The reactions of diazo compounds with lactones. Part 1. Cyclopropanespiro-β-lactones from diketene: synthesis and reactions

Paul V. Murphy,† Timothy J. O'Sullivan and Niall W. A. Geraghty *

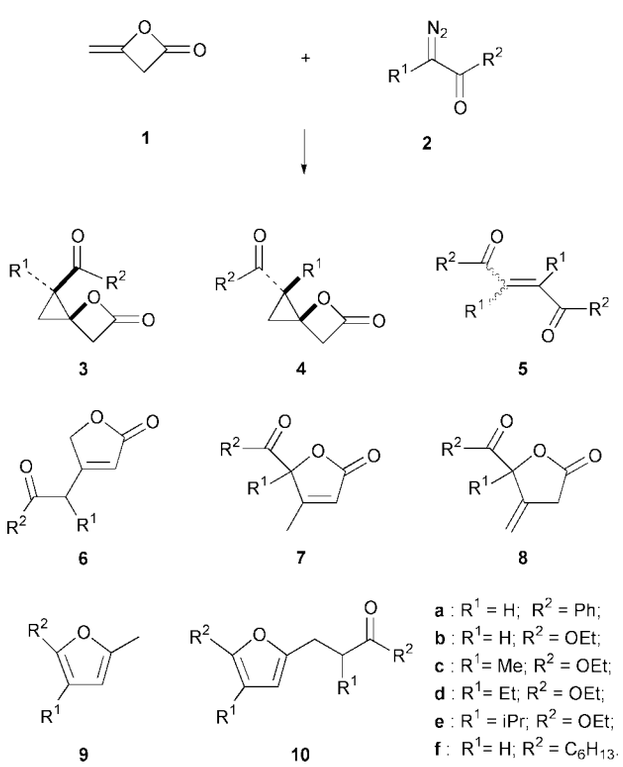
Department of Chemistry, National University of Ireland, Galway, Republic of Ireland.
E-mail: niall.geraghty@nuigalway.ie

Received (in Cambridge, UK) 21st February 2000, Accepted 19th April 2000
Published on the Web 8th June 2000

The cyclopropanespiro-β-lactones **3**, **4** and **12** can be prepared by the metal catalysed, or photochemically promoted decomposition reactions of diazocompounds in the presence of diketene. The thermal reactions of these compounds give a variety of products depending on the nature of the spirolactone; these include a furan **9a**, 1,4-dicarbonyl compounds **18a–c** and **19b**, a pyranone **20b**, furanones **21a**, **21f** and **22a** and the enol **16**. The boron trifluoride promoted reaction of a mixture of **3b** and **4b** gives a β-ketoacid. Mechanisms are proposed for the formation of these products. The rearrangment of the cyclopropanespiro-β-lactones to furan-2(5*H*)-ones and furan-2-(3*H*)-ones **6–8**, **21a, 21f**, **22a** and **24** is shown to be a general reaction that involves metal catalysis. A mechanism based on formation of a metallocycle by a novel insertion of the metal into the C–O bond of the β-lactone ring is proposed for this rearrangement. This accounts for the observed features of the reaction.

Introduction

The reactions of carbenes or carbenoids from diazocompounds with diketene[1] **1** (Scheme 1) gives in most cases the expected



Scheme 1

products of addition to the exocyclic double bond. Diazoacetophenone **2a**, for example, has been reported to give the expected mixture of diastereoisomeric 5-oxo-4-oxaspiro[2.3]-hexanes (cyclopropanespiro-β-lactones) **3a** and **4a** under metal catalysis.[2] In some cases other products have been isolated: metal catalysed reaction of ethyl diazoacetate **2b** with diketene is reported[2] to give a mixture of spirolactone **4b** and furanones **6b–8b**, whereas the photochemical reaction of ethyl diazoacetoacetate with diketene gives a levulinate (4-oxopentanoate).[3] The formation of furanones in these reactions is particularly interesting and it has been suggested that this occurs by rearrangement of initially formed spiro-β-lactones. However this was not confirmed experimentally nor considered from a mechanistic point of view. In a preliminary communication[4] we provided evidence that the spiro-β-lactone to furanone rearrangement is general and requires metal catalysis. We now give a full account of this work which describes the synthesis of a range of spiro-β-lactones and a study of their thermal, metal catalysed and Lewis acid catalysed rearrangements.

Results and discussion

Initial experiments focused on an investigation of how furanone formation occurred in the copper powder or copper(II) sulfate catalysed reactions of ethyl diazoacetate **2b** and diketene.[2] The spiro-β-lactone **4b** (*trans* isomer) and the furanones **6b–8b** were originally isolated by fractional distillation of the crude filtered product obtained from reactions carried out at 100 °C. When this reaction was repeated, ^{1}H-NMR showed that the crude product contained only a mixture of spiro-β-lactones **3b**[2] and **4b**[5] (2 : 3) as well as the products of carbene dimerisation **5b**; **3b** and **4b** could be isolated from this mixture by rapid distillation and chromatography. The fact that formation of the furanones **6b–8b** could be avoided in this way clearly supports the contention that they are formed *via* the spiro-β-lactones and that this process is at least in part thermal. However, when pure samples of the spirolactones were heated for prolonged periods at 113 °C in toluene, the approximate pot temperature during distillation, no reaction occurred. Thermal reactions were also carried out at higher temperatures by heating **3b** and **4b** in sealed glass tubes at 180 °C. Analysis (^{1}H-NMR) of the crude product showed that although reactions occurred (see below), the furanones **6b–8b**

† *Current address*: Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland.

DOI: 10.1039/b001393p

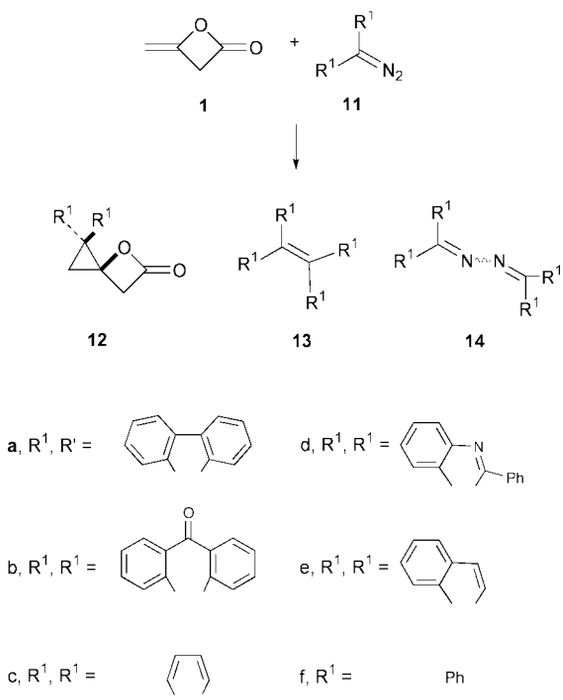
Table 1 Synthesis of spiro-β-lactones from diazo compounds and diketene

