The reactions of diazo compounds with lactones. Part 2.† The reaction of cyclic 2-diazo-1,3-dicarbonyl compounds with diketene: benzofuran formation

Paul V. Murphy,‡ Timothy J. O'Sullivan, Bryan D. Kennedy and Niall W. A. Geraghty *

Department of Chemistry, National University of Ireland, Galway, Republic of Ireland.
*E-mail: niall.geraghty@nuigalway.ie*

Cyclic 2-diazo-1,3-dicarbonyl compounds react with diketene in the presence of rhodium(II) salts to give benzofurans as the major isolated products. The formation of intermediate products with exocyclic double bonds which isomerise to benzofurans provides support for the proposed mechanism which involves initial formation of a dioxaspirooctenone by a formal dipolar cycloaddition reaction of a carbenoid to the exocyclic double bond of diketene followed by the loss of carbon dioxide. Acyclic 2-diazo-1,3-dicarbonyl compounds give furans in poor yield.

Introduction

We and others have described the synthesis of cyclopropane-spiro-β-lactones **2** by means of the reaction of carbene or
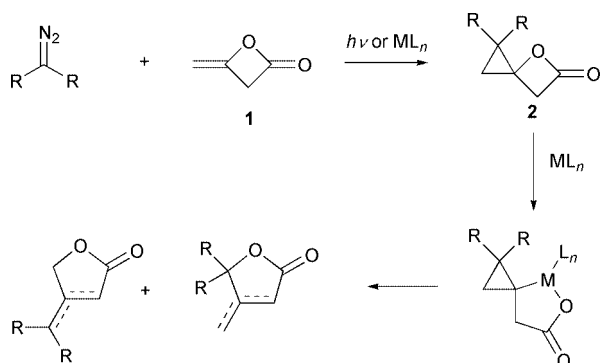
Scheme 1

carbenoid species, generated by the photochemical or metal catalysed decomposition of diazo compounds, respectively, with the exocyclic double bond of diketene **1**.[1–6] The metal catalysed and thermal rearrangements of these compounds have also been studied.[6] We have shown, for example, that the conversion of **2** to furanones (Scheme 1) is a general metal catalysed process and have proposed a mechanism involving the insertion of a metal species into the O–C bond of the β-lactone ring.

In view of these results, it might have been expected that the metal catalysed reaction of acyclic and cyclic 2-diazo-1,3-dicarbonyl compounds with diketene would give cyclopropane-spiro-β-lactones arising from cyclopropanation of the exocyclic double bond or furanones resulting from insertion of the metal into the O–C bond of the initially formed spirolactone. Herein we present the results relating to the reactions of 2-diazo-1,3-dicarbonyl compounds with diketene which in contrast to the behaviour of other diazo compounds[6] give furans and benzofurans as the isolated products.[7]

---

† For Part 1, see ref. 6(*b*).
‡ *Current address*: Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland.

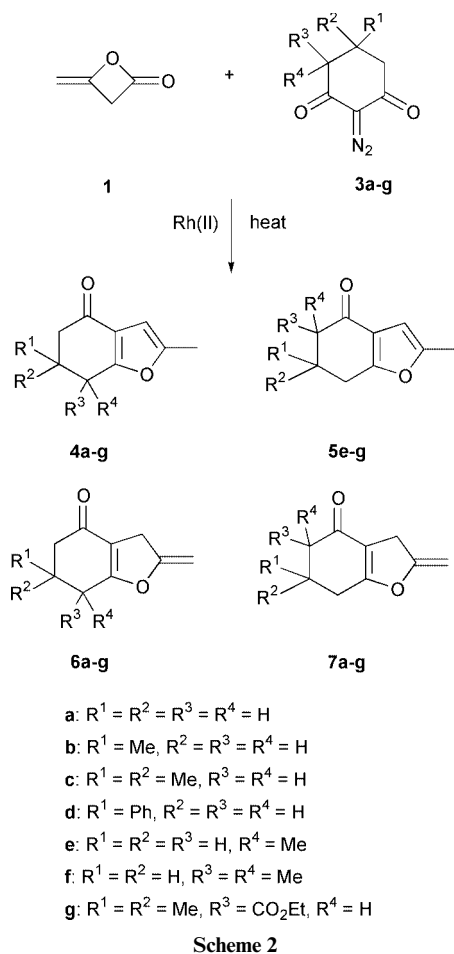**Table 1** Rh₂(OAc)₄ catalysed reactions of cyclic diazo compounds with diketene

Diazo compound	Reaction time/h[a]	Product (yield %)[b]
3a[8]	15	**4a** (28)[b]
3a	15	**4a** (29)
3a	15	4 : 1 mixture of **4a** + **6a** (30)
3b[9]	15	**4b** (44)
3c[8]	22	**4c** (26)[c]
3d[10]	24	**4a** (43)
3e[11]	8	**4e**[d] (35), **5e** (6)
3f	24	**4f** (28), **5f** (14)
3g	24	**4g** (21), **5g** (8)
8[12]	6[e]	**9** (28), **10** (21)

