl_3$ at 28 °C. Queries (?) indicate that bands should be present but could not be identified. Signals are singlets if no multiplicities are given. [b] d, 9 Hz. [c] dd, 8 and 1 Hz. [d] m, 8, 7 and 1 Hz. [e] d, 16 Hz. [f] d, 8.5 Hz. [g] d, 8 Hz with further ill-defined splitting. [h] d, 10 Hz. [i] dd, 8 and 2 Hz. [j] Very broad. [k] 8′-H.

protons adjacent to carbonyl but large enough (*ca.* 0.6 p.p.m.) for the β-protons [4] to bring them into a clear region of the spectrum.

It is unfortunate that no protons of ring E could be assigned their resonances, for these should reflect by upfield shifts the presence of a μ-aryl group in an adjacent plane. The effect would offer a configuration criterion when, as in certain spirans below, a 3′-vinylic proton is not available. (A proton at the 2′-position would lie



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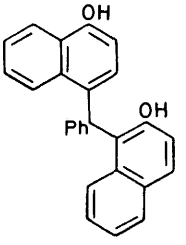

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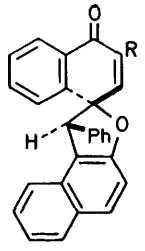
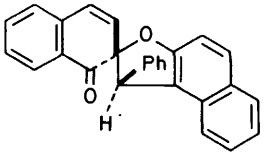


(13) a ; R = H
b ; R = Br



(14)

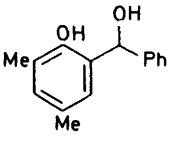
on the edge of the shielding/deshielding cone and so yield no information.) However, a general upfield shift in benzenoid resonances is usually obvious in the spectra though not easily quantified.

We turn now to a discussion of the preparation and orientation of the rest of the spirans mentioned in the previous paper.[1] Attempts to reduce 2-hydroxy-1-naphthaldehyde to the corresponding alcohol by means of aluminium amalgam led instead to the furofuran (5) described by earlier workers [3] who obtained it by zinc–acid reduction. To avoid this trouble we reduced the methyl ether with borohydride and condensed the product (6) with 1-naphthol in acid conditions to obtain the dinaphthylmethane derivative (7a); if the conditions were too stringent a second substitution gave (8). Demethylation of the dinaphthylmethane by several of the usual methods proved unsatisfactory, but the method of Wilds and McCormack [5] worked well; the salt formed by treating the dinaphthylmethane with methylmagnesium iodide supplied the desired phenol (7b) when heated at 140 °C. Oxidation of the phenol with (diacetoxyiodo)benzene gave spiran (9) in poor yields (*ca.* 20%) but oxidation with hexacyanoferrate(III), hypobromite, or peroxydisulphate gave none. This spiran is isomeric with Abel's ketone (10) and is an unsaturated ketone ($\nu_{max.}$ 1 680 cm^{-1}) displaying low-field multiplets appropriate for an aromatic proton with an *ortho*-carbonyl group, a methylenic quartet, and a vinylic quartet (Table 2). The shifts of the vinylic quartet accord reasonably with those calculated by the use of structural shifts increments and very well if, as models suggest would be the case, ring B deshields the nearer vinylic proton by 0.10—0.15 p.p.m. In the absence of a μ-phenyl group there are no broad bands and all the aromatic multiplets resonate at fields lower than 7.1.

Next, condensation of the diarylmethanol (11) with 1-naphthol furnished the triarylmethane (12) which, by oxidation with hexacyanoferrate(III) or by (diacetoxyiodo)benzene, was cyclised to the spiran (13a) and recovered therefrom by reduction with zinc in acetic acid. The n.m.r. spectrum of the spiran (Table 2) includes a vinylic AB quartet in which the 3′-proton clearly suffers a marked upfield shift in comparison with that in the analogue (9) without the μ-phenyl group. The configuration is confirmed by the scant aromatic resonance above δ 7.1. A very broad band (*ca.* 2 H) near 6.8 is attributed to the *ortho* protons of the hindered μ-phenyl group.

In passing, we compared this spectrum with that of spiran (14) (spiran C), the configuration of which had not been securely established by the previous study.[6] Again one vinylic proton shows the marked upfield shift associated with a μ-phenyl group on the same side of the molecule.

Hypobromite oxidises the triarylmethane (12) to a brominated spiran for which structure (13b) is advanced.