Diazo compound	Conditions	Spiro-β-lactone (isolated yield, %)	Other products (isolated yield, %)
2a[6]	$Rh_2(OAc)_4$, Et_2O, 40 °C	**3a** (18), **4a** (37)	**9a** (2), **10a** (6)
	$Cu(acac)_2$, C_6H_6, 60 °C	**3a** (5), **4a** (31)	**5a** (22), **6a** (5), **8a** (1), **9a** (1), **10a** (3)
2b[a]	Cu powder, 80 °C, rapid distillation and/or chromatography	**3b** (12), **4b** (21)	**5b** (13)
2c[7]	$Rh_2(OAc)_4$, rt	**4c** (32)	**5c** (27)
2d[8]	*hv*, CH_3CN, Ph_2CO	**3d** (18), **4d** (26)	—
2e[8]	*hv*, CH_3CN, Ph_2CO	**3e** (13), **4e** (17)	—
2f[9]	$Rh_2(OAc)_4$	**3f** (10), **4f** (32)	—
11a[11]	$Rh_2(OAc)_4$, rt, Et_2O	**12a** (84)	—
	hv	**12a** (85)	—
11b[12]	$Rh_2(OAc)_4$, C_6H_6, rt	**12b** (15–60)[b]	Anthraquinone (4)
11c[13]	$Rh_2(OAc)_4$, C_6H_6, 80 °C	**12c** (31)	**13c** (37)
11e[15]	$Rh_2(OAc)_4$, C_6H_6, 80 °C	**12e** (26)	**15** (10)[c]
11f[10]	*hv*, CH_3CN	**12f** (14)	**14f** (50)

[a] Used as supplied (Aldrich). [b] The yield is reduced significantly on chromatography. However, the crude product can be used for further manipulation of the spiro-β-lactone. [c] Could not be obtained analytically pure.

were not formed. These results show that the conversion of spirolactones to furanones is not a simple thermal reaction. As the preparation of the spiro-β-lactones involved the reaction of ethyl diazoacetate with diketene in the presence of copper powder, the possibility existed that the rearrangement to furanones was catalysed by a metal species formed during the course of their preparation. Thus a mixture of the spirolactones **3b** and **4b** was heated for 72 h in the presence of copper powder. This reaction gave a 3 : 1 mixture (^{1}H-NMR) of **6b** and **7b**, establishing unambigiously that the formation of furanones does involve spiro-β-lactones and is metal catalysed. It remained to explore the scope of the reaction and to identify the exact role played by the metal catalyst. The possibility that the metal was behaving as a Lewis acid was considered and as preliminary experiments had led to some unusual products, the basic thermal rearrangement of these highly strained lactones was investigated.

Cyclopropanespiro-β-lactones were prepared by metal catalysed or photochemical decomposition of α-diazocarbonyl compounds[6–10] **2** (Scheme 1) and other diazocompounds[11–15] **11** (Scheme 2) in the presence of diketene (Table 1). Thus, spirolactones **3a** and **4a** can be prepared as previously described[2] by the copper powder catalysed decomposition of diazoacetophenone in the presence of diketene. Spirolactones **3a** and **4a** as well as alkenes **5a**,[2] furanones **6a** and **8a**, and furans **9a**[16] and **10a** were isolated when $Cu(acac)_2$ was used as catalyst in the reaction of diketene and diazoacetophenone. The $Rh_2(OAc)_4$ catalysed reactions gave spirolactones **3a** and **4a** as well as the furans **9a** and **10a** but no furanones (^{1}H-NMR). In common with all the spiro-β-lactones the IR spectra of both **3a** and **4a** contain a carbonyl band at 1830 cm^{-1} characteristic of the β-lactone group. The stereochemistry of **3a** and **4a** (and of the related **3b/4b** and **3e/4e** systems) was assigned on the basis of the pattern observed for the lactone methylene protons. Thus these protons appear as a pair of AB doublets for **4b** in which they are *cis* to the ethoxycarbonyl group, and as a singlet for **3b**, in which they have a *trans* relationship with this group. The $Rh_2(OAc)_4$ catalysed decomposition of ethyl diazopropionate **2c** in the presence of diketene gave the spiro-β-lactone **4c** as the only isolable product. The cyclopropane protons in this compound appear as a pair of AB doublets in the ^{1}H-NMR spectrum at δ 1.72 and 1.38, the lower signal being due to the proton *cis* to the oxetane oxygen atom. The *trans* stereochemistry of **4c** was assigned on the basis of NOE difference spectra which showed that on irradiating the methyl signal at δ 1.44, a 3.2% enhancement of the doublet at δ 1.72 was obtained. This enhancement indicates that this proton and the methyl group



Scheme 2

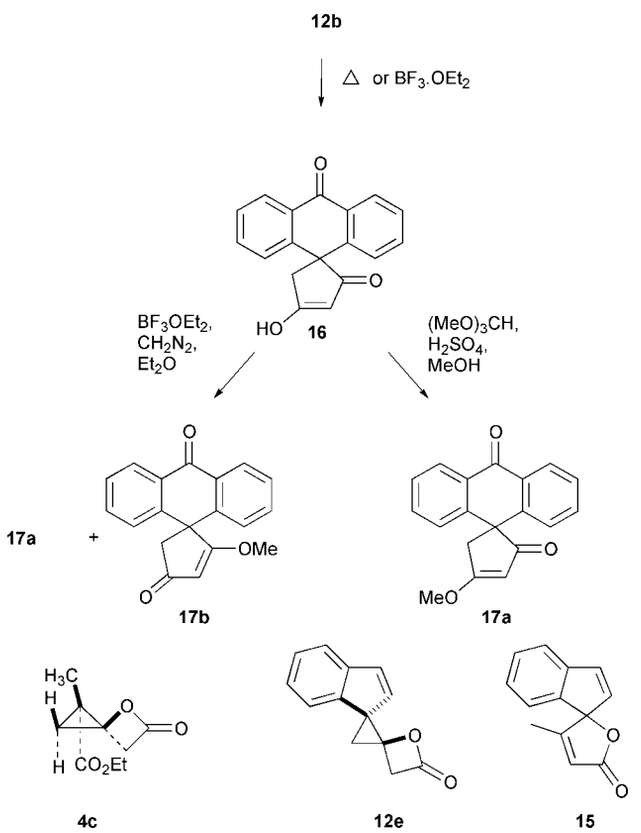
are *cis* to each other and thus also *cis* to the oxetane oxygen. In keeping with the pattern outlined above the lactone protons in **4c** which are *cis* to the ethoxycarbonyl group appear as AB doublets at δ 3.74 and δ 3.63. The benzophenone sensitized photolysis of ethyl diazobutyrate **2d** and ethyl diazoisovalerate **2e** was used to prepare **3d/4d**, and **3e/4e**, respectively, as metal catalysis led to very complex mixtures in these cases. Unlike the other compounds in the series the lactone protons in both **3d** and **4d** appear as pairs of doublets. However in one isomer the diastereotopic methylene protons of the cyclopropane ethyl group appear as multiplets at δ 1.76 and 1.48, and at δ 2.30 and 0.85 in the other. This indicates that the latter is **4d** in which these protons are *cis* to the oxetane oxygen.

