

Dibenzofuranones from 1 : 1 Condensations between Cyclohexanones and Cyclohexane-1,3-diones

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Like aldehydes, cyclopentanone and pentan-2-one react with dimedone in a 1 : 2 ratio to give xanthenes. With a series of cyclohexanones, however, both dimedone and cyclohexane-1,3-dione give octahydrodibenzofuranones which are readily aromatised. In some cases, the intermediate 2-cyclohexenyldimedones have been isolated.

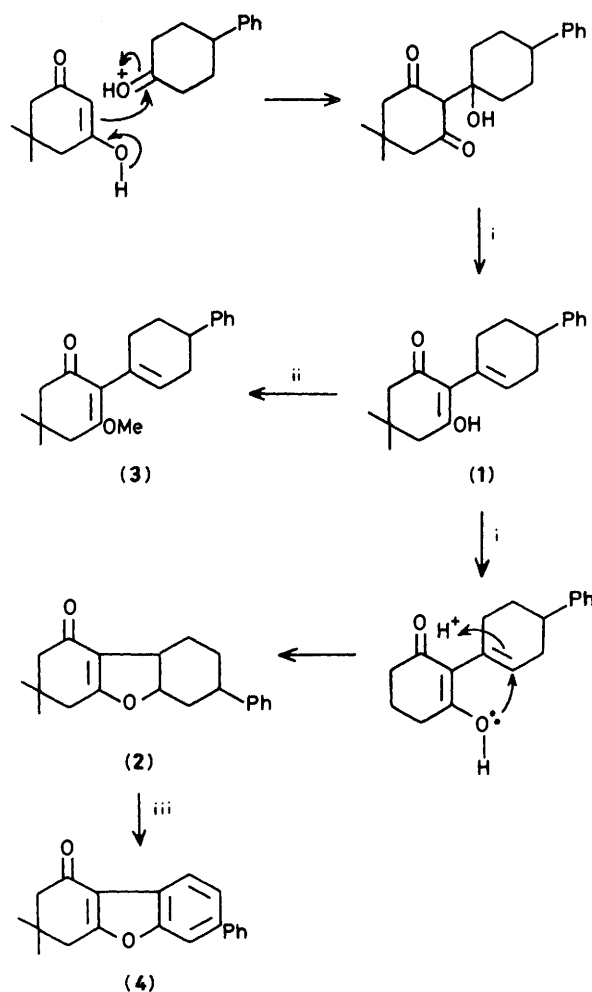
Methylenebisdimedones and their derived xanthenes are well known aldehyde derivatives. However, condensation reactions with ketones do not appear to have been studied in detail. Our discovery of an acid-catalysed tetramerisation of dimedone and our suggested mechanism for the reaction¹ led to a wider investigation of ketone reactions with cyclohexane-1,3-diones.

The reaction between dimedone (5,5-dimethylcyclohexane-1,3-dione) and cyclopentanone or pentan-2-one catalysed by toluene-*p*-sulphonic acid in refluxing xylene gave the expected xanthenediones. Under the same conditions with 4-phenylcyclohexanone, however, a 1 : 1 reaction occurred to give either the 2-substituted dimedone (1) or the dibenzofuranone (2) depending upon the reflux period (Scheme 1).

Compound (1) was obtained in up to 75% yield after being refluxed for 1½ h. It was soluble in sodium hydroxide and showed a characteristic u.v. absorption for the un-ionised enol [$\lambda_{\text{max.}}$ (0.1M-HCl) 268 nm (ϵ 11 000)] and for the anion [$\lambda_{\text{max.}}$ (0.1M-NaOH) 294 nm (ϵ 18 900)]. It had a strong i.r. band at 1 570 cm^{-1} (KBr), also characteristic of dimedone, and gave the expected ¹H n.m.r. spectrum with the vinyl proton appearing as a broad signal centred at δ 5.75. Treatment with diazomethane converted it into the vinylogous ester (3) in which the vinyl proton gave a broadened triplet at δ 5.48. When compound (1) was refluxed with toluene-*p*-sulphonic acid in xylene for 11 h a 56% yield of the dibenzofuranone (2) was obtained. This product was most readily prepared by running the original reaction for at least 8 h.

Compound (2) had strong i.r. bands at 1 625 and 1 650 cm^{-1} , characteristic of the vinylogous ester system. The n.m.r. spectrum showed one proton multiplets at δ 2.9 (9a-H) and 4.7 (5a-H). Dehydrogenation over palladium gave the dihydrodibenzofuranone (4) which showed $\nu(\text{C}=\text{O})$ at 1 670 cm^{-1} . The proton at C-9 was shifted downfield, clear of the other aromatic protons in the n.m.r. spectrum, by the anisotropy of the carbonyl group. It appeared as an *ortho* coupled doublet (J 8 Hz) at δ 8.02. This confirmed the position of the phenyl substituent. The ¹³C n.m.r. spectrum of the dibenzofuranone (2) was completely consistent with the assigned structure (see Experimental section).