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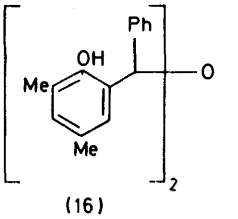

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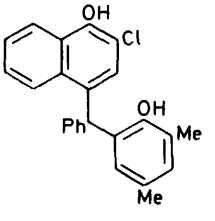

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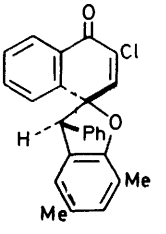
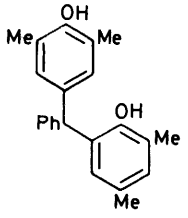


(18)

The only aromatic resonances above δ 7.0 form a broad, two-proton band at 6.9 emanating from the *ortho*-protons of the μ-phenyl group. Hence this group is distant from ring E and the configuration is that shown. At δ 7.1 there appears a singlet that has to be assigned to one surviving vinylic proton, the other having been replaced by bromine. Incremental-shift calculations agree, provided that the μ-phenyl group has little influence; as explained above, this is the case for a proton at the 2′-position and structure (13b) follows.

We did not observe the highly specific *ortho*-chlorin-

ation of 1-naphthol by t-butyl hypochlorite claimed by others,[7] gas-liquid chromatography showing the product to contain about 20% of a dichloronaphthol; however, this mixture was satisfactory for preparative work. Borohydride reduction of the appropriate benzophenone derivative [8] gave the desired alcohol (15) along with the related ether (16) and condensation of the alcohol with



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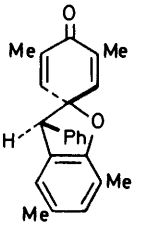

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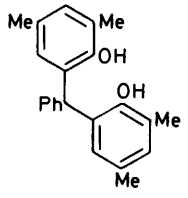

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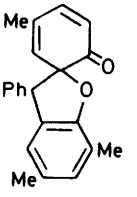

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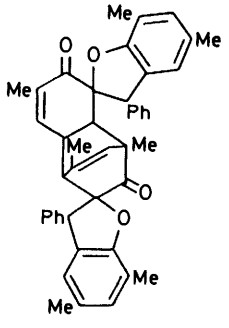

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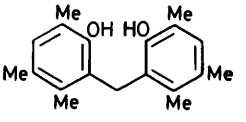

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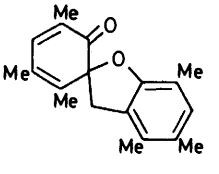

(25)

the mixture of chloronaphthols supplied the triarylmethane (17) without difficulty.

(Diacetoxyiodo)benzene oxidised this triarylmethane to the spiran (18). Above δ 7 this compound displays bands equivalent to five protons, two of which have to be assigned to the isolated aromatic protons of the dimethylphenol residue. Two more have to be assigned to the heavily shielded *ortho*-protons of the μ-phenyl group. The fifth appears as a sharp peak—the only sharp singlet in this region—at δ 6.83 and is thereby recognised as the vinylic proton at the 2′-position. Since incremental shifts for a proton in this position lead to a value close to 6.83 the μ-phenyl group cannot be assigned a configuration on this basis; however, all other aromatic resonance is at fields below δ 7.1 so that, as indicated in (18), the μ-phenyl group must be remote from ring E.

The same diarylmethanol (15) condensed with 2,6-dimethylphenol to give another triarylmethane derivative (19) and thence spiran (20) by oxidation with (diacetoxyiodo)benzene. The spiran is of interest in that it contains no rings A or E so that the μ-phenyl group can now rotate more freely. Accordingly the n.m.r. spectrum shows no broadening at ordinary temperatures. Anisotropic shielding effects are evident at both positions on one side of the hexadienone ring; thus on that side the vinylic proton resonates at δ 6.20 and the methyl group at 1.54; on the other side, the corresponding shifts are 6.78 and 1.94, respectively.

An isomeric triarylmethane (21) was made by condensing the diarylmethanol (15) with 2,4-dimethylphenol. Oxidation presumably gave the spiran (22) but only a dimer was isolated. From the n.m.r. spectra it appeared that a single stereoisomer or regioisomer was formed although in theory several are possible. Some possibilities are rendered improbable by major repulsions between various parts of the molecule and others by considerations based upon secondary overlap in (2 + 4) cycloaddition. Such dimers are well known for cyclohexadienones with small or few substituents and the structure (23), though provisional, agrees with similar examples.[9] (Diacetoxyiodo)benzene oxidation of the more substituted diarylmethanol (24) gave the known spiran [10] (25) without difficulty.

