Chemoselectivity and stereoselectivity of cyclisation of α-diazocarbonyls leading to oxygen and sulfur heterocycles catalysed by chiral rhodium and copper catalysts

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Good levels of enantioselectivity have been achieved in intramolecular C–H insertion reactions of α-diazocarbonyl compounds leading to six-membered oxygen heterocycles (chromanones) through the use of chiral rhodium(II) carboxylates as catalysts. Competition between C–H insertion and sigmatropic rearrangement, the latter leading to five-membered oxygen heterocycles (furanones), was observed with precursors containing a proximal *O*-allyl side chain. Whereas rhodium carboxylates produced C-H insertion products predominantly, a copper catalyst produced sigmatropic rearrangement products exclusively. A precursor with an *S*-allyl side chain exhibited cyclisation *via* sigmatropic rearrangement with both copper and rhodium catalysts.

The opportunities for asymmetric synthesis employing diazocarbonyl precursors are numerous. The fact that many of the more synthetically useful reactions of this versatile class of compounds, *viz.* cyclopropanation, X–H insertion (X = C, N, O, S, Si), cycloaddition and sigmatropic rearrangement, require metal catalysis makes the option of using chiral catalysts particularly attractive. Very substantial progress has already been made, especially in the area of cyclopropanation, and there are now several rhodium- and copper-based complexes capable of achieving high levels (> 90%) of enantioselectivity in both intermolecular and intramolecular cyclopropanation over a range of substrates. Of the various X–H insertion reactions amenable to asymmetric synthesis, those leading to C–C bond formation have received most attention, though high enantioselectivities over a range of different substrate types have yet to be realised. The small number of asymmetric N–H and O–H insertion reactions that have been examined display only low levels of enantioselection.[1]

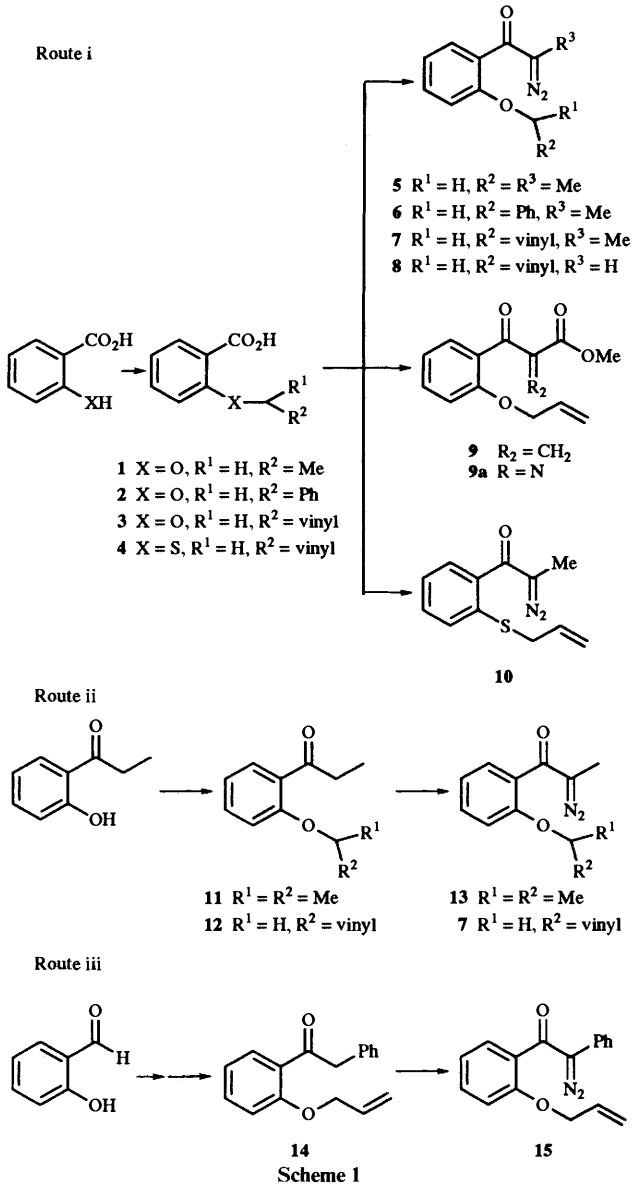
Unfortunately, the copper-based chiral complexes which have proved so effective in cyclopropanation have limited chemical reactivity and are more or less inert in X–H insertion. On the other hand, rhodium(II) carboxylates are catalytically active across the entire spectrum of keto carbenoid reactions including X–H insertion and the question naturally arose therefore as to the efficacy of chiral rhodium(II) complexes in catalysed asymmetric synthesis.

Several years ago, we introduced chiral rhodium(II) carboxylates derived from (*S*)-mandelic acid,[2] *N*-phenylsulfonyl-L-proline[3] and *N*-acetyl-L-phenylalanine for intramolecular C–H insertion of a diazo sulfone and although very efficient cyclisation to a substituted cyclopentanone did occur, the enantioselection was low (*ca.* 12%).[4] More recently, Hashimoto *et al.*,[5] have found enantiomeric excess (ee) values up to 76% in the cyclisation of α-diazo-β-keto esters to substituted cyclopentanones catalysed by the rhodium(II) carboxylate of *N*-phthaloyl-(*S*)-phenylalanine. Doyle's Rh^{II}-MEPY[6] [MEPY: methyl (*S*)-(−)-5-oxopyrrolidine-2-carboxylate], which is derived from a chiral carboxamide rather than a carboxylate, is also catalytically active in C–H insertion and there are now examples of intramolecular processes leading to lactones and lactams where this catalyst is capable of producing good to excellent enantioselectivity. Other examples of heterocyclic synthesis *via* C–H insertion include the formation of disubstituted 2*H*-furan-3-ones from α-alkoxy diazo ketones[7] and of 2*H*-furan-3-one esters from γ-alkoxy-α-diazo-β-keto esters.[8] In the latter process the combination of a chiral auxiliary in the ester moiety of the precursor and a chiral catalyst leads to asymmetric induction with diastereoselectivites up to 61%. We now report the first examples of asymmetric synthesis of six-membered oxygen heterocycles and demonstrate that good levels of enantioselectivity can be obtained using chiral rhodium(II) catalysts. We also report the catalyst-dependent behaviour of substrates capable of cyclising *via* C–H insertion and/or sigmatropic rearrangement.

