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# Condensations of benzil with phenols and aryl ethers mediated by tin(IV) chloride pentahydrate

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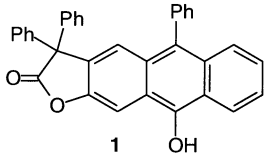
**Abstract**—The reaction of benzil with phenol at 180°C in the presence of $SnCl_4{\cdot}5H_2O$ produces a benzofuran, a benzofuranol, a benzodifuran, and a benzofuranone. Anhydrous tin(IV) chloride also gives a benzofuranofuranone. Other phenols and their methyl ethers yield related products. The good yields of the benzo- and naphtho-furanones make the method an attractive alternative to the benzilic acid route to such compounds. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

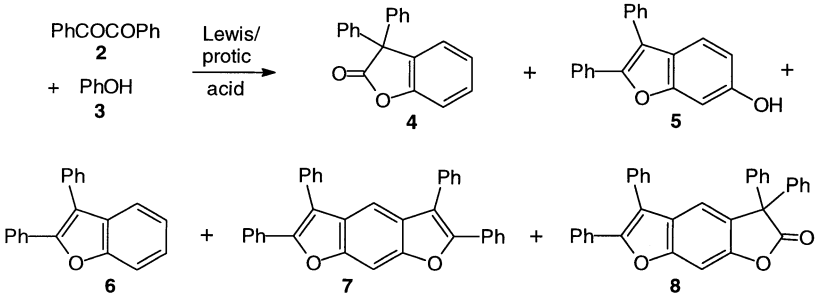
Hans von Liebig reported[1] in 1908 that benzil reacted with phenol at 180°C in the presence of 'Zinnchlorid' to give the polycyclic lactone **1**. His explanation for its formation assumed an *acid-catalysed* benzil–benzilic acid rearrangement and a novel anthracene synthesis. We found his arguments unconvincing and have reinvestigated this reaction; we have also extended it by the use of other phenols and their methyl ethers.




**1**

## 2. Results and discussion

Liebig did not specify the type of tin(IV) chloride used and we chose to employ the hydrated form which behaves as both a Lewis and a protic acid and which is handled more easily than is the anhydrous compound. Repetition of the reaction between benzil **2**, phenol **3**, and $SnCl_4{\cdot}5H_2O$ using Liebig's conditions and subsequent separation of the products by PLC gave the lactone **4** and the benzofuranol **5** together with smaller amounts of the benzofuran **6** and the benzodifuran **7** but the lactone **1** was not present (Scheme 1).The yields are given in Table 1. Both the use of a lower temperature (130°C) and the substitution of anhydrous zinc chloride in place of $SnCl_4{\cdot}5H_2O$ gave generally similar results but anhydrous aluminium chloride provided a significantly larger (59%) yield of the lactone **4**. In contrast polyphosphoric acid gave mainly the benzofuranol **5** even after prolonged heating. Finally the use of anhydrous tin(IV) chloride produced a substance $C_{34}H_{22}O_3$, mp 235–236°C, which we believe to be the compound with the same molecular formula, mp 239°C, reported by Liebig and thought by him to be the lactone **1**. We formulate the substance as the benzofuran lactone **8**. It shows the characteristic behaviour of a γ-lactone, absorbing strongly




**Scheme 1.**

*Keywords*: benzofurans; diones; furanones; phenols.

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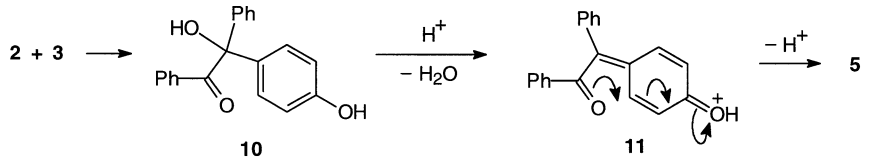
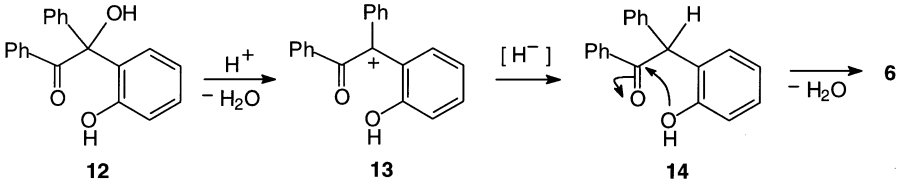
**Table 1.** Products (%) from benzil–phenol reactions (8 h at 180°C)