EXPERIMENTAL

U.v. spectra were determined on *ca.* 10^{-3}M solutions in ethanol. I.r. spectra were determined on mulls in paraffin. N.m.r. spectra were usually determined at 100 MHz on solutions in trichloromethane with tetramethylsilane as internal standard, and at temperatures near 25 °C. Molecular weights were determined by means of the mass spectra. Light petroleum refers to the fraction b.p. 60—80 °C.

Methylene-1,1′-bisnaphthalene-2,4′-diol (7b).—In preference to the published method,[11] 2-methoxy-1-naphthylmethanol (6) was prepared by reduction of 2-methoxy-1-naphthaldehyde (10 g) in ethanol (120 ml) with sodium borohydride (2.5 g), and crystallised from ether–light petroleum as needles (10 g), m.p. 102 °C (lit.,[11] 100—101 °C). The naphthylmethanol (1.0 g) and 1-naphthol (5.0 g) were shaken in ether containing concentrated hydrochloric acid (4 drops) for 20 h; then the solution was washed with water, dried (Na_2SO_4), and evaporated to a brown gum. This was chromatographed on silica (300 g) from benzene–light petroleum (4 : 1 v/v) and furnished as one fraction a solid (0.55 g) that supplied 4-(*2-methoxy-1-naphthylmethyl*)-*naphth-2-ol* (7a) which separated from benzene–light petroleum as needles, m.p. 161—162 °C, $\nu_{max.}$ 3 230 cm^{-1} (Found: C, 84.0; H, 5.9%; *M*, 314. $C_{22}H_{18}O_2$ requires C, 84.05; H, 5.8%; *M*, 314). The *acetate* crystallised from benzene–light petroleum as needles, m.p. 130—131 °C, $\nu_{max.}$ 1 740 cm^{-1}, δ 2.50 (3 H, OAc), 3.88 (3 H, OMe), 4.48 (2 H, CH_2), 6.89 (1 H, d, *J* 10 Hz; ArH with *ortho*-OMe),

7.04—7.60 (7 H, mm; ArH), and 7.60—7.94 (4 H, mm; ArH) (Found: C, 81.0; H, 5.65%; *M*, 356. $C_{24}H_{20}O_3$ requires C, 80.9; H, 5.7%; *M*, 356).

The reaction between 2-methoxy-1-naphthylmethanol (7a) (0.25 g) and 1-naphthol (0.2 g) in boiling acetic acid (5 ml) for 30 min gave a solid which, purified from benzene–light petroleum, supplied *2,4-bis-(2-methoxy-1-naphthylmethyl)naphth-1-ol* (8) as needles (0.10 g), m.p. 210 °C $\nu_{max.}$ 3 380 cm^{-1}; δ 3.76 (3 H, OMe), 4.04 (3 H, OMe), 4.20 (2 H, CH_2), 4.80 (2 H, CH_2), and 6.72—8.50 (17 H, mm, ArH). The *acetate* formed needles, m.p. 194—194.5 °C, $\nu_{max.}$ 1 755 cm^{-1} (Found: C, 82.2; H, 5.9%; *M*, 526. $C_{36}H_{30}O_4$ requires C, 82.1; H, 5.7%; *M*, 526).

To demethylate 4-(2-methoxy-1-naphthylmethyl)naphth-2-ol, this compound (1.0 g) was added slowly to an ethereal solution of methylmagnesium iodide [from magnesium (0.5 g)], the ether was removed *in vacuo*, and the residue was heated at 140 °C for 1 h. The product was cooled in ice while being treated with dilute hydrochloric acid, and the resulting solution was repeatedly extracted with ether. The product was transferred from the ether into 5% aqueous potassium hydroxide (3 × 50 ml) and, after exact neutralisation of that solution, back into ether (3 × 50 ml). Recovered in the usual way, the product now crystallised from benzene–light petroleum giving the *diol* as pale fawn plates (0.83 g), m.p. 177—178 °C, $\nu_{max.}$ 3 280 cm^{-1} (Found: C, 83.7; H, 5.2%; *M*, 300. $C_{21}H_{16}O_2$ requires C, 84.0; H, 5.4%; *M*, 300). The *diacetate* separated from benzene–light petroleum as needles, m.p. 160—161 °C, $\nu_{max.}$ 1 740 cm^{-1}, δ 2.24 (3 H, OAc), 2.52 (3 H, OAc), 4.36 (2 H, CH_2), 6.87 (1 H, d, *J* 10 Hz; ArH with *o*-OMe), 7.10—7.56 (7 H, mm, ArH), and 7.56—7.69 (4 H, mm, ArH).

