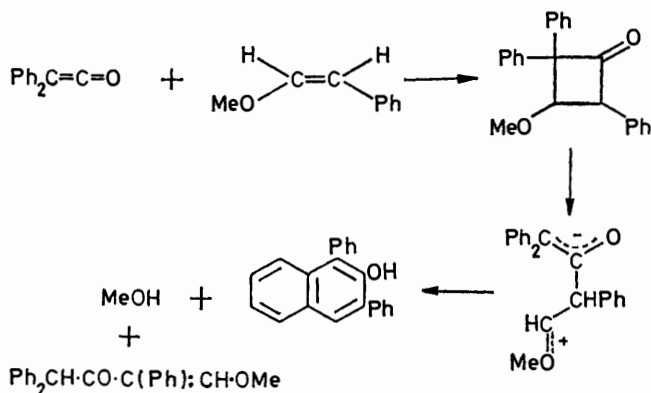


## Overcrowded Molecules. Part VIII.<sup>1</sup> Addition of Diphenylketen to (*Z*)-2-Benzylidene-3-diphenylmethylene-2,3-dihydro-5-methylbenzofuran

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Diphenylketen, through its carbonyl double bond, adds to the 1,4-positions of the conjugated diene. (*Z*)-2-benzylidene-3-diphenylmethylene-2,3-dihydro-5-methylbenzofuran, to give the vinyl ether, 3-diphenylmethylene-3,4-dihydro-8-methyl-1,1,4-triphenyl-1*H*-pyrano[4,3-*b*]benzofuran (7; X = O, R = Me). The mechanism of this unusual keten–diene reaction is discussed.

HUISGEN and his co-workers have reported that cycloadditions of diphenylketen to 1,3-dienes yield cyclobutanones and that Diels–Alder adducts cannot be detected.<sup>2</sup> Kinetic and stereochemical results are consistent with a concerted mechanism for cyclobutanone formation from diphenylketen with vinyl ethers, involving  $[\pi^{2s} + \pi^{2a}]$  cycloaddition where the keten is the antarafacial component.<sup>3</sup> The cyclobutanone derivatives, obtained from vinyl ethers, ring-open on heating to give dipolar intermediates which rearrange. 3-Methoxy-2,2,4-triphenylcyclobutanone, from diphenylketen and (*Z*)- $\beta$ -methoxystyrene at room temperature, gave 1,3-diphenyl-2-naphthol and 4-methoxy-1,1,3-triphenylbut-3-en-2-one at 100° (see Scheme 1).<sup>4</sup>



SCHEME 1

The reaction of diphenylketen with the (*Z*)-benzofuran (3; X = O, R = Me) to yield the vinyl ether (7; X = O, R = Me) by 1,4-addition of the carbonyl double bond of the keten to the diene, can be rationalised on the basis of these elegant studies.

It is suggested that cycloaddition of diphenylketen with diene occurs to form the cyclobutanone derivative (5; R = Me) through a transition state with unequal closure of the two  $\sigma$  bonds. The necessary stabilisation of partial charges accounts for the reactivity of the diene, the double bond which is attacked, and for the orientation of diphenylketen in the cycloaddition. One of the

newly formed  $\sigma$ -bonds of the cyclobutanone (5; R = Me) then opens to form a dipolar intermediate (6; R = Me), which cyclises to the vinyl ether (7; X = O, R = Me) (see Scheme 2). The structure of the vinyl ether (7; X = O, R = Me) follows from combustion analysis, molecular weight determination by mass spectrometry, the absence of a carbonyl absorption in the i.r. spectrum, n.m.r. studies which showed methine and methyl singlets at  $\tau$  4.86 and 7.75 respectively, and ozonolysis which gave benzophenone. The alternative structure for the adduct (9; R = Me) is less likely on mechanistic considerations. A small amount of adduct (7; X =  $\text{CH}_2$ , R = H) has been isolated from the reaction of diphenylketen with (*E*)-2-benzylideneindan-1-one (1; X =  $\text{CH}_2$ , R = H).<sup>5</sup> It is believed that ketone (8; R = Me) is not formed because of steric interactions between four phenyl groups on two adjacent carbon atoms. Similar steric effects account for the failure of diphenylketen to react with diphenylethylene to give 2,2,3,3-tetraphenylcyclobutanone.<sup>6-8</sup> In this reaction, a 2 : 1 diphenylketen–diphenylethylene adduct is obtained which, from Baldwin's studies,<sup>8</sup> we conclude is the enol ester (13) obtained from the naphthalenone (12) by further reaction with diphenylketen. On alkaline hydrolysis, the ester (13) yields diphenylacetic acid and the hydroxy-ketone<sup>9</sup> (14) (see Scheme 3) and not 4-hydroxy-1,1,4,4-tetraphenylbutan-2-one as reported by Farooq and Abraham.<sup>7</sup>