| Lewis/protic acid | Benzofuran **6** | Benzodifuran **7** | Lactone **4** | Benzofuranol **5** | Benzofuran lactone **8** |
|---|---|---|---|---|---|
| $SnCl_4 \cdot 5H_2O$ | 4 | 6 | 23 | 29 | 0 |
| $SnCl_4 \cdot 5H_2O$ (130°C) | 3 | 6 | 17 | 41 | 0 |
| $ZnCl_2$ (anhydrous) | 4 | 4 | 29 | 31 | 0 |
| $AlCl_3$ (anhydrous) | 5 | 1 | 59 | 13 | 0 |
| Polyphosphoric acid | 1 | 1 | 0 | 36 | 0 |
| Polyphosphoric acid (24 h) | 1 | 2 | 2 | 40 | 0 |
| $SnCl_4$ (anhydrous) | 6 | 16 | 0 | 35 | 25 |

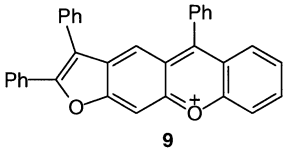



**Scheme 2.**




**Scheme 3.**

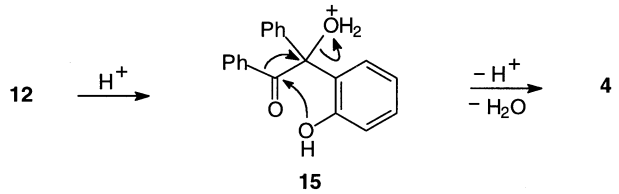
in the IR at 1797 $cm^{-1}$ and losing carbon monoxide followed by a hydrogen atom in the mass spectrometer to give, as the base peak, an ion which may be written as the pyrylium ion **9**. Its UV absorption resembles that of the benzofuranol **5**; all its $^1H$ NMR signals are those of aromatic protons.



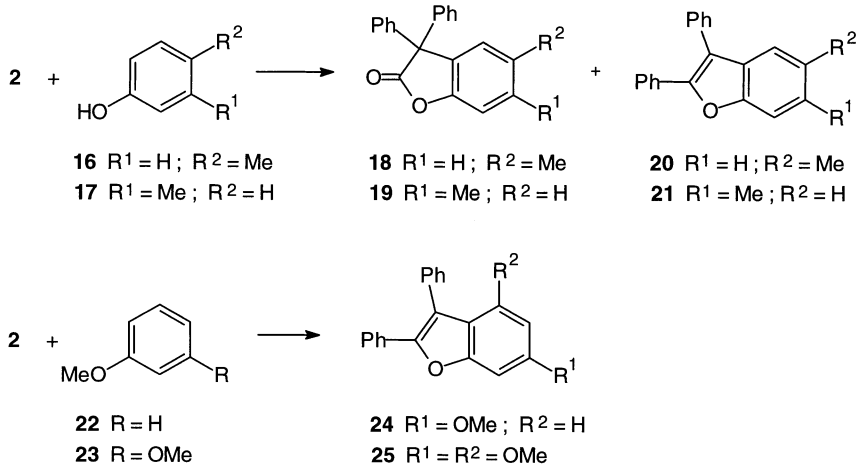

The formation of the benzofuranol **5** in which a second oxygen function has been introduced *meta* to the original hydroxy group appears to involve the reaction of one of the benzil carbonyl groups at the *para* position of phenol to give the hydroxyketol **10** (Scheme 2) followed by acid-induced dehydration to give the protonated *p*-quinonemethide **11** and subsequent cyclisation to form the furan ring. The formation of the minor product, the benzofuran **6**, requires *ortho* alkylation of the phenol and this would be favoured by the coordination of the oxygen atoms of both reactants with the Lewis acid used. Before the furan ring can be formed the arylbenzoin intermediate must undergo reduction presumably via the α-ketocarbocation **13**[2] (Scheme 3). The reducing agent would appear to be phenol two molecules of which, probably coordinated with the Lewis acid, would provide the necessary hydrogen producing a dihydroxybiphenyl in the process. This explanation receives support from the corresponding reaction with 1-naphthol which gave as a minor product the difuran **34**. The latter clearly results from the reaction of the intermediate dihydroxybinaphthyl **32** with benzil.

The same cation **13** may also participate in the formation of the lactone **4**, addition of the hydroxy group to the carbonyl group of **13** being accompanied by migration of a phenyl group to the electron-deficient site but a synchronous mechanism, as in structure **15**, would seem to be more appropriate (Scheme 4). This 1,2-shift of a phenyl group bears some resemblance to the benzpinacol–benzpinacone rearrangement;[3] it is favoured energetically by the stability of the resulting γ-lactone system. A similar rearrangement has been postulated[4] to account for the formation of the lactone **4** (in 17% yield) during the anodic oxidation of the benzofuran **6**. The tricyclic products **7** and **8** clearly result from further reactions of the benzofuranol **5** with benzil.