Oxidation of the Diol (7b); *Spiran* (9).—(Diacetoxyiodo)-benzene (0.50 g) in benzene (20 ml) was slowly added to a stirred solution of methylene-1,1′-bisnaphthalene-2,4′-diol (7b) (0.40 g) in benzene (100 ml) and the mixture was stirred for a further 30 min. The benzene was removed under reduced pressure at 22 °C leaving a deep red gum which was chromatographed on silica (30 g) from benzene. The main fraction formed a yellow solid that crystallised from ether–cyclohexane to give *naphtho*[2,1-b]*furan*-2(1H)-*spiro*-1′(4′H)-*naphthalen*-4′-*one* (9) as small yellow rhombs (70 mg), m.p. 159—160 °C, $\lambda_{max.}$ 243, 269, 279, 281, 329, and 341 nm (log ε 4.22, 3.89, 3.90, 3.76, 3.64, and 3.64), $\nu_{max.}$ 1 680 cm^{-1} (Found: C, 84.5; H, 4.9%; *M*, 298. $C_{21}H_{14}O_2$ requires C, 84.5; 4.7%; *M*, 298).

Benzylidene-1,1′-bisnaphthalene-2,4′-diol (12).—(2-Hydroxy-1-naphthyl)phenylmethanol[12] (11) (7.0 g) was condensed with 1-naphthol (14 g) in dichloromethane (50 ml) and light petroleum (50 ml) by means of a stream of hydrogen chloride led in until the solution was saturated. A solid separated and was collected after a further 30 min; a second crop was obtained after concentration of the mother-liquor. The solid crystallised from dichloromethane–light petroleum as needles (10.0 g), m.p. 230—231 °C, $\nu_{max.}$ 3 400 and 3 575 cm^{-1} (Found: C, 85.9; H, 5.5%; *M*, 376. $C_{27}H_{20}O_2$ requires C, 86.15; H, 5.35%; *M*, 376). The *diacetate* separated from ethyl acetate–light petroleum as needles, m.p. 210—211 °C, $\nu_{max.}$ 1 748 and 1 760 cm^{-1}; δ 1.64 (3 H, OAc), 2.41 (3 H, OAc), 6.91br (1 H, Ar_3CH), 6.94—7.24 (mm, 8 H, ArH), 7.24—7.56 (mm, 4 H, ArH), and 7.56—8.10 (mm, 5 H, ArH) (Found: C, 81.1; H, 5.4%; *M*, 460. $C_{31}H_{24}O_4$ requires C, 80.85; H, 5.25%; *M*, 460).

Oxidation of the Diol (12); *Spirans* (13a) *and* (13b).—(i) (Diacetoxyiodo)benzene (0.17 g) was added in small portions to a stirred solution of the diol (12) (0.20 g) in benzene (20 ml). After 30 min the solvent was removed at 20 °C under reduced pressure, and the residue was chromatographed on neutral alumina (3% H_2O; 35 g) from benzene, which eluted (1R*,2R*)-1-*phenylnaphtho*[2,1-b]*furan*-2(1H)-*spiro*-1′(4′)-*naphthalen*-4′-*one* (13a) crystallising from benzene as very faintly yellow needles (0.125 g), m.p. 185 °C, $\lambda_{max.}$ 244, 268, 279, 291, 327, and 342 nm (log ε 4.23, 4.04, 4.04, 3.92, 3.56, and 3.60); $\nu_{max.}$ 1 670 cm^{-1} (Found: C, 86.4; H, 5.0%; *M*, 374. $C_{27}H_{18}O_2$ requires C, 86.6; H, 4.85%; *M*, 374).