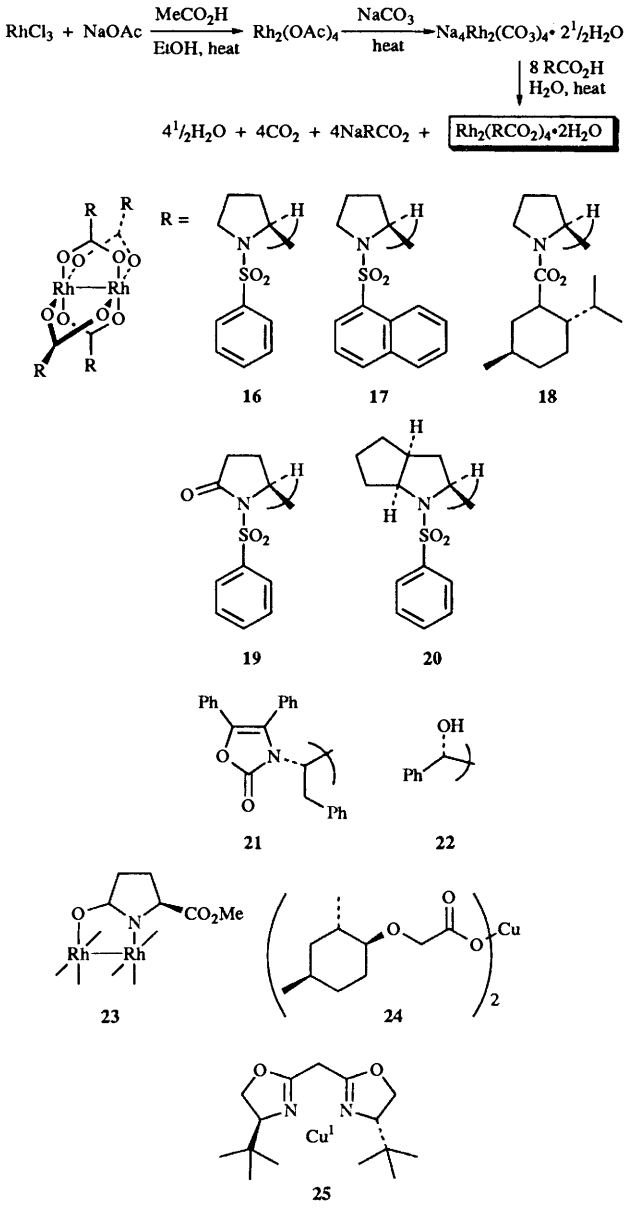
Results and discussion

The substrates selected for exploring six-membered heterocycle formation are summarised in Scheme 1. In route i, salicylic acid [or thiosalicylic acid (2-sulfanylbenzoic acid)] was bis-alkylated with the appropriate alkyl bromide and potassium carbonate in acetone. Alkaline hydrolysis of the esters afforded the acids **1**–**4**. Diazo ketones **5**–**8** were prepared *via* acyl chloride formation followed by exposure to ethereal diazoethane or diazomethane. Acid **3** was also converted into the corresponding acyl imidazole which was treated with the chelated enolate, magnesium monomalonate,[9] to form a β-keto ester. Diazo transfer with mesyl azide[10] completed the conversion of **9** into the diazocarbonyl **9a**. Diazo ketone **10** was prepared from the acid **4** *via* the mixed anhydride[11] and ethereal diazoethane. Route ii was used to convert 1-(2-hydroxyphenyl)propan-1-one into the *O*-alkyl derivatives **11** and **12** which were then transformed into diazo ketones **13** and **7** (**7** was obtained in high yield following this route) using Danheiser's procedure.[12] Salicylaldehyde served as the starting material for route iii, sequential alkylation with allyl bromide, addition of benzylmagnesium bromide and oxidation to ketone **14** followed by diazo transfer, again with mesyl azide, affording diazo ketone **15**.

The design and synthesis of chiral carboxylic acids, which serve as ligands of the catalyst, play a key role in the development of new chiral rhodium(II) carboxylates. The catalysts used in this study are shown in Scheme 2. Most of the ligands are based on N-protected proline derivatives. Rhodium(II) carboxylates **16**–**22** were generally prepared from the sodium salt of rhodium(II) carbonate[13] and the appropriate carboxylic acid by a displacement reaction.[14] The sulfonyl derivatives of the amino acids were obtained by treatment of a basic solution of the amino acid with the correspondent sulfonyl chloride according to standard procedures. The (−)-(1*R*)-menthoxycarbonyl protected proline was similarly prepared



Scheme 1



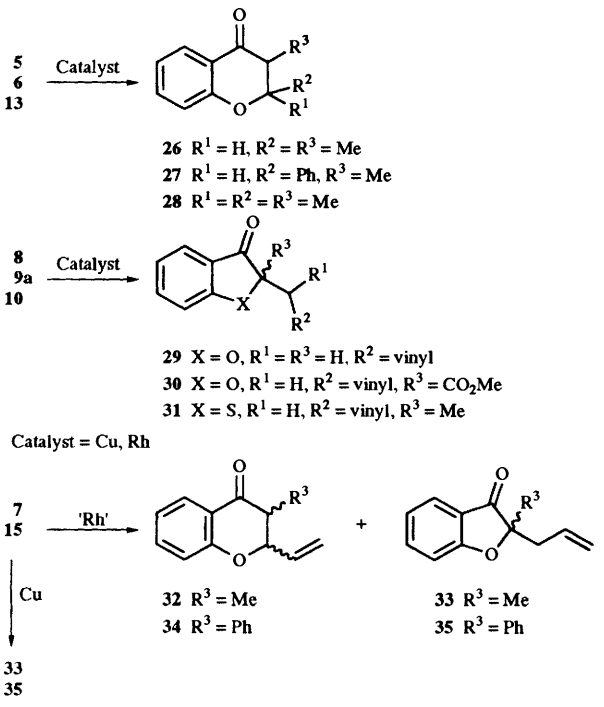
Scheme 2

from (−)-menthyl chloroformate. The carboxylic acid used to prepare **19** was obtained following the procedure of Gibian and Klieger.[15] The bicyclic amino acid which served as ligand of catalyst **20** was prepared from the benzyl ester of (1*S*,3*S*,5*S*)-2-azabicyclo[3.3.0]octane-3-carboxylic acid *via* hydrogenation[16] followed by N-protection. Finally, the catalyst **21** was obtained from the 4,5-diphenyl-4-oxazolin-2-one derivative of L-phenylalanine, prepared according to Sheehan's procedure.[17] Doyle's catalyst,[6] Rh^{II}MEPY **23**, and the chiral copper catalysts **24** [derived from (−)-menthyloxyacetic acid] and **25**[18] completed the catalysts studied.

Decomposition of the diazo ketones shown in Scheme 1 was studied in dichloromethane or benzene at various temperatures using 1–2% by mass of Rh^{II} or Cu catalysts (Scheme 3). All of the rhodium catalysts were active with the exception of Rh^{II}MEPY **23** which was either completely ineffectual or produced very low reaction rates. The copper catalysts were active towards some substrates, though their mode of action differed significantly from that of their rhodium counterparts (*vide infra*). The behaviour of diazo ketones **5** and **6** with rhodium(II) was temperature dependent: only at 40 °C (refluxing dichloromethane) was intramolecular cyclisation observed; at 0 °C or room temperature intermolecular dimerisation was the dominant reaction pathway.

Intramolecular C–H insertion leading to chromanone formation was the sole mode of reaction with diazo ketone **13** and rhodium catalysts **16**–**22**. ^{1}H NMR chiral shift studies employing [Eu(hfc)$_3$]{tris[(heptafluoropropylhydroxymethylene)camphorato]europium(III)} were used to quantify the extent of enantioselectivity (ee) in the cyclisation product **28**. With the *N*-phenylsulfonylproline catalyst **16** in dichloromethane at 40 °C **28** was formed in quantitative yield with an ee of 50%. The variation of enantioselectivity with catalyst, summarised in Table 3, shows that catalyst **16** comprising an *N*-phenylsulfonylproline was more effective than either **17** with an *N*-naphthalenesulfonate or **20** which is an *N*-benzenesulfonate of a bicyclic proline analogue. That the enantioselectivity could also be modulated by temperature and solvent was shown by the observation that 0 °C in dichloromethane the ee of **28** increased to 70% whereas in benzene under reflux the ee decreased to 43%.

