Alternatives to α-Diazo Ketones for Tandem Cyclization–Cycloaddition and Carbenoid–Alkyne Metathesis Strategies. Novel Cyclic Enol–Ether Formation *via* Carbonyl Ylide Rearrangement Reactions

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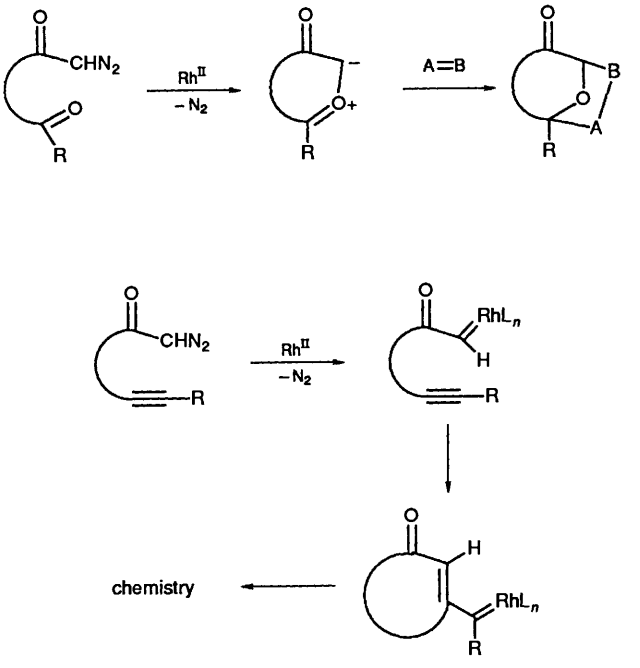
Attempts to form carbonyl ylides from free carbenes derived from diazirines or diazo compounds lacking electron-withdrawing substituents resulted in azine formation or Wolff rearrangement, respectively. Iodonium ylides proved to be a possible alternative to α-diazo compounds for metallocarbenoid generation, similar reactivity being observed for both systems. Studies into the rearrangement chemistry of carbonyl ylides provided a novel cyclic enol–ether synthesis *via* a 1,4-hydrogen shift process.

In recent years increasing attention has been paid to the application of carbenes or their synthetic equivalents toward organic synthesis.[1] Following the initial report of Stork and Ficini,[2] the transition metal-catalysed cyclopropanation reaction of α-diazo ketones as a method for producing bicyclic ring compounds has been extensively studied both from a mechanistic[3] and synthetic viewpoint.[4] Synthetic uses for metal-catalysed decomposition of diazocarbonyls are not limited to cyclopropanation, even though the focus of many studies has centred on this transformation.[5] Intramolecular reactions involving either carbon–hydrogen insertion[6] or ylide generation[7] have also been used to prepare complex synthetic targets. Rhodium(II) carboxylates are particularly effective catalysts for the decomposition of diazo compounds and an increasing number of chemical syntheses are based on this catalytic methodology.[8] The rhodium(II) catalysed reaction is believed to involve a metallocarbenoid intermediate which retains the highly electrophilic properties associated with free carbenes.[9] Recent studies within our group have been concentrated in two main areas, the utilization of a α-diazo ketones in the formation of carbonyl ylides[10,11] and the application of carbenoid-alkyne metathesis reactions to produce vinyl carbenoids as reactive intermediates.[12,13] The general strategies for both of these areas of research are shown in Scheme 1.



Scheme 1

Despite the fact that both these methods have resulted in the construction of a variety of polycyclic systems, several pertinent questions arose during the course of our studies. How do classical free carbenes compare to rhodium carbenoids with respect to ylide formation? How necessary is the vicinal carbonyl group? Are α-diazo compounds the only viable carbenoid source? Can carbonyl ylides undergo useful transformations other than dipolar cycloaddition?

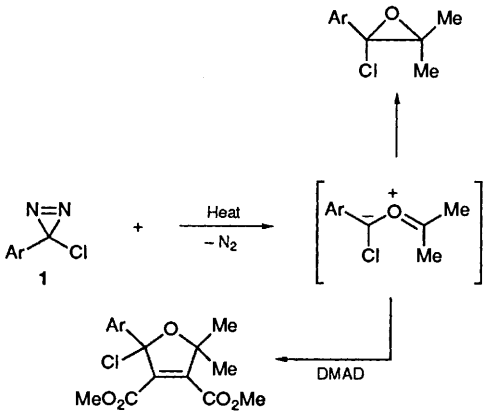
The ability to extend the carbonyl ylide and carbenoid-alkyne metathesis methodology to related systems would greatly enhance their synthetic potential. Likewise, the hazards associated with the handling of α-diazo compounds merits the study of other carbene or carbenoid sources. This paper documents results obtained in our efforts to answer the above questions.

Results and Discussion

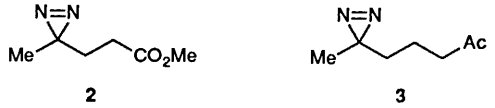
Initial studies were concerned with the determination and preparation of an appropriate free carbene precursor. Diazirines appeared to meet our requirements, the decomposition of these species *via* a diazo intermediate to afford free carbenes being well documented.[14] Furthermore, precedent exists for the bimolecular formation of carbonyl ylides from diazirine precursors **1**. For instance, carbonyl ylide formation of phenylchlorocarbene with acetone and several of its *para*-substituted derivatives have been well documented.[15–18] Product analysis demonstrated that the carbonyl ylides are readily intercepted with dipolarophiles [*i.e.* dimethyl acetylenedicarboxylate (DMAD)] or, in the absence of an ylide trap, ring-close to give the three-membered oxirane ring (Scheme 2). Laser flash photolysis experiments have directly detected the transient absorption spectra of the phenylchlorocarbene acetone ylide (λ_{max} 450 nm) and the acetone ylides of the corresponding *p*-Cl,[16] *p*-CF_3[16] and *p*-NO_2[15] derivatives, which have absorption maxima at 480, 480 and 590 nm, respectively. As expected, an increase in the electron-withdrawing ability of the *para*-substituents facilitated ylide formation.

In order to study the intramolecular variant of this reaction, diazirines **2** and **3** were prepared by the method of Church and Weiss.[19] Although, the preparation of the diazirine **2** was fairly routine, that of **3** was slightly more involved, differentiation between the two keto groups of the diazirine precursor being necessary. An alkylation–decarboxylation protocol was therefore employed (see Scheme 3).