Nine further dibenzofuranones were prepared from dimedone and three from cyclohexane-1,3-dione (Table 1). In some cases the 2-cyclohexenyl intermediate was also isolated (see Experimental section). Dimedone and 2-methylcyclohexanone gave only one product (9) in low yield. The quaternary carbon atom (C-5a) gave a singlet (δ 91.92 p.p.m.) in the ¹³C n.m.r. spectrum. The ring closure required attack by an enol oxygen atom at a tetra-alkylated olefin. Should the (possible, but less stable) trialkylated olefin form, the alternative ring closure to



Scheme 1. Reagents: i, H⁺; ii, CH₂N₂; iii, Pd

give the 9-methyl dibenzofuran would be severely hindered by a non-bonding interaction between the methyl group and the dimedone carbonyl oxygen. No reaction was observed between dimedone and 2,6-dimethylcyclohexanone. This compound (9) was the only dibenzofuranone lacking a proton signal in the δ 4.2–4.8 region. All the others had a multiplet in this region except for compound (13) which, with a *gem* dimethyl group at C-6, showed a sharp doublet (J 9 Hz) at δ 4.25 for the 5a-H

Table 1. Physical data for the dihydrofuranones (2) and (5)–(6)

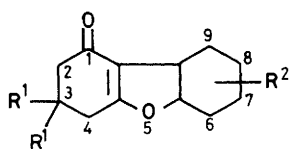
Compound	Yield (%)	B.p. (°C) (mmHg)	M.p. (°C)	Required (%)		Molecular formula	Found (%)	
				C	H		C	H
(5)	14.1	128–140 (1.0)		75.0	8.3	C ₁₂ H ₁₆ O ₂	75.1	8.7
(6)	32.2	146–148 (0.5)		77.4	9.7	C ₁₆ H ₂₄ O ₂	77.1	9.8
(7)	50.7	182 (0.2)		80.6	7.5	C ₁₈ H ₂₀ O ₂	80.6	7.7
(8)	71.8	114–116 (0.1)	66–67 ^a	76.4	9.1	C ₁₄ H ₂₀ O ₂	76.4	9.4
(9)	26.5	98–100 (0.1)	50–51 ^a	76.9	9.4	C ₁₅ H ₂₂ O ₂	76.9	9.7
(10)	55.6	123–125 (0.5)	48 ^a	76.9	9.4	C ₁₅ H ₂₂ O ₂	76.6	9.6
(11)	56.0	132–136 (1.0)		76.9	9.4	C ₁₅ H ₂₂ O ₂	76.7	9.5
(12) ^c	41.1	136–144 (1.0)	123–124 ^b	77.4	9.7	C ₁₆ H ₂₄ O ₂	77.0	9.7
(13)	23.2	136–140 (0.8)						
(14)	30.4	146–166 (0.4)	104–105 ^a	78.3	10.1	C ₁₈ H ₂₈ O ₂	78.1	10.1
(2)	21.0	192–194 (0.5)	90–91 ^b	81.1	8.1	C ₂₀ H ₂₄ O ₂	81.1	8.5
(15)	54.0	146–160 (0.2)						
(16) ^d	29.1	130–132 (0.3)	65–66 ^a	76.9	9.4	C ₁₅ H ₂₀ O ₂	76.9	9.5

^a From light petroleum, b.p. 40–60 °C. ^b From light petroleum, b.p. 80–100 °C. ^c Prepared from 3,5-dimethylcyclohexanone.² ^d Compound derived from cycloheptanone, ring c seven membered.

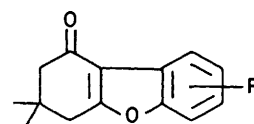
Table 2. Spectral data of the dihydrofuranones (2) and (5)–(16)