[a] All reactions were carried out at room temperature unless otherwise stated and % yields are those obtained after chromatography. [b] A yield of 72% was obtained by direct distillation of the crude product. [c] A yield of 46% was obtained by direct distillation of the crude product. [d] **6e** rearranged to **4e** on standing. [e] The reaction with diketene was carried out in refluxing benzene.
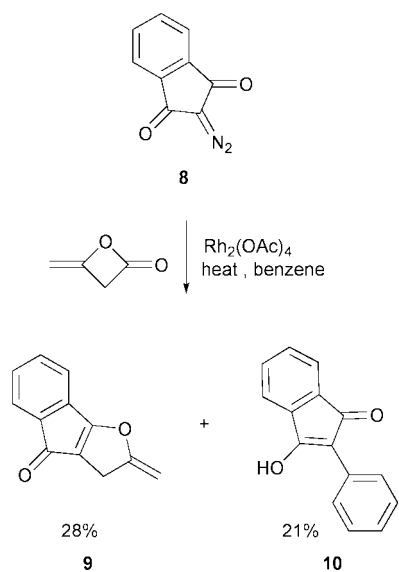
Results and discussion

The Rh(II) catalysed reactions of the cyclic 2-diazo-1,3-diketones[8–11] **3a**–**g** with diketene ultimately give moderate to good yields of benzofurans **4** and **5** in a process that is moderately regioselective (Table 1, Scheme 2). The exocyclic double bond isomers **6** and **7** were observed by NMR spectroscopy of the crude reaction mixtures. These intermediates isomerise to the endocyclic isomers **4** and **5** during chromatography, distillation of the crude product mixture or simply on standing at room temperature. The regioisomeric products **4** and **5** can be distinguished using ¹H-NMR as the methylene protons α to the furan ring occur at consistently lower field than the protons α to the keto group. The reaction is under steric control as cyclisation occurs at the carbonyl group furthest from the ring substituent. The reaction of 2-diazoindane-1,3-dione[12] **8** with diketene in benzene gave the furan **9** which has an exocyclic double bond, but unlike **6** and **7** one which does not isomerise on standing or heating (Scheme 3), and the product **10** resulting from carbene insertion into the C–H bond of the aromatic ring.[13]

In contrast to the reactions of **3** and **8**, the Rh(II) catalysed decompositon reactions of the cyclic 2-diazo-1,3-dicarbonyl

Scheme 2

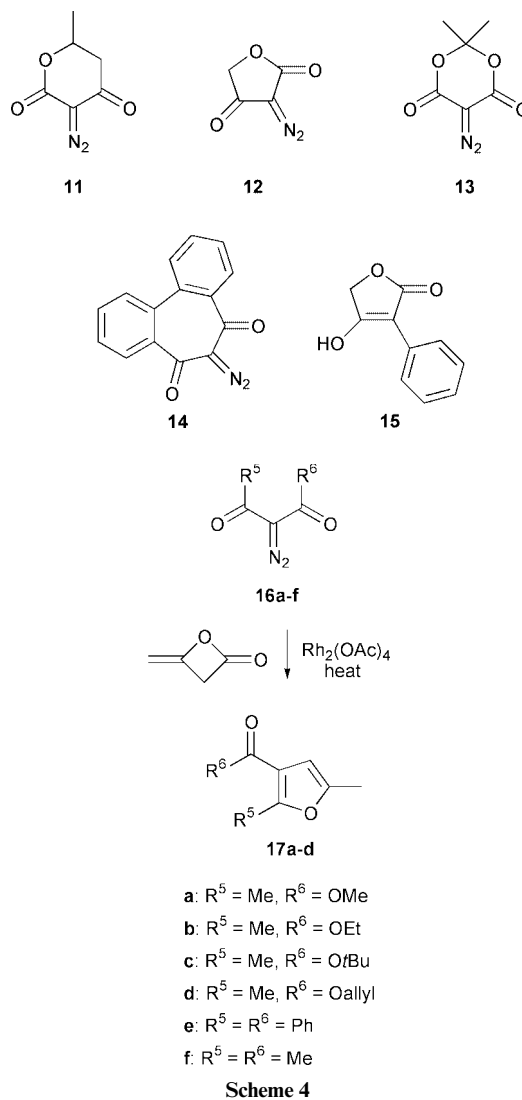a: $R^1 = R^2 = R^3 = R^4 = H$
b: $R^1 = Me$, $R^2 = R^3 = R^4 = H$
c: $R^1 = R^2 = Me$, $R^3 = R^4 = H$
d: $R^1 = Ph$, $R^2 = R^3 = R^4 = H$
e: $R^1 = R^2 = R^3 = H$, $R^4 = Me$
f: $R^1 = R^2 = H$, $R^3 = R^4 = Me$
g: $R^1 = R^2 = Me$, $R^3 = CO_2Et$, $R^4 = H$

Scheme 3

Table 2 $Rh_2(OAc)_4$ catalysed reactions of acyclic 2-diazo-1,3-dicarbonyl compounds with diketene