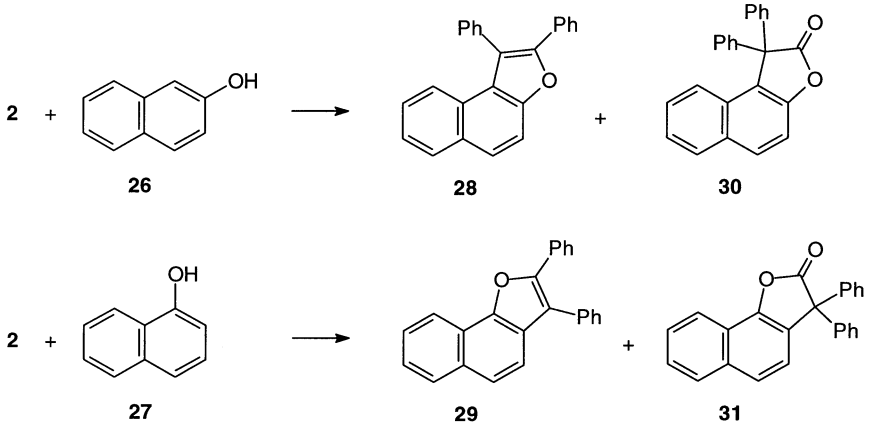
The replacement of phenol in the benzil–$SnCl_4 \cdot 5H_2O$ reaction by other phenols and their methyl ethers resulted in the formation of analogous products. In particular *p*-cresol **16** and *m*-cresol **17** gave good yields of the corresponding lactones **18** (65%) and **19** (91%) together with small amounts of the related benzofurans **20** and **21**. In contrast the less reactive methyl ethers anisole **22** and *m*-dimethoxybenzene **23** afforded only the methoxybenzofurans **24** and **25**, respectively (Scheme 5). 2-Naphthol **26** and 1-naphthol




**Scheme 4.**



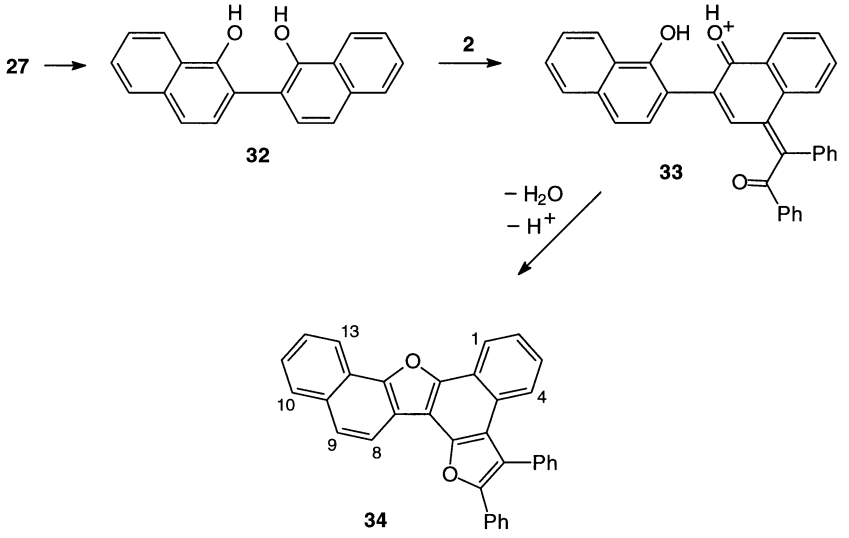

**Scheme 5.**



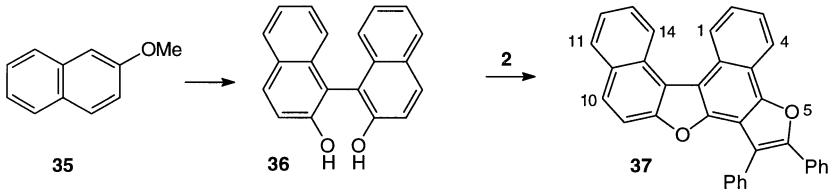

**Scheme 6.**

**27** provided the naphthofurans **28** and **29** and the related naphthofuranones **30** and **31**, respectively, the latter again in good yields (70 and 65%) (Scheme 6).