Compound	I.r. (cm ⁻¹)		U.v. EtOH)		¹ H n.m.r. δ(CDCl ₃)		
	ν(C=O)	ν(C=C)	λ _{max} (nm)	ε	5a-H	9a-H	Others
(5)	1 655	1 630 ^a			4.58	2.90	
(6)	1 650	1 625 ^a			4.68	2.84	1.04 (s, Me ₃)
(7)	1 660	1 630 ^a			4.60	2.80	7.15 (s, Ph)
(8)	1 645	1 620 ^b	274	13 600	4.60	3.00	
(9)	1 650	1 635 ^b	274	14 000		2.82	1.33 (s, 5a-Me)
(10)	1 655	1 630 ^b			4.62	2.86	0.92 (d, 7-Me)
(11)	1 655	1 630 ^a			4.43	2.90	0.93 (d, 8-Me)
(12)	1 645	1 620 ^b	274	12 800	4.26	2.75	1.10 (d, 6-Me), 0.85 (d, 8-Me)
(13)		1 635 ^a			4.25	3.20	0.90, 0.93, 1.01, 1.03, 1.06 (all s, Me's)
(14)	1 640	1 620 ^b	274	12 500	4.80	3.00	0.85 (s, Me ₃)
(2)	1 650	1 625 ^b	273	11 500	4.70	2.90	7.22 (Ph)
(15)	1 630	1 660 ^a			4.50	2.95	
(16)		1 630 ^a	274	13 100	4.88	3.23	

^a Neat liquid. ^b KBr.



	R ¹	R ²
(5)	H	H
(6)	H	7-Bu ¹
(7)	H	7-Ph
(8)	Me	H
(9)	Me	5a-H
(10)	Me	7-Me
(11)	Me	8-Me
(12)	Me	6,8-Me ₂
(13)	Me	6,6,8,8-Me ₄
(14)	Me	7-Bu ¹
(15)	Me	6,7-[CH ₂] ₄ + 7,8-[CH ₂] ₄
(16)	Me	-CH ₂ -



	R
(17)	H
(18)	8-Me
(19)	6,8-Me ₂
(20)	7-Bu ¹
(21)	6,7-CH=CH-CH=CH
(22)	7,8-CH=CH-CH=CH

(Table 2). A one proton multiplet for 9a-H at about δ 2.9 was present in every spectrum. This was shown to be coupled to the C-5a signal for several examples by double resonance experiments.

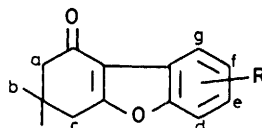
Several of the octahydrodibenzofuranones were aromatised to give the dihydrodibenzofuranones (4), and (17)–(22) or the

hydroxydibenzofurans (23), and (24) (Table 3); compound (17) has been prepared³ by the reaction between dimedone and *O*-phenylhydroxylamine, and compound (23) has been obtained⁴ from its tetra-*t*-butyl derivative by transalkylation. Each of the aromatic compounds (4), (17)–(22) showed the 9-H signal shifted downfield by the carbonyl group. Compounds with C-8 substituents showed singlets [broadened by *meta* coupling for (18) and (19), sharp for (22)]. Those with C-7 substituents (4), (20), and (21) showed *ortho* coupled doublets (all with *J* 8 Hz). Only one product (18) could be obtained from the derivative of 3-methylcyclohexanone. No indication of a 6-methyl isomer was shown by t.l.c. or by n.m.r. on the mother-liquors after

Table 3. Physical data of the aromatised derivatives (4) and (17)–(24)

Compound	Yield (%)	M.p. (°C)	Solvent ^c	Required (%)		Molecular formula	Found		I.r. (cm ⁻¹) ν(C=O)	U.v. (nm)		
				C	H		C	H		λ _{max.} (EtOH) (ε)		
(17)	51.4	121–123	A	78.5	6.5	C ₁₄ H ₁₄ O ₂	78.6	6.6	1 665	229 (22 200)	248 (8 400)	
(18)	44.6	122–123	C	79.0	7.0	C ₁₅ H ₁₆ O ₂	78.9	7.2	1 665	266 (7 500)	281 (5 800)	
(19)	30.7	151–152	B	79.3	7.4	C ₁₆ H ₁₈ O ₂	79.5	7.6	1 665	237 (20 800)	270 (7 800)	
(20)	51.1	119–120	A	80.0	8.2	C ₁₈ H ₂₂ O ₂	80.2	8.5	1 665	236 (24 200)	278 (8 600)	
(4)	40.8	203	EtOAc	82.8	6.2	C ₂₀ H ₁₈ O ₂	82.5	6.2	1 670	231 (29 100)	270 (7 400)	
(21)	5.2	165–166	MeOH	81.8	6.1	C ₁₈ H ₁₆ O ₂	81.9	6.1	1 660	245 (19 400)	273 (26 000)	
(22)	5.0	204–205	Toluene	81.8	6.1	C ₁₈ H ₁₆ O ₂	81.6	6.2	1 660	245 (74 400)	317 (3 800)	
										326 (3 700)	331 (3 600)	
(23) ^b	55.9	144	Toluene	78.3	4.3	C ₁₂ H ₈ O ₂	78.0	4.4	3 300	241 (70 300)	293 (17 000)	
									ν(OH)	λ _{max.} (H ₂ O)	λ _{max.} (0.1M-MeOH)	
										223 (32 700)	236 (8 200)	
										256 (13 500)	267 (9 700)	
										268 (11 000)	275 (11 000)	
										275 (14 000)	325 (9 900)	
										295 (4 900)		
										306 (7 100)		
(24)	17.2	168–169	Toluene	83.1	4.6	C ₁₈ H ₁₂ O ₂	83.0	4.6	3 300	213 (36 000)	223 (41 800)	
										290 (29 300)	247 (22 800)	
										316 (17 200)	292 (22 300)	
											340 (18 200)	