Cyclisation of diazo ketones **5** and **6** in dichloromethane at 40 °C using the rhodium(II) prolinate catalyst **16** produced disubstituted chromanones **26** and **27**, respectively. Both products were a mixture of diastereoisomers containing predominantly the *cis*-isomer to the extent of 75–89%. The



Scheme 3

Table 1 Catalyst dependence: chemoselectivity

Catalyst	32 (%)	33 (%)
$Rh_2(OAc)_4$	97	3
16	97	3
17	96	4
18	96	4
19	82	18
20	97	3
21	90	10
22	88	12
23	96	4
$Cu(acac)_2$	—	100
24	—	100
25	—	100

individual isomers *cis*-**26** and *cis*-**27** had ee values of 82 and 62%, respectively.[19]

These intramolecular cyclisation studies were then extended to include a series of diazocarbonyl substrates, *viz.* **7**–**9a**, **10** and **15** in which the putative C–H insertion site adjacent to the heteroatom was also part of an allyl system. This arrangement introduces the possibility of an alternative mode of cyclisation namely, tandem oxonium ylide formation–2,3-sigmatropic rearrangement. The reactivity in this series highlights some of the differences between rhodium and copper catalysts and it is nicely illustrated by the product distributions from diazo ketones **7** and **15**. Whereas decomposition of **7** with all rhodium(II) carboxylates in dichloromethane at 40 °C furnished predominantly *cis*-disubstituted chromanone **32**, the product of the C–H insertion, with minor amounts of benzofuranone **33**, the product of the oxonium ylide–2,3-sigmatropic rearrangement pathway, the corresponding reaction employing all three copper catalysts yielded the latter product exclusively (Table 1). In the rhodium-catalysed series the proportion of benzofuranone **33** varied slightly depending on the nature of the carboxylate ligand (3–18%, Table 1). The reactivity of the rhodium(II) carboxylates was considerably greater than that of Rh^{II}MEPY **23**. Whereas with the carboxylates decomposition of **7** was complete within 10 min, Rh^{II}MEPY, with a ten-fold

Table 2 Catalyst dependence: stereoselectivity

	32	
Catalyst	*cis* (%)	*trans* (%)
$Rh_2(OAc)_4$	74	26
16	93	7
17	85	15
18	83	17
19	75	25
20	92	8
21	92	8
22	86	20
23	74	26

Table 3 Catalyst dependence: enantioselectivity

	Ee (%)[a]		
	32		
Catalyst	*trans*	*cis*	**28**
$Rh_2(OAc)_4$	0	0	0
16	—	60	50
17	18	31	23
18	7	10	18
19	—	20	—
20	—	40	30
21	—	8	—
22	11	20	10
23	0	0	—

[a] The reaction was carried out at 40 °C in CH_2Cl_2.

increase in quantity, required 3 days for completion. While chromanone **32** was uniformly produced with the *cis*-geometry, the *cis*:*trans* ratio (Table 2) did vary somewhat with catalyst, that containing the *N*-phenylsulfonylproline moiety **16** giving the highest stereoselectivity (93:7). Enantioselectivities, again measured by ^1H NMR using [Eu(hfc)$_3$], were higher in the *cis*-isomer than in the *trans*-isomer and were markedly catalyst dependent with **16** producing the highest value of 60% ee (Table 3) for *cis*-chromanone **32**. When cyclisation of **7** with catalyst **16** was conducted at 0 °C in dichloromethane the ee value for **32** improved to 79%. Rather similar behaviour was observed with diazocarbonyl precursor **15**, though this compound was not studied in the same detail as its counterpart **7**. Decomposition of **15** with catalyst **16** in dichloromethane at 40 °C furnished *cis*-disubstituted chromanone **34** (95%) with an ee value of 45%. Use of copper catalysts, in contrast, led exclusively to benzofuranone **35**. Attempts to measure the ee of **35** were not successful. This preference for intramolecular oxonium ylide–[2,3]sigmatropic rearrangement with copper catalysts and suitable substrates has precedent in the work of Doyle's group on intermolecular reactions between allyl ethers and ethyl diazoacetate.[20,21] Interestingly, however, there are situations in which rhodium catalysts will promote this pathway even when the alternative C–H insertion pathway is also an option. This is illustrated by the behaviour of diazo ketones **8**, **9a** and **10** (Scheme 3). With either copper or rhodium catalysis all three substrates furnished heterocycles **29**, **30** and **31**, respectively, in excellent yield. Benzofuranone **29** proved to be rather unstable and we suspected that racemization may have occurred during chromatographic purification making the ee determination unreliable. In furanones **30** and **31**, the centre of chirality is now quaternary thus precluding easy racemization. Nevertheless, neither chiral shift NMR measurements nor chiral HPLC revealed the ee value for **31**. [Eu(hfc)$_3$]-NMR measurements with furanone **30** were successful, however, showing that this product possessed an ee of 25% when catalyst **16** was used. This

degree of asymmetric induction in an oxonium ylide-[2,3]sigmatropic rearrangement reaction of a diazocarbonyl precursor is somewhat less than that obtained earlier using a rhodium(II) phosphate catalyst.[22]

In conclusion, these results indicate that the rhodium(II) carboxylates are highly efficient catalysts for carbenoid generation leading to C–H insertion and six-membered oxygen-heterocycles. In some cases, there are significant levels of enantiocontrol when chiral rhodium(II) prolinate catalysts are employed. The chemoselectivity in a particular molecule depends on both the nature of the diazocarbonyl precursor and the type of catalyst. The construction of furanones and chromanones can be modulated with rhodium and copper catalysts.

Experimental

Mps were determined on a Reichert microscope hot stage apparatus and are uncorrected. IR spectra were obtained using a Perkin-Elmer 983G grating spectrophotometer. ^{1}H NMR (300 MHz) and ^{13}C (75 MHz) spectra were recorded on a GE-300 spectrometer with $SiMe_4$ as internal standard and $CDCl_3$ as solvent. *J* Values are given in Hz. Mass spectra and accurate masses were measured with a AEI-MS902 spectrometer using a heated inlet system. Elemental analyses were determined on a Perkin-Elmer 2400CHN microanalyser.

Flash column chromatography was performed using Rhone-Poulenc silica gel C60-H (40–60 mm). Solvents and commercially available reagents were dried and purified by standard procedures.[23] Ether refers to diethyl ether.

Ethereal diazomethane was prepared from Diazald according to the literature procedure.[24]

Ethereal diazoethane was prepared from *N*-ethyl-*N*-nitrosourea according to the literature procedure.[25] *N*-Ethyl-*N*-nitrosourea was prepared following a published procedure.[26]

Hydrogen methyl malonate was prepared *via* a literature procedure.[27]

Synthesis of o-allyl salicylic acid derivatives

General procedure. A mixture of salicylic acid (2-sulfanylbenzoic acid) (0.22 mol) and potassium carbonate (0.54 mol) in acetone (400 cm^3) was refluxed while stirring under nitrogen for 45 min. The mixture was then cooled to room temperature. A solution of the alkyl (or allyl) bromide (0.54 mol) in acetone (250 cm^3) was added over 10 min and heating was continued for 36 h. The cooled mixture was filtered and concentrated at reduced pressure to an oil which was dissolved in dichloromethane (300 cm^3) and washed with water (300 cm^3). The organic layer was separated, dried and concentrated at reduced pressure to give a clear, pale yellow oil which was used in the next experiment without purification.