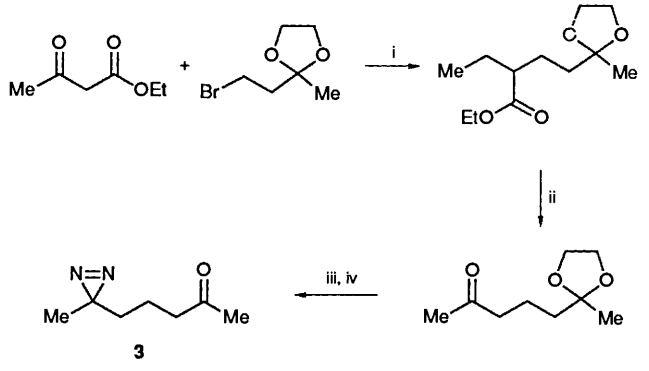
Our attempts to generate a carbonyl ylide from the decom-



Scheme 2



2 3



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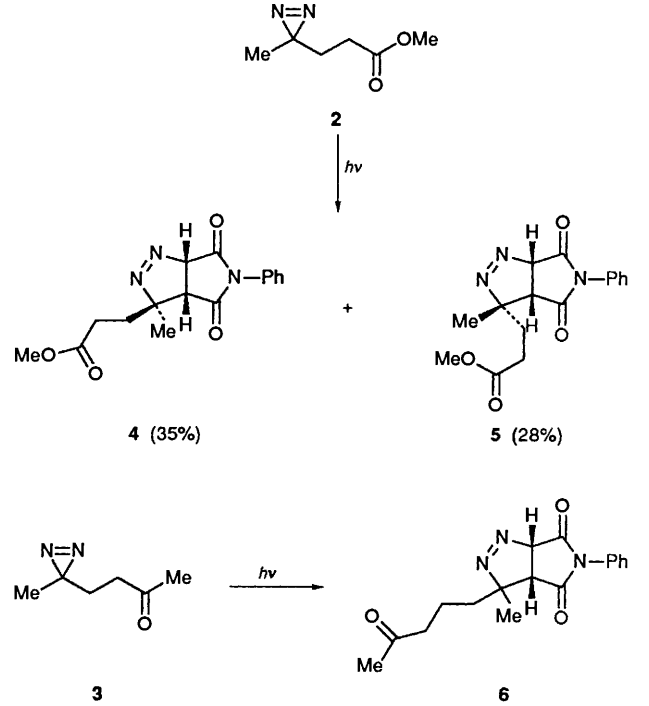
Scheme 3 *Reagents and conditions:* i, KOBu^t, THF, 25 °C; ii, $Ba(OH)_2$, H_2O, 100 °C; iii, ref. 9; iv, HCl (2 mol dm^{-3}), THF



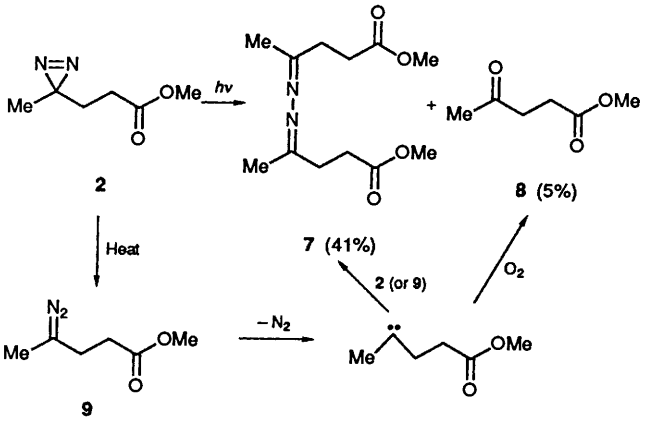
4 (35%) 5 (28%)

3 6

Scheme 4

position of diazirine **2** failed to give rise to any dipolar cycloadduct. Instead of ylide formation, rearrangement of the diazirine to the diazo compound occurred, which subsequently underwent 1,3-dipolar cycloaddition to *N*-phenylmaleimide, affording the bicyclic pyrazoline derivatives **4** and **5** in 63% combined yield (Scheme 4). Similarly, photochemical decomposition of diazirine **3** afforded the pyrrolopyrazole **6** as a 4:1 mixture of diastereoisomers in 41% yield. Analogous results, with somewhat diminished yields, were obtained in the thermal decomposition of the diazirines **2** and **3**.

Photolysis of diazirine **2** in the absence of a dipolarophile resulted in the formation of the azinobipentanoate **7** as the major product along with ketoester **8** (Scheme 5). The



2 8 (5%)

7 (41%)

9

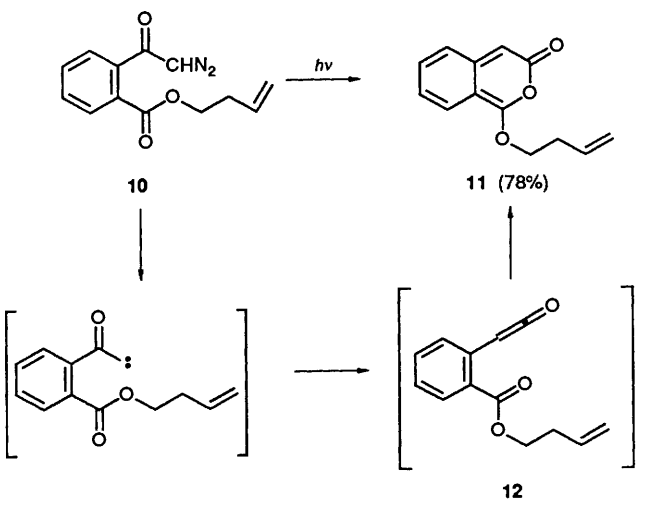
Scheme 5

formation of azine **7** occurs by the attack of a free carbene, derived from the diazo intermediate **9**, upon a second diazo species. The thermal and photochemical rearrangement of diazirines to diazo compounds is well documented in the literature[14] thereby providing good precedence for this suggestion. Ketoester **8** derives from insertion of the resulting free carbene into residual oxygen present in the reaction medium.

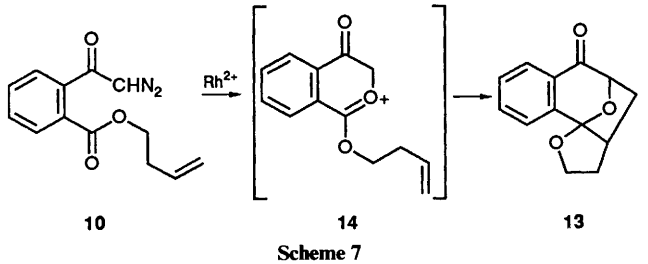
A possible explanation for the reluctance of the above diazines to form carbonyl ylides could be due to the flexibility of the carbon skeleton, thus preventing the carbonyl group and carbene centre from achieving a proximal orientation. It was envisaged that by replacing the carbon chain by an aromatic ring, the two reacting centres of the molecule would be held in close proximity, facilitating carbonyl ylide formation. To this end, α-diazoketone **10** was synthesized by a previously published method[10] and subjected to photolysis. This resulted in a 78% yield of the bicyclic lactone **11**. Structure **11** is derived from a Wolff rearrangement[20] of the initially produced carbene and this is followed by cyclization of the resulting ketene **12**.

Previous reports from this laboratory[10] have described the rhodium-catalysed decomposition of α-diazoketone **10**, which resulted in the formation of the oxapolycyclic species **13**, produced *via* the intramolecular trapping of the derived carbonyl ylide **14** (Scheme 7). From this and the above results it becomes apparent that carbenes are inferior to carbenoids with respect to carbonyl ylide formation. In the diazirine case, loss of nitrogen from the intermediate diazo compound is slow compared to 1,3-dipolar cycloaddition with the added dipolarophile. Likewise, Wolff rearrangement is the more facile process in the decomposition of α-diazoketone **10**.