Thermochromic yellow needles of the (*Z*)-benzofuran (3; X = O, R = Me), which turns red on heating, were obtained together with the vinyl ether (7; X = O, R = Me) by heating the (*Z*)-benzofuranone (1; X = O, R = Me) with diphenylketen at 56°. Reaction of (*E*)-2-benzylideneindan-1-one (1; X =  $\text{CH}_2$ , R = H) with diphenylketen only takes place at 140° to give the corresponding (*E*)-indane (3; X =  $\text{CH}_2$ , R = H).<sup>5</sup> The milder conditions for the former reaction are attributed to the greater polarity of the benzylidenebenzofuranone and hence the increased susceptibility of the carbonyl oxygen atom to electrophilic attack by diphenylketen.

At 140°, the diene (3; X = O, R = H) undergoes

<sup>1</sup> Part VII, R. J. Hart and H. G. Heller, *J.C.S. Perkin I*, 1972, 1321.

<sup>2</sup> R. Huisgen and P. Otto, *Chem. Ber.*, 1969, **102**, 3475.

<sup>3</sup> R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, 1969, **102**, 3444.

<sup>4</sup> R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, 1969, **102**, 3405.

<sup>5</sup> N. Campbell, P. S. Davison, and H. G. Heller, *J. Chem. Soc.*, 1963, 993.

<sup>6</sup> H. Staudinger and E. Suter, *Ber.*, 1920, **53**, 1092.

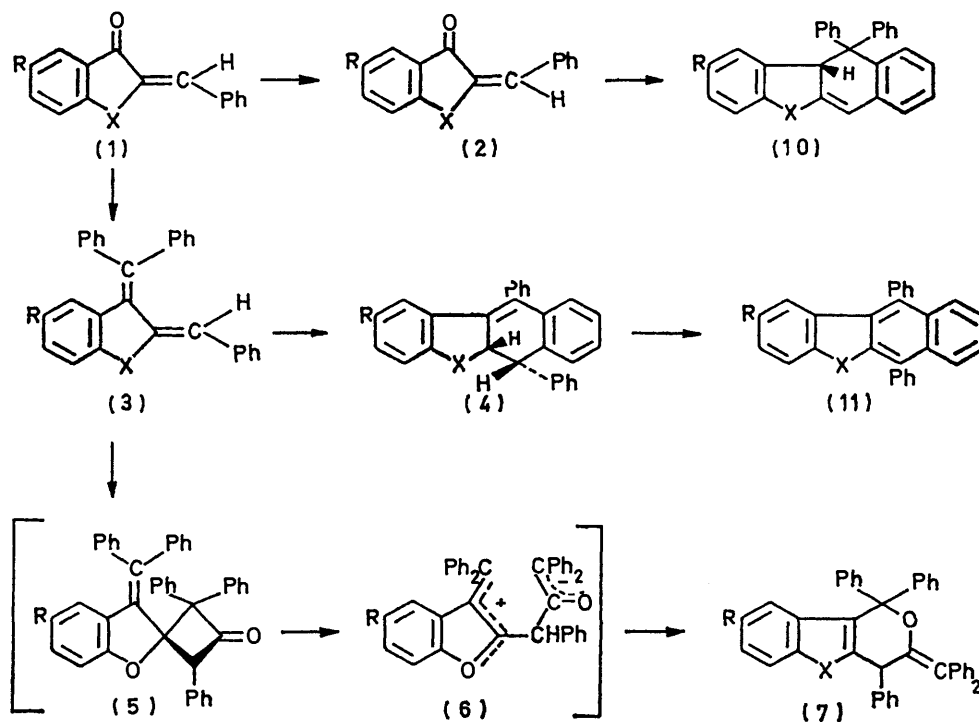
<sup>7</sup> M. O. Farooq and N. A. Abraham, *Bull. Soc. chim. France*, 1958, 832.