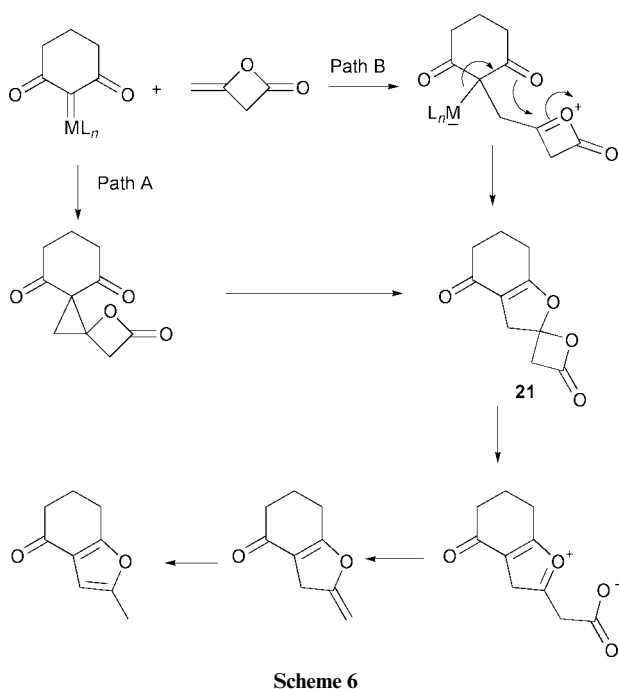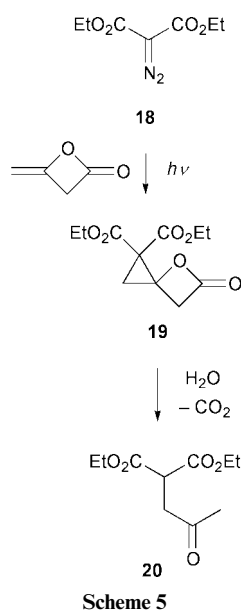| Diazo compound	Reaction time/h[a]	Product (yield, %)[b]
16a[17]	24	**17a** (6)
16b[18]	72	**17b** (7)
16c[19]	24	**17c** (3)
16d[20]	72[c]	**17d** (18)

[a] All reactions were carried out at room temperature unless otherwise stated. [b] Isolated yields after chromatography. [c] The reaction was carried out at 70 °C.

Scheme 4

a: $R^5 = Me$, $R^6 = OMe$
b: $R^5 = Me$, $R^6 = OEt$
c: $R^5 = Me$, $R^6 = OtBu$
d: $R^5 = Me$, $R^6 = Oallyl$
e: $R^5 = R^6 = Ph$
f: $R^5 = R^6 = Me$

compounds **11**–**14** in the presence of diketene gave complex mixtures from which furans, cyclopropanespiro-β-lactones or other identifiable products could not be obtained. When benzene was used as a solvent for the reaction of **12**[14] the product of insertion into the C–H bond of the aromatic ring **15**[15] was again obtained. This appears to be a general reaction for cyclic-2-diazo-1,3-dicarbonyl compounds[13,15,16] and renders aromatic solvents unsuitable for these reactions.

Furan formation also occurs in the $Rh_2(OAc)_4$ catalysed reactions of acyclic 2-diazoacetoacetates[17–20] **16a**–**d** with diketene giving **17a**–**d** (Table 2, Scheme 4) in low yield. However, furans are not formed in $Rh_2(OAc)_4$ catalysed reactions of

acyclic 2-diazo-1,3-diketones **16e** and **16f** both of which give intractable mixtures. Diethyl diazomalonate[21] **18** is recovered unreacted after prolonged exposure to $Rh_2(OAc)_4$ in the presence of diketene; photolysis of **18** in the presence of diketene leads to formation of the cyclopropanespiro-β-lactone **19** which was readily converted to the levulinate **20**[22] presumably due to the reaction with traces of adventitious water (Scheme 5).[6,23]

Pirrung has shown[24] that vinyl acetate reacts with cyclic 2-diazo-1,3-dicarbonyl compounds under conditions of metal catalysis to give benzofurans and thus diketene is behaving as a vinyl acetate equivalent in these reactions. The isolation of products with exocyclic double bonds such as **6** and **7** which isomerise in most cases to benzofurans provides an indication of how the reaction proceeds. Such products could be formed by thermal elimination of carbon dioxide (Scheme 6) from a dioxaspirooctenone **21** formed *via* rearrangement of an initially

18

19

EtO₂C, CO₂Et ... (structures)

H_2O
$-CO_2$

20

Scheme 5

Path B

Path A

21

Scheme 6

sible explanation for this may lie in the smaller resonance energy gain that accrues to the already extensively conjugated **9** relative to that which results from the isomerisation of the less conjugated **6** or **7**. Although the mechanism proposed here suggests that electrophilic catalysts with electron-withdrawing ligands should be the most effective, this is not true in general (see Table 3). The least electrophilic catalyst, Rh₂(acetamide)₄, is inactive but when catalysts such as Rh₂(butyrate)₄ and Rh₂(perfluorobutyrate)₄, were compared the yield of benzofuran obtained was lower for the fluorinated catalyst. The larger ligands are in general more effective and this may be due to the increased soublity of the catalyst in these cases.

Although acyclic 2-diazo-1,3-dicarbonyl compounds also form furans on reaction with diketene they do so in very low yield. Although the cyclic systems are locked in a W-configuration facilitating formation of dioxaspirooctenone **21**, the acyclic analogues are conformationally free allowing other processes, such as a Wolff rearrangement, to compete with furan formation.