Next we turned our attention to the role of the vicinal carbonyl group in promoting carbonyl ylide formation. The total absence of any products derived from carbonyl ylide in the decomposition of diazirines **2** and **3** already suggested that the carbene was not susceptible to attack by the pendant carbonyl group, though other factors may come into play in these

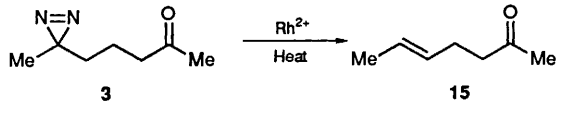


Scheme 6



Scheme 7

systems. Firmer evidence was provided by carrying out the decomposition of diazirine **3** in the presence of rhodium(II) acetate and DMAD. Doyle has reported that rhodium(II) carboxylates are very effective in the interception of α-diazo compounds formed by isomerisation of the corresponding diazirine.[21] However, the thermolysis of diazirine **3** in the presence of rhodium(II) acetate only resulted in the formation of the 1,2-hydrogen migration product **15** (Schene 8).

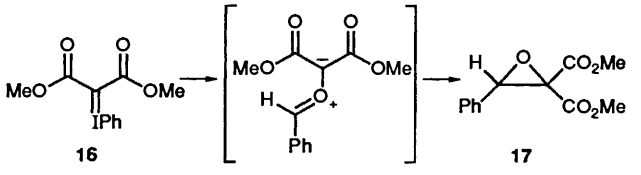


Scheme 8

The rhodium-catalysed decomposition of α-diazo ketone **10** and the subsequent trapping of the intermediate carbonyl ylide has been reported,[11] the reaction proceeding in high yield. From these observations it becomes apparent that the vicinal carbonyl group is indeed necessary for carbonyl ylide formation. We assume that the electron-deficient rhodium–carbene complex is further destabilized by the presence of the electron-withdrawing carbonyl group and that this facilitates cyclization to the dipole. Simple carbenes or carbenoids derived from diazirines of the type **2** and **3** do not possess sufficient electrophilic character in order for carbonyl ylide formation to take place. It is noteworthy that the bimolecular examples reported in the literature employ arylchlorocarbenes, which are highly electrophilic species and therefore more susceptible to nucleophilic attack.[15–18]

Having established that carbenoids are superior to carbenes with respect to ylide formation, and that a vicinal carbonyl group strongly promotes this process, we focused our attention on the possibility that precursors other than diazo compounds could be used for ylide formation. Several reports in the literature have described the thermal, photochemical, and metal-catalysed[22,23] decomposition of iodonium ylides which afford products consistent with a carbene or carbenoid intermediate, although an ionic pathway has also been suggested.[24] Consequently, we turned our attention to the synthesis and decomposition of a suitable iodonium ylide precursor.

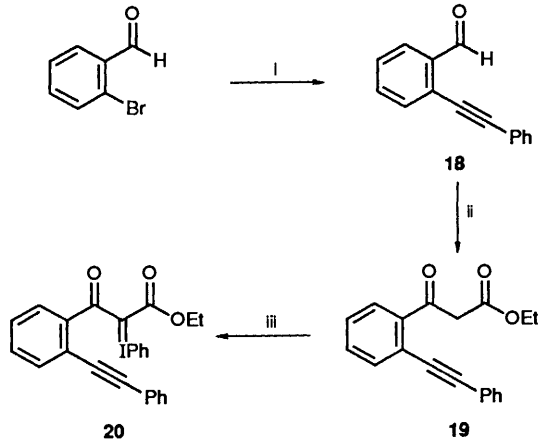
Our initial attempts to produce carbonyl ylides concentrated on bimolecular dipole formation. Iodonium ylide **16** was prepared by the method of Varvoglis *et al.*[23] Treatment of **16** with copper(I) chloride in the presence of a large excess of benzaldehyde results in the formation of oxirane **17** in fair yield (Scheme 9); but none of the dipolar cycloaddition product was



Scheme 9

observed. Oxirane **17** results from bimolecular carbonyl ylide formation followed by intramolecular ring closure. The formation of **17** compares favourably with the results of Huisgen[25] who reported that the copper powder-catalysed decomposition of dimethyl diazomalonate resulted in a 72% yield of the same oxirane product, again a carbonyl ylide being the proposed intermediate.

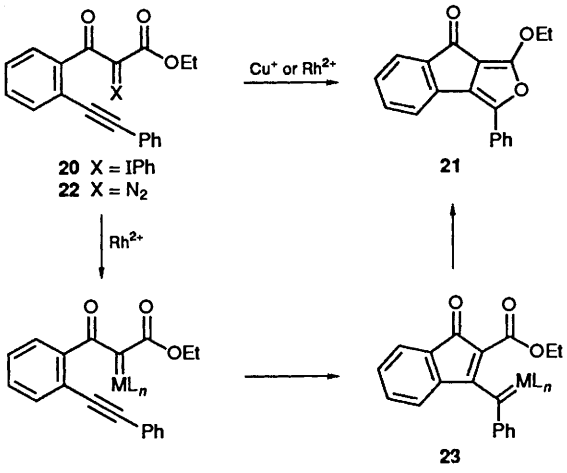
Encouraged by this result, we examined the possibility of intramolecular dipole formation. The system we decided to study was based upon the acetylenic ketoester **19**, which was readily available *via* the synthetic sequence shown in Scheme 10. Castro–



Scheme 10 *Reagents:* i, $PdCl_2(PPh_3)_2$, CuI, Et_3N, PhC≡CH; ii, $SnCl_2$, ethyl diazoacetate; iii, MeOH, KOH, $PhI(OAc)_2$

Stephens[26] coupling of 2-bromobenzaldehyde and phenylacetylene afforded aldehyde **18** which was treated with ethyl diazoacetate in the presence of tin(II) chloride.[27] Reaction of a methanolic solution of the resulting ketoester **19** with potassium hydroxide and bis-acetoxyiodosobenzene afforded iodonium ylide **20**. The copper(I)-catalysed decomposition of **20** afforded furan **21** in 57% yield. Likewise the rhodium(II)-catalysed decomposition of α-diazoketone **22** gave an identical furan in similar yield. The mechanism for the formation of furan **21** from **22** involves the initial formation of a rhodium carbenoid with concomitant loss of nitrogen.[12,13] Addition of this carbenoid to the acetylene π-system results in formation of the vinyl carbenoid **23** (Scheme 11). Subsequent carbonyl ylide generation and aromatization produces **21**. A similar mechanism can be envisaged for the formation of **21** from iodonium ylide **20**, although an ionic mechanism cannot be totally ruled out.

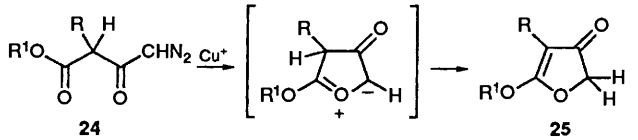
The above two examples clearly demonstrate that iodonium



Scheme 11

ylides are comparable to diazo compounds in both carbonyl ylide and vinyl carbenoid formation. However, a drawback does exist using these compounds. In our hands, the above iodonium ylides were quite prone to decomposition, making storage and prolonged handling a problem.