The reaction with 1-naphthol also afforded a minor product, $C_{34}H_{20}O_2$, which gave mass and UV spectra typical of a polycyclic aromatic structure. Its molecular formula shows it to be composed of two molecules of 1-naphthol plus one of benzil less two molecules of water and two atoms of hydrogen. We suggest that two molecules of 1-naphthol



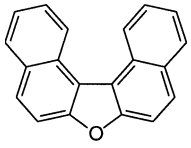

**Scheme 7.**




**Scheme 8.**

**27**, coordinated to tin(IV), couple to give 2,2[1]-binaphthyl-1,1[1]-diol **32** (and in so doing provide the hydrogen needed for the formation of the naphthofuran **29**). The diol then reacts with benzil to form the protonated quinonemethide **33** which cyclises as in structure **11**; elimination of water from the two phenolic hydroxy groups gives the dinaphthodifuran **34** (Scheme 7). The proton NMR spectrum supports this formulation. The *peri* protons at C-1 and -13 appear as a multiplet at $\delta$ 8.50–8.60, similar to that at $\delta$ 8.30–8.45 shown by the *peri* proton in the naphthofuran **29** while the AB quartet centred at $\delta$ 7.86 and 8.35 can be assigned to H-9 and -8 the low-field shift of the latter proton being a consequence of the proximity of the oxygen at position 7. The multiplet at $\delta$ 7.97–8.05 corresponds to H-10; similar *peri* protons in the dinaphthofuran **38** resonate at $\delta$ 8.00.

2-Methoxynaphthalene **35** underwent cleavage of the methoxy group during reaction with benzil and $SnCl_4{\cdot}5H_2O$ giving the same compounds as were obtained from 2-naphthol together with a minor product, $C_{34}H_{20}O_2$, isomeric with the dinaphthodifuran **34** and having generally similar spectroscopic properties. A mechanistic argument similar to that proposed above when applied to 2-naphthol leads via the binaphthyldiol **36** to the structure **37** which receives support from the proton NMR spectrum (Scheme 8). Of the four low-field signals those at $\delta$ 9.11 and 8.89 can be assigned to H-1 and -14 which are in close proximity; the corresponding signals for the dinaphthofuran **38** appear as a broad doublet at $\delta$ 9.12. The signal at $\delta$ 8.54 can be attributed to H-4 being similar to that (at $\delta\sim$8.37) of H-9 of the naphthofuran **29**. The signal at $\delta$ 8.01 can be assigned to H-11 as the corresponding proton of the dinaphthofuran **38** resonates at $\delta$ 8.00. Finally its UV absorption shows a marked resemblance to that[5] of the latter compound.




**38**

## 3. Experimental

### 3.1. General

IR spectra were measured for KBr discs, and UV absorptions for methanolic solutions. $^1H$ and $^{13}C$ NMR spectra were recorded for $CDCl_3$ solutions at 220 and 20 MHz, respectively, using $Me_4Si$ as internal standard. Mass spectra were obtained using EI at 70 eV. 'Light petroleum' refers to the fraction bp 60–80°C. All the products are colourless solids. Their yields are based on the initial weights of benzil used, no account being taken of the varying amounts of starting materials that were recovered from all the reactions.