In conclusion, the metal catalysed reactions of cyclic 2-diazo-1,3-diketones and acyclic 2-diazoacetoacetates are significantly different to those of other diazocarbonyl compounds as the carbenoid on reaction with diketene give furans as the major products. Most other diazo compounds, with the exception of diazoacetophenone which gives traces of a furan, give cyclopropanes exclusively. The mechanism suggested for furan formation provides a rationalisation for this process, but the structure–activity relationship observed for the catalysts suggests that the reaction is more complex. Studies designed to clarify the precise nature of the process are currently under way.

Experimental

The general experimental conditions have already been described.[6b]

Synthesis of diazo compounds

General procedure[8] for the preparation of 2-diazo-1,3-dicarbonyl compounds. *p*-Tosyl azide (0.1 mol) in dichloromethane (75 cm³) and powdered potassium fluoride (0.1 mol) or triethylamine (0.1 mol) were added to a stirred solution of the appropriate 1,3-dicarbonyl compound (0.075 mol) in dichloromethane (260 cm³). The mixture was protected from light and stirred for 18 h. It was then washed with 5% NaOH (2 × 100 cm³) and water (2 × 200 cm³) and was dried over anhydrous Na₂SO₄. Filtration, removal of solvent and chromatography (ether–petroleum ether) gave the pure diazo compound.

4-Methylcyclohexane-1,3-dione gave **3b**[9] (83%); δ_H 2.73–2.21 (5H, overlapping m, CH₂CH₂CH), 1.14 (3H, m, CH₃); δ_C 189.4 (C=O), 83.5 (s), 44.8 (d), 25.7 (t) and 20.2 (q); ν_{max} (Nujol)/cm⁻¹ 2155, 2127 (N₂), 1636 (C=O).

5-Phenylcyclohexane-1,3-dione gave **3d**[10] (98%): δ_H 7.42–7.18 (5H, m, Ph), 3.34 (1H, m, CH), 2.82 (4H, d, *J* 7.1, C*H₂*CHC*H₂*);

formed cyclopropanespiro-β-lactone (Path A) or *via* formal dipolar addition (Path B). The formal dipolar cycloaddition of α-ketocarbenoids to alkenes forming dihydrofurans is known[25] whereas a study of the rearrangement reactions of cyclopropanespiro-β-lactones[6] provided no precedence for their conversion to dihydrofurans. Thus it would appear more likely that formation of the dioxaspirooctenone **21** occurs by an independent dipolar cycloaddition type process which is competitive with cyclopropanation. These processes have been reviewed by Doyle[25] who suggested that increasing nucleophilicity of the carbonyl group adjacent to the carbenoid centre can alter the reaction pathway from cyclopropanation to dihydrofuran formation. Although not apparently important for cyclopropanespiro-β-lactones[6] decarboxylation is a standard reaction of β-lactones in general and is reported to involve the build up of positive charge at C(4).[26] The decarboxylation of **21** is thus facilitated as a result of the resonance stabilisation provided by the oxygen atom of the dihydrofuran ring. As indicated above the resulting methylene compound is either not observed or else is unstable, rearranging readily to the corresponding furan. The behaviour of **9** is in marked contrast to this general trend as it appears to be indefinitely stable. A pos-

Table 4 Physical and IR data for benzofurans and furans

Furan (molecular formula)	Mp/°C (solvent)	Found (%) [Requires (%)] C	H	ν_{max}/cm^{-1} C=O
4a ($C_9H_{10}O_2$)	Oil[9]		—	1674
4b ($C_{10}H_{12}O_2$)	Oil	73.1 [73.2]	7.2 [7.3]	1670
4c ($C_{11}H_{14}O_2$)	76–77 (ether–petroleum ether) (lit. 74–75)[27]		—	1669
4d ($C_{15}H_{14}O_2$)	91–92 (ether–petroleum ether)	79.5 [79.7]	5.9 [6.2]	1672
4e ($C_{10}H_{12}O_2$)	Oil	72.9 [73.2]	7.1 [7.3]	1680
5e ($C_{10}H_{12}O_2$)	Oil	72.9 [73.2]	7.5 [7.3]	1679
4f ($C_{11}H_{14}O_2$)	70–72 (ether–petroleum ether)	73.9 [74.2]	7.7 [7.9]	1673
5f ($C_{11}H_{14}O_2$)	71–73 (ether–petroleum ether)	73.9 [74.2]	7.6 [7.9]	1671
4g ($C_{14}H_{18}O_4$)	Oil	67.0 [67.2]	7.0 [7.2]	1733, 1686
5g ($C_{14}H_{18}O_4$)	58–60 (ether–petroleum ether)	67.0 [67.2]	7.0 [7.2]	1725, 1679
17a ($C_8H_{10}O_3$)	Oil	62.1 [62.3]	6.2 [6.5]	1721
17b ($C_9H_{12}O_3$)	Oil	64.0 [73.2]	6.9 [7.3]	1722
17c ($C_{10}H_{12}O_3$)	Oil	66.4 [66.7]	6.4 [6.7]	1726
17d ($C_{15}H_{14}O_2$)	Oil	67.0 [67.3]	7.9 [8.2]	1719