^a Lit.,³ m.p. 118–119 °C. ^b Lit.,⁴ m.p. 142–143 °C. ^c A = Light petroleum, b.p. 40–60 °C; B = light petroleum, b.p. 60–80 °C; C = light petroleum, b.p. 80–100 °C.

Table 4. ¹H N.m.r. data of the aromatic ketones (4) and (17)–(24)

Compound	δ(CDCl ₃)							Others
	a	b	c	d	e	f	g	
(17)	2.40	1.15	2.82				8.10 (m)	7.2–7.6 (m, 3 H)
(18)	2.36	1.12	2.75	7.30 (d)	7.02 (br d)		7.82 (s)	2.38 (s, 3 H)
(19)	2.38	1.14	2.81		6.90 (br s)		7.66 (br s)	2.40 (s, 6 H)
(20)	2.36	1.10	2.75	7.45 (s)		7.35 (dd)	7.95 (d)	1.34 (s, 9 H)
(4)	2.40	1.12	2.81				8.02 (d)	7.2–7.7 (m, 7 H)
(21)	2.44	1.18	2.10				8.12 (d)	7.2–8.0 (m, 5 H)
(22)	2.42	1.15	2.80	7.78 (s)			8.48 (s)	7.30–7.60 (m, 2 H) 7.80–8.10 (m, 2 H)

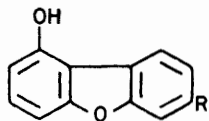
the recrystallisation. 2-Decalone clearly gave a mixture of dodecahydrobenzofuranones (15). After aromatisation, fractional recrystallisation produced small yields of the angular (21) and linear (22) derivatives. There were clear differences in both the u.v. and n.m.r. spectra of these compounds (Tables 3 and 4). We were not surprised when the cyclohexane-1,3-dione derivatives (5) and (7) were aromatised to phenolic compounds. The u.v. spectra showed typical multiple bands and the expected profound changes when re-run at high pH.

Further confirmation of the structure of (14) was obtained when it was found to hydrogenate readily to give the saturated dibenzofuranone [$\nu(\text{C}=\text{O})$ 1 700 cm⁻¹]. In the preparation of the dibenzofuranones (2) and (6), secondary neutral products were isolated and shown to be the hexahydrodibenzofuranones (25) and (26). Presumably air oxidation was responsible.

A reaction between cyclohexane-1,3-dione and 4-*t*-butylcyclohexanone was run with methanesulphonic acid in benzene. On

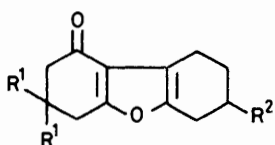
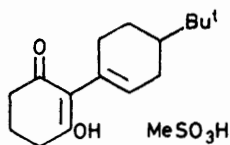
cooling, a crystalline precipitate was obtained which analysed for a 1:1 mixture of the 2-cyclohexenylcyclohexanedione and methanesulphonic acid (27). It would appear that the two components co-crystallised.

The product showed typical cyclohexane-1,3-dione characteristics in its i.r. and the u.v. spectra. In the mass spectrum, there was no peak above m/z 276 which is the molecular weight of the olefin. The presence of a 1:1 mixture of olefin and sulphonic acid in solution was established by the ¹H n.m.r. spectrum which showed a broadened triplet at δ 5.22 for the vinyl proton and a two proton singlet at δ 10.5 for the two acidic protons. In the ¹³C n.m.r. spectrum a doublet at δ 125.12 p.p.m. and a singlet at 129.40 p.p.m. confirmed the presence of the olefin link. Three other co-crystalline mixtures were obtained from reactions with cyclohexane-1,3-dione. 4-Phenylcyclohexanone gave a product containing methanesulphonic acid after reaction in benzene, and one with toluene-*p*-sulphonic acid after reaction in toluene. The first of these underwent ring-closure to give compound (7)



(23) R = H

(24) R = Ph

(25) R¹ = H, R² = Bu^t(26) R¹ = Me, R² = Ph

(27)

in refluxing xylene. Also in toluene, cyclohexanone gave 2-cyclohexenylcyclohexane-1,3-dione as a mixture (exactly 1:1) with toluene-*p*-sulphonic acid. The spectral characteristics of the three further products were closely similar to those of (27).