The bis-alkylated compound thus obtained (0.21 mol) and sodium hydroxide (0.63 mol) in 90% aqueous ethanol (300 cm^3) were refluxed for 15 h while stirring under nitrogen. The cooled reaction mixture was then acidified with dilute hydrochloric acid and extracted with benzene. Subsequent evaporation of the solvent yielded crude product which was purified by recrystallisation.

2-Benzyloxybenzoic acid 2. Salicylic acid (10 g, 72.4 mmol) was alkylated with benzyl bromide (2.5 equiv.) to provide the crude ester which was hydrolysed by the general procedure described to produce the pure acid **2** (13.9 g, 84%) as pale white crystals, mp 73.5–74.5 °C (from ethyl acetate–hexane) (Found: C, 73.8; H, 5.4. Calc. for $C_{14}H_{12}O_3$ C, 73.7; H, 5.3%); ν_{max}/cm^{-1} 3500–2100 (CO_2H) and 1673 (C=O); δ_H 5.30 (2 H, s, $PhCH_2$), 7.14 (2 H, m, ArH), 7.30 (5 H, s, ArH), 7.53 (1 H, m, ArH), 8.20 (1 H, d, *J* 8, ArH) and 10.80 (1 H, br s, CO_2H).

2-Allyloxybenzoic acid 3. Following the general procedure, a mixture of salicylic acid (30 g, 0.22 mol) and potassium carbonate (75 g, 0.54 mol) in acetone (400 cm^3) was refluxed while stirring under nitrogen for 45 min. A solution of allyl bromide (65.7 g, 0.54 mol) in acetone (250 cm^3) was added over 10 min and heating was continued for 36 h. After work up, the crude ester and sodium hydroxide (25.7 g, 0.63 mol) in 90% aqueous ethanol (300 cm^3) were refluxed for 15 h. Evaporation of the solvent yielded crude product which was recrystallised from ether–hexane to give the acid **3** (30.1 g, 82%) as pale white crystals, mp 63–64 °C (lit.,[28] 64–65 °C); ν_{max}/cm^{-1} 3500–2120 (CO_2H), 1689 (C=O) and 1611 (C=C); δ_H 4.80 (2 H, d, *J* 5.6, OCH_2CHCH_2), 5.47 (2 H, m, OCH_2CHCH_2), 6.10 (1 H, m, OCH_2CHCH_2), 7.06 (1 H, d, *J* 7.5, ArH), 7.13 (1 H, t, 7.5, ArH), 7.56 (1 H, t, *J* 7.5, ArH), 8.18 (1 H, d, *J* 7.5, ArH) and 10.90 (1 H, br s, CO_2H).

2-Allylsulfanylbenzoic acid 4. Thiosalicylic acid (2-sulfanylbenzoic acid) (5 g, 0.032 mol) was allylated with allyl bromide (2.7 cm^3, 0.032 mol) and potassium carbonate (11 g, 0.08 mol) in acetone (60 cm^3). The crude ester was treated with sodium hydroxide (3.2 g, 0.08 mol) in 90% aqueous ethanol (40 cm^3) at reflux for 12 h. The acid **4** was obtained as pale yellow crystals, mp 109–111 °C; ν_{max}/cm^{-1} 3320–2800 (CO_2H), 1670 (C=O) and 1600 (C=C); δ_H 3.63 (2 H, d, *J* 6.6, OCH_2CHCH_2), 5.28 (2 H, m, OCH_2CHCH_2), 5.93 (1 H, m, OCH_2CHCH_2), 7.20 (1 H, d, *J* 7.5, ArH), 7.35 (1 H, d, *J* 8.2, ArH), 7.48 (1 H, t, *J* 8.4, ArH) and 8.13 (1 H, d, *J* 7.8, ArH).

α-Diazo ketone formation[29] from acid chlorides[30]

General procedure. The acid chloride was prepared by stirring the carboxylic acid (1 equiv.) with oxalyl chloride (1.2 equiv.) and dimethylformamide (DMF) (2 drops, catalytic) in dichloromethane (0.52 mol dm^{-3}) at 0 °C under a nitrogen atmosphere for 3 h. The solution was then concentrated at reduced pressure and the crude acid chloride taken up in ether or tetrahydrofuran (THF) and added *via* a pressure-equalised dropping funnel to a freshly prepared ethereal diazomethane (or diazoethane) solution (3–4 equiv.) over 1 h at 0 °C (−20 °C for reaction with diazoethane) under a nitrogen atmosphere. The reaction solution was then allowed to warm to room temperature over 3–4 h. The solvent was removed under reduced pressure to yield the crude α-diazo ketone which was purified by flash chromatography on silica gel with ethyl acetate–hexane as eluent.

2-Diazo-1-(2-ethoxyphenyl)propan-1-one 5. 2-Ethoxybenzoyl chloride, prepared from 2-ethoxybenzoic acid (2.0 g, 17.2 mmol), was treated with diazoethane to give a crude product which was purified by chromatography on silica gel with ethyl acetate–hexane (1:4) as eluent to afford the diazo ketone **5** (1.77 g, 50%) as a yellow oil (Found: C, 64.6; H, 5.9; N, 14.0. Calc. for $C_{11}H_{12}N_2O_2$: C, 64.7; H, 5.9; N, 13.7%); ν_{max}/cm^{-1} 2076 (C=N_2) and 1598 (C=O); δ_H 1.42 (3 H, *J* 7, CH_3CH_2O), 2.10 (3 H, br s, CH_3CH_2), 4.07 (2 H, q, *J* 7, CH_3CH_2O), 6.89 (1 H, d, *J* 8.6, ArH), 6.98 (1 H, t, *J* 7.7, ArH) and 7.36 (2 H, m, ArH).

1-(2-Benzyloxyphenyl)-2-diazopropan-1-one 6. 2-Benzyloxybenzoyl chloride (prepared from 4.0 g, 17.5 mmol) 2-benzyloxybenzoic acid) was converted using diazoethane into the diazo ketone **6** which was purified by chromatography on silica gel with ethyl acetate–hexane (1:4) as eluent to give pure diazo ketone **6** (1.96 g, 42%) as a yellow oil (Found: C, 72.0; H, 5.5; N, 10.5. Calc. for $C_{16}H_{14}N_2O_2$ C, 72.1; H, 5.3; N, 10.5%); ν_{max}/cm^{-1} 2085 (C=N_2) and 1600 (C=O); δ_H 2.06 (3 H, s, CH_3CN_2), 5.11 (2 H, s, $PhCH_2$), 7.30 (2 H, m, ArH) and 7.39 (8 H, m, ArH).