Table 5 ^{1}H-NMR spectroscopic data for benzofurans **4** and **5**

Benzofuran	δ_H
4a	6.23 (1H, s, CH), 2.82 (2H, m, CH$_2$C=C), 2.46 (2H, m, CH$_2$C=O), 2.13 (2H, m, CH$_2$CH$_2$CH$_2$), 2.28 (3H, s, CH$_3$) and 1.41 (3H, d, J 6.4, CH$_3$)
4b	6.23 (1H, s, CH, furan), 2.98–2.18 (1H, overlapping multiplets), 1.16 (3H, d, J 6.0, CH$_3$CH)
4c	6.33 (1H, s, CH), 2.68 (2H, m, CH$_2$C=C), 2.33 (2H, m, CH$_2$C=O), 2.28 (3H, s, CH$_3$C=C) and 1.12 (6H, s, (CH$_3$)$_2$C)
4d	7.35–7.21 (5H, m, Ar H), 6.28 (1H, br s, CH, furan), 3.43 (1H, m, CHPh), 3.05 (2H, d, J 7.2, CH$_2$C=C), 2.75 (2H, d, J 8.0, CH$_2$C=O), 2.31 (3H, s, CH$_3$)
4e	6.24 (1H, s, CH, furan), 3.04 (1H, m, CHC=C), 2.61–2.38 (2H, m, CH$_2$C=O), 2.28 (3H, s, CH$_3$C=C), 2.26–2.19 and 1.88–1.73 (each 1H, each m, CHCH$_2$CH$_2$)
5e	6.32 (1H, s, CH, furan), 2.85 (2H, m, CH$_2$C=C), 2.47 (1H, m, CHC=O), 2.24 (4H, m, CH$_3$C=C and CH(H)CH$_2$), 1.88 (1H, m, CH(H)CH$_2$), 1.19 (3H, d, J 7.0, CH$_3$CH)
4f	6.19 (1H, s, CH), 2.38–2.04 (2H, m, CH$_2$C=O), 2.28 (3H, s, CH$_3$C=C), 2.05–1.85 (2H, m, CH$_2$CH$_2$), 1.35 (6H, s, (CH$_3$)$_2$C)
5f	6.21 (1H, s, CH), 2.84 (2H, t, J 6.5, CH$_2$C=C), 2.28 (3H, s, CH$_3$C=C), 1.97 (2H, t, J 6.5, CH$_2$CH$_2$), 1.16 (6H, s, (CH$_3$)$_2$C)
4g	6.27 (1H, s, CH, furan), 4.21 (2H, q, J 7.1, CH$_2$CH$_3$), 3.60 (1H, m, CHCO$_2$), 2.86 and 2.19 (each 1H, each d, J 17.9, CH$_2$C=O), 2.29 (3H, s, CH$_3$C=C), 1.29 (3H, t, J 7.1, CH$_2$CH$_3$), 1.16 (6H, s, (CH$_3$)$_2$C)
5g	6.16 (1H, s, CH, furan), 4.09 (2H, q, J 7.1, CH$_2$CH$_3$), 3.14 (1H, m, CHCO$_2$), 3.02 and 2.52 (each 1H, each d, J 16.0, CH$_2$C=C), 2.20 (3H, s, CH$_3$C=C), 1.18 (3H, t, J 7.1, CH$_2$CH$_3$), 1.07 and 1.04 (each 3H, each s, (CH$_3$)$_2$C)

δ_C 189.1 (C=O), 141.4–126.5 (Ar), 84.4 (s), 44.2 (d), 36.5 (t); ν_{max} (Nujol)/cm^{-1} 2139, (N$_2$), 1667 (C=O), 1636 (C=C).

4,4-Dimethylcyclohexane-1,3-dione gave **3f** (90%) which could not be obtained analytically pure; δ_H 2.70–2.50 (2H, m, CH$_2$C=O), 1.95–1.80 (2H, s, CH$_2$CH$_2$C=O), 1.24 (6H, s, (CH$_3$)$_2$C); δ_C 194.3 (C=O), 189.4 (C=O), 82.7, 40.6 (s), 32.7, 31.7 (t), 23.6 and 23.4 (q); ν_{max} (Nujol)/cm^{-1} 2157 (N$_2$), 1645 (C=O); mp 96–98 °C.

Ethyl 5,5-dimethylcyclohexane-1,3-dione-4-carboxylate[28] gave **3g** (56%) (Found C, 55.3; H, 5.9; N, 11.6. $C_{11}H_{14}N_2O_4$ requires C, 55.5; H, 5.9; N, 11.8%); δ_H 4.24 (2H, q, J 7.0, OCH$_2$), 3.31 (1H, s, CHCO$_2$), 2.91 (1H, d, J 16.1, CH(H)C=O), 2.34 (1H, d, J 16.1, CH(H)C=O), 1.30 (3H, q, J 7.0, CH$_2$CH$_3$), 1.16 (6H, s, (CH$_3$)$_2$C); δ_C 189.2 (C=O), 186.4 (s), 168.0 (C=O, ester), 83.9 (s), 64.2 (d), 62.1, 48.4 (t), 33.7 (s), 27.8, 27.9 and 13.7 (q); ν_{max} (Nujol)/cm^{-1} 2140, 2183 (N$_2$), 1735 (C=O, ester), 1651 (C=O, ketone).