Experimental

Ether refers to diethyl ether.

General Method for the Preparation of 3,4,5a,6,7,8,9,9a-Octahydrodibenzofuran-1(2H)-ones.—A solution of cyclohexane-1,3-dione (40 mmol) or dimedone (40 mmol), the appropriate ketone (40 mmol), and toluene-*p*-sulphonic acid (1 g) in xylene (250 ml) was refluxed under a Dean-Stark water separator for 8–12 h. The cooled product was washed with sodium hydroxide solution (2 × 100 ml) add water (100 ml), and dried (MgSO₄). After filtration, the solvent was evaporated under reduced pressure and the residue distilled. The products are listed in Tables 1 and 2. 3,3-Dimethyl-7-phenyl-3,4,5a,6,7,8,9,9a-octahydrodibenzofuran-1(2H)-one (2), δ_c(CDCl₃) 194.76 (C-1), 176.47 (C-4a), 146.46 (C-1'), 128.60 and 126.85 (C-2' and C-3'), 126.33 (C-4'), 119.89 (C-9b), 85.90 (C-5a), 51.11 (C-2), 37.94 (C-4), 38.00 and 36.32 (C-7 and C-9a), 35.18, 29.39 and 28.94 (C-6, C-8 and C-9), 34.21 (C-3), and 29.58 and 27.80 p.p.m. (*gem* dimethyl group). 3,3,5a-Trimethyl-3,4,5a,6,7,8,9,9a-octahydrodibenzofuran-1(2H) (9), δ_c(CDCl₃) 195.09 (C-1), 175.45 (C-4a), 115.35 (C-9b), 91.92 (C-5a), 51.30 (C-2), 43.77 (C-9a), 38.19 (C-4), 33.99 (C-3), 32.12, 27.23, 24.16, 18.57 (C-6, C-7, C-8, and C-9), 29.02 (5a-Me), and 28.29 p.p.m. (*gem* dimethyl group).

The following compounds were also obtained by the above general method, modified as indicated.

(i) 3,3,6,6-Tetramethyl-3,4,5,6-tetrahydroanthene-9-spirocyclopentane-1(2H),8(7H)-dione. After 2 h reflux the spirodiketone (76%) was obtained, m.p. 248–250 °C (from toluene-light petroleum, b.p. 40–60 °C) (Found: C, 76.9; H, 8.8. C₂₁H₂₈O₃ requires C, 76.8; H, 8.5%); ν_{max}(KBr) 1 655 and 1 605 cm⁻¹; λ_{max}(EtOH) 232 (ε 11 800) and 306 nm (4 400); δ(CDCl₃) 1.05 (12 H, s, 4 × s, Me), 1.80–2.07 (8H, m, 4 × CH₂), 2.22 (4H, s, 2 × CH₂), and 2.33 (4H, s, 2 × CH₂).

(ii) 3,3,6,6,9-Pentamethyl-9-propyl-3,4,5,6-tetrahydroanthene-1(2H),8(7H)-dione. After 2 h reflux the diketone (61%) was obtained, m.p. 162–164 °C (from light petroleum, b.p. 80–100 °C) (Found: C, 76.4; H, 9.3. C₂₁H₃₀O₃ requires C, 76.4; H, 9.1%); ν_{max}(KBr) 1 660 and 1 610 cm⁻¹; λ_{max}(EtOH) 307 nm (ε 4 400); δ(CDCl₃) 0.81–0.95 (5 H, m, CH₂CH₃), 1.05 (12 H, s, 4 × Me), 1.58 (3 H, s, Me), and 2.20 and 2.29 (10 H, 2s, 5 × CH₂).

(iii) 2-Cyclohex-1-enyl-5,5-dimethylcyclohexane-1,3-dione.

From the alkaline extract after a 2 h reflux the cyclohexanedione (75%) was obtained, m.p. 117–119 °C (from ethanol-water) (Found: C, 76.1; H, 9.5. C₁₄H₂₀O₂ requires C, 76.4; H, 9.1%); ν_{max}(KBr) 1 600 and 1 560 cm⁻¹; λ_{max}(H₂O) 270 nm (ε 9 650); λ_{max}(0.1M-HCl) 268 nm (ε 10 500); λ_{max}(0.1M-NaOH) 294 nm (ε 22 200).