1-(2-Allyloxyphenyl)-2-diazoethanone 8. 2-Allyloxybenzoic acid **3** (7 g, 0.036 mol) was converted into the acid chloride which on reaction with diazomethane gave an oil. Chromatography on silica gel with CH_2Cl_2–EtOAc (95:5) as eluent yielded diazo ketone **8** (6.26 g, 87%) as a yellow solid, mp 56–57 °C

(Found: C, 64.9; H, 5.0; N, 13.6. Calc. for $C_{11}H_{10}N_2O_2$: C, 65.3; H, 5.0; N, 13.8%); ν_{max}/cm^{-1} 2095 (C=N_2) and 1590 (C=O); δ_H 4.64 (2 H, d, *J* 5.5, OCH_2CHCH_2), 5.41 (2 H, m, OCH_2CHCH_2), 6.10 (1 H, m, OCH_2CHCH_2), 6.39 (1 H, br s, CHN_2), 6.94 (1 H, d, *J* 8.4, ArH), 7.04 (1 H, t, *J* 7.6, ArH), 7.43 (1 H, m, ArH) and 7.94 (1 H, d, *J* 6.6, ArH).

Methyl 2-diazo-3-(2-allyloxyphenyl)-3-oxopropionate 9a

To a solution of the carboxylic acid **3** (3 g, 15.6 mmol) in THF was added 1,1'-carbonyldiimidazole (18.7 mmol) and the resulting solution was stirred for 12 h at room temperature. Treatment of hydrogen methyl malonate (23.4 mmol) with isopropylmagnesium bromide (46.8 mmol) at 0 °C for 0.5 h, then at room temperature for 0.5 h and finally at 40 °C for 0.5 h, generated the malonate dianion as its magnesium chelate. To this solution at 0 °C was added the imidazolide solution, and a gummy precipitate began to form immediately. After warming to room temperature and stirring for 4 h, the reaction mixture was poured into ice-cold 1 mol dm^{-3} H_3PO_4. Extraction with ethyl acetate (3 × 150 cm^3), was followed by washing the combined organic extracts with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, and drying over Na_2SO_4. Evaporation of the solvent left the crude β-keto ester **9**. The crude ester (2.3 g, 9.3 mmol) was dissolved in acetonitrile (50 cm^3) and methanesulfonyl azide[10] (**CAUTION:** Although we have never had any trouble with mesyl azide, it is potentially explosive!) (1.23 g, 10.2 mmol) and triethylamine (2.58 cm^3, 18.6 mmol) were added to provide a brown oil. Chromatography on silica gel with ethyl acetate–hexane (1:4) as eluent afforded pure β-keto ester **9a** (2.32 g, 91%) as a yellow oil (Found: C, 61.2; H, 5.2; N, 10.0. Calc. for $C_{14}H_{14}N_2O_4$ C, 61.3; H, 5.1; N, 10.2%); ν_{max}/cm^{-1} 2131 (C=N_2), 1731 and 1694 (dicarbonyl); δ_H 3.76 (3 H, s, CH_3O), 4.34 (2 H, m, OCH_2CHCH_2), 5.26 (2 H, m, OCH_2CHCH_2), 6.00 (1 H, m, OCH_2CHCH_2) and 7.18 (3 H, m, ArH).

1-(2-Allylsulfanylphenyl)-2-diazopropan-1-one 10

To a solution of the carboxylic acid **4** (2 g, 0.01 mol) in THF at −20 °C was added triethylamine (1.4 cm^3, 0.01 mol) and isobutyl chloroformate (1.3 cm^3, 0.01 mol) under a dry nitrogen atmosphere. The solution was stirred for 30 min and then allowed to warm to −10 °C. At this temperature, a solution of diazomethane in ether was added *via* a pressure-equalised dropping funnel during 1 h. The reaction mixture was stirred for a further 3 h while allowing it to reach room temperature. The solvent was removed using a rotatory evaporator with an acetic acid trap and the residue was diluted with ether (50 cm^3) and washed with water (50 cm^3) and saturated aqueous sodium hydrogen carbonate (50 cm^3). The organic phase was dried ($MgSO_4$), filtered and evaporated to give the crude diazo ketone which was purified by flash chromatography on silica gel with ether–hexane (1:7) as eluent to afford diazo ketone **10** (1.2 g, 50%), as a yellow oil, ν_{max}/cm^{-1} 2100 (C=N_2) and 1630 (C=O); δ_H 2.11 (3 H, br s, CH_3CN_2), 3.53 (2 H, d, *J* 6.8, OCH_2CHCH_2), 5.09 (2 H, m, OCH_2CHCH_2), 5.83 (1 H, m, OCH_2CHCH_2), 7.25 (2 H, m, ArH) and 7.40 (2 H, m, ArH); *m/z* 232 (M^+, 4%), 204 (21), 177 (21) and 163 (100).

1-(2-Isopropoxyphenyl)propan-1-one 11

Reaction of 1-(2-hydroxyphenyl)propan-1-one (2'-hydroxypropiophenone) (15.0 g, 0.1 mol) with 2-bromopropane (24.6 g, 0.2 mol) in the presence of potassium carbonate (27.6 g, 0.2 mol) according to the procedure described for compounds **1**–**4** gave ketone **11** (11.2 g, 58%) as a clear colourless oil (Found: C, 74.7; H, 8.3. Calc. for $C_{12}H_{16}O_2$: C, 75.0; H, 8.4%); ν_{max}/cm^{-1} 1673 (C=O); δ_H 1.17 [3 H, t, *J* 7.2, $CH_3CH_2C(O)$], 1.38 [6 H, d, *J* 6.2, $(CH_3)_2CH$], 3.00 [2 H, q, *J* 7.2, $CH_3CH_2C(O)$], 4.67 [1 H, m, $(CH_3)_2CH$], 6.94 (2 H, t, *J* 7.8, ArH), 7.39 (1 H, m, ArH) and 7.66 (1 H, m, ArH).

1-(2-Allyloxyphenyl)propan-1-one 12

A mixture of 1-(2-hydroxyphenyl)propan-1-one (20.0 g, 0.133 mol) and potassium carbonate (36.7 g, 0.27 mol) in acetone (200 cm^3) was refluxed while stirring under nitrogen for 30 min then the mixture was cooled to room temperature. A solution of allyl bromide (32.2 g, 0.27 mol) in acetone (150 cm^3) was added to the mixture over 15 min and heating was continued for 36 h. The cooled mixture was filtered and concentrated at reduced pressure to an oil which was dissolved in benzene (300 cm^3), washed with aqueous potassium hydroxide (1 mol dm^{-3}; 3 × 100 cm^3), then washed with water (100 cm^3) and brine (100 cm^3), dried and concentrated at reduced pressure to give the pure title compound **12** (22.2 g, 88%) as a clear colourless oil; ν_{max}/cm^{-1} 1675 (C=O); δ_H 1.17 (3 H, t, *J* 7.2, CH_3CH_2O), 3.02 (2 H, q, *J* 7.2, CH_3CH_2O), 4.61 (2 H, m, OCH_2CHCH_2), 5.36 (2 H, m, OCH_2CHCH_2), 6.06 (1 H, m, OCH_2CHCH_2), 6.96 (2 H, m, ArH), 7.40 (1 H, m, ArH) and 7.67 (1 H, m, ArH).