<sup>8</sup> J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, 1970, **92**, 4868.

<sup>9</sup> J. E. Baldwin, M. F. Brechinridge, and D. S. Johnson have made the same assignments in an independent study, *Tetrahedron Letters*, 1972, 1635.

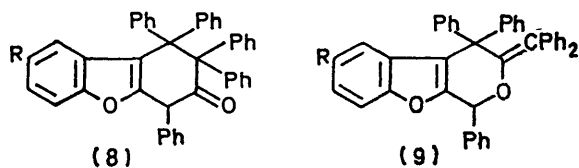
disrotatory electrocyclic ring closure followed by a [1,5] hydrogen shift to yield *cis*-5a,6-dihydrobenzofuran (4; X = O, R = H) in almost quantitative yield. On prolonged heating at 160°, the benzofuranone (11; X = O, R = H) is also obtained.<sup>10</sup>

R = Me) were obtained, indicating that thermal (*E*) → (*Z*) reversal of the benzylidenefuranone occurred more rapidly than reaction of the (*E*)-isomer with diphenylketen. The (*E*)-benzofuranone (2; X = O, R = Me) isomerises to the (*Z*)-isomer (1; X = O, R = Me) on

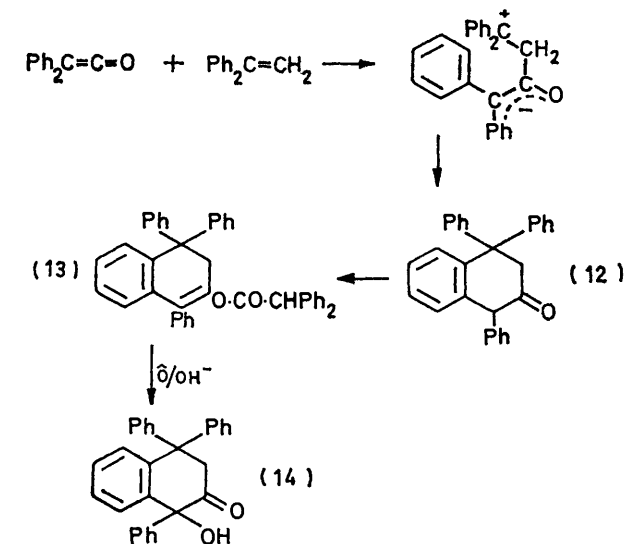


The *cis* arrangement of 5a and 6 protons in the dihydro-compound (4; X = O, R = H) is indicated by coupling of 8 Hz in the n.m.r. spectrum.<sup>11</sup> (*E*) and (*Z*)-2-Benzylideneindan-1-ones (1; X = CH<sub>2</sub>, R = H) and (2; X = CH<sub>2</sub>, R = H) with diphenylketen yield the dihydrobenzofluorene (4; X = CH<sub>2</sub>, R = H) and (10; X = CH<sub>2</sub>, R = H), respectively.

heating at 100°. The non-methylated (*Z*)-benzofuranone (1; X = O, R = H) also reacted with di-



Analogous reactions of (*Z*)- and (*E*)-2-benzylidene-5-methylbenzofuran-3(2*H*)-ones (1; X = O, R = Me) and (2; X = O, R = Me) would have confirmed chemically the stereochemistry of benzylidenefuranones.<sup>12</sup> The (*E*)-benzofuranone (2; X = O, R = Me), produced by photochemical isomerisation of the (*Z*)-isomer, did not react with diphenylketen at 56°. At 100°, diene (3; X = O, R = Me) and adduct (7; X = O,



phenylketen at 56° to give a mixture of diene (3; X = O, R = H) and vinyl ether (7; X = O, R = H).