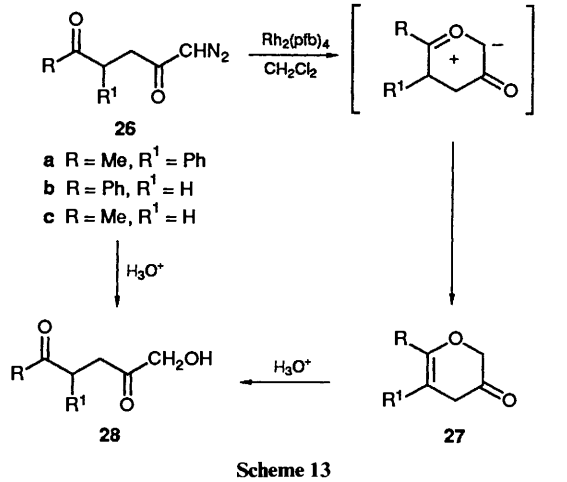
Our final area of study was to examine the chemical outcome of forming a carbonyl ylide in the absence of a dipolarophile, and to ascertain whether any synthetically useful transformations would arise. Although the vast majority of reactions of carbonyl ylides involve trapping with dipolarophiles, Bien[28] has reported that hydrogen migration can also occur in these systems. Thus, treatment of ethyl 4-diazo-2-phenylacetoacetate **24a** with either copper(I) sulfate or copper(I) iodide–trimethyl phosphite complex was reported to result in the formation of furanone **25a** (Scheme 12). Likewise, the diazo ketones **24b** and **24c** furnished the furanones **25b** and **25c**, respectively.



a R = Ph, R^1 = Et
b R = R^1 = Et
c R = Ph, R^1 = Me

Scheme 12

We were intrigued as to whether this chemistry was general to five-ring carbonyl ylides, so to this end the α-diazo ketones **26a–c** were synthesized and subjected to rhodium(II) perfluorobutyrate-catalysed decomposition (Scheme 13). The decomposition of **26a–c** resulted in the formation of the cyclic enol ethers **27a–c**, respectively. In the case of the α-diazo ketones **26a** and **26b**, isolation of the enol ethers was possible, but in the case of the diazo ketone **26c** the resulting enol-ether was presumed to have hydrolysed upon work-up, affording the hydroxyketone **28c**. The structures of the hydrolysis products from the enol-ethers **27b** and **27c** were further substantiated by comparison to the products obtained from the hydrolysis of their respective α-diazo ketone precursors. To our knowledge these results are the first examples of hydrogen migration in the six membered carbonyl ylide series. Moreover, recent deuterium labelling studies by Landgrebe[29] have provided strong evidence that the hydrogen shift observed in carbonyl ylides is an intramolecular process. Hence, a relatively rare 1,4-hydrogen shift[30] is occurring in the above reactions.



Scheme 13

In conclusion, the studies described herein have addressed the questions that arose during our earlier investigations dealing with the transition metal-catalysed decomposition of α-diazo ketones. Firstly, classical free carbenes do not show the same reactivity profiles as transition metal carbenoids and, consequently, are of limited use for the formation of carbonyl ylides. Secondly, it is apparent that a vicinal carbonyl group or other electron-withdrawing functionality is necessary for efficient carbonyl ylide formation. Presumably, increasing the electrophilic nature of the resulting carbenoid promotes attack by the lone pair of electrons on the tethered carbonyl group. Thirdly, iodonium ylides are a possible alternative to diazo compounds, as they display similar reactivity when subjected to transition metal-catalysed decomposition. However, the difficulties experienced in both the synthesis and handling of these compounds at present limits their general applicability. Finally, we have demonstrated that carbonyl ylides undergo a facile 1,4-hydrogen shift in the absence of a trapping agent affording cyclic enol–ethers. From the above studies it can be seen that α-diazo ketones still remain the favourable precursors for both the tandem cyclization–cycloaddition and carbenoid-alkyne metathesis methods.

Experimental

M.p.s were determined on a Thomas–Hoover capillary m.p. apparatus and are uncorrected. IR spectra were run on a Perkin-Elmer Model 283 IR spectrometer. ^{1}H NMR spectra were obtained on a Varian EM-390 and a GE QE-300 spectrometer. ^{13}C NMR spectra were recorded on a GE QE-300 75 MHz spectrometer. *J*-Values in Hz. Microanalyses were performed at Atlantic Microlabs, Atlanta, Ga. Mass spectra were determined with a VG MM-7070S mass spectrometer at an ionizing voltage of 70 eV.

Preparation and Reactions of Methyl 3-(3-*Methyldiazirin*-3-*yl*)*propanoate* **2**.—The title compound was prepared according to a procedure described by Church and Weiss.[19] A solution containing compound **2** (0.40 g, 2.8 mmol) and *N*-phenylmaleimide (0.97 g, 5.6 mmol) in distilled dichloromethane (70 cm^3) was degassed with argon and photolysed using a 450 W mercury lamp equipped with a Pyrex filter sleeve. The photolysis was complete in 3 h and the solution was concentrated under reduced pressure. The crude oil was chromatographed on silica gel using hexane–ethyl acetate (2:1) eluent to give (4*R*)-3,3a-dihydro-3-(2-methoxycarbonylethyl)-3-methyl-5-phenyl-5*H*-pyrrolo[3,4-*c*]pyrazole-4,6-dione **4** (0.31 g, 35%) and the (4*S*)-isomer **5** (0.25 g, 28%).

Compound **4**. M.p. 110–111 °C; ν(CHCl$_3$)/cm^{-1} 1710, 1370 and 1170; δ_H(300 MHz; CDCl$_3$) 1.58 (s, 3 H), 2.20–2.30 (m, 2 H), 2.43–2.46 (m, 2 H), 3.07 (d, 1 H, *J* 7.5), 3.71 (s, 3 H), 5.98 (d, 1 H, *J* 7.5), 7.18–7.26 (m, 2 H) and 7.40–7.52 (m, 3 H); δ_C(75

MHz; $CDCl_3$) 20.4, 28.4, 34.8, 45.2, 51.8, 94.2, 97.0, 126.1, 128.9, 129.1, 130.7, 168.2, 172.5 and 172.6 (Found: C, 60.9; H, 5.5; N, 13.3. Calc. for $C_{16}H_{17}N_3O_4$: C, 60.94; H, 5.43; N, 13.3%).

Compound **5**. M.p. 111–112 °C; $\nu(CHCl_3)/cm^{-1}$ 1700, 1370 and 1170; δ_H(300 MHz; $CDCl_3$) 1.49 (s, 3 H), 2.12–2.23 (m, 1 H), 2.38–2.48 (m, 1 H), 2.72–2.79 (m, 2 H), 3.03 (d, 1 H, *J* 6.0), 3.68 (s, 3 H), 5.97 (d, 1 H, *J* 7.5), 7.21–7.26 (m, 2 H) and 7.41–7.48 (m, 3 H); δ_C(75 MHz; $CDCl_3$) 24.7, 29.5, 30.7, 47.2, 51.8, 93.6, 96.6, 126.2, 129.0, 129.2, 130.8, 168.1, 172.4 and 172.8 (Found: C, 60.9; H, 5.4; N, 13.3. Calc. for $C_{16}H_{17}N_3O_4$: C, 60.94; H, 5.43; N, 13.3%).