Preparation of 3-diazotetrahydrofuran-2,4-dione 12[14]. Tetrahydrofuran-2,4-dione (2.0 g, 0.02 mol) was dissolved in acetonitrile (50 cm³), *p*-tosyl azide (3.7 g, 0.02 mol) was added and the mixture was stirred at room temp. Triethylamine (1.98 g, 0.02 mol) was added dropwise over 10 min resulting in a darkening of the solution. The reaction mixture was stirred for a further hour and was then concentrated. The residue was extracted with ether (300 cm³) and the extract was passed through a short column of silica (10 g) which was further eluted with dichloromethane (200 cm³). The combined eluant was concentrated to give a mixture of unreacted *p*-tosyl azide, **12** and *p*-tosyl amide. Chromatography (dichloromethane–petroleum ether gradient) gave **12** (1.4 g, 57%); δ_H 4.68 (2H, s,

CH$_2$); δ_C 185.6 (C=O), 163.6 (C=O), 72.8 (s) and 72.7 (t); ν_{max} (Nujol)/cm^{-1} 2169 (N$_2$), 1754 (C=O, lactone), 1690 (C=O, ketone).

**The reactions of 2-diazo-1,3-dicarbonyl compounds with diketene**

General procedure. The diazo compound (2–10 mmol) and Rh(II) catalyst (5–10 µmol) were added to freshly distilled diketene (0.04–0.1 mol) and the mixture was stirred at room temperature until the diazo compound had completely reacted (checked by IR). Excess diketene was then removed at room temp. (0.1 mmHg). The products (Table 1) were isolated from the residue by Kugelrohr distillation (bath temperature 80–200 °C, 0.1 mmHg) or by silica gel chromatography (ether–petroleum ether gradient elution). Spectroscopic and physical data for the products are given in Tables 4–7.

The reaction of 2-diazocyclohexane-1,3-dione with diketene. 2-Diazocyclohexane-1,3-dione (**3a**, 1.0 g, 7.3 mmol) gave 2-methyl-4,5,6,7-tetrahydro-1-benzofuran-4-one (**4a**, 0.75 g, 72%) after Kugelrohr distillation of the residue (bath temperature 80–120 °C, 0.1 mmHg). Physical and spectroscopic data for **4a** are given in Tables 4–6.

In a separate experiment the residue (0.5 g) was dissolved in an ether–petroleum ether mixture (1:20, 100 cm³) and was rapidly eluted through a short column of silica (5 g). The eluant was concentrated (20 °C, 15 mmHg) and was shown (^{1}H- and ^{13}C-NMR) to contain a 2.5:1 mixture (0.18 g) of **4a** and 2-methylene-2,3,4,5,6,7-hexahydro-1-benzofuran-4-one (**6a**). Distillation (0.1 mmHg, 50–80 °C) of this mixture gave only **4a** (0.17 g). When a sample that contained **6a** as the major

Table 6 ^{13}C-NMR spectroscopic data for benzofurans **4** and **5**
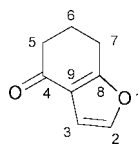
Benzofuran	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	Other signals
4a	152.4	101.8	194.3	35.4	22.4	23.1	165.8	121.9	21.1, 13.3 (q)
4b	152.7	101.8	194.1	46.0	30.8	31.4	165.7	121.9	20.4 (q)
4c	158.3	102.2	196.0	53.2	36.2	38.8	165.2	120.4	29.2, 2.8 (q)
4d	152.6	101.0	194.7	40.4	43.9	30.2	166.1	126.5	141.6–125.8 (Ar)
4e	152.7	102.2	196.9	41.2	22.7	30.7	165.5	121.4	15.0, 13.4 (q)
5e	152.8	102.0	194.8	37.1	31.6	29.6	169.5	121.1	17.4, 13.5 (q)
4f	152.4	101.8	194.1	42.4	21.5	36.2	171.6	119.1	24.8, 13.9 (q)
5f	152.4	101.8	194.1	38.3	32.5	37.9	171.6	119.7	25.9, 13.0 (q)
4g	153.1	102.1	188.5	65.1	37.6	35.8	165.5	119.8	168.7 (C=O), 60.9, (t), 28.5, 26.2, 14.2, 13.4 (q)
5g	153.9	102.1	193.2	49.4	37.8	51.7	160.6	121.9	169.4 (C=O), 61.3, (t), 28.7, 26.5, 14.2, 13.4 (q)

Table 7 NMR spectroscopic data for furans **17**

Furan	δ_H	δ_C
17a	6.19 (1H, s, CH), 3.79 (3H, s, CH$_3$O), 2.51 (3H, s, CH$_3$C=CC=O), 2.23 (3H, s, CH$_3$C=C)	163.3 (C=O), 156.3, 148.5, 112.4 (s), 104.7 (d), 13.1, 12.9, and 12.1 (q)
17b	6.21 (1H, s, CH), 4.26 (2H, q, J 7.0, OCH$_2$), 2.52 (3H, s, CH$_3$C=CC=O), 2.23 (3H, s, CH$_3$C=C)	165.6 (C=O), 153.8, 149.8, 114.0 (s), 106.2 (d), 59.8 (t), 14.3, 13.6 and 13.0 (q)
17c	6.16 (1H, s, CH), 2.49 (3H, s, CH$_3$C=CC=O), 2.23 (3H, s, CH$_3$C=C), 1.49 (9H, s, (CH$_3$)$_3$C)	163.8 (C=O), 156.9, 149.6, 115.5 (s), 106.5 (d), 80.2 (s), 28.4 (q), 13.7 and 13.1 (q)
17d	6.23 (1H, s, CH, furan), 6.00 (1H, m, CH=CCH$_2$), 5.32 (2H, m, CH=CH_2), 4.71 (2H, m, CH$_2$O), 2.53 (3H, s, CH$_3$C=CC=O), 2.23 (3H, s, CH$_3$C=C)	163.8 (C=O), 157.8, 149.9, 132.5 (d), 117.6 (t), 106.2 (d), 64.5 (t), 13.6 and 13.0 (each q)