(iv) 5,5-Dimethyl-2-[2-(3,4,4a,5,6,7,8,8a-octahydronaphthyl)]-cyclohexane-1,3-dione. From the alkaline extract after 2 h reflux the naphthyl diketone (58%) was obtained, m.p. 109–111 °C (from ethanol-water) (Found: C, 78.7; H, 9.9. C₁₈H₂₆O₂ requires C, 78.8; H, 9.5%); ν_{max}(KBr) 1 580 cm⁻¹; λ_{max}(H₂O) 270 nm (ε 9 600); λ_{max}(0.1M-HCl) 268 nm (ε 10 300); λ_{max}(0.1M-NaOH) 294 nm (ε 20 650); δ(CDCl₃) 1.06 (6 H, s, 2 × Me), 1.46–2.55 (18 H, m, 8 × CH₂ + 2 × CH), 5.50 (1 H, br s, =CH), and 7.00 (1 H, br s, OH).

(v) 5,5-Dimethyl-2-(3,3,5,5-tetramethylcyclohex-1-enyl)cyclohexane-1,3-dione. From the alkaline extract after a 2 h reflux the diketone (65%) was obtained, m.p. 167–168 °C (from ethanol-water) (Found: C, 78.2; H, 9.9. C₁₈H₂₈O₂ requires C, 78.3; H, 10.1%); ν_{max}(KBr) 1 620 and 1 600 cm⁻¹; δ(CDCl₃) 1.07 (18 H, s, 6 × Me), 1.39 (2 H, s, CH₂), 1.85 (2 H, s, CH₂), 2.22 (2 H, s, CH₂), 2.37 (2 H, s, CH₂), 5.40 (1 H, br s, =CH), and 6.60 (1 H, br s, OH).

(vi) 5,5-Dimethyl-2-(4-phenylcyclohex-1-enyl)cyclohexane-1,3-dione. From the alkaline extract after a 3 h reflux the diketone (75%) was obtained, m.p. 140–142 °C (from ethanol-water) (Found: C, 81.3; H, 8.2. C₂₀H₂₄O₂ requires C, 81.1; H, 8.1%); ν_{max}(KBr) 1 570 cm⁻¹; λ_{max}(H₂O) 290 nm (ε 11 800); λ_{max}(0.1M-HCl) 268 nm (ε 11 000); λ_{max}(0.1M-NaOH) 294 nm (ε 18 900); δ(CDCl₃) 1.08 (6 H, s, 2 × Me), 1.60–2.63 (11 H, m, 5 × CH₂ + CH), 5.75 (1 H, br s, =CH), and 7.26 (6 H, s, Ph + OH).

(vii) 7-*t*-Butyl-3,4,6,7,8,9-hexahydrodibenzofuran-1(2H)-one (25). After a 6 h reflux period using toluene as solvent were obtained compound (6) (Table 1) (24.4%), b.p. 148–152 °C (0.4 mmHg) and compound (25) (8.1%), b.p. 180–186 °C (0.4 mmHg), m.p. 70 °C (from light petroleum, b.p. 40–60 °C) (Found: C, 77.7; H, 9.2. C₁₆H₂₂O₂ requires C, 78.1; H, 8.9%); ν_{max}(KBr) 1 670 cm⁻¹; λ_{max}(H₂O) 284 nm (ε 3 130). It gave the thiosemicarbazone, m.p. 242–243 °C (from toluene) (Found: C, 64.1; H, 8.0; N, 13.1; S, 9.9. C₁₇H₂₅N₃OS requires C, 64.0; H, 7.8; N, 13.2; S, 10.0%).

(viii) 3,3-Dimethyl-3,4,6,7,8,9-hexahydro-7-phenylbenzofuran-1(2H)-one (26). After a 7 h reflux period using toluene as solvent the neutral residues gave compound (26) (6.1%), m.p. 133.5–134.5 °C (from ethanol) (Found: C, 81.4; H, 7.6. C₂₀H₂₂O₂ requires C, 81.6; H, 7.5%); ν_{max}(KBr) 1 580 and 1 660 cm⁻¹; λ_{max}(H₂O) 286 nm (ε 3 210); δ(CDCl₃) 1.11 (6 H, s, 2 × Me), 2.00 (2 H, m, 8-CH₂), 2.30 (2 H, s, 2-CH₂), 2.67 (2 H, s, 4-CH₂), 2.80 (5 H, m, 2 × CH₂ + CH), and 7.25 (5 H, s, Ph); δ_c(CDCl₃) 194.79 (C-1), 165.11 (C-4a), 150.83 (C-5a), 145.53 (C-1'), 128.60 and 126.91 (C-2' and C-3'), 126.53 (C-4'), 119.11 (C-9b), 115.07 (C-9a), 52.44 (C-2), 40.72 (C-7), 37.58, 30.75, 30.30, and 21.43 (C-4, C-6, C-8, and C-9), 35.25 (C-3), and 28.71, 28.58 p.p.m. (*gem* dimethyl group).