A solution of **2** (0.25 g, 1.8 mmol) in distilled dichloromethane (45 cm^3) was de-gassed with argon and photolysed using a 450 W mercury lamp equipped with a Pyrex filter sleeve. The photolysis was complete in 3 h and the solution was concentrated under reduced pressure. Chromatography of the crude oil on silica gel with hexane–ethyl acetate (5:1) eluent gave dimethyl 4,4′-azinobipentanoate **7** (190 mg, 41%), together with methyl 4-oxopentanoate **8** (12 mg, 5%).

Compound **7**. $\nu(CHCl_3)/cm^{-1}$ 3000, 1720, 1640, 1430 and 1360; δ_H(90 MHz; $CDCl_3$) 1.77 (s, 6 H), 2.56–2.66 (m, 8 H) and 3.66 (s, 6 H); δ_C (75 MHz; $CDCl_3$) 17.2, 29.7, 32.9, 51.4, 160.1 and 173.5 (Found: C, 56.2; H, 7.9; N, 11.0. Calc. for $C_{12}H_{20}N_2O_4$: C, 56.24; H, 7.87; N, 10.93%).

Preparation and Reactions of 5-(3-*Methyldiazirin*-3-*yl*)-*pentan*-2-*one* **3**.—To a flask charged with ethyl acetoacetate (6.4 g, 49 mmol) and 2-(2-bromoethyl)-2-methyl-1,3-dioxolane[31] (8.0 g, 41 mmol) in THF (50 cm^3) was added potassium *tert*-butoxide (5.5 g, 59 mmol) in three portions over a period of 40 min. The resulting mixture was stirred at 25 °C for 16 h and then quenched with water, extracted with ether, concentration of the extract under reduced pressure left an orange oil which was chromatographed using hexane–ethyl acetate (6:1) eluent to provide ethyl (6,6-ethylenedioxy-2-oxoheptan-3-yl)formate (7.3 g, 73%).

A sample containing this formate (3.0 g, 12 mmol) and barium hydroxide (3.0 g) in water (35 cm^3) was heated at reflux for 5 h. The mixture was extracted twice with ether. Concentration of the extract under reduced pressure left an oil which upon chromatography on silica gel using hexane–ethyl acetate (6:1) eluent gave 6,6-ethylenedioxyheptan-2-one (1.74 g, 82%); ν(neat)/cm^{-1} 2985, 1717, 1376, 1256 and 1136; δ_H(300 MHz; $CDCl_3$) 1.31 (s, 3 H), 1.60–1.68 (m, 4 H), 2.13 (s, 3 H), 2.45 (t, 2 H, *J* 7.5) and 3.91–3.95 (m, 4 H); δ_C(75 MHz; $CDCl_3$) 17.8, 23.2, 29.3, 37.7, 43.0, 64.1, 109.2 and 208.0.

To a flask containing liquid ammonia (30 cm^3) was added the above ketone (1.40 g, 8.1 mmol). The resulting solution was maintained at reflux for 3 h and then cooled to −78 °C. To the solution was added hydroxylamine-*O*-sulfonic acid (1.1 g, 9.8 mmol) in methanol (20 cm^3). The resulting mixture was kept at reflux for 1 h and the ammonia was allowed to evaporate overnight. The white slurry thus obtained was filtered through a pad of Celite and washed with portions of methanol. The combined washings were concentrated to *ca.* 20 cm^3 and used directly for oxidation without further purification. This crude methanol solution was cooled to 0 °C and treated with triethylamine (20 cm^3). Iodine crystals were then added to the mixture; the red colour of iodine persisted after *ca.* 1.9 g had been added. The solution was concentrated to *ca.* 20 cm^3, diluted with brine (30 cm^3) and extracted several times with ether. The combined extracts were concentrated under reduced pressure to leave an oil chromatography of which on silica gel using hexane–ethyl acetate (4:1) as the eluent gave 1-(3-methyldiazirin-3-yl)-4,4-ethylenedioxypentane (0.80 g, 53%); δ_H(300 MHz; $CDCl_3$) 1.00 (s, 3 H), 1.29 (s, 3 H), 1.20–1.35 (m, 4 H), 1.55–1.62 (m, 2 H) and 3.90–3.96 (m, 4 H); δ_C(75 MHz; $CDCl_3$) 18.4, 19.6, 23.6, 25.5, 34.2, 38.4, 64.5 and 109.5.

To a solution containing the above acetal (0.50 g, 2.7 mmol) in THF (20 cm^3) was added HCl (2 mol dm^{-3}; 5 cm^3). The resulting mixture was stirred at 25 °C for 8 h and then extracted with ether. The extract was washed with concentrated aqueous sodium hydrogen carbonate and brine and evaporated under reduced pressure to leave an oil. This when chromatographed on silica gel using hexane–ethyl acetate (4:1) eluent gave the pentanone **3** (0.33 g, 87%) as a colourless oil; ν(neat)/cm^{-1} 2957, 1717, 1453, 1364 and 1167; δ_H(300 MHz; $CDCl_3$) 1.00 (s, 3 H), 1.34 (t, 2 H, *J* 7.5), 1.48 (quin, 2 H, *J* 7.5), 2.14 (s, 3 H) and 2.42 (t, 2 H, *J* 7.5); δ_C(75 MHz; $CDCl_3$) 17.9, 19.4, 25.3, 29.6, 33.3, 42.3 and 207.6.

A solution containing compound **3** (0.40 g, 2.9 mmol) and *N*-phenylmaleimide (0.99 g, 5.7 mmol) in distilled chloromethane (50 cm^3) was de-gassed with argon and photolysed using a 450 W mercury lamp equipped with a Pyrex filter sleeve. The photolysis was complete in 2 h and the solution was concentrated under reduced pressure. The crude oil was chromatographed on silica gel using hexane–ethyl acetate (5:1) as eluent to give the cycloadduct 3,3a-dihydro-3-methyl-3-(4-oxopentyl)-5-phenyl-5*H*-pyrrolo[3,4-*c*]pyrazole-4,6-dione **6** as a white solid (0.39 g, 46%, a 4:1 mixture of diastereoisomers); m.p. 105–107 °C; $\nu(CHCl_3)/cm^{-1}$ 3000, 1640, 1490 and 1450; δ_H(300 MHz; $CDCl_3$) 1.42–1.63 (m, 2 H), 1.70–1.82 (m, 1 H), 1.90–2.00 (m, 1 H), 2.15 (s, 1 H), 2.52 (t, 2 H, *J* 7.5), 3.22 (d, 1 H, *J* 7.5), 5.95 (d, 1 H, *J* 7.5), 7.20–7.25 (m, 2 H) and 7.40–7.50 (m, 3 H) (Found: C, 65.0; H, 6.1; N, 13.3. Calc. for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41%).