component, was allowed to stand for 4 days at room temp. complete conversion to **4a** was found to have occurred. Spectroscopic data for **6a**: δ_H 4.76 (1H, q, J 2.6, C=C(H)H), 4.41 (1H, q, J 2.6, C=C(H)H), 3.47 (m, CH_2C=CH$_2$); δ_C 193.8 (C=O), 175.0, 160.5, 114.1 (s), 87.7, 36.2, 29.2, 22.9, 21.3 (t); ν_{max} (film)/cm^{-1} 1674 (C=O) and 1582 (C=C).

The reaction of 2-diazo-4-methylcyclohexane-1,3-dione with diketene. 2-Diazo-4-methylcyclohexane-1,3-dione (**3e**, 0.5 g, 3.3 mmol) gave two fractions after chromatography using a 30 : 70 ether–petroleum ether mixture. The first was identified as 5-methyl-2-methylene-2,3,4,5,6,7-hexahydro-1-benzofuran-4-one (**6e**, 0.19 g, 35%) (Found: C, 72.9; H, 7.5. C$_{10}$H$_{12}$O$_2$ requires C, 73.2; H, 7.3); δ_H 4.73 (1H, q, J 3.0, C=C(H)H), 4.40 (1H, q, J 3.0, C=C(H)H), 3.45 (2H, m, CH_2C=CH$_2$), 2.65–1.67 (5H, overlapping multiplets, CH$_2$CH$_2$CH), 1.16 (3H, d, J 7.1, CH$_3$); δ_C 196.2 (C=O), 173.9, 173.4, 160.8 (s), 87.7 (t), 39.9 (d), 29.4, 29.3, 22.2 (t), 14.8 (q); ν_{max} (film)/cm^{-1} 1671 (C=O) and 1585 (C=C). The second fraction was 2,7-dimethyl-4,5,6,7-tetrahydro-1-benzofuran-4-one (**5e**, see Tables 4–6 for physical and spectroscopic data).

5-Methyl-2-methylene-2,3,4,5,6,7-hexahydro-1-benzofuran-4-one **6e** rearranged to **5e** on standing at room temperature for 4 days.

The reaction of 2-diazoindane-1,3-dione with diketene. 2-Diazoindane-1,3-dione [12] (**8**, 1.0 g, 5.8 mmol) gave two major fractions after chromatography. The first fraction was 2-methylene-3,4-dihydro-2H-indeno[1,2-b]furan-4-one (**9**, 0.31 g, 28%) (Found: C, 78.1; H, 4.0. C$_{12}$H$_{8}$O$_2$ requires C, 78.3; H, 4.35%); δ_H 7.38–7.05 (4H, m, Ar H), 4.97 (1H, q, J 3.0, CH(H)=C), 4.58 (1H, q, J 3.0, CH(H)=C), 3.52 (2H, t, J 3.0, C=C–CH$_2$); δ_C 185.6 (C=O), 166.9 (s), 138.8–118.1 (Ar), 114.3 (s), 90.9, 28.5 (t); ν_{max} (Nujol)/cm^{-1} 1693 (C=O) and 1674 (C=C); mp 128–130 °C (ether–petroleum ether). The second

major fraction was 2-phenylindane-1,3-dione (**10**, 0.25 g, 21%) whose structure was confirmed by comparison of its NMR spectroscopic data with those of an authentic sample (Aldrich).

The reaction of allyl diazoacetoacetate with diketene. Allyl diazoacetoacetate [20] (**16d**, 0.84 g, 5 mmol) and Rh$_2$(OAc)$_4$ (5 mg, 10 μmol) were added to freshly distilled diketene (**1**, 5.0 g, 0.06 mol) and the mixture was heated at 70 °C for 3 days. Additional catalyst (5 mg) was added to the reaction mixture each day. Allyl 2,5-dimethylfuran-3-carboxylate (**17d**, 0.16 g, 18%) was isolated by silica gel chromatography of the reaction residue. Physical and spectroscopic data for **17d** are given in Tables 4 and 7.