The $Rh_2(OAc)_4$ catalysed reactions of 1-diazooctan-2-one **2f**, diazofluorene **11a**, diazoanthrone **11b** and diazocyclopentadiene **11c** with diketene gave, respectively, the expected spirocyclopropanes, **3f** and **4f**,[17] **12a**, **12b** and **12c**. It was also possible to prepare **12a** by photolysis of diazofluorene in diketene. Diazocyclopentadiene **11c** also gave some of the dimer **13c**. The Rh(II) catalysed reaction of 3-diazo-2-phenyl-

3*H*-indole **11d** in the presence of diketene led only to the isolation of 2,2′-diphenyl-3,3′-azinodi-3*H*-indole **14d**.[18] Only one of the two possible diastereoisomeric spiro-β-lactones was obtained from the Rh(II) catalysed reaction of diazoindene **11e** and diketene; this product was assigned the structure **12e** on the basis of the similarities between its ^{1}H-NMR spectrum and that of **12c**. The chemical shifts of the lactone methylene protons (δ 3.84 and 3.62) and the cyclopropane proton *trans* to the oxetane oxygen (δ 2.09) in **12e** are essentially identical to those of the corresponding protons in **12c** (δ 3.90, 3.67 and 2.09, respectively) suggesting that the environment of these protons is the same in both cases. The furanone **15** was also isolated from this reaction but this compound was unstable decomposing after 3 days at room temperature. Photolysis of diphenyldiazomethane **11f** in acetonitrile solutions of diketene and benzophenone was used to prepare **12f**, as the metal catalysed reaction of the diazocompound was again not successful in this case. The spectroscopic data used to assign the structures of these spiro-β-lactones are presented in Table 4.

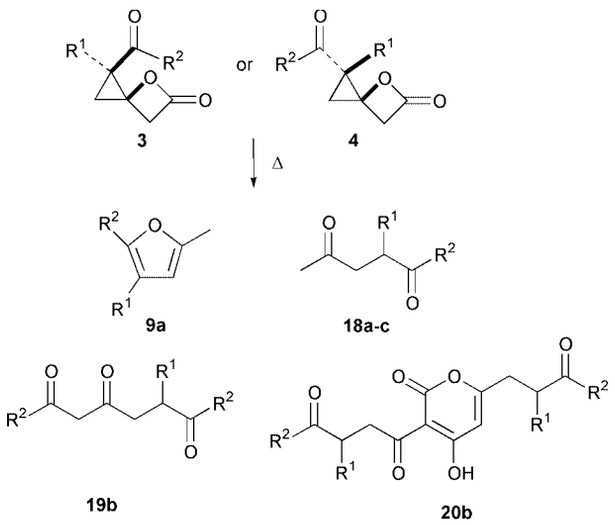
Furans rather than spiro-β-lactones are formed when acyclic and cyclic 2-diazo-1,3-dicarbonyl compounds react with diketene under metal catalysis.[19] A preliminary account of these reactions has been described and a full description will be appear in a subsequent paper.

The simple thermal rearrangement of these spiro-β-lactones led to the formation of a variety of products (Schemes 3–5;



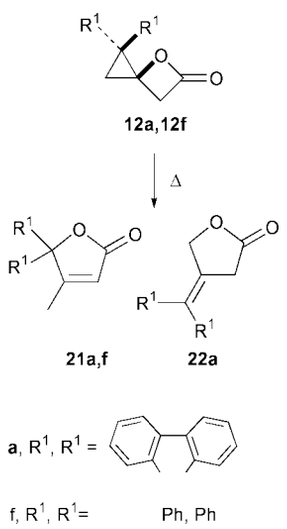
Scheme 3

Table 2). They were in general more thermally stable than might have been expected given the presence of a strained β-lactone ring and all were indefinitely stable at room temperature. Thus, the spiro-β-lactones **3a**–**c**, **4a**–**c**, **12a** and **12f**, were recovered unchanged after prolonged heating in refluxing toluene. However, the enol **16** (Scheme 3) was obtained by heating the anthrone derivative **12b** under these conditions for 72 h. The acid catalysed methylation of **16** using trimethyl orthoformate in methanol giving **17a** and its boron trifluoride catalysed reaction with diazomethane giving a mixture of ethers **17a** and **17b** confirmed its structure.



a, R^1 = H; R^2 = Ph
b, R^1 = H; R^2 = OEt
c, R^1 = Me; R^2 = OEt

Scheme 4



Scheme 5

The sealed tube pyrolysis of spiro-β-lactones at higher temperatures resulted in reaction in all cases (Table 2, Schemes 4, 5). The 1,4-dicarbonyl derivatives **18a**,[20] **18b**, and **18c**[21] were formed from the corresponding spirolactones, **3a**/**4a**, **3b**/**4b** and **4c**, respectively, and **3b**/**4b** produced a further 1,4-dicarbonyl compound **19b**. A furan **9a** was obtained in low yield from **3a** and **4a** and most unexpectedly **4b** gave a dimeric pyranone **20b**. Furan and pyranone formation was not observed for any other spiro-β-lactone studied during the course of this work. Although in general metal catalysis (see below) was required for their formation, furanones were obtained on pyrolysis of the spiro-β-lactones **12a** and **12f**. Thus **21a** and **22a** (77 : 13) were obtained from the fluorene derivative **12a** and **21f** was isolated in excellent yield from **12f** (Scheme 5).

The boron trifluoride catalysed rearrangement of **3b** and **4b** in the presence of catalytic amounts of boron trifluoride gave the β-ketoacid **23a** which was converted to its methyl ester **23b** on treatment with an ethereal solution of diazomethane (Scheme 6). The boron trifluoride catalysed reaction of **12b** gave **16**. Reaction of other spiro-β-lactones gave complex mixtures which did not contain any furanones (^{1}H-NMR). In all cases spectroscopic analysis (^{1}H-NMR) of the crude product provided no evidence for the formation of furanones ruling out the possibility that the metal catalyst is behaving simply as a Lewis acid.