Rhodium(II) *Acetate-catalysed Reaction of Compound* **3**.—A solution containing compound **3** (50 mg, 0.36 mmol) in benzene (5 cm^3) was added dropwise to a refluxing solution containing DMAD (103 mg, 0.73 mmol) in benzene (5 cm^3) and rhodium(II) acetate (15 mg). The reaction mixture was heated at reflux for 2 h and then transferred to a sealed tube and heated at 150 °C for an additional 6 h. The mixture was cooled, concentrated under reduced pressure and chromatographed on silica gel to give hept-5-en-2-one[32] **15** (20 mg, 43%) as a 3:1 mixture of *E*- and *Z*-isomers; δ_H(300 MHz; $CDCl_3$) *E*: 1.62 (d, 2 H, *J* 8), 2.12 (s, 3 H), 2.25 (m, 2 H), 2.47 (t, 2 H, *J* 10) and 5.40 (m, 2 H); *Z*: 1.62 (d, 2 H, *J* 8), 2.15 (s, 3 H), 2.32 (m, 2 H), 2.41 (t, 2 H, *J* 10) and 5.40 (m, 2 H).

Photolysis of But-3-*enyl* 2-(*Diazomethylcarbonyl*)*benzoate* **10**.—The title compound was prepared following the procedure described by Padwa and co-workers.[10] A solution containing **10** (0.65 g, 2.7 mmol) in distilled dichloromethane (50 cm^3) was de-gassed with argon and photolysed using a 450 W mercury lamp equipped with a Pyrex filter sleeve. The photolysis was completed in 5 h and the solution was concentrated under reduced pressure. The crude oil was chromatographed on silica gel using hexane–ethyl acetate (6:1) eluent to give 1-(but-2-enyloxy)benzo[*c*]pyran-3-one **11** (0.45 g, 78); ν(neat)/cm^{-1} 1933, 1727, 1573, 1266 and 1077; δ_H(300 MHz; $CDCl_3$) 2.50–2.57 (m, 2 H), 4.38 (t, 2 H, *J* 7.5), 5.09–5.23 (m, 2 H), 5.82–5.95 (m, 1 H), 7.25 (t, 1 H, *J* 7.9), 7.41 (t, 1 H, *J* 7.5), 7.60 (d, 1 H, *J* 7.8), 7.67 (s, 1 H) and 7.92 (1 H, *J* 7.9); δ_C(75 MHz; $CDCl_3$) 33.0, 64.0, 95.6, 117.3, 126.8, 127.8, 128.5, 130.8, 131.9, 133.9, 134.4, 167.0 and 210.2 (Found: M^+, 216.0785. Calc. for $C_{13}H_{12}O_3$: *M*, 216.0786).

Preparation and Reaction of Dimethyl Phenyl-λ^3-*iodanylidenemalonate* **16**.—To a solution containing potassium hydroxide (70 mg, 12.4 mmol) in methanol (3 cm^3) was added dimethyl malonate (50 mg, 3.12 mmol) and the reaction mixture was stirred at −10 °C for 15 min. After this time iodobenzene-diacetate (1.0 g, 3.12 mmol) was added in small portions so as to maintain the temperature below 0 °C. The reaction flask was

placed in a freezer for 8 h and the resulting precipitate was filtered off and dried *in vacuo* to yield the title compound **16** (0.49 g, 47%); m.p. 59–60 °C; ν(KBr)/cm^{-1} 3063, 2920, 1755, 1559, 1471 and 1254; δ_H(300 MHz; $CDCl_3$) 3.72 (s, 6 H), 7.38 (m, 2 H), 7.45 (m, 1 H) and 7.72 (m, 2 H); δ_C(75 MHz; $CDCl_3$) 53.9, 94.4, 127.5, 130.3, 137.4, 139.8 and 162.5.

A solution containing the above iodonium ylide (350 mg, 1.04 mmol) and benzaldehyde (2.0 g, 18.9 mmol) in methylene dichloride (2.5 cm^3) was cooled to 0 °C and copper(I) chloride (15 mg) was added. The resulting suspension was stirred at 0 °C for 2 h and then warmed to room temperature. The mixture was filtered and the filtrate evaporated under reduced pressure. The crude product was purified by chromatography on silica gel to give dimethyl 3-phenyloxirane-2,2-dicarboxylate **17** (0.106 g, 43%) as a clear oil; ν(neat)/cm^{-1} 3037, 2951, 1738, 1431, 1231 and 1101; δ_H(300 MHz; $CDCl_3$) 3.85 (s, 6 H), 5.79 (s, 1 H), 7.43 (m, 2 H), 7.58 (m, 1 H) and 8.11 (m, 2 H); δ_C(75 MHz; $CDCl_3$) 53.3, 71.7, 128.4, 130.1, 133.8 and 164.8.

Preparation and Reaction of Ethyl 3-Oxo-3-(2′-phenylethynylphenyl)-2-phenyl-λ^3-iodanylidenepropionate **20**.—To a 250 cm^3 flask equipped with a magnetic stirring bar and reflux condenser was added 2-bromobenzaldehyde (9.37 g, 50.6 mmol), phenylacetylene (6.70 g, 66.8 mmol), bis-(triphenylphosphine)-palladium dichloride (18.5 mg), copper(I) iodide (180 mg) and triphenylphosphine (12 mg) in dry triethylamine (100 cm^3). The mixture was heated at reflux under nitrogen for 48 h, filtered to remove the triethylammonium iodide, and the filtrate was concentrated under reduced pressure to remove most of the triethylamine. The residue was redissolved in ether (100 cm^3) and washed with aqueous HCl (5%; 25 cm^3) and then with water (25 cm^3). Vacuum distillation of the resulting dark brown oil afforded 2-(2′-phenylethynyl)benzaldehyde **18** (8.37 g, 80%) as a light yellow oil; b.p. 120–125 °C (0.15 mmHg); ν(neat)/cm^{-1} 3056, 2834, 2738, 2213, 1695, 1592, 1488, 1266 and 1192; δ_H-(300 MHz; $CDCl_3$) 7.35–7.47 (m, 4 H), 7.53–7.67 (m, 4 H), 7.96 (m, 1 H) and 10.68 (s, 1 H); δ_C(75 MHz; $CDCl_3$) 85.0, 96.4, 122.3, 126.8, 127.2, 128.6, 129.1, 131.6, 132.5, 133.2, 133.7, 135.8 and 191.5 (Found: M$^+$, 206.0732. Calc. for $C_{15}H_{10}O$: *M*, 206.0732).

A flask containing the aldehyde **18** (1.0 g, 4.84 mmol) and ethyl diazoacetate (0.83 g, 7.26 mmol) in methylene dichloride (5 cm^3) was cooled to 0 °C and tin(II) chloride (50 mg) was added. Initial rapid revolution of nitrogen occurred and the reaction was subsequently stirred at room temperature for 2 h. After this time additional tin(II) chloride (50 mg) was added, and the reaction was stirred for a further 2 h. The mixture was filtered and the filtrate evaporated under reduced pressure. Purification of the residue by column chromatography gave ethyl 3-oxo-3-(2′-phenylethynylphenyl)propionate **19** (0.80 g, 57%) as a 1:1.6 mixture of enol and keto tautomers; ν(neat)/cm^{-1} 3057, 2980, 1734, 1681, 1620, 1215 and 1188; δ_H(300 MHz; $CDCl_3$) enol: 1.30 (t, 3 H, *J* 7.1), 4.25 (q, 2 H, *J* 7.1), 6.22 (s, 1 H), 7.33–7.43 (m, 5 H), 7.51–7.59 (m, 3 H) and 7.76–7.79 (m, 1 H); keto: 1.16 (t, 3 H, *J* 7.1), 4.13 (q, 2 H, *J* 7.1), 4.24 (s, 2 H), 7.33–7.43 (m, 5 H), 7.51–7.59 (m, 3 H) and 7.76–7.79 (m, 1 H); δ_C(75 MHz; $CDCl_3$) 14.0, 14.3, 48.5, 60.4, 61.3, 88.0, 92.3, 95.8, 121.9, 122.6, 128.2, 128.3, 128.4, 128.45, 128.5, 128.7, 129.0, 129.2, 130.0, 131.5, 131.6, 131.9, 133.7, 134.04?, 135.3, 139.2, 167.5, 170.4, 173.1 and 194.5 (Found: M$^+$, 292.1098. Calc. for $C_{19}H_{16}O_3$: *M*, 292.1099).