<sup>10</sup> H. Tucker, Ph.D. Thesis, University College of Wales, Aberystwyth, 1967.

<sup>11</sup> H. G. Heller and K. Salisbury, *J. Chem. Soc. (C)*, 1970, 399.

<sup>12</sup> J. S. Hastings and H. G. Heller, *J.C.S. Perkin I.*, 1972, in the press.

## EXPERIMENTAL

U.v. spectra were measured for solutions in ethanol with a Unicam SP 500 spectrometer unless stated otherwise; n.m.r. spectra were obtained for solutions in deuteriochloroform with a Perkin-Elmer R12 (60 MHz) spectrometer (tetramethylsilane as internal standard). Molecular weight determinations were obtained using an AEI MS9 mass spectrometer.

(Z)-2-Benzylidene-5-methylbenzofuran-3(2H)-one<sup>13</sup> (1; X = O, R = Me).—This was obtained by condensation of 5-methylbenzofuran-3(2H)-one with benzaldehyde in ethanol in presence of a few drops of hydrochloric acid, yellow prisms, m.p. 117–118° (from ethanol) (lit.<sup>13</sup> 119°) (Found: C, 81.5; H, 5.0. Calc. for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>: C, 81.3; H, 5.1%),  $\lambda_{\max}$  215, 260, 323, and 385 nm (log  $\epsilon$  4.06, 4.06, 4.30, and 4.02),  $\nu_{\max}$  1710s (C=O) and 1660s (C=C) cm<sup>-1</sup>  $\tau$  2.10 (2H, q, 2'- and 6'-H<sub>2</sub>), 2.45–2.78 (6H, complex m, remaining Ar- and Ar'-H), 3.16 (1H, s, C:CHPh), and 7.63 (3H, s, Me).

(E)-2-Benzylidene-5-methylbenzofuran-3(2H)-one (2; X = O, R = Me).—The (Z)-isomer (1; X = O, R = Me) (0.5 g) in benzene (1 l) was irradiated (8 h) using a Hanovia 1-l Photoreactor fitted with a medium-pressure mercury lamp and Pyrex thimbles. Solvent was removed and the residue recrystallised from ethanol to give (E)-2-benzylidene-5-methylbenzofuran-3(2H)-one (0.4 g), which isomerised on heating above 80° (Found: C, 81.5; H, 5.1. C<sub>16</sub>H<sub>12</sub>O<sub>2</sub> requires C, 81.3; H, 5.1%),  $\lambda_{\max}$  220, 260, 325, and 395 nm (log  $\epsilon$  4.12, 4.12, 4.30, and 3.86),  $\nu_{\max}$  1700s (C=O) and 1665w cm<sup>-1</sup> (C=C),  $\tau$  1.78 (2H, q, 2'- and 6'-H<sub>2</sub>), 2.4–2.8 (6H, complex m, Ar- and Ar'-H), 3.05 (1H, s, C:CHPh), and 7.63 (3H, s, Me).

Reaction of Diphenylketen with (Z)-2-Benzylidene-5-methylbenzofuran-3(2H)-one (1; X = O, R = Me).—(Z)-2-Benzylidene-5-methylbenzofuran-3(2H)-one (2 g) and diphenylketen (1.8 g) were heated (16 h) at 56°. The product was chromatographed (silica gel; benzene). The orange first fraction yielded a 1:1 mixture of diene (3; X = O, R = Me) and vinyl ether (7; X = O, R = Me) (1.8 g) (see later). Composition and concentration followed from comparison of the n.m.r. spectrum of the mixture to those of pure components. Repeated crystallisation of the mixture from benzene-light petroleum gave (Z)-2-benzylidene-3-diphenylmethylene-2,3-dihydro-5-methylbenzofuran (3; X = O, R = Me) (0.3 g), yellow needles, m.p. 174–176°. On heating, the crystals turn from yellow to red and the reverse colour change occurs on cooling (Found: C, 89.0; H, 5.7. C<sub>29</sub>H<sub>22</sub>O requires C, 90.1; H, 5.7%),  $\lambda_{\max}$  (CHCl<sub>3</sub>) 284 and 408 nm (log  $\epsilon$  4.40 and 4.10),  $\tau$  2.3–3.0 (17H, complex m, ArH), 4.48 (1H, s, C:CHPh), 3.73 (1H, s, 4-H), and 7.92 (3H, s, Me). A second fraction yielded unchanged (Z)-isomer (1.4 g).