Table 2 Thermal and Lewis acid catalysed reactions of spiro-β-lactones

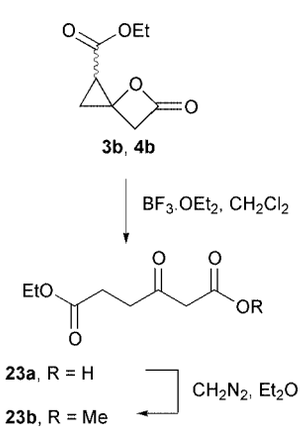
Spiro-β-lactone	Conditions	Product (isolated yield, %)
3a or **4a**	Sealed tube, 180 °C, 50 min	**9a** (5), **18a** (20)
3b	Sealed tube, 180 °C, 50 min	**18b** (34), **19b** (17)
4b	Sealed tube, 180 °C, 50 min	**20b** (43), **18b** (17), **19b** (10)
4c	Sealed tube, 180 °C, 50 min	**18c** (65)
12a	Sealed tube, 180 °C, 50 min	**21a** (76), **22a**[a] (12)
12b	Toluene, 113 °C	**16** (66)
12f	Sealed tube, 180 °C, 50 min	**21f** (85)
3b and **4b**	(i) $BF_3{\cdot}OEt_2$; (ii) CH_2N_2	**23b** (37)
12b	$BF_3{\cdot}OEt_2$, ether	**16** (67)

[a] Isolated by crystallisation from chloroform.

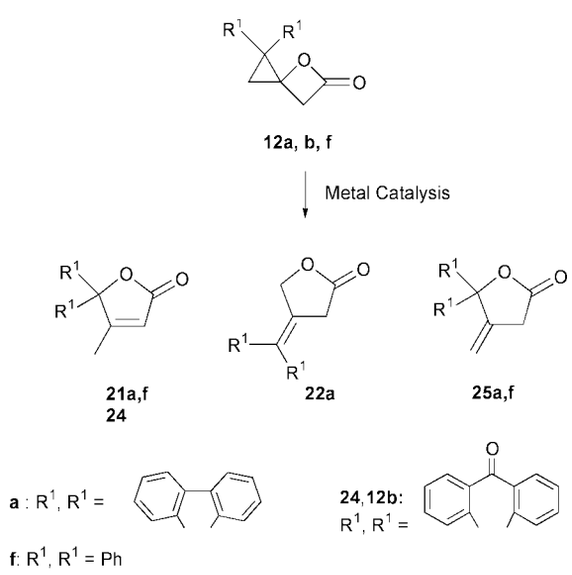
Table 3 Metal catalysed rearrangement of spiro-β-lactones

Spiro-β-lactone	Conditions[a]	Time	Furanones (isolated yield, %)
3a	$Cu(acac)_2$, toluene, 113 °C	6 h	**6a** (56), **8a** (39)
4a	$Cu(acac)_2$, toluene, 113 °C	6 h	**6a** (65), **8a** (29)
3b	$Cu(acac)_2$, toluene, 113 °C	6 h	**6b** (52), **7b** + **8b** (42)
4b	$Cu(acac)_2$, toluene, 113 °C	6 h	**6b** (61), **7b** + **8b** (31)
4b	Cu powder, neat, 125 °C	24 h	**6b** (75), **7b** (22)
4c	$Cu(acac)_2$, toluene, 113 °C	5 h	**7c** (82)
3d	$Cu(acac)_2$, toluene, 113 °C	5 h	**7d** (94)
4d	$Cu(acac)_2$, toluene, 113 °C	5 h	**7d** (92)
3e	$Cu(acac)_2$, toluene, 113 °C	5 h	Recovered **3e**
3e	Cu powder, neat, 200 °C	24 h	Complex mixture
4e	$Cu(acac)_2$, toluene, 113 °C	5 h	Recovered **4e**
4e	Cu powder, neat, 200 °C	24 h	Complex mixture
4f	$Cu(acac)_2$, toluene, 113 °C	5 h	Complex mixture
12a	$Cu(acac)_2$, toluene, 113 °C	15 min	**21a** (78),[b] **22a** (18)[c]
12b	$Cu(acac)_2$, toluene, 113 °C	10 min	**24** (85)
12c	$Cu(acac)_2$, toluene, 113 °C	5 h	Complex mixture
12f	$Cu(acac)_2$, toluene, 113 °C	5 h	**21f** (60)[b]

[a] Identical product mixtures were obtained when reactions were carried out with diazo compound present. [b] Obtained after chromatography or by heating crude product at 125 °C for 36 h. [c] Obtained from the crude product by recrystallisation from chloroform.



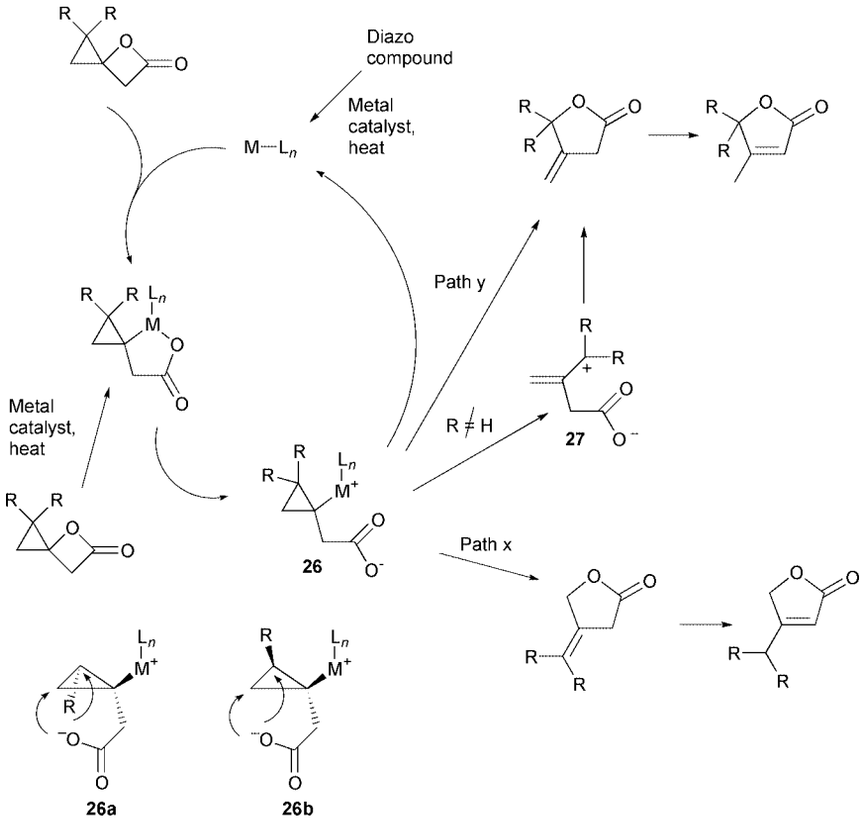
Scheme 6



Scheme 7

In general, the metal catalysed rearrangement of spiro-β-lactones to furanones (Schemes 1 and 7, Table 3) can be effected in excellent yield by heating in refluxing toluene in the presence of a soluble metal catalyst such as $Cu(acac)_2$. Thus the spiro-β-lactones **3a** and **4a** gave mixtures of **6a** and **8a** (56 : 39 from the *cis* isomer **3a** and 65 : 29 from the *trans* isomer **4a** (^{1}H-NMR)). Similar results were obtained for the rearrangement of **3b** and **4b**, the furan-2(5*H*)-one **6b** being the major product in both cases, although the selectivity is lower in the case of the *cis* isomer **3b**. Chromatography on silica resulted in the isomerization of **8b** to the furan-2(5*H*)-one **7b**. The corresponding furanone **8a** was stable to rapid chromatography; prolonged stirring in ether containing silica resulted in decomposition.

The regiochemistry of the metal catalysed rearrangement was reversed for the other compounds studied (Schemes 1, 7), a furan-2(5*H*)-one being formed selectively or, in some cases, specifically. The ^{1}H-NMR of the crude product mixture obtained from rearrangement of **4c** indicated that **8c** was formed regiospecifically and was converted to its endocyclic isomer **7c** during chromatography. The rearrangements of **3d** and **4d** gave the furanone **7d** directly whereas **3e**, **4e** and **4f** gave complex mixtures containing no furanones. The furanone **25a**, formed initially from rearrangement of **12a** (^{1}H-NMR), was converted to **21a** on chromatography; the furanone **22a** was also isolated from this reaction. The rearrangement of **12f** gave

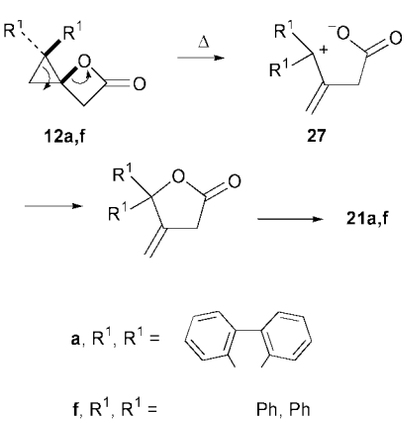


Scheme 8

25f which isomerised to **21f** after chromatography. Reaction of **12b** gave **24** directly but the reaction of **12d** gave a complex mixture containing no furanones.

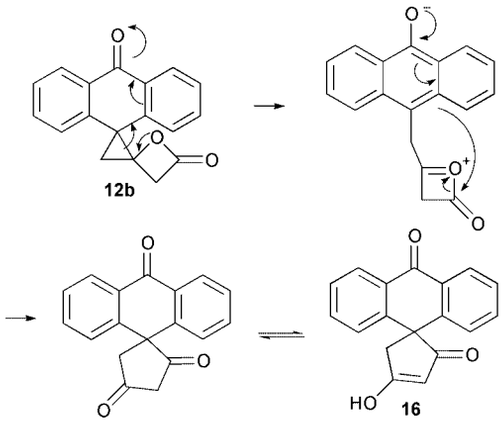
The principal objective of this work was to confirm that the spiro-β-lactones were indeed involved in the formation of the furanones and to establish the generality and nature of the reaction. The preliminary experiments indicated that furanones were formed directly from the spiro-β-lactones, but that the reaction was not a simple thermal rearrangement nor one in which a residual metal species from the preparation of the spiro-β-lactones acted as a Lewis acid. It has been shown previously[4] that an induction period of varying length is a characteristic feature of this rearrangement and that it can be significantly reduced by the addition of a diazo compound (2 equiv., relative to the catalyst) without affecting the ultimate reaction kinetics nor the product ratio. This suggests that the diazo compound promotes the formation of the catalytically active species[22] which is probably a metal carbenoid. Such a mechanistic framework accounts not only for the results presented here, but also for the earlier observation that the slow distillation of the crude filtered product from the copper promoted reaction of diazo compounds with diketene leads to the formation of furanones. The cyclopropanation reaction involves metal carbenoids and these are clearly stable and soluble enough to survive to the distillation stage of the process. We suggest that the thermal cracking of the metal carbenoid produces a coordinatively unsaturated metal species which forms a metallocycle[23] and initiates a catalytic cycle (Scheme 8). In the absence of a diazo compound the coordinatively unsaturated metal species or the metallocycle is formed in a slower process, accounting for the observation of an induction period. However once initiated the catalytic process in both cases gives the same product ratio and similar kinetics. Other features of the reaction that have emerged in investigating the behaviour of these spiro-β-lactones can also be rationalised using the proposed mechanism. Thus the higher selectivity observed for the formation of the furan-2(5*H*)-ones **6a** and **6b** (Path x) from the *trans* spiro-β-lactones **4a** and **4b**, respectively, can be interpreted in terms of greater steric hindrance encountered in the key intermediate **26a** during the formation of furan-2(3*H*)-ones (Path y); the *cis* isomer displays no such selectivity, a fact which is entirely in keeping with the structure of the intermediate **26b** formed in this case.

The significant inversion of selectivity which is observed for the 1,1-disubstituted spiro-β-lactones **4c**, **3d** and **4d**, **12a**–**b** and **12e**–**f**, all of which initially form furan-2(3*H*)-ones selectively or specifically, is understandable if cyclopropane ring cleavage occurs prior to furanone ring formation in these cases. This would produce intermediates **27** which involve a tertiary carbocation and can close to furan-2(3*H*)-ones without the steric problems associated with **25a**. The stability of intermediates such as **27** explain why **12a** and **12f** rearrange thermally to furan-2(3*H*)-ones and hence to **21a** and **21f**, respectively, the process being regiospecific in the latter case (Scheme 9). Facile



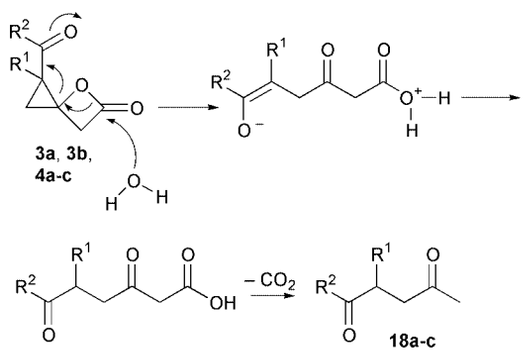
Scheme 9

cyclopropane cleavage due to the relative stability of the zwitterion thus formed may also explain why the spiroanthrone **16** is formed in good yield thermally or under BF_3 catalysis from the anthrone derived spiro-β-lactone **12b** (Scheme 10).



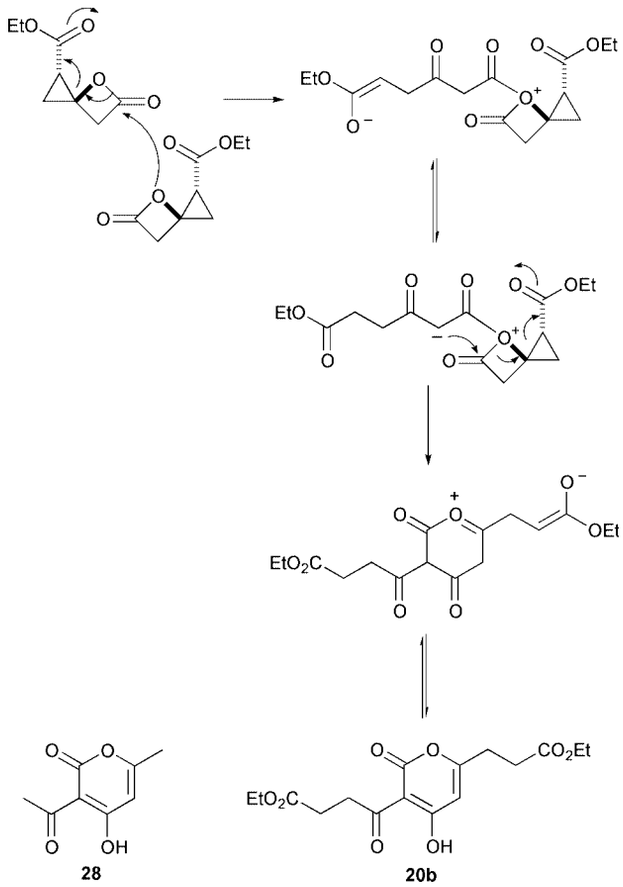
Scheme 10

The formation of 1,4-dicarbonyl products (**18a–c**) in sealed tube reactions of **3a**, **3b** and **4a–c** presumably involves the nucleophilic attack of adventitious water at the carbonyl of the lactone, with subsequent ring opening and proton transfer giving a β-ketoacid which then undergoes decarboxylation to the observed product (Scheme 11). The BF_3 promoted formation of **23a** from **3b** and **4b** can also be explained by nucleophilic attack of water at the oxetanone carbonyl group. Decarboxylation does not occur under these milder conditions and the β-ketoacid can be isolated as its methyl ester. The formation of **20b** from **3b** or **4b** is surprising. However dehydroacetic acid **28** is formed thermally[24] from the dimerisation of diketene by a mechanism which presumably involves the nucleophilic attack of one diketene molecule on another. A similar mechanism can be used to explain the formation of the pyranone **20b** from **4b** (Scheme 12). The fact that the *cis* isomer **3b** does not give the pyranone may be due to a reduction in the nucelophilicity of the oxetane oxygen atom as a result of steric hindrance by the ethoxycarbonyl group. The formation of **19b** can be rationalised, using a mechanism related to that described above for formation of **18a–c** (Scheme 11), by the nucleophilic attack of adventitious ethanol, presumably formed by ethyl ester hydrolysis, at the carbonyl of the lactone. However levulinic acid, an expected by-product of such a process, could not be detected in the crude reaction product.



Scheme 11

The furans **9a** and **10a** are formed in very low yield together with the spiro-β-lactones **3a** and **4a** in the reaction of diazoacetophenone with diketene. Furan **9a** is also formed in the sealed tube pyrolysis of **3a** and **4a**. Thus it would appear that furans are secondary products arising from initially formed spiro-β-lactones. Although thermal elimination of CO_2 is a characteristic reaction of β-lactones, there is no evidence to suggest that cyclopropanespiro-β-lactones undergo this reaction. Thus a mechanism involving an initial cyclopropane ring opening (Path b, Scheme 13) is preferred to one involving decarboxylation of the spiro-β-lactone (Path a, Scheme 13). Decarboxylation of the intermediate dioxaspiro[3,4]octenone is however more probable as an electron releasing group at C-4 is known to accelerate this process.[25] The formation of **10a** is presumably due to cyclopropanation of the furan precursor **29** and subsequent ring cleavage.



Scheme 12

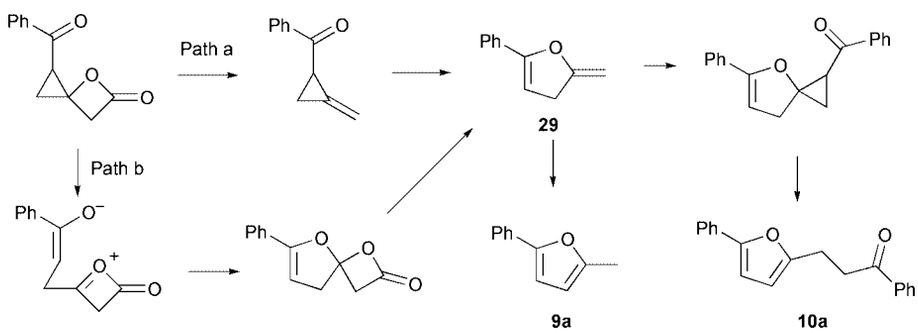
In conclusion, the synthesis of a range of cyclopropanespiro-β-lactones by the reactions of diazo compounds with diketene has been described. The thermal, Lewis acid and metal catalysed reactions of these compounds have been studied and give a diverse range of products depending on the nature of the spirolactone. The rearrangment of cyclopropanespiro-β-lactones to furanones has been shown to be a general reaction that involves metal catalysis and a novel mechanism involving insertion of the metal into C_β–O bond of the lactone ring has been proposed. This accounts for the key features of the reaction including its regiochemistry. The synthetic potential of the metal catalysed ring opening reactions of other β- and γ-lactones and of small ring molecules is currently under investigation.

Experimental

Melting points were obtained using an Electrothermal melting point apparatus and are uncorrected. TLC analyses were carried out on pre-coated sheets of Merck Kieselgel 60 F_{254}. Spots were located by UV illumination using a portable Spectroline Hanovia lamp (λ 254 nm). Column chromatography was carried out with Merck Silica Gel 60 (70–230 mesh, 40–60 mesh). GC analyses were carried out using a Shimadzu GC 8A equipped with a flame ionisation detector and a glass column (2 m × 3 mm) containing 3% OV-17 on Chromosorb W AW-DCMS (100–120 mesh). IR spectra (Nujol mull and liquid film) were obtained using a Perkin-Elmer 1600 series (FT) or a Perkin-Elmer 983G spectrometer. ^{1}H-NMR spectra were obtained using a JEOL EX90 FT NMR or a JEOL EX270 FT NMR spectrometer at probe temperatures with $CDCl_3$ as solvent and using tetramethylsilane as internal standard, unless

Table 4 Physical and IR data for the spiro-β-lactones

Spiro-β-lactone (molecular formula)	Mp/°C (solvent)	Found (%) [Requires (%)] C	H	ν_{max}/cm^{-1} Lactone C=O	Other C=O
3a	73–74 (petroleum ether) (lit. 74–75)[2]	—		1830	1665
4a	68–70 (petroleum ether) (lit. 73–74)[2]	—		1830	1662
3b	Oil[5]	—		1843	1728
4b	Oil[2]	—		1843	1728
4c ($C_9H_{12}O_4$)	Oil	58.7 [59.0]	6.5 [6.3]	1848	1724
3d ($C_{10}H_{14}O_4$)	Oil	60.5 [60.6]	6.8 [7.1]	1844	1724
4d ($C_{10}H_{14}O_4$)	Oil	60.3 [60.6]	7.0 [7.1]	1844	1724
3e ($C_{11}H_{16}O_4$)	Oil	62.0 [62.3]	7.4 [7.6]	1852	1728
4e ($C_{11}H_{16}O_4$)	Oil	62.1 [62.3]	7.5 [7.6]	1850	1726
4f	66–68 (Et_2O) (lit. 64–65)[17]	—		1867	1691
12a ($C_{17}H_{12}O_2$)	191–193 (Et_2O)	82.0 [82.2]	4.9 [4.9]	1841	—
12b ($C_{18}H_{12}O_3$)	125–127 (EtOH)	78.2 [78.3]	4.2 [4.4]	1839	1658
12c ($C_9H_8O_2$)	Oil	72.5 [73.0]	5.3 [5.4]	1832	—
12e ($C_{13}H_{10}O_2$)	Oil	78.4 [78.8]	4.7 [5.0]	1843	—
12f ($C_{17}H_{14}O_2$)	91–93 (Et_2O)	81.2 [81.6]	5.4 [5.6]	1821	—



Scheme 13

otherwise indicated; *J* values are given in Hz. ^{13}C-NMR spectra were obtained on the same instruments with $CDCl_3$ or DMSO-d_6 or a mixture of both, as solvent and internal standard ($CDCl_3$, δ 77.0; DMSO-d_6, δ 39.5). ^{13}C-NMR signals were assigned by off-resonance, ^{13}C-*J*-resolved or 135° DEPT spectra or by a combination of the above techniques. Elemental analyses were obtained using a Perkin-Elmer model 2400 CHN analyser. Photolyses were carried out in a Pyrex vessel using a Rayonet reactor model RPR-100 equipped with sixteen 254 nm lamps. Solvents were dried and distilled before use and petroleum ether is the fraction of light petroleum with bp 40–60 °C. All reactions were carried out under an atmosphere of N_2.

cis-1-(Phenylcarbonyl)-4-oxaspiro[2.3]hexan-5-one 3a and *trans*-1-(phenylcarbonyl)-4-oxaspiro[2.3]hexan-5-one 4a[2]

A solution of diazoacetophenone[6] (2.5 g, 0.17 mol) in ether was added dropwise, over 2 h at 40 °C, to a suspension of $Rh_2(OAc)_4$ (20 mg, 4.5×10^{-5} mol) in diketene (7.2 g, 0.085 mol). After the addition was complete, the mixture was stirred for a further 2 h at this temperature to ensure complete decomposition of the diazocompound. The crude reaction mixture was eluted through a short column of silica with ether (300 cm^3) and was concentrated to give a brown oil. Chromatography (ether–petroleum ether gradient) gave four products. The first product was 2-methyl-5-phenylfuran[17] **9a** (0.05 g, 5%); δ_H 7.64–7.16 (5H, m, Ar H), 6.52 (1H, d, *J* 3.1, PhC=C*H*), 6.03 (1H, dq, *J* 3.1 and 0.9, C*H*=CCH$_3$), 2.35 (3H, d, *J* 0.9, CH_3); δ_C 152.4, 152.0, 131.3 (s), 128.7, 126.8, 123.4, 107.7, 105.9 (d), 13.8 (q); ν_{max} (film)/cm^{-1} 1667 (C=C).

The second fraction was 1-phenyl-3-(5-phenyl-2-furyl)-propan-1-one **10a** (0.15 g, 6%), which was further purified by recrystallisation from petroleum ether (Found C, 82.6; H, 5.8. $C_{19}H_{16}O_2$ requires C, 82.6; H, 5.8%); δ_H 7.99–7.17 (10H, m, Ar H), 6.52 (1H, d, *J* 2.7, PhC=C*H*), 6.12 (1H, d, *J* 2.7, C*H*=CCH$_2$), 3.37 (2H, t, *J* 7.3, CH_2CH$_2$COPh), 3.14 (2H, t, *J* 7.3, CH$_2$CH_2COPh); δ_C 198.7 (C=O), 154.6, 152.6, 136.8 (s), 133.2 (d), 131.1 (s), 128.7, 128.1, 127.0, 123.5, 107.7, 105.8 (d), 37.1 and 22.9 (t); ν_{max} (Nujol)/cm^{-1} 1675 (C=O); mp 112–113 °C.

The third fraction was **4a** (1.2 g, 37%), which was recrystallised from petroleum ether. The fourth fraction, **3a** (0.6 g, 18%), was an oil and was crystallised from petroleum ether. Physical and spectroscopic data are given for **3a** and **4a** in Tables 4 and 5 and were in good agreement with those previously reported.[2]

Ethyl *cis*-5-oxo-4-oxaspiro[2.3]hexane-1-carboxylate 3b[5] and ethyl *trans*-5-oxo-4-oxaspiro[2.3]hexane-1-carboxylate 4b[2]

Ethyl diazoacetate (11.4 g, 0.1 mol) was added dropwise over 1.5 h to a stirred suspension of copper powder (1 g, 0.02 mol) and freshly distilled diketene (40 g, 0.5 mol). The reaction was maintained at a temperature between 81 and 84 °C and after the addition was complete the mixture was stirred at this temperature until an IR spectrum of the mixture showed the absence of a diazo band. The mixture was cooled and filtered, and excess diketene was removed by distillation (15 mmHg). Rapid distillation (60–130 °C, 0.1 mmHg) of the crude residue followed by chromatography (ether–petroleum ether gradient) of the mixture gave three fractions. The first fraction was a mixture of diethyl maleate and diethyl fumarate (1.1 g), confirmed by comparison with authentic samples (GC and ^{1}H-NMR). The second fraction, after further purification by distillation (80 °C, 0.5 mmHg), gave **4b** (3.75 g, 21%), The third fraction after further purification by distillation (80 °C, 0.5 mmHg) gave **3b** (2.0 g, 12%). The spectroscopic data for the title compounds (Tables 4 and 5) were in agreement with those previously reported.[2,5]

Table 5 NMR spectroscopic data for the spiro-β-lactones

Spiro-β-lactone	δ_H	δ_C
3a	8.02–7.27 (5H, m, ArH), 3.82 (2H, s, CH_2COO), 3.14 (1H, dd, *J* 7.0 and 8.1, C*H*CH_2), 2.44 (1H, t, *J* 7.0, CHC*H*(H)), 1.52 (1H, dd, *J* 7.0 and 8.1, CHCH(*H*))	Not determined
4a	8.04–7.51 (5H, m, ArH), 3.82 and 3.61 (2H, 2d, *J* 15.9, CH_2COO), 3.45 (1H, dd, *J* 7.0 and 8.4, C*H*CH_2), 1.92 (2H, m, CHCH_2)	Not determined
3b	4.21 (2H, q, *J* 7.1, CH_2CH_3), 3.72 (2H, s, CH_2CO_2), 2.11 (1H, dd, *J* 10.4 and 7.0, C*H*CH_2), 2.05 (1H, t, *J* 7.0 CH(*H*)CH), 1.43 (1H, dd, *J* 10.4 and 7.0, C*H*(H)H), 1.29 (3H, t, *J* 7.1 CH_2CH_3)	168.5 (C=O), 165.7 (C=O), 64.4 (s), 61.1, 43.3 (t), 22.1 (d), 14.8 (t), 14.0 (q)
4b	4.15 (2H, q, *J* 7.2, CH_2CH_3), 3.74 and 3.65 (2H, 2d, *J* 17.0, CH_2CO_2), 2.32 (1H, dd, *J* 10.5 and 6.9, CH(H)C*H*), 1.72 (1H, dd, *J* 10.5 and 6.9, C*H*(H)CH), 1.52 (1H, t, *J* 6.9, CH(*H*)CH), 1.25 (3H, t, *J* 7.2, CH_2CH_3)	170.4 (C=O), 165.8 (C=O), 64.5 (s), 61.1, 41.8 (t), 21.2 (d), 14.8 (t), 14.0 (q)
4c	4.17 (2H, q, *J* 7.1, CH_2CH_3), 3.74 and 3.63 (2H, 2d, *J* 17.2, CH_2CO_2), 1.72 and 1.38 (2H, 2d, *J* 17.2, cyclopropyl CH_2), 1.44 (3H, s, CH_3), 1.27 (3H, t, *J* 7.1, CH_2CH_3)	171.7 (C=O), 166.3 (C=O), 67.9 (s), 61.1, 42.2 (t), 25.3 (s), 21.4 (t), 14.0 and 13.6 (q)
3d	4.02 (2H, m, $CO_2CH_2CH_3$), 3.55 and 3.45 (2H, 2d, *J* 17.2, CH_2CO_2), 1.76 (1H, m, CH(*H*)CCO_2), 1.50 and 1.19 (2H, 2d, *J* 7.3 cyclopropyl H), 1.48 (1H, m, C*H*(H)CCO_2), 1.12 (3H, t, *J* 7.3, $CO_2CH_2CH_3$), 0.90 (3H, t, *J* 7.3, $CH_3CH(H)CCO_2$)	171.1 (C=O), 166.3 (C=O), 68.2 (s), 61.0, 42.5 (t), 31.1 (s), 21.5 (t), 20.0 (t), 14.0 and 11.5 (q)
4d	4.21 (2H, m, $CO_2CH_2CH_3$), 3.64 and 3.54 (2H, 2d, *J* 17.1, CH_2CO_2), 2.30 (1H, m, $CH_3CH(H)CCO_2$), 2.19 and 1.05 (2H, 2d, *J* 7.0 cyclopropyl H), 1.26 (3H, t, *J* 7.3, $CO_2CH_2CH_3$), 0.99 (3H, t, *J* 7.3, $CH_3CH(H)CCO_2$), 0.85 (1H, m, $CH_3CH(H)CCO_2$)	169.1 (C=O), 165.8 (C=O), 67.1 (s), 61.2, 40.8 (t), 31.6 (s), 24.2, 17.9 (t), 14.0 and 10.5 (q)
3e	4.11 (2H, m, CH_2CH_3), 3.64 (2H, s, CH_2CO_2), 1.65–1.58 (2H, overlapping signals, *i*Pr H and cyclopropyl H), 1.30 (1H, d, *J* 6.7, cyclopropyl H), 1.29–1.09 (9H, overlapping signals, CH_3)	168.6 (C=O), 165.9 (C=O), 67.1 (s), 61.0, 40.9 (t), 35.0 (s), 31.9 (d), 19.5 and 18.9 (q), 18.3 (t) and 14.0 (q)
4e	4.14 (2H, m, CH_2CH_3), 3.74 and 3.75 (2H, 2d, *J* 16.8, CH_2CO_2), 2.07 (1H, d, *J* 7.4, cyclopropyl H), 1.36 (1H, m, *i*Pr H), 1.31–1.16 (7H, overlapping signals, *i*Pr H and cyclopropyl H), 0.99 (3H, t, *J* 7.4, CH_2CH_3)	170.4 (C=O), 166.4 (C=O), 68.4 (s), 60.7, 42.9 (t), 34.4 (s), 30.2 (d), 20.9 (t), 19.6, 19.0 and 14.0 (q)
12a	7.88–6.80 (8H, m, Ar H), 3.92 and 3.64 (2H, 2d, *J* 16.4, CH_2CO_2), 2.46 and 2.12 (2H, 2d, *J* 7.8, cyclopropyl H)	165.8 (C=O), 143.5, 142.2, 140.8, 139.5 (s), 126.7, 126.4, 121.9, 121.6, 120.1, 119.8 (d), 69.2 (s), 41.0 (t), 34.9 (s), 21.2 (t)
12b	8.48–6.71 (8H, m, Ar H), 3.82 and 3.33 (2H, 2d, *J* 16.7, CH_2CO_2), 2.75 and 2.45 (2H, 2d, *J* 9.0, cyclopropyl H)	183.3 (C=O), 165.7 (C=O), 140.3, 138.2 (s), 133.7, 133.3, 133.0 (d), 132.6, 132.4 (s), 128.5, 128.0, 127.3, 125.2, 122.7 (d), 71.5 (s), 42.6 (t), 28.6 (s), 24.8 (t)
12c	6.61–6.50 (2H, m, cyclopentadienyl H), 6.34–6.24 (1H, m, cyclopentadienyl H), 3.90 and 3.67 (2H, 2d, *J* 17.2, CH_2CO_2), 2.47 and 2.09 (2H, 2d, *J* 17.2, cyclopropyl H)	165.4 (C=O), 135.0–131.6 (d), 70.9, 44.2 (s), 43.5 (t), 19.6 (t)
12e	7.43–7.15 (4H, m, Ar H), 6.95 (1H, d, *J* 5.5, ArC*H*=CH), 6.02 (1H, d, *J* 5.5, ArCH=C*H*), 3.84 and 3.62 (2H, 2d, *J* 16.1, CH_2CO_2), 2.29 and 2.09 (2H, 2d, *J* 16.1, cyclopropyl CH_2)	165.4 (C=O), 143.6–120.8 (Ar), 69.3 (s), 43.3 (t), 39.1 (s), 20.5 (t)
12f	7.39–7.12 (10H, m, Ar H), 3.60 and 3.49 (2H, 2d, *J* 16.6, CH