#### 3.1.1. Reactions of benzil with benzene derivatives.

*(a) With phenol using $SnCl_4{\cdot}5H_2O$.*

A mixture of benzil (5.0 g, 23.8 mmol), phenol (5.0 g, 53.2 mmol), and $SnCl_4{\cdot}5H_2O$ (5.0 g, 14.2 mmol) was heated at 180°C for 8 h, cooled, diluted with chloroform (75 ml), and washed with water (800 ml). Evaporation of the solvent gave an oil which was separated by PLC using light petroleum–chloroform (1:1) followed in the case of the less polar constituents by light petroleum into four fractions. The fastest-moving component crystallised from ether–light petroleum to give 2,3-diphenylbenzofuran **6** (4%) as needles mp 119–120°C (lit.,[6] 120°C) (Found: $M^+$, 270.1039. Calcd for $C_{20}H_{14}O$: *M*, 270.1045); *m/z* 270 (100%, $M^+$), 268 (11, M−2H), 241 (18, M−CHO), and 239 (18, 268−CHO); $\lambda_{max}$ (nm) 238 (log $\varepsilon$ 4.27), 273infl (3.95), 305 (4.29) and 313infl (4.25); $\nu_{max}$ ($cm^{-1}$) 1600 (aromatic C=C), 764 (4 adjacent ArH), 748 and 694 (5 adjacent ArH); $\delta_H$ 7.17–7.80 (14H, m, ArH). Next came 2,3,5,6-tetraphenylbenzo[1,2-*b*:5,4-*b*[1]]difuran **7** (6%) which crystallised from ether-light petroleum as needles, mp 220–221.5°C (lit.,[7] 221–222°C) identical (IR, UV, mixed mp) with an authentic specimen (Found: $M^+$, 462.1622. Calcd for $C_{34}H_{22}O_2$: *M*, 462.1620; *m/z* 462 (100%, $M^+$) and 231 (13, $M^{2+}$); $\lambda_{max}$ (nm) 231 (log $\varepsilon$ 4.48), 245 (4.49), 300 (4.48), 331infl (4.55), 339 (4.60), and 349infl (4.50); $\nu_{max}$ ($cm^{-1}$) 1600 (aromatic C=C), 890 (isolated ArH), 762 and 693 (5 adjacent ArH); $\delta_H$ 7.15–7.83 (22H, m, ArH). The third component crystallised from chloroform–light petroleum to give 3,3-diphenyl-2(3*H*)-benzofuranone **4** (23%) as plates, mp 119–120°C (lit.,[1] 120°C) (Found: $M^+$, 286.0996. Calcd for $C_{20}H_{14}O_2$: *M*, 286.0994); *m/z* 286 (45%, $M^+$), 258 (52, M−CO), 257 (100, 258−H), 242 (8, $M-CO_2$), 241 (10, $M-CHO_2$) and 181 (44, M−PhCO); $\lambda_{max}$ (nm) 260 (log $\varepsilon$ 3.15), 266.5 (3.19), 272 (3.24), and 280 (3.18); $\nu_{max}$ ($cm^{-1}$) 1795 ($\gamma$-lactone C=O), 1590 (aromatic C=C), 763 (4 adjacent ArH), 749 and 695 (5 adjacent ArH); $\delta_H$ 7.13–7.48 (14H, m, ArH). The slowest-moving component crystallised from ether–light petroleum to give 2,3-diphenylbenzofuran-6-ol **5** (29%) as needles, mp 117–119°C (lit.,[7] 118–120°C) (Found: $M^+$, 286.0998. Calcd for $C_{20}H_{14}O_2$: *M*, 286.0994); *m/z* 286 (100%, $M^+$), and 257 (16, M−CHO); $\lambda_{max}$ (nm) 236 (log $\varepsilon$ 4.25), 320 (4.31), and 347infl (3.74); $\nu_{max}$ ($cm^{-1}$) 3300 (phenolic OH), 1622, 1600 (aromatic C=C), 795 (2 adjacent ArH), 761 and 689 (5 adjacent

ArH); $\delta_H$ 5.02 (1H, s, 6-OH), 6.84 (1H, dd, *J*=1 and 9 Hz, H-5), 7.10 (1H, d, *J*=1 Hz, H-7) and 7.29–7.72 (11H, m, ArH).

*(b) With phenol using anhydrous $SnCl_4$.*

A similar reaction in a sealed ampoule using anhydrous $SnCl_4$ (5.0 g, 19.2 mmol) in place of the hydrate gave, in addition to the above benzofurans, *3,3,5,6-tetraphenyl-2(3H)benzo [1,2-b:5,4-b']furanofuranone* **8** (25%) which crystallised from ethanol, mp 235–236°C (Found: $M^+$, 478.1568. $C_{34}H_{22}O_3$ requires: *M*, 478.1569); *m/z* 478 (61%, $M^+$), 450 (56, M−CO), 449 (100, 450−H), 373 (28, 450−$C_6H_5$), 105 (17, PhCO) and 77 (19, $C_6H_5$); $\lambda_{max}$ (nm) 304infl (log $\varepsilon$ 4.03), 317 (4.14), and 324infl (4.11); $\nu_{max}$ ($cm^{-1}$) 1797 (γ-lactone C═O), 1600 (aromatic C═C), 903 (isolated ArH), 763, 752 and 695 (5 adjacent ArH); $\delta_H$ 7.08–7.65 (22H, m, ArH).