Potassium hydroxide (0.44 g, 7.85 mmol) was dissolved in methanol (2 cm^3) and the solution was cooled to −10 °C and the ketoester **19** (0.57 g, 1.96 mmol) was added and the mixture stirred for 15 min. To this mixture was added iodobenzene diacetate (0.63 g, 1.96 mmol) in small portions so as to maintain the temperature below 0 °C. When the addition was complete the reaction flask was placed in a freezer for 12 h and the resulting precipitate was filtered off and dried *in vacuo* to give the title iodonium ylide (0.34 g, 35%); m.p. 87–88 °C; ν(neat)/cm^{-1} 3053, 2974, 2217, 1741, 1647, 1272 and 991; δ_H(300 MHz; $CDCl_3$) 0.85 (t, 3 H, *J* 7.1), 3.82 (q, 2 H, *J* 7.1), 7.05 (m, 2 H), 7.18–7.32 (m, 9 H), 7.49 (m, 1 H) and 7.82 (m, 2 H); δ_C(75 MHz; $CDCl_3$) 14.1, 60.7, 88.51, 91.5, 113.0, 120.4, 123.4, 126.9, 127.7, 128.0, 128.1, 130.3, 130.8, 131.2, 131.5, 131.9, 132.74, 137.4, 143.7, 164.9 and 184.4.

A solution containing **20** (0.15 g, 0.3 mmol) in methylene dichloride (1 cm^3) was cooled to 0 °C and then treated with copper(I) chloride (15 mg). After 1 h the mixture became deep yellow in colour. Filtration and removal of the solvent under reduced pressure afforded a dark yellow solid that was purified by column chromatography to give 1-ethoxy-3-phenylindeno-[1,2-*c*]furan-8-one **21** (0.05 g, 58%) as a yellow solid; m.p. 159–161 °C; ν(neat)/cm^{-1} 3053, 2966, 1695, 1595, 1465 and 919; δ_H(300 MHz; $CDCl_3$) 1.51 (t, 3 H, *J* 7.1), 4.87 (q, 2 H, *J* 7.1), 7.24–7.34 (m, 2 H), 7.43–7.49 (m, 3 H) and 7.70–7.75 (m, 4 H); δ_C(75 MHz; $CDCl_3$) 14.8, 100.8, 122.2, 124.5, 126.8, 127.9, 128.0, 128.4, 130.1, 131.2, 131.7, 140.2, 160.5 and 186.9 (Found: M$^+$, 290.0941. Calc. for $C_{19}H_{14}O_3$: *M*, 290.0943).

Preparation and Reaction of Ethyl 2-Diazo-3-oxo-3-(2′-phenylethynylphenyl)propionate **22**.—To a solution of **19** (0.18 g, 0.62 mmol) in methylene dichloride (5 cm^3) was added mesyl azide (0.08 g, 0.62 mmol) and triethylamine (0.19 g, 1.9 mmol) and the reaction mixture was stirred at 0 °C for 5 h. The mixture was then warmed to room temp. and aqueous sodium hydroxide (2 mol dm^{-3}; 5 cm^3) was added. The aqueous layer was extracted several times with methylene dichloride and the combined extracts were dried (Na_2SO_4) evaporated under reduced pressure. Purification of the residue by silica gel chromatography gave the title compound **22** (0.15 g, 76%) as a clear oil; ν(neat)/cm^{-1} 3053, 2974, 2133, 1718, 1694, 1298, 1115 and 926; δ_H(300 MHz; $CDCl_3$) 1.08 (t, 3 H, *J* 7.1), 4.14 (q, 2 H, *J* 7.1) and 7.32–7.55 (m, 9 H); δ_C(75 MHz; $CDCl_3$) 13.6, 42.4, 61.3, 86.3, 93.7, 120.6, 122.3, 126.8, 127.9, 128.0, 128.4, 130.1, 131.2, 131.7, 140.2, 160.5 and 186.9.

To a solution containing compound **22** (0.15 g, 0.47 mmol) in methylene dichloride (2 cm^3) was added rhodium(II) octanoate (5 mg) and the reaction mixture was stirred at room temperature for 18 h. The solvent was removed under reduced pressure and the resulting green solid was purified by chromatography furnishing compound **21** (0.08 g, 54%) as a bright yellow solid.

Preparation and Rhodium(II) Perfluorobutyrate-catalysed Reaction of 1-Diazo-4-phenylhexane-2,5-dione **26a**.—To a solution containing potassium bis(trimethylsilyl)amide (16.5 cm^3, 8.2 mmol) in THF (50 cm^3) was added phenylacetone (1.0 cm^3, 7.5 mmol) dropwise and the mixture stirred for 0.75 h at −78 °C. The solution was then treated with ethyl 2-bromoacetate (1.9 g, 11.2 mmol) and stirred for 3 h, after which water (10 cm^3) was added at 0 °C. The solution was diluted with methylene dichloride (50 cm^3), washed with water (2 × 25 cm^3) and brine (1 × 25 cm^3), dried (Na_2SO_4) and concentrated under reduced pressure. The crude oil was chromatographed on silica get to give ethyl 4-oxo-3-phenylpentanoate (1.5 g, 91%); ν(neat)/cm^{-1} 3064, 2983, 1719 and 1601; δ_H($CDCl_3$; 300 MHz) 1.10 (t, 3 H, *J* 7.0), 2.00 (s, 3 H), 2.40 (dd, 1 H, *J* 16.9, 5.0), 3.10 (dd, 1 H, *J* 16.9, 9.8), 4.00 (dd, 1 H, *J* 9.8, 5.0), 4.10 (q, 2 H, *J* 7.0) and 7.10–7.30 (m, 5 H); δ_C($CDCl_3$; 75 MHz) 13.4, 28.1, 36.3, 54.1, 59.8, 127.0, 127.5, 128.4, 136.8, 171.2 and 205.9.