α-Diazo ketone formation *via* Danheiser's procedure[12]

General procedure. A 50 cm^3, three-necked, round-bottomed flask equipped with a rubber septum, nitrogen inlet adapter, and a 25 cm^3 pressure-equalising addition funnel was charged with a solution of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (4.7 mmol) in THF (12 cm^3) and then cooled at 0 °C in an ice–water bath while butyllithium solution (2.2 mol dm^{-3} in hexane; 4.71 mmol) was added rapidly dropwise. After 10 min, the resulting solution was cooled at −78 °C in a solid CO_2–acetone bath while a solution of ketone (4.29 mmol) in THF (8 cm^3) was added dropwise over 15 min. The reaction mixture was stirred at −78 °C for 30 min, and then 2,2,2-trifluoroethyl trifluoroacetate (5.14 mmol) was added rapidly by syringe in one portion. After 10 min, the reaction mixture was poured into a separatory funnel containing 5% aqueous HCl (25 cm^3) and Et_2O (30 cm^3). The aqueous phase was extracted with two portions of Et_2O (30 cm^3) and the combined organic phases were then washed with saturated aqueous NaCl (25 cm^3) and concentrated at reduced pressure to give an oil which was immediately dissolved in MeCN (15 cm^3) and transferred to a 50 cm^3, three-necked, round-bottomed flask equipped with a rubber septum, nitrogen inlet adapter, and a 25 cm^3 pressure-equalising addition funnel. Water (4.29 mmol) and Et_3N (6.44 mmol) were added, and a solution of methanesulfonyl azide (6.44 mmol) in MeCN (15 cm^3) was then added dropwise over 20 min. The resulting solution was stirred at room temperature for 2.5 h and then concentrated to a volume of *ca.* 10 cm^3. The residue was diluted with Et_2O (30 cm^3) and washed with three portions of 10% aqueous NaOH (20 cm^3) and saturated aqueous NaCl (15 cm^3), dried over Na_2SO_4, filtered, and then concentrated to afford crude product as a yellow–orange oil. Flash chromatography on silica gel (ethyl acetate–hexane) provided pure diazoketone.

2-Diazo-1-(2-isopropoxyphenyl)propan-1-one 13. Reaction of 1-(2-isopropoxyphenyl)propan-1-one **11** (6.5 g, 33.8 mmol) with LiHMDS (37.2 mmol) and 2,2,2-trifluoroethyl trifluoroacetate (40.5 mmol) in THF (80 cm^3) following the above general procedure provided a yellow oil which was treated with H_2O (33.8 mmol), Et_3N (50.1 mmol) and methanesulfonyl azide (50.1 mmol) in MeCN (120 cm^3) at room temperature for 12 h to yield a brown oil. Flash chromatography on silica gel (ethyl acetate–hexane, 1:3) provided the diazo ketone **13** (3.73 g, 51%) as a yellow oil (Found: C, 65.9; H, 6.7; N, 13.1. Calc. for $C_{12}H_{14}N_2O_2$: C, 66.0; H, 6.5; N, 12.9%); ν_{max}/cm^{-1} 2073 (C=N_2) and 1590 (C=O); δ_H 1.33 [6 H, d, *J* 6.2, $(CH_3)_2CH$], 2.10 (3 H, br s, CH_3CN_2), 4.54 [1 H, m, $(CH_3)_2CH$], 6.89 (1 H, t, *J* 7.8, ArH), 6.97 (1 H, t, *J* 7.4, ArH) and 7.37 (2 H, m, ArH).

1-(2-Allyloxyphenyl)-2-diazopropan-1-one 7. Reaction of 1-(2-allyloxyphenyl)propan-1-one **12** (5.44 g, 28.6 mmol) with LiHMDS (31.4 mmol) and 2,2,2-trifluoroethyl trifluoroacetate

(34.3 mmol) in THF (80 cm^3) according to the general procedure provided a yellow oil which was then treated with H_2O (28.6 mmol), Et_3N (42.9 mmol), and methanesulfonyl azide (42.9 mmol) in MeCN (100 cm^3) at room temperature for 12 h to yield a brown oil. Flash chromatography on silica gel (ethyl acetate–hexane, 1:4) afforded diazo ketone **7** (3.35 g, 54%) as a yellow oil (Found: C, 66.4; H, 5.6; N, 12.9. Calc. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.95%); ν_{max}/cm^{-1} 2080 (C=N_2) and 1600 (C=O); δ_H 2.09 (3 H, s, CH_3CN_2), 4.57 (2 H, m, OCH_2CHCH_2), 5.35 (2 H, m, OCH_2CHCH_2), 6.04 (1 H, m, OCH_2CHCH_2), 6.99 (2 H, m, ArH) and 7.39 (2 H, m, ArH).

1-(2-Allyloxyphenyl)-2-phenylethanone 14

Reaction of salicylaldehyde (17.5 cm^3, 0.16 mol) and allyl bromide (21.3 cm^3, 0.24 mol) in the presence of potassium carbonate (33.1 g, 0.24 mol) according to the procedure described for compounds **1–4** gave the 2-allyl derivative as a clear colourless oil. To a solution of benzylmagnesium bromide, prepared from magnesium turnings (1.7 g, 52 mmol) and benzyl bromide (7.7 cm^3, 47.5 mmol) in THF (60 cm^3), was added dropwise a solution of the 2-allyl aldehyde (7.0 g) in THF (30 cm^3) at −10 °C and the resulted mixture was refluxed for 3 h. The solution was poured into crushed ice (200 g), followed by dilute sulfuric acid and the mixture concentrated under reduced pressure. Extraction of the residue with ether (3 × 200 cm^3) gave the desired alcohol (86.5%) after removal of solvent, which was used in the next experiment without purification.

A 100 cm^3 two-necked round-bottomed flask equipped with a condenser and nitrogen inlet was charged with a solution of pyridinium chlorochromate (3.88 g, 18 mmol) in anhydrous dichloromethane (24 cm^3) and cooled at 0 °C in an ice–water bath while the above alcohol (3.0 g, 12 mmol) in anhydrous dichloromethane (5 cm^3) was added in one portion. After 5 min the ice bath was removed and the reaction was stirred at room temperature for 3 h. The suspension was filtered over Celite and washed with ether. The solvent was removed under reduced pressure and chromatography of the residue on silica gel (ethyl acetate–hexane, 1:5) afforded ketone **14** (2.3 g, 77%) as a colourless oil (Found: C, 80.5; H, 6.55. Calc. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4%); ν_{max}/cm^{-1} 1672 (C=O) and 1592 (C=C); δ_H 4.33 [2 H, s, C(O)CH_2Ph], 4.60 (2 H, d, *J* 5.3, OCH_2CHCH_2), 5.36 (2 H, m, OCH_2CHCH_2), 6.04 (1 H, m, OCH_2CHCH_2), 6.93 (2 H, m, ArH), 7.24 (5 H, m, ArH), 7.38 (1 H, m, ArH) and 7.64 (1 H, m, ArH).