(ii) Oxidation of the diol (12) (0.40 g) in benzene (40 ml) with potassium hexacyanoferrate(III) (6.0 g) in 3M-aqueous potassium hydroxide (60 ml) for 1 h gave material which, separated from the organic layer and chromatographed on alumina as before but with benzene–light petroleum (4 : 1 v/v), afforded the spiran (13a) (0.20 g), identified spectroscopically.

Dissolved in acetic acid (5 ml) and reduced with zinc dust (1 g) at 50 °C for 1 h, the spiran (0.5 g) regenerated the diol (12), isolated in the usual way and purified from dichloromethane–light petroleum to give needles (0.33 g), m.p. 230 °C.

(iii) To the diol (0.20 g) in toluene (40 ml) at 0 °C was added, with vigorous stirring, a freshly prepared solution of potassium hypobromite in water from bromine (1 g) in 10% aqueous potassium hydroxide also at 0 °C. After 30 min the toluene layer was washed with water and dried (Na_2SO_4). The yellow residue from evaporation of the solvent under reduced pressure was fractionated on a column of neutral alumina (3% H_2O; 25 g) from which benzene–light petroleum (4 : 1 v/v) eluted (1R*,2S*)-3′-*bromo*-1-*phenylnaphtho*[2,1-b]*furan*-(21H)-*spiro*-1′(4′)-*naphthalen*-4-*one* (13b), which formed yellow needles (0.19 g), m.p. 215—217 °C; $\nu_{max.}$ 1 676 cm^{-1} (Found: C, 71.8; H, 3.9%; *M*, 458, 456. $C_{27}H_{17}BrO_2$ requires C, 71.5; H, 3.8%; *M*, 458, 456).

(*2-Hydroxy-3,5-dimethylphenyl*)*phenylmethanol* (15).—This compound was obtained from 2-hydroxy-3,5-dimethylbenzophenone for which two methods of preparation were compared, the second being the better. (i) Aluminium chloride (126.6 g) was gradually added to a stirred solution of 2,4-dimethylphenol (12.2 g) and benzoyl chloride (12 ml) in nitrobenzene (100 ml) and the mixture was kept at 50—60 °C for 18 h then poured into 5M-hydrochloric acid. The aqueous layer was extracted once with ether and the combined organic phases were washed with 2M-sodium hydroxide and then with a little dilute hydrochloric acid. Steam distillation removed the nitrobenzene and the organic residue was chromatographed on silica from which benzene–light petroleum (1 : 9 v/v) eluted a mixture of an ester and a ketone. The mixture (10 g) was hydrolysed with aqueous sodium hydroxide to destroy the ester and chromatography on alumina from benzene then gave 2-hydroxy-3,5-dimethylbenzophenone as pale yellow needles (6.2 g), m.p. 40—41 °C (lit.,[8] 40—41°), from light petroleum. Continued elution of the silica column with benzene–light petroleum (1 : 1 v/v) supplied 2,2′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl as large rods (1.8 g), m.p. 137—138 °C (lit.,[12] 134 °C), δ 2.25 (12 H, Me), 5.12 (2 H, removed by D_2O, OH), 6.85 (m, 2 H, ArH), and 7.00 (m, 2 H, ArH) (Found: C, 79.4; H, 7.4%; *M*, 242. Calc. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5%; *M*, 242).

(ii) 2,4-Dimethylphenyl benzoate (35 g) and aluminium

chloride (28 g) were heated together at 140—160 °C for 20 min, then cooled and mixed with 5M-hydrochloric acid. After 1 h, the organic products were isolated by means of ether and the resulting oil heated under reflux with 2M-*sodium* hydroxide (250 ml) for 2 h. The material liberated by neutralisation was chromatographed on silica (300 g) and benzene–light petroleum (1 : 1 v/v) eluted the benzophenone, which crystallised as before forming needles (29 g), m.p. 40—41 °C.