Yellow solutions of the diene in chloroform rapidly decolourised in daylight to give 2-methyl-6,11-diphenylbenzo[b]naphtho[2,3-d]furan (11; X = O; R = Me), needles with a blue-green fluorescence, m.p. 169–170° (from benzene-light petroleum),  $\tau$  2.3–3.26 (17-H, complex m, ArH) and 7.73 (3H, s, Me). Its u.v. spectrum [ $\lambda_{\max}$  (CHCl<sub>3</sub>) 273, 330, 349, and 364 nm (log  $\epsilon$  4.37, 4.03, 3.92, and 3.95)] closely resembled the spectra of benzo[b]naphtho[2,3-d]furan<sup>14</sup> and its 6,11-diphenyl derivative.

Reaction of Diphenylketen with (E)-2-Benzylidene-5-

methylbenzofuran-3(2H)-one (2; X = O, R = Me).—(E)-2-Benzylidene-5-methyl-3(2H)-benzofuranone (0.35 g) and diphenylketen (0.29 g) were heated (4 h) at 100°. Work-up as before gave diene (3; X = O, R = Me) (0.12 g), m.p. 174–176°. A second reaction with diphenylketen (0.58 g) gave 3-diphenylmethylene-3,4-dihydro-8-methyl-1,1,4-triphenyl-1H-pyrano[4,3-b]benzofuran (7; X = O, R = Me) (0.75 g), crystals, with a sharp m.p. in the range 231–239°, which varies with the rate of heating (from benzene-light petroleum) (Found: C, 88.9; H, 5.5%; M, 580. C<sub>43</sub>H<sub>32</sub>O<sub>2</sub> requires C, 88.9; H, 5.6%; M, 580),  $\tau$  2.73–3.22 (28H, complex m, ArH), 4.86 (1H, s, methine proton), and 7.75 (3H, s, Me),  $\nu_{\max}$  1625m cm<sup>-1</sup> (C=C). The vinyl ether (100 mg) was also obtained from heating diene (3; X = O, R = Me) (70 mg) with diphenylketen (36 mg) at 140°. Ozone was passed through the vinyl ether (0.5 g) in carbon tetrachloride until the ozonide separated. Steam distillation gave first solvent, then benzophenone (identified from its i.r. and n.m.r. spectra, and characterised as the 2,4-dinitrophenylhydrazone).

Reaction of Diphenylketen with (Z)-2-Benzylidenebenzofuran-3(2H)-one (1; X = O, R = H).—(Z)-2-Benzylidenebenzofuran-3(2H)-one<sup>15</sup> (0.7 g) and diphenylketen (1 g) were heated (24 h) at 56°. Work-up as before gave a 1:1 mixture of diene (3; X = O, R = H) and vinyl ether (7; X = O, R = H), which could not be separated by chromatography or fractional crystallisation. The mixture (0.25 g) was heated with diphenylketen at 100° and the product chromatographed (alumina; benzene). The first fraction yielded the vinyl ether (7; X = O, R = H), crystals, m.p. 198–199° (from ethanol) (Found: C, 88.9; H, 5.3%; M, 566. C<sub>42</sub>H<sub>30</sub>O<sub>2</sub> requires C, 89.0; H, 5.3%; M, 566),  $\tau$  2.45–3.2 (29H, complex m, ArH) and 4.84 (1H, s, methine proton),  $\nu_{\max}$  1625m cm<sup>-1</sup> (C=C).