5,5-Dimethyl-3-methoxy-2-(4-phenylcyclohex-1-enyl)cyclohex-1-enylcyclohexane-1,3-dione (1 g) in methanol (15 ml) was added to diazomethane (1 g) in ether (50 ml) and the mixture swirled on an ice-bath for 2 h. The solvent was evaporated and the residue dissolved in toluene and chromatographed through a silica-gel column eluted with 20% ethyl acetate-toluene to give the methoxy derivative as an oil (0.94 g, 90%); *m/z* 310; ν_{max}(neat) 1 650 and 1 600 cm⁻¹; λ_{max}(H₂O) 275 nm (ε 8 500); δ(CDCl₃) 1.00 (6 H, s, 2 × Me), 2.17 (2 H, s, CH₂), 2.32 (2 H, s, CH₂), 1.70–2.90 (7 H, m, 3 × CH₂ + CH), 3.70 (3 H, s, OMe), 5.48 (1 H, br s, =CH), and 7.25 (5 H, s, Ph).

3,3-Dimethyl-7-*t*-butyl-3,4,4a,5a,6,7,8,9,9a,9b-decahydrodibenzofuran-1(2H)-one.—A stirred mixture of 10% palladium-on-charcoal (1 g) and 3,3-dimethyl-7-*t*-butyl-3,4,4a,5a,6,7,8,9,9a,9b-decahydrodibenzofuran-1(2H)-one (14) (1.4 g) in methanol (30 ml) took up 1 equiv. of hydrogen at room temperature and pressure within 3 h. Evaporation gave the *ketone* (0.3 g, 21.4%), m.p. 126–127 °C (from light petroleum, b.p. 40–60 °C) (Found: C, 77.4; H, 11.1. C₁₈H₃₀O₂ requires C, 77.7; H, 10.8%); ν_{\max} (Nujol) 1 700 cm⁻¹; δ (CDCl₃) 0.83 (9 H, s, CMe₃), 0.88 (3 H, s, Me), 1.03 (3 H, s, Me), 1.00–2.50 (12 H, m), 3.02 (1 H, t, 9b-CH), 3.93 (1 H, m, 5a-CH), and 4.32 (1 H, m, 4a-CH).

2-(4-*t*-Butylcyclohex-1-enyl)cyclohexane-1,3-dione–Methanesulphonic Acid (27).—A solution of cyclohexane-1,3-dione (5.6 g, 50 mmol), 4-*t*-butylcyclohexanone (7.7 g 50 mmol), and methanesulphonic acid (1 ml) in benzene (250 ml) was refluxed under a Dean–Stark water separator for 9 h, during which the theoretical volume of water was collected. The mixture was allowed to cool overnight and the crystals collected to give the *methanesulphonic acid mixture* (27) (3.6 g, 20.9%), m.p. 176–177 °C (from acetone) (Found: C, 59.4; H, 8.2; S, 9.1. C₁₇H₂₈O₅S requires C, 59.3; H, 8.1; S, 9.3%); ν_{\max} (KBr) 3 450 (enol OH), 2 550 (acid OH), and 1 535 cm⁻¹ (dione); λ_{\max} (H₂O) 264 nm (ϵ 11 100); λ_{\max} (0.1M-HCl) 265 nm (ϵ 10 600); λ_{\max} (0.1M-NaOH) 292 nm (ϵ 22 000); δ [(CD₃)₂SO] 0.84 (9 H, s, CMe₃), 1.0–2.5 (15 H, m), 2.64 (3 H, s, MeSO₃H), 5.25 (1 H, br t, =CH), 10.06 (2 H, s, 2 × OH); δ^{\dagger} [(CD₃)₂SO] 182.46 (C-1 and C-3), 129.40 (C-1'), 125.12 (C-2'), 117.29 (C-2), 41.83 (C-4'), 38.33 (MeSO₃H), 31.60 (C-4 and C-6), 30.68 (C-Bu'), 28.32, 25.34, and 22.53 (C-3', C-5', and C-6'), 25.83 (CMe₃), and 19.18 p.p.m. (C-5). In the same way the following were prepared.

(i) 2-(4-Phenylcyclohex-1-enyl)cyclohexane-1,3-dione–methanesulphonic acid. The methanesulphonic acid (74%) was obtained, m.p. 189 °C (from acetone) (Found: C, 62.7; H, 6.6; S, 8.5. C₁₉H₂₄O₅S requires C, 62.6; H, 6.6; S, 8.8%); ν_{\max} (KBr) 3 460, 2 500, and 1 535 cm⁻¹; λ_{\max} (H₂O) 264 nm (ϵ 11 800); λ_{\max} (0.1M-HCl) 264 nm (ϵ 11 700); λ_{\max} (0.1M-NaOH) 291 nm (ϵ 21 700); δ (CD₃OD) 2.71 (3 H, s, MeSO₃H), 1.6–2.9 (15 H, m), 5.50 (1 H, br t, =CH), and 7.24 (5 H, s, Ph); δ [(CD₃)₂SO] 11.80 (2 H, s, 2 × OH).