The foregoing benzophenone (10 g) in methanol (100 ml) was reduced by sodium borohydride (5 g) in methanol (20 ml) and water (10 ml) during 20 min, and the products were isolated by chloroform after neutralisation with dilute hydrochloric acid. Chromatography on silica from benzene–light petroleum (1 : 4 v/v) supplied *bis*-[α-(2-*hydroxy*-3,5-*dimethylphenyl*)*benzyl*] *ether* (16) which formed a glass (2.9 g), $\nu_{max.}$ 3 470 cm^{-1}; δ 2.17 (12 H, Me), 5.63 (2 H, ArC*H*-O), 6.65 (m, 2 H, ArH), 6.98 (m, 2 H, ArH), 6.76 (2 H, removed by D_2O; OH), and 7.3br (10 H, ArH) (Found: C, 82.15; H, 6.8. $C_{30}H_{30}O_3$ requires C, 82.2; H, 6.9%). The mass spectrum included peaks at *m/e* 226 (40), 225 (35), 210 (50), and 209 (100%) but no molecular ion (*m/e* 438) was observed. The compound gave negative tests for halogen but a deep red solution in sulphuric acid. Elution of the column with benzene then gave (2-hydroxy-3,5-dimethylphenyl)phenylmethanol (15), which separated from aqueous methanol as feathery needles (5.6 g), m.p. 104—106 °C, $\nu_{max.}$ 3 350 and 3 400 cm^{-1}; δ 2.15 (6 H, Me), 5.80 (1 H, ArC*H*-O), 3.5 (m, 2 H, Ar*H*), 6.85 (m, 2 H, ArH), 7.3 (5 H, ArH), and 3.0 and 7.8 (both s, 1 H, removed by D_2O; OH) (Found: C, 79.2; H, 6.9%; *M*, 228. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.1%; *M*, 228). This compound also gave a deep-red solution in sulphuric acid.

2-*Chloro*-4-(2-*hydroxy*-3,5-*dimethylphenyl*)*phenylmethyl*-1-*naphthol* (17).—Freshly prepared t-butyl chlorate(I) (23 g) in tetrachloromethane (25 ml) was added dropwise to 1-naphthol (30 g) in the same solvent (250 ml) and the mixture refluxed for 2 h. The solvent was removed under reduced pressure and the residue chromatographed on silica. Light petroleum eluted a product that crystallised from trichloromethane–light petroleum giving needles (27 g), m.p. 65—67 °C, as reported by Ginsburg.[7] Gas-liquid chromatography showed that this product is not pure 2-chloro-1-naphthol but a mixture that separated into two fractions, one with retention time 24 min, the other with retention time 47 min. The former supplied the requisite 2-chloro-1-naphthol as needles, m.p. 64 °C, *m/e* 178, and 180. The latter (*ca.* 20% of the mixture) appeared to be 2,4-dichloro-1-naphthol; it had m.p. 104—106 °C and *m/e* 212 and corresponding isotope peaks. For preparative purposes, the mixture was employed.

(2-Hydroxy-3,5-dimethylphenyl)phenylmethanol (15) (2.28 g) and the mixture (1.78 g) of chloronaphthols were kept at 90 °C for 3 h in acetic acid (20 ml) containing concentrated hydrochloric acid (1 ml). Water (50 ml) was added, and the products extracted into ether and recovered in the usual way leaving a red oil. From trichloromethane–light petroleum (1 : 9 v/v) this material separated as a pink powder, and recrystallisation from aqueous methanol then gave the *phenylmethylnaphthol* as colourless rods (2.1 g), m.p. 161—163 °C (Found: C, 77.1; H, 5.4; Cl, 9.1. $C_{25}H_{21}ClO_2$ requires C, 77.2; H, 5.4; Cl, 9.1%). The *diacetate* formed needles, m.p. 221—223 °C, with $\nu_{max.}$ 1 740 (alkyl acetate) and 1 760 cm^{-1} (aryl acetate) (Found: C, 73.4; H, 5.35. $C_{29}H_{25}ClO_4$ requires C, 73.6; H, 5.3%).

(2R*,3S*)-3′-*Chloro*-5,7-*dimethyl*-3-*phenylbenzofuran*-2(3H)-*spiro*-1′-(4′H)-*naphthalen*-4′-*one* (18).—The foregoing phenylmethylnaphthol (17) (0.39 g) in acetic acid (25 ml) was mixed with (diacetoxyiodo)benzene (0.325 g) also in acetic acid (15 ml). After 90 min, the mixture was diluted with water and extracted with ether; the ether layer was freed from acid by means of water and then aqueous sodium hydrogen carbonate and dried (Na_2SO_4). Spontaneous evaporation of the solvent left an orange residue that was purified by chromatography on silica from benzene–light petroleum (1 : 1 v/v), which eluted the *spiran*, obtained from methanol as rods (0.107 g), m.p. 162—163 °C, $\lambda_{max.}$ 245infl, 285, and 294infl nm (log ε 5.14, 4.95, and 4.90); $\nu_{max.}$ 1 680, 1 640, and 1 603 cm^{-1}; δ 2.23 (3 H, ArMe), 2.26 (3 H, ArMe), 5.00 (1 H, Ar_2CH), 6.73br (2 H, phenolic ArH), 6.83 (1 H, vinylic H), 6.88 (2 H, mm, *o*-H in Ph), 7.18 (3 H, mm, other H in Ph), and 8.1 (1 H, dd, *J* 8 Hz, ArH with *o*-C:O) (Found: C, 77.6; H, 5.2%; *M*, 386, 388. $C_{25}H_{19}ClO_2$ requires C, 77.6; H, 4.95%; *M*, 386, 388).