1-(2-Allyloxyphenyl)-2-diazo-2-phenylethanone 15

A flame-dried, two-necked flask equipped with a nitrogen inlet, septum, and a pressure-equalising addition funnel was charged with the ketone **14** (2.8 g, 11 mmol), methanesulfonyl azide (1.4 g, 11 mmol) and MeCN (5 cm^3). The solution was cooled at 0 °C in an ice–water bath while 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.7 cm^3, 11 mmol) was added dropwise over 10 min. The reaction mixture was stirred overnight, then diluted with 10% aqueous NaOH and extracted with ether (3 × 30 cm^3). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residual brown oil was purified by chromatography on silica gel with ethyl acetate–hexane (1:4) as eluent to afford diazo ketone **15** (1.2 g, 40%) as a yellow oil (Found: M, 278.1060. Calc. for $C_{17}H_{14}N_2O_2$: *M*, 278.1055); ν_{max}/cm^{-1} 2080 (C=N_2) and 1610 (C=O); δ_H 4.53 (2 H, d, *J* 4.9, OCH_2CHCH_2), 5.22 (1 H, d, *J* 10.6, OCH_2CHCH_2), 5.35 (1 H, d, *J* 17, OCH_2CHCH_2), 5.94 (1 H, m, OCH_2CHCH_2), 6.90 (1 H, d, *J* 8.7, ArH), 7.04 (1 H, t, *J* 7.6, ArH), 7.23 (1 H, m, ArH), 7.40 (1 H, m, ArH) and 7.56 (2 H, m, ArH).

Preparation of rhodium(II) carboxylates 16–22 [14]

The carbonate complex $Na_4Rh_2(CO_3)_4 \cdot 2.5H_2O$ [13] (0.13 mmol) and the carboxylic acid (8 equiv.) in water (8 cm^3) were refluxed for 1 h. The blue colour of the carbonate faded and the volume of the resulting solution was reduced to 4 cm^3 by evaporation. After cooling the mixture, the precipitate was isolated by filtration, washed with water, recrystallised from methanol–water to afford the rhodium(II) carboxylates **16–22**.

Catalytic decomposition of diazocarbonyl compounds

General procedure. The α-diazocarbonyl precursor in dry solvent (CH_2Cl_2 or C_6H_6, 0.01 mol dm^{-3}) was added dropwise over 1–2 h to a suspension of the catalyst (Cu^I, Cu^{II} or Rh^{II}, 0.5–1.0 mmol% based on diazocarbonyl precursor) in the same solvent at 0 °C, 25 °C or refluxing under nitrogen. The reaction was followed by TLC until the diazocarbonyl compound was consumed (30 min–12 h). The solution was filtered through a silica gel pathway and the solvent was removed under reduced pressure to give the crude product.

2,3-Dimethyl-3,4-dihydro-2*H*-1-benzopyran-4-one 26. 2-Diazo-1-(2-ethoxyphenyl)propan-1-one **5** (100 mg, 0.49 mmol) was treated with the rhodium(II) catalyst in CH_2Cl_2 at reflux. Chromatography on silica gel with ethyl acetate–hexane (1:4) as eluent afforded the title compound **26** (85 mg, 99%) (Found: C, 74.7; H, 6.8. Calc. for $C_{11}H_{12}O_2$: C, 74.9; H, 6.9%); ν_{max}/cm^{-1} 1685 (C=O); δ_H(*cis* isomer): 1.15 [3 H, d, *J* 7.4, $CH_3CHC(O)$], 1.35 (3 H, d, *J* 6.5, CH_3CHO), 2.65 [1 H, m, $CH_3CHC(O)$], 4.63 (1 H, m, CH_3CHO), 6.99 (2 H, m, ArH), 7.51 (1 H, m, ArH) and 7.81 (1 H, d, *J* 7.6, ArH); (*trans* isomer): 1.21 [3 H, d, *J* 6.9, $CH_3CHC(O)$], 1.52 (3 H, d, *J* 6.4, CH_3CHO), 2.55 [1 H, m, $CH_3CHC(O)$], 4.24 (1 H, m, CH_3CHO), 6.99 (2 H, m, ArH), 7.51 (1 H, m, ArH) and 7.81 (1 H, d, *J* 7.6, ArH). Decoupling of C-2–CH_3 showed: *cis* isomer, 2-H–3-H, *J* 2.2; *trans* isomer, 2-H–3-H, *J* 10.2.

2-Phenyl-3-methyl-3,4-dihydro-2*H*-1-benzopyran-4-one 27. 1-(2-Benzyloxyphenyl)-2-diazopropan-1-one **6** (118 mg, 0.52 mmol) was treated with the rhodium(II) catalyst in CH_2Cl_2 at reflux. Chromatography on silica gel with ethyl acetate–hexane (1:9) as eluent afforded the title compound **27** (97 mg, 92%) (Found: C, 80.4; H, 6.1. Calc. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.9%); ν_{max}/cm^{-1} 1680 (C=O); δ_H(*cis* isomer): 0.99 [3 H, d, *J* 7.2, $CH_3CHC(O)$], 2.82 [1 H, m, $CH_3CHC(O)$], 5.57 (1 H, d, *J* 2.5, $PhCHO$), 7.06 (2 H, m, ArH), 7.37 (6 H, m, ArH) and 7.94 (1 H, d, *J* 7.6, ArH); (*trans* isomer): 1.01 [3 H, d, *J* 6.7, $CH_3CHC(O)$], 3.04 [1 H, m, $CH_3CHC(O)$], 5.04 (1 H, d, *J* 12.4, $PhCHO$), 7.06 (2 H, m, ArH), 7.37 (6 H, m, ArH) and 7.94 (1 H, d, *J* 7.6, ArH).

2,2,3-Trimethyl-3,4-dihydro-2*H*-1-benzopyran-4-one 28. Diazo ketone **13** (120 mg, 0.56 mmol) was decomposed with the rhodium(II) catalyst at 0 °C, 25 °C, refluxing in CH_2Cl_2 or refluxing in C_6H_6 to provide the crude product in quantitative yield. Chromatography on silica gel with ethyl acetate–hexane (1:3) as eluent afforded the title compound **28** (94 mg, 90%) (Found: C, 75.5; H, 7.7. Calc. for $C_{12}H_{14}O_2$: C, 75.7; H, 7.4%); ν_{max}/cm^{-1} 1687 (C=O); δ_H 1.20 [3 H, d, *J* 7, $CH_3CHC(O)$], 1.30 (3 H, s, CH_3CCH_3), 1.49 (3 H, s, CH_3CCH_3), 2.72 [1 H, q, *J* 7, $CH_3CHC(O)$], 6.94 (2 H, m, ArH), 7.47 (1 H, m, ArH) and 7.84 (1 H, m, ArH).

2-Allyl-2,3-dihydrobenzofuran-3-one 29. Diazo ketone **8** (100 mg, 0.5 mmol) in CH_2Cl_2 was added to a refluxing suspension of rhodium(II) catalyst in CH_2Cl_2. Chromatography on silica gel with dichloromethane as eluent afforded the title compound **29** (90% yield) as a clear colourless oil, ν_{max}/cm^{-1} 1710 (C=O) and 1608 (C=C); δ_H 2.52 (1 H, m, $OCHCH_2CHCH_2$), 2.79 (1 H, m, $OCHCH_2CHCH_2$), 4.62 (1 H, dd, *J* 4.2 and 9.7, $OCHCH_2CHCH_2$), 5.22 (2 H, m, $OCHCH_2CHCH_2$), 5.81 (1 H, m, $OCHCH_2CHCH_2$), 7.09 (2 H, m, ArH) and 7.62 (2 H, m, ArH); δ_C 35.48, 84.60, 113.57, 118.96, 121.04, 121.95, 124.29, 131.77, 138.07, 172.76 and 201.28.