1,1-Bis(ethoxycarbonyl)-5-oxo-4-oxaspiro[2.3]hexane (19). A solution of diethyl diazomalonate [21] (3 g, 0.016 mol), diketene (13.4 g, 0.16 mol) and benzophenone (2.9 g, 0.016 mol) in dichloromethane (60 cm^3) was irradiated in a Rayonet reactor until the diazo compound had been consumed (IR). After removal of the solvent (rotary evaporator) and residual diketene (30 °C, 1.0 mmHg), the resulting oil was chromatographed to give **19** (2.5 g, 65%) (Found C, 54.2, H, 5.8. C$_{11}$H$_{14}$O$_6$ requires C, 54.5; H, 5.8%); δ_H 4.32–4.11 (4H, overlapping m, CH$_3$CH_2), 4.02 and 3.75 (each 1H, each d, J 17.4, CH$_2$C=O), 2.41 and 1.80 (each 1H, each d, J 7.7, cyclopropyl CH$_2$), 1.30 (6H, t, J 7.3, CH$_3$); δ_H 167.3, 165.1 and 164.3 (C=O), 62.3, 62.1 (t), 61.6 (s), 42.8 (t), 34.8 (s), 20.9 (t), 14.0 (q); ν_{max}/cm^{-1} 1852 (C=O) and 1728 (C=O). Trace amounts of diethyl acetonylmalonate **20** [22] are formed on standing at room temp. for 3 days.

4-Hydroxy-3-phenyl-2,5-dihydrofuran-2-one (15) [15]

The diazo compound **12** (0.92 g, 7.4 mmol) was added to a mixture of diketene (5 g, 0.06 mol) and Rh$_2$(OAc)$_4$ (3 mg, 7 μmol) over 1 h at room temp. The mixture was stirred for 48 h

after which time no reaction had occurred (IR and TLC). Benzene was then added and the mixture was heated at reflux until complete consumption of the diazo compound had occurred (22 h, IR). Concentration of the reaction mixture gave a black product which was subjected to chromatography (silica, 80 g). Elution with chloroform gave a complex mixture of unidentified products. Further elution with ethyl acetate gave 4-hydroxy-3-phenyl-2,5-dihydrofuran-2-one (**15**, 0.26 g, 20%), mp 254–25 °C (lit., 259–264 °C, EtOH).[15]

Acknowledgements

References

1 R. J. Clemens, *Chem. Rev.*, 1986, **86**, 241.
2 T. Kato and N. Katagiri, *Chem. Pharm. Bull.*, 1973, **21**, 729.
3 T. Kato, N. Katagiri and R. Sato, *Chem. Pharm. Bull.*, 1979, **27**, 1176.
4 T. Kato, N. Katagiri and R. Sato, *J. Chem. Soc., Perkin Trans. 1*, 1979, 525.
5 S. Takano, T. Sugahara, M. Ishiguro and K. Ogasawara, *Heterocycles*, 1977, **6**, 1141.
6 (*a*) N. W. A. Geraghty and P. V. Murphy, *Tetrahedron Lett.*, 1994, **35**, 6737; (*b*) P. V. Murphy, T. J. O'Sullivan and N. W. A. Geraghty, *J. Chem. Soc., Perkin Trans. 1*, 2000, DOI: 10.1039/b001393p (preceding paper).
7 P. D. Cunningham, N. W. A. Geraghty, P. J. McArdle, P. V. Murphy and T. J. O'Sullivan, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1.
8 V. V. Popic, S. M. Korneev, V. A. Nikolaev and I. K. Korobitsyna, *Synthesis*, 1991, 195.
9 M. C. Pirrung and Y. R. Lee, *Tetrahedron Lett.*, 1994, **35**, 6231.
10 M. Regitz and A. Liedegener, *Chem. Ber.*, 1967, **100**, 1817.
11 J. Cossy, D. Belotti and C. Leblanc, *J. Org. Chem.*, 1993, **58**, 2351.
12 G. Staudinger, *Chem. Ber.*, 1916, **49**, 1917.
13 M. J. Rosenfield, B. K. Shankar and H. Schechter, *J. Org. Chem.*, 1988, **53**, 2699.
14 H. D. Stachel, H. Poschenrieder, J. Redlin, J. Schachtner and K. Zeitler, *Liebigs Ann. Chem.*, 1994, 129.
15 A. C. Campbell, M. S. Maidment, J. H. Pick and D. F. M. Stevenson, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1567.
16 M. C. Pirrung, J. C. Zhang, K. Lackey, D. D. Sternbach and F. Brown, *J. Org. Chem.*, 1995, **60**, 2112.
17 G. Staudinger and H. Becker, *Chem. Ber.*, 1916, **49**, 1985.
18 M. Regitz, *Chem. Ber.*, 1966, **99**, 3128.
19 K. Vorlander, *Justus Liebigs Ann. Chem.*, 1897, **294**, 323.
20 H. Mastalerz and M. Menard, *J. Org. Chem.*, 1994, **59**, 3223.
21 M. Regitz, *Synthesis*, 1972, 363.
22 G. Griffiths, P. D. Howes and C. J. Stirling, *J. Chem. Soc., Perkin Trans.*, 1, 1977, 912.
23 T. Kato, N. Katagiri and R. Sato, *Chem. Pharm. Bull.*, 1979, **27**, 1176.
24 M. C. Pirrung, J. C. Zhang and A. T. Morehead, Jr., *Tetrahedron Lett.*, 1994, **35**, 6229.
25 M. P. Doyle, *Chem. Rev.*, 1986, **86**, 919.
26 S. Searles, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1994, vol. 7, p. 363.
27 S. R. Ramadas and S. Padmanabhan, *Curr. Sci.*, 1979, **48**, 52.
28 M. Scheiber, *Chem. Ber.*, 1915, **48**, 264.