(Z)-2-Benzylidenebenzofuran-3(2H)-one (6 g) and diphenylketen (7.9 g) were heated (20 h) at 160°. The mixture was chromatographed (alumina; benzene). The first fraction, which had a deep blue fluorescence in u.v. light, gave 6,11-diphenylbenzo[b]naphtho[2,3-d]furan (11; X = O, R = H) (1.8 g), needles, m.p. 193–194° [from benzene-light petroleum (b.p. 100–120°)] (Found: C, 90.8; H, 5.0. C<sub>28</sub>H<sub>18</sub>O requires C, 90.8; H, 4.9%),  $\lambda_{\max}$  (CHCl<sub>3</sub>) 270, 326, 345, and 360 nm (log  $\epsilon$  5.1, 4.49, 4.29, and 4.30). The second fraction yielded cis-5a,6-dihydro-6,11-diphenylbenzo[b]naphtho[2,3-d]furan (4; X = O, R = H) (1.2 g), plates, m.p. 197–198° [from benzene-light petroleum (b.p. 100–120°)] (Found: C, 90.4; H, 5.4. C<sub>28</sub>H<sub>20</sub>O requires C, 90.3; H, 5.4%),  $\lambda_{\max}$  248, 295, 305, 375, and 390 nm (log  $\epsilon$  4.48, 4.04, 4.03, 4.40, and 4.07),  $\tau$  2.78–3.6 (18H, complex m, ArH), 4.1 (1H, d, J 8 Hz, 5a-H), and 5.41 (1H, d, J 8 Hz, 6-H). Further reaction of diphenylketen (1.5 g) with (Z)-2-benzylidenebenzofuran-3(2H)-one (1.1 g) at 140° for 0.5 h gave the dihydro-compound (4; X = O, R = H) in quantitative yield.

Hydrolysis of Diphenylketen-Diphenylethene 2:1 Adduct, 1,2-Dihydro-1,1,4-triphenyl-2-naphthyl Diphenylacetate (13) (with R. M. MEGIT).—The 2:1 adduct<sup>6</sup> (m.p. 182°; 1 g) was boiled (2 h) with ethanolic sodium ethoxide [prepared by dissolving sodium (2 g) in ethanol (100 ml)]. The solution was cooled, carefully acidified with dilute hydrochloric acid to pH 6, and ethanol was removed under reduced pressure. The aqueous suspension was extracted

<sup>13</sup> K. Auwers and K. Müller, *Ber.*, 1908, **41**, 4233; K. Fries and G. Finck, *ibid.*, p. 4271.

<sup>14</sup> G. M. Badger and B. J. Christie, *J. Chem. Soc.*, 1956, 3438.  
<sup>15</sup> J. Gripenberg, *Acta Chem. Scand.*, 1953, **7**, 1323.

with ether, and the combined ether extracts were washed with *m*-sodium carbonate. The carbonate extract was acidified and extracted with ether. Work-up of this ether extract gave diphenylacetic acid (0.3 g, 80%), identified by m.p. and mixed m.p. The first ether extract yielded 3,4-dihydro-1-hydroxy-1,4,4-triphenylnaphthalen-2(1*H*)one (0.45 g, 67%), m.p. 195—196° (after repeated recrystallisation from benzene–light petroleum) (lit.,<sup>7</sup> 195—196°; but considered to be 4-hydroxy-1,1,4,4-tetra-

phenylbutan-2-one). (Found: <sup>7</sup> C, 86.0; H, 5.6%; *M*, 390.161. C<sub>28</sub>H<sub>22</sub>O<sub>2</sub> requires C, 86.1; H, 5.7%; *M*, 390.161),  $\tau$  2.0—3.2 (about 19H, complex m, ArH), 5.9 (1H, d, *J* 13 Hz, CH<sub>2</sub>), and 6.75 (1H, d, *J* 13 Hz, CH<sub>2</sub>),  $\nu_{\max}$  (1% in CCl<sub>4</sub>) 3450 (OH) and 1725 (C=O) cm<sup>-1</sup>.

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