*(c) With p-cresol using $SnCl_4 \cdot 5H_2O$.*

A similar reaction between benzil (5.0 g, 23.8 mmol), *p*-cresol (5.0 g, 46.3 mmol) and $SnCl_4 \cdot 5H_2O$ (5.0 g, 14.2 mmol) provided two products. The faster-moving component gave 2,3-diphenyl-5-methylbenzofuran **20** (3.5%) which crystallised from chloroform as needles mp 112–113°C (lit.,[6] 114°C) (Found: $M^+$, 284.1201. Calcd for $C_{21}H_{16}O$: *M*, 284.1201); *m/z* 284 (100%, $M^+$), 282 (9, M−2H), 255 (8, M−CHO), and 239 (8, M−CO–Me); $\lambda_{max}$ (nm) 237 (log $\varepsilon$ 4.19), 288infl (4.09), 299infl (4.18), 305 (4.22), and 315 (4.15); $\nu_{max}$ ($cm^{-1}$) 1599 (aromatic C═C), 797 (2 adjacent ArH), 759 and 692 (5 adjacent ArH); $\delta_H$ 2.42 (3H, s, Me) and 7.16–7.75 (13H, m, ArH). The slower-moving component was 3,3-diphenyl-5-methyl-2(3)-benzofuranone **18** (65%) which crystallised from chloroform as plates mp 128–129°C (lit.,[8] 130°C) (Found: $M^+$, 300.1158. Calcd for $C_{21}H_{16}O_2$: *M*, 300.1150); *m/z* 300 (20%, $M^+$), 272 (49, M−CO), 271 (100, M−CHO), 255 (7, M−$CO_2$–H), 241 (8, M−$CO_2$–Me), 228 (7, 271−CO–Me), and 195 (35, M−CO–Ph); $\lambda_{max}$ (nm) 233 (log $\varepsilon$ 4.14), 258infl (3.17), 266infl (3.13), 271infl (3.18), 279 (3.29) and 288 (3.22); $\nu_{max}$ ($cm^{-1}$) 1801 (γ-lactone C═O), 1614, 1593 (aromatic C═C), 809 (4 adjacent ArH), 770, 749, 738, and 699 (5 adjacent ArH); $\delta_H$ 2.30 (3H, s, Me), 7.04–7.41 (13H, m, ArH); $\delta_C$ 21.2 (q), 61.5 (s), 110.7, 126.6, 127.8, 128.2, 128.6 and 129.7 (all d), 131.0, 134.2, 140.9, 150.5, and 177.1 (all s).

*(d) With m-cresol.*

A similar reaction with *m*-cresol (5.0 g, 46.3 mmol) gave two products. The faster-moving component was 2,3-diphenyl-6-methylbenzofuran **21** (2%) which crystallised from chloroform–light petroleum in needles mp 87–88°C (lit.,[6] 89°C) (Found: $M^+$, 284.1200, Calcd for $C_{21}H_{16}O$: *M*, 284.1201); *m/z* 284 (100%, $M^+$), 255 (15, M−CHO) and 239 (19, M−CO–Me); $\lambda_{max}$ (nm) 239 (log $\varepsilon$ 4.30), 301infl (4.28), 309 (4.32), and 328infl. (4.26); $\nu_{max}$ ($cm^{-1}$) 1602 (aromatic C═C), 818 (2 adjacent ArH), 764 and 695 (5 adjacent ArH); $\delta_H$ 2.46 (3H, s, Me), 7.04 (1H, dd, *J*=9 and 1 Hz, H-5). and 7.20–7.75 (12H, m, ArH). The slower-moving component crystallised from chloroform to give 3,3-diphenyl-6-methyl-2(3*H*)-benzofuranone **19** (91%) as plates mp 122–124°C (lit.,[9] 125°C) (Found: $M^+$, 300.1156. Calcd for $C_{21}H_{16}O_2$: *M*, 300.1150); *m/z* 300 (32%, $M^+$), 272 (51, M−CO), 271 (100, M−CHO), 255 (6, M−$CO_2$−H), 241 (12, 271−CO–Me), and 195 (M−Ph–CO); $\lambda_{max}$ (nm) 235 (log $\varepsilon$ 4.13), 267 (3.17), 275 (3.20), and 282 (3.24); $\nu_{max}$ ($cm^{-1}$) 1796 (γ-lactone C═O), 1620, 1595 (aromatic C═C), 817 (2 adjacent ArH), 767, 752, and 698 (5 adjacent ArH); $\delta_H$ 2.34 (3H, s, Me), 6.98 (1H, br.s, H-7), 7.11 (1H, br.d, *J*=8 Hz, H-5), and 7.17–7.45 (11H, m, ArH); $\delta_C$ 21.6 (q), 61.2 (s), 111.7, 125.3, 125.8 (all d), 126.9 (s), 127.7, 128.1, 128.7 (all d), 139.7, 140.9, 152.7, and 177.1 (all s).

*(e) With anisole.*

A similar reaction between benzil (5.0 g, 23.8 mmol), anisole (5.0 g, 46.3 mmol) and $SnCl_4 \cdot 5H_2O$ (5.0 g, 14.2 mmol) gave 6-methoxy-2,3-diphenylbenzo[*b*]furan **24** (29%) which crystallised from light petroleum as needles, mp 121–122°C (lit.,[10] 120–121°C) (Found: C, 84.00; H, 5.40%; $M^+$, 300.1152. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37%; *M*, 300.1150); *m/z* 300 (100%, $M^+$), 285 (71, M−Me), 228 (3, 285−CHO–CO) and 150 (3, $M^{2+}$); $\lambda_{max}$ (nm) 230 (log $\varepsilon$ 4.26), 316 (4.40), and 350infl (3.26); $\nu_{max}$ ($cm^{-1}$) 1610 (aromatic C═C), 820 (2 adjacent ArH), 765 and 700 (5 adjacent ArH); $\delta_H$ 3.81 (3H, s, MeOAr), 6.85 (1H, dd, *J*=2 and 8 Hz, H-5), 7.05 (1H, d, *J*=2 Hz, H-7), and 7.13–7.75 (11H, m, ArH).