(ii) 2-Cyclohex-1-enylcyclohexane-1,3-dione–toluene-*p*-sulphonic acid. With toluene as solvent the *dione* (8.2%) was obtained, m.p. 185–186 °C (from butanone) (Found: C, 62.7; H, 6.6; S, 9.2. C₁₉H₂₄O₅S requires C, 62.6; H, 6.6; S, 8.8%); ν_{\max} (KBr) 2 500 and 1 540 cm⁻¹; λ_{\max} (H₂O) 262 nm (ϵ 10 000);

λ_{\max} (0.1M-HCl) 262 nm (ϵ 10 100); λ_{\max} (0.1M-NaOH) 289 nm (ϵ 20 000); δ (CD₃OD) 1.40–2.20 (10 H, m), 2.32 (3 H, s, MeC₆H₄), 2.3–2.9 (4 H, m), 7.23 (2 H, d), and 7.74 (2 H, d) (C₆H₄); the CD₃OH signal at δ 5.4 obscured the vinyl proton; δ^{\dagger} [(CD₃)₂SO] 184.01 (C-1, C-3) 131.18 (C-1'), 126.48 (C-2'), 119.23 (C-2), 33.08 (C-4, C-6), 28.32, 25.16 (C-3', C-6'), 22.71, 21.92 (C-4', C-5'), and 20.64 p.p.m. (C-4); for the toluene-*p*-sulphonic acid, δ^{\dagger} 144.63 (C-1), 138.86 (C-4), 128.63 (C-3, C-5), 125.84 (C-2), (C-6), and 20.98 p.p.m. (Me).

(iii) 2-(4-Phenylcyclohex-1-enyl)cyclohexane-1,3-dione–toluene-*p*-sulphonic acid. With toluene as solvent, the *dione* (19.5%) was obtained, m.p. 177 °C (from butanone) (Found: C, 67.8; H, 6.4; S, 7.3. C₂₅H₂₈O₅S requires C, 68.2; H, 6.4; S, 7.3%); ν_{\max} (KBr) 2 520, and 1 535 cm⁻¹; λ_{\max} (H₂O) 264 nm (ϵ 11 500); λ_{\max} (0.1M-HCl) 264 nm (ϵ 11 300); λ_{\max} (0.1M-NaOH) 290 nm (ϵ 20 100); δ (CD₃OD) 2.31 (3 H, s, Me), 1.4–2.9 (15 H, m), 5.50 (1 H, br, =CH), 7.23 (7 H, m, Ph + 2 from C₆H₄), and 7.75 (2 H, d, 2 from C₆H₄); δ^{\dagger} [(CD₃)₂SO] 184.10 (C-1, C-3), 147.54 (C-1'), 131.15 (C-1'), 128.57 (C-3', C-5'), 127.09 (C-2'), 126.30 (C-2'), 118.77 (C-2), 39.37 (C-4'), 33.63, 30.02, 29.05 (C-3', C-5', and C-6'), 33.11 (C-4, C-6), and 20.67 p.p.m. (C-5); for the toluene-*p*-sulphonic acid, δ^{\dagger} 144.78 (C-1), 138.8 (C-4), 128.63 (C-3, C-5), 125.87 (C-2, C-6), and 21.01 p.p.m. (Me).

General Method for Aromatisation—A mixture of 10% palladium-on-charcoal (1 g) and the dibenzofuranone (2 g) in *p*-cymene (50 ml) was heated to the boiling point. About 15 ml of the solvent was removed by distillation and the residue refluxed for 6 h. The solution was filtered, the solvent removed at the water pump, and the residue recrystallised to give the products listed in Tables 3 and 4. Compounds (15) (Table 1) failed to aromatise by this method but a mixture of dehydrogenated derivatives was obtained after reflux for 12 h in decalin and separated by fractional recrystallisation. For 3,3-Dimethyl-3,4-dihydrodibenzofuran-1(2H)-one, δ^{\dagger} (CDCl₃) 194.21 (C-1), 170.05 (C-4a), 155.09 (C-5a), 124.94, 124.52, (C-7, C-9), 123.76 (C-9a), 121.85 (C-8), 115.47 (C-9b), 111.22 (C-6), 52.33 (C-2), 37.82 (C-4), 35.27 (C-3), and 28.72 p.p.m. (2 × Me).

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† In the n.m.r. assignments, primed numbers refer to the cyclohexenyl moiety; double primes are used for the phenyl substituent when present.