A solution containing ethyl 4-oxo-3-phenylpentanoate (1.0 g, 4.5 mmol), potassium hydroxide (2.5 g, 45 mmol), water (6 cm^3) and methanol (30 cm^3) was stirred for 4 h at room temp. The reaction mixture was washed with ether (2 × 50 cm^3) and acidified to pH 2 with HCl solution (1.5 mol dm^{-3}). The product was extracted with methylene dichloride (2 × 75 cm^3), washed with brine (1 × 50 cm^3), dried (Na_2SO_4) and concentrated

under reduced pressure to give 4-oxo-3-phenylpentanoic acid (0.6 g, 69%); m.p. 98–99 °C; ν(neat)/cm^{-1} 3031, 1710, 1600 and 1162; δ_H($CDCl_3$; 300 MHz) 2.10 (s, 3 H), 2.60 (dd, 1 H, *J* 17.4, 4.7), 3.30 (dd, 1 H, *J* 17.4, 9.9), 4.10 (dd, 1 H, *J* 9.9, 4.7), 7.20–7.40 (m, 5 H) and 11.30 (s, 1 H); δ_C($CDCl_3$; 75 MHz) 28.1, 36.1, 53.9, 127.2, 127.6, 128.6, 136.5, 177.5 and 206.2.

To a solution containing 4-oxo-3-phenylpentanoic acid (0.5 g, 2.6 mmol) and methyl chloroformate (3.0 mmol) in ether (75 cm^3) was added triethylamine (0.26 g, 2.6 mmol). The resulting white suspension was stirred for 1 h at room temp. The precipitated triethylamine hydrochloride was filtered off and the resulting clear solution was immediately treated with freshly prepared diazomethane (20 mmol) at 0 °C. The mixture was stirred for 12 h while warming to room temp. Excess of diazomethane was removed under reduced pressure and the resulting crude oil was chromatographed on silica gel to give the title dione **26a** (0.4 g, 65%); ν(neat)/cm^{-1} 3101, 2107, 1715 and 1640; δ_H($CDCl_3$; 300 MHz) 2.00 (s, 3 H), 2.50 (dd, 1 H, *J* 16.3, 4.5), 3.10–3.20 (m, 1 H), 4.20 (dd, 1 H, *J* 9.7, 4.5), 5.20 (s, 1 H) and 7.10–7.30 (m, 5 H); δ_C($CDCl_3$; 75 MHz) 28.3, 42.6, 53.7, 54.2, 127.0, 127.5, 128.5, 137.0, 192.2 and 206.3.

A solution containing the α-diazo ketone **26a** (0.28 g, 1.29 mmol) in methylene dichloride (25 cm^3) was treated with rhodium(II) perfluorobutyrate (5 mg). The solution was stirred for 0.5 h and was then concentrated under reduced pressure and chromatographed to give 6-methyl-5-phenyl-4*H*-pyran-3(2*H*)-one **27a** (82%) as a light yellow oil; ν(neat)/cm^{-1} 3406, 1733, 1684 and 1602; δ_H($CDCl_3$; 300 MHz) 1.90 (s, 3 H), 3.25 (s, 2 H), 4.35 (s, 2 H) and 7.20–7.45 (m, 5 H); δ_C($CDCl_3$; 75 MHz) 16.7, 40.1, 71.2, 108.2, 126.1, 127.7, 138.5, 149.2 and 207.4 (Found: M$^+$, 188.0837. Calc. for $C_{12}H_{12}O_2$: *M*, 188.0837).

Rhodium(II) *Perfluorobutyrate-catalysed Reaction of 5-Diazo-1-phenylpentane-1,4-dione* **26b**.—A solution containing the α-diazo ketone **26b**[10] (0.25 g, 1.23 mmol) in methylene dichloride (25 cm^3) was treated with rhodium(II) perfluorobutyrate (5 mg). The solution was stirred for 1 h after which it was concentrated under reduced pressure and then chromatographed on silica gel to give 6-phenyl-4*H*-pyran-3(2*H*)-one **27b** (60%) as fine white needles; m.p. 65–66 °C; ν(neat)/cm^{-1} 3074, 2981, 1733, 1685 and 1661; δ_H($CDCl_3$; 300 MHz) 3.10 (d, 2 H, *J* 3.9), 4.45 (s, 2 H), 5.65 (t, 1 H, *J* 3.9) and 7.20–7.65 (m, 5 H); δ_C($CDCl_3$; 75 MHz) 35.5, 72.7, 95.2, 124.6, 128.3, 128.7, 133.9, 153.1 and 207.0 (Found: C, 75.7; H, 5.8. Calc. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79%).

To a solution containing the dihydropyran **27b** (0.20 g, 1.15 mmol) in THF (14 cm^3) was added HCl solution (1.0 mol dm^{-1}; 1 cm^3) dropwise at 0 °C and the mixture was stirred for 12 h. The solution was then diluted with ether (50 cm^3), washed with water (2 × 50 cm^3) and brine (1 × 50 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to give 5-hydroxy-1-phenylpentane-1,4-dione **28b** (0.12 g, 52%);[33] ν(neat)/cm^{-1} 3381, 1717, 1683 and 1401; δ_H($CDCl_3$; 300 MHz) 2.80 (t, 2 H, *J* 6.1), 3.15 (s, 1 H), 3.45 (t, 2 H, *J* 6.1), 4.44 (s, 2 H), 7.50 (t, 2 H, *J* 7.5), 7.65 (t, 1 H, *J* 7.5) and 8.05 (d, 2 H, *J* 7.5); δ_C($CDCl_3$; 75 MHz) 31.3, 31.8, 67.7, 127.4, 128.0, 132.8, 135.6, 197.3 and 208.1.

A sample of the dione **28b** was also prepared by acid hydrolysis of the diazo ketone **26b**. To a solution containing **26b** (1.0 g, 4.9 mmol) in water–diethyl ether (30 cm^3, 2:1) was added concentrated sulfuric acid (1 cm^3) dropwise at 0 °C. The solution was stirred for 1 h and then washed with ether (2 × 10 cm^3), dried (sodium sulfate) and concentrated under reduced pressure to give **28b** (0.38 g, 41%).

Rhodium(II) *Perfluorobutyrate-catalysed Reaction of 1-Diazohexane-2,5-dione* **26c**.—A solution containing the α-diazo ketone (0.25 g, 1.80 mmol) **26c**[10] in methylene dichloride (20 cm^3) was treated with rhodium(II) perfluorobutyrate (15 mg). The solution was stirred for 1 h and then concentrated under reduced pressure and chromatographed on silica gel to give 1-hydroxyhexane-2,5-dione **28c**[33] (0.20 g, 85%) as a clear liquid; ν(neat)/cm^{-1} 3454, 2914, 1713 and 1403; δ_H($CDCl_3$; 300 MHz) 2.15 (s, 3 H), 2.60 (t, 2 H, *J* 6.1), 2.85 (t, 2 H, *J* 6.1), 3.10 (s, 1 H) and 4.35 (s, 2 H); δ_C($CDCl_3$; 75 MHz) 29.0, 31.0, 36.2, 67.5, 206.1 and 208.0.

A sample of the dione **28c** was also prepared from the acid hydrolysis of the diazo ketone **26c**. To a solution containing **26c** (0.5 g, 3.6 mmol) in water–diethyl ether (20 cm^3, 2:1) solution was added concentrated sulfuric acid (0.75 cm^3) dropwise at 0 °C. The solution was stirred for 1 h and then washed with ether (2 × 10 cm^3), dried (sodium sulfate) and concentrated under reduced pressure to give the dione **28c** (0.17 g, 37%).

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