2-Allyl-2-methoxycarbonyl-2,3-dihydrobenzofuran-3-one 30. The diazo ketone **9** (214 mg, 0.78 mmol) in CH_2Cl_2 was added

dropwise to a refluxing suspension of rhodium(II) catalyst in CH_2Cl_2. Chromatography on silica gel with ethyl acetate–hexane (1:4) as eluent afforded the title compound **30** (176 mg, 92%) as a clear colourless oil (Found: C, 68.3; H, 5.7. Calc. for $C_{14}H_{14}O_4$: C, 68.3; H, 5.7%); ν_{max}/cm^{-1} 1750 and 1720 (C=O); δ_H 2.85 (1 H, dd, *J* 7.1 and 14.5, CCH_2CHCH_2), 3.07 (1 H, dd, *J* 7.1 and 14.5, CCH_2CHCH_2), 3.76 (3 H, s, OCH_3), 5.16 (2 H, m, CCH_2CHCH_2), 5.66 (1 H, m, CCH_2CHCH_2), 7.02 (1 H, t, *J* 7.5, ArH) and 7.47 (2 H, m, ArH).

2-Allyl-2-methyl-2,3-dihydro-1-benzothiophen-3-one 31. To a suspension of catalyst in CH_2Cl_2 (10 cm^3) at reflux a solution of the diazo ketone **10** (50 mg, 0.21 mmol) in CH_2Cl_2 (10 cm^3). Chromatography on silica gel with ethyl acetate–hexane (1:20) as eluent afforded the title compound **31** (43 mg, 97%) as a clear oil (Found: C, 70.1; H, 6.2. Calc. for $C_{12}H_{12}OS$: C, 70.5; H, 5.9%); δ_H 1.56 (3 H, s, CH_3), 2.58 (2 H, d, *J* 7.1, CCH_2CHCH_2), 5.13 (2 H, m, CCH_2CHCH_2), 5.75 (1 H, m, CCH_2CHCH_2), 7.19 (1 H, td, *J* 7.6 and 0.8, ArH), 7.36 (1 H, dd, *J* 7.4 and 0.8, ArH), 7.54 (1 H, ddd, *J* 7.8, 7.2 and 1.5, ArH) and 7.76 (1 H, dd, *J* 7.8 and 1.5, ArH); δ_C 24.58, 43.45, 61.98, 119.54, 123.93, 124.47, 126.95, 130.00, 132.48, 135.78, 151.70 and 204.42.

3-Methyl-2-vinyl-3,4-dihydro-2*H*-1-benzopyran-4-one 32 and 2-allyl-2-methyl-2,3-dihydrobenzofuran-3-one 33. The diazo ketone **7** (120 mg, 0.56 mmol) was treated with the rhodium(II) or copper catalyst at 0 °C, 25 °C, refluxing CH_2Cl_2 or refluxing C_6H_6 to provide crude products in quantitative yield. Chromatograhy on silica gel with ethyl acetate–hexane as eluent achieved separation and afforded the title compounds **32** and **33**. The distribution of products is summarised in Table 1. 2-Benzopyran-4-one **32** was obtained as a clear colourless oil (Found: C, 76.5; H, 6.7. Calc. for $C_{12}H_{12}O_2$: C, 76.6; H, 6.4%); ν_{max}/cm^{-1} 1685 (C=O); δ_H (*cis* isomer): 1.15 (3 H, d, *J* 7.3, CH_3CH), 2.80 (1 H, m, CH_3CH), 4.97 (1 H, m, $OCHCHCH_2$), 5.46 (2 H, m, $OCHCHCH_2$), 5.93 (1 H, m, $OCHCHCH_2$), 7.02 (2 H, m, ArH), 7.48 (1 H, m, ArH) and 7.88 (1 H, m, ArH); (*trans* isomer): 1.20 (3 H, d, *J* 7, CH_3CH), 2.71 (1 H, m, CH_3CH), 4.57 (1 H, dd, *J* 7.1 and 11.1, $OCHCHCH_2$), 5.43 (2 H, m, $OCHCHCH_2$), 6.04 (1 H, m, $OCHCHCH_2$), 7.02 (2 H, m, ArH), 7.48 (1 H, m, ArH) and 7.88 (1 H, m, ArH). (Decoupling of C-3–CH_3 showed: *cis* isomer, 2-H–3-H, *J* 3.5; *trans* isomer, 2-H–3-H, *J* 11).

Benzofuran-3-one **33** was obtained as a clear colourless oil (Found: C, 76.3; H, 6.7. Calc. for $C_{12}H_{12}O_2$: C, 76.6; H, 6.4%); ν_{max}/cm^{-1} 1710 (C=O) and 1603 (C=C); δ_H 1.44 (3 H, s, CH_3), 2.55 (2 H, m, CCH_2CHCH_2), 5.11 (2 H, m, CCH_2CHCH_2), 5.67 (1 H, m, CCH_2CHCH_2), 7.07 (2 H, m, ArH) and 7.62 (2 H, m, ArH).

3-Phenyl-2-vinyl-3,4-dihydro-2*H*-1-benzopyran-4-one 34 and 2-allyl-2-phenyl-2,3-dihydrobenzofuran-3-one 35. Diazo ketone **15** (115 mg, 0.36 mmol) was treated with the rhodium(II) catalyst according to the general procedure (refluxing, CH_2Cl_2) to provide crude products containing two compounds **34** and **35** in the ratio 95:5. Chromatography on silica gel with ethyl acetate–hexane (1:4) as eluent afforded pure title compounds **34** (85 mg, 94%) and **35** (2 mg). 1-Benzopyran-4-one **34** was obtained as a clear colourless oil (Found: M, 250.1000. Calc. for $C_{17}H_{14}O_2$: *M*, 250.0994); ν_{max}/cm^{-1} 1680 (C=O) and 1600 (C=C); δ_H (*cis* isomer): 3.81 [1 H, d, *J* 3.7, C(O)C*H*Ph], 5.18 (1 H, m, $OCHCHCH_2$), 5.24–5.46 (2 H, m, $OCHCHCH_2$), 5.82 (1 H, m, $OCHCHCH_2$), 7.09 (2 H, m, ArH), 7.22 (4 H, m, ArH), 7.30 (1 H, m, ArH), 7.53 (1 H, m, ArH) and 7.93 (1 H, m, ArH); (*trans* isomer): 3.86 [1 H, d, *J* 10, C(O)C*H*Ph], 5.12 (1 H, m, $OCHCHCH_2$), 5.24–5.46 (2 H, m, $OCHCHCH_2$), 5.82 (1 H, m, $OCHCHCH_2$), 7.09 (2 H, m, ArH), 7.22 (4 H, m, ArH), 7.30 (1 H, m, ArH), 7.53 (1 H, m, ArH) and 7.93 (1 H, m, ArH).

Benzofuran-3-one **35** was obtained as a clear colourless oil, δ_H 2.95 (2 H, m, CCH_2CHCH_2), 5.09 (2 H, m, CCH_2CHCH_2), 5.63 (1 H, m, CCH_2CHCH_2), 7.08 (1 H, m, ArH), 7.36 (4 H, m, ArH) and 7.64 4 H, m, ArH).

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