*(f) With m-dimethoxybenzene.*

A similar reaction with *m*-dimethoxybenzene (5.0 g, 36.2 mmol) in place of anisole gave *4,6-dimethoxy-2,3-diphenylbenzo[b]furan* **25** (23%) which crystallised from benzene-light petroleum in needles mp 129–130°C (Found: $M^+$, 330.1258. $C_{22}H_{18}O_3$ requires: *M*, 330.1255); *m/z* 330 (100%, $M^+$), 315 (70, M−Me), 299 (3, M−MeO) and 287 (6, 315−CO); $\lambda_{max}$ (nm) 246 (log $\varepsilon$ 4.24) and 324 (4.26); $\nu_{max}$ ($cm^{-1}$) 1602 (aromatic C═C), 755 and 690 (5 adjacent ArH); $\delta_H$ 3.60 and 3.82 (each 3H, s, MeO at C-4 and -6), 6.25 (1H, d, *J*=2 Hz, H-5), 6.67 (1H, d, *J*=2 Hz, H-7), and 6.91–7.60 (10H, m, ArH).

### 3.1.2. Reactions of benzil with naphthalene derivatives.

*(a) With 1-naphthol.*

A mixture of benzil (5.2 g, 24.8 mmol), 1-naphthol (3.6 g, 25.0 mmol) and $SnCl_4 \cdot 5H_2O$ (5.0 g, 14.2 mmol) after treatment as in (a) above gave three products. The fastest-moving material crystallised from acetone–ethanol to give 2,3-diphenylnaphtho[1,2-*b*]furan **29** (13%) as needles, mp 99–100°C (lit.,[11] 100°C) (Found: $M^+$, 320.1206. Calcd for $C_{24}H_{16}O$: *M*, 320.1201); *m/z* 320 (100%, $M^+$), 291 (9, M−CHO), 289 (13, 291−2H), 215 (7, M−PhCO), and 160 (7, $M^{2+}$); $\lambda_{max}$ (nm) 252 (log $\varepsilon$ 4.52), 265infl (4.46), 279infl (4.36), 316 (4.26), 325infl (4.21), 333infl (4.09) and 349 (3.76); $\nu_{max}$ ($cm^{-1}$) 1595 (aromatic C═C), 817 (2 adjacent ArH), 770 (4 adjacent ArH), 741 and 699 (5 adjacent ArH); $\delta_H$ 7.17–7.95 (15H, m, ArH) and 8.30–8.45 (1H, m, H-9). Next came 5,6-*diphenylnaphtho[1',2'-b]naphtho[1,2-b:3,4-b']difuran* **34** (2%) which crystallised from acetone–methanol in needles, mp 171–173°C (Found:

$M^+$, 460.1473. $C_{34}H_{20}O_2$ requires: *M*, 460.1463); *m/z* 460 (100%, $M^+$), and 230 (5, $M^{2+}$); $\lambda_{max}$ (nm) 236 (log $\varepsilon$ 4.56), 267infl (4.61), 273 (4.63), 300 (4.57), 308infl (4.53), 335 (4.32), 343infl (4.25), and 362 (3.96); $\nu_{max}$ ($cm^{-1}$) 1600 (aromatic C=C), 805 (2 adjacent ArH), 764 (4 adjacent ArH), 755 and 701 (5 adjacent ArH); $\delta_H$ 7.21–7.45 (5H, m, ArH), 7.48–7.72 (10H, m, ArH), 7.86 (1H, d, *J*=8 Hz, H-9), 7.97–8.05 (1H, m, H-10), 8.35 (1H, d, *J*=8 Hz, H-8) and 8.50–8.60 (2H, m, H-1 and -13). The slowest-moving material was 3,3-diphenyl-2(3*H*)-naphtho[1,2-*b*]furanone **31** (65%) which crystallised from chloroform–light petroleum as needles, mp 188–189°C (lit.,[12] 190°C) (Found: $M^+$, 336.1147. Calcd for $C_{24}H_{16}O_2$: *M*, 336.1150); *m/z* 336 (24%, $M^+$), 308 (49, M−CO), 307 (100%, 308-H), 278 (6, 307−CHO), 231 (42, 308−$C_6H_5$), 202 (16, 231−CHO), and 154 (12, $308^{2+}$); $\lambda_{max}$ (nm) 239 (log $\varepsilon$ 4.67), 286 (3.78), 296infl (3.73), 311 (3.48), 318 (3.34), and 325 (3.50); $\nu_{max}$ ($cm^{-1}$) 1800 (γ-lactone C=O), 1596 (aromatic C=C), 806 (2 adjacent ArH), 766 (4 adjacent ArH), 749 and 699 (5 adjacent ArH); $\delta_H$ 7.20–7.73 (14H, m, ArH), 7.83–7.91 (1H, m, ArH) and 8.06–8.15 (1H, m, ArH).