2-[(4-*Hydroxy*-3,5-*dimethylphenyl*)*phenylmethyl*]-4,6-*dimethylphenol* (19).—The phenylmethanol (15) (1 g) was condensed with 2,6-dimethylphenol (0.55 g) in acetic acid (10 ml) containing sulphuric acid (0.2 ml) at 100 °C for 90 min. Water and ether were added, and the organic phase was freed from acid by means of aqueous sodium hydrogen carbonate and evaporated leaving a residue that crystallised from aqueous methanol giving the *phenol* as faintly yellow rosettes (1.11 g), m.p. 137—139 °C, $\nu_{max.}$ 3 500 and 3 600 cm^{-1}; δ 2.15 (12 H, Me), 4.5br (2 H, diminished by D_2O, OH), and 5.50 (1 H, Ar_3CH) (Found: C, 83.4; H, 7.3%; *M*, 332. $C_{23}H_{24}O_2$ requires C, 83.1; H, 7.3%; *M*, 332). The *diacetate* crystallised from aqueous methanol as plates, m.p. 162—164 °C, $\nu_{max.}$ 1 750 cm^{-1} (Found: C, 77.6; H, 7.0. $C_{17}H_{28}O_4$ requires C, 77.9; H, 6.8%).

3′,5,5′,7-*Tetramethyl*-3-*phenylbenzofuran*-2(3H)-*spiro*-1′-*cyclohex*-2′,5′-*dien*-4′-*one* (20).—The foregoing phenol (19) (0.35 g) in benzene (80 ml) was treated with (diacetoxyiodo)benzene (0.39 g) added gradually during 2 h. Removal of solvent *in vacuo* left an orange solid that was fractionated on silica (40 g) from benzene–trichloromethane (9 : 1 v/v) giving, as the first fraction eluted, the *spiran* which crystallised from aqueous methanol as needles (0.12 g), m.p. 102—103 °C, $\lambda_{max.}$ 235, 284, and 293infl nm, (log ε 5.34, 4.67, and 4.60); $\nu_{max.}$ 1 650 cm^{-1}; δ 1.50 (3 H; vinylic Me), 1.88 (vinylic Me), 2.20 (6 H, ArMe), 4.60 (1 H, Ar_2CH), 6.16br (1 H, vinylic H), and 6.68—7.20 (mm, 8 H, ArH + vinylic H) (Found: C, 83.6; H, 6.7%; *M*, 330. $C_{23}H_{22}O_2$ requires C, 83.6; H, 6.7%; *M*, 330).

Elution of the second fraction with trichloromethane supplied an orange powder (80 mg), believed to consist of a mixture of the quinone methide 2′-hydroxy-4-diphenylmethylene-2,3′,5′,6-tetramethylcyclohexa-2,5-dien-1-one and its hydrate (*i.e.* the corresponding triarylmethanol), with m.p. 257—262 °C (decomp.), $\lambda_{max.}$ 218, 256, 279, and 361 nm (log ε 5.10, 4.84, 4.78, and 4.97), $\lambda_{max.}$ (with NaOH) 245infl, 305, 401, and 600 nm (log ε 5.06, 4.79, 4.80, and 4.56) (acidification restored the spectrum in neutral solvent), $\nu_{max.}$ ($CHCl_3$) 3 580 (OH) and 1 610 (strong; quinonoid C:O); δ 1.98 (3 H, vinylic Me), 2.12 (3 H, vinylic Me), 2.21 (6 H, ArMe), 6.60br (1 H, vinylic H), 6.97 (mm, vinylic H + one phenolic ArH), and 7.17—7.50 (mm, ArH) (Found: C, 79.5; H, 6.5; Calc. for $C_{23}H_{22}O_2 \cdot H_2O$; C, 79.2; H, 7.0%). Accurate mass measurements gave for the parent ion *m/e* 330.161 38; $C_{23}H_{22}O_2$ requires *m/e* 330.161 97.

When the spirobenzofuranone was heated in toluene at 110 °C for 3 h the solution became orange and chromatography and the u.v. and i.r. spectra indicated the formation of small amounts of this orange quinone methide.

3′,4,5,5′,6′,7-Hexamethylbenzofuran-2(3H)-spiro-1′-cyclohexa-3′,5′-dien-2′-one (25).—Methylene-2,2′-bis-(3,5,6-trimethylphenol)(24) (1.0 g) formed a suspension in acetic acid (80 ml) to which (diacetoxyiodo)benzene (1.2 g) in acetic acid (50 ml) was added dropwise with stirring. After 3 h, the resulting clear yellow solution was poured into water and the product was collected, purified on a column of alumina from benzene, and crystallised from ethanol to give the *spiran* as bright yellow needles (0.55 g), m.p. 139—140 °C (lit.,[10] 137 °C), $\lambda_{max.}$ 220, 283, 289, and 340 nm (log ε 5.09, 4.53, and 4.55); δ 1.83 (9 H, vinylic Me), 2.02 (3 H, ArMe), 2.15 (3 H, ArMe), 2.18 (3 H, ArMe), 3.27 (d, 1 H, *J* 16 Hz) with 2.98 (d, 1 H, *J* 16 Hz, CH_2), 6.63br (1 H, vinylic H), and 6.75br (1 H, ArH).

Spiran Dimer (23).—Kept in ethanol (10 ml) and concentrated hydrochloric acid (2 ml) for 48 h, 2,4-dimethylphenol (2.44 g) and benzaldehyde (1.06 g) formed a solid that was washed with 5M-sodium hydroxide and then water and crystallised from light petroleum to give *benzylidene-2,2′-bis-(4,6-dimethylphenol)* (21) as needles (1.8 g), m.p. 110—112 °C, $\nu_{max.}$ 3 500 cm^{-1} (Found: C, 82.85; H, 7.4%; *M*, 332. $C_{23}H_{24}O_2$ requires C, 83.0; H, 7.3%; *M*, 332). The *diacetate* crystallised from aqueous methanol as prisms, m.p. 155—157 °C, $\nu_{max.}$ 1 745 cm^{-1} (Found: C, 77.9; H, 7.0. $C_{27}H_{28}O_4$ requires C, 77.9; H, 6.8%).

(Diacetoxyiodo)benzene (1.1 g) in acetic acid (50 ml) was added dropwise to a stirred solution of the bisphenol (1.1 g) in acetic acid (100 ml) at 20 °C. After 3 h the yellow solution was poured into water and the products collected into ether, freed from acetic acid by washing with sodium hydrogen carbonate and then water, and recovered by evaporation of the solvent. A yellowish gum remained; a little methanol induced it to form a solid (0.31 g). The yellow material from the mother liquor was chromatographed on alumina from benzene to provide a further quantity (0.16 g) of this solid, and the combined solids, purified by crystallisation from benzene–light petroleum, furnished the *dimer* as needles, m.p. 201—203 °C, $\lambda_{max.}$ 223, 285, and 294 nm (log ε 5.46, 4.75, and 4.75); $\nu_{max.}$ 1 723 and 1 690 cm^{-1}; δ 0.53 (3 H, angular Me), 0.82 (d, *J* 1.5 Hz, 3 H, vinylic Me), 1.09 (3 H, angular Me), 1.83 (d, *J* 1.5 Hz, 3 H, vinylic Me), 1.97 (3 H, ArMe), 2.09 (3 H, ArMe), 2.11 (3 H, ArMe), 2.16 (3 H, ArMe), 3.12 (d, *J* 3 Hz, 1 H; angular H), 3.47 (d?, 1 H, angular H), 4.01 (1 H, Ar_2CH), 4.56 (1 H, Ar_2CH), 4.88 (m, 1 H, vinylic H), 5.94 (m, 1 H, vinylic H), 6.38 (mm, 2 H, phenolic ArH), 6.72 (mm, 2 H, phenolic ArH), 7.00 (mm, 4 H, *o*-H in Ph), and 7.3 (mm, 6 H, other ArH).

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