*(b) With 2-naphthol.*

A similar reaction using 2-naphthol (5.0 g, 34.7 mmol) gave two products. The faster-moving material crystallised from chloroform–light petroleum to give 2,3-diphenylnaphtho[2,1-*b*]furan **28** (6%) as needles mp 105–106°C (lit.,[13] 106°C) (Found: $M^+$, 320.1198. Calcd for $C_{24}H_{16}O$: *M*, 320.1201); *m/z* 320 (100%, $M^+$), 291 (7, M−CHO), 289 (15, 291−2H), 215 (7, M−PhCO), 160 (5, $M^{2+}$), and 105 (PhCO); $\lambda_{max}$ (nm) 251infl (log $\varepsilon$ 4.13), 301infl (4.15), 309 (4.17), 315 (4.16), 329 (4.28), and 344 (4.35); $\nu_{max}$ ($cm^{-1}$) 1594 (aromatic C=C), 803 (2 adjacent ArH), 765 (4 adjacent ArH), 755 and 701 (5 adjacent ArH); $\delta_H$ 7.17–7.90 (16H, m, ArH). The slower-moving material crystallised from chloroform-light petroleum to give 3,3-diphenyl-2(3*H*)-naphtho[2,1-*b*]furanone **30** (70%) as plates, mp 182–183°C (lit.,[9] 183°C) (Found: $M^+$, 336.1152. Calcd for $C_{24}H_{16}O_2$: *M*, 336.1150); *m/z* 336 (96%, $M^+$), 308 (53, M−CO), 307 (100, 308−H), 292 (11, M−$CO_2$), 291 (8, 292−H), and 231 (37, 308−$C_6H_5$); $\lambda_{max}$ (nm) 233 (log $\varepsilon$ 4.57), 265 (3.53), 271 (3.55), 282 (3.66), 295 (3.66), 316 (3.27), 324 (3.20), and 330 (3.34); $\nu_{max}$ ($cm^{-1}$) 1805 (γ-lactone C=O), 1627 and 1580 (aromatic C=C), 809 (2 adjacent ArH), 766 (4 adjacent ArH). 741 and 691 (5 adjacent ArH); $\delta_H$ 7.19–7.65 (14H, m, ArH), and 7.79–7.97 (2H, m, 8- and 9-H).

*(c) With 2-methoxynaphthalene.*

A similar reaction between benzil (4.2 g, 20.0 mmol), 2-methoxynaphthalene (3.l6 g, 20.0 mmol) and $SnCl_4{\cdot}5H_2O$ (5.0 g, 14.2 mmol) gave three products. The fastest-moving material, the naphthofuran **28** (4%) was followed by *6,7-diphenylnaphtho[2′,1′-g]naphtho[1,2-b:3,4-b′]difuran* **37** (4%) which crystallised from acetone as needles, mp 190–192°C (Found: $M^+$, 460.1455. $C_{34}H_{20}O_2$ requires: *M*, 460.1463); *m/z* 460 (100%, $M^+$), and 230 (11, $M^{2+}$); $\lambda_{max}$ (nm) 263.5 (log $\varepsilon$ 4.42), 293 (4.45), 303 (4.44), 313infl (4.36), 327 (4.32), 343 (4.27), 360 (4.30), and 378 (4.27); $\nu_{max}$ ($cm^{-1}$) 1599 (aromatic C=C), 798 (2 adjacent ArH), 745 and 692 (5 adjacent ArH); $\delta_H$ 7.29–7.94 (16H, m, ArH), 8.01 (1H, br.d, *J*=7.5 Hz, H-11), 8.54 (1H, br.d, *J*=8 Hz, H-4), 8.89 (1H, br.d, *J*=8 Hz, H-1), and 9.11 (1H, br.d, *J*=7.5 Hz, H-14). The final product was the naphthofuranone **30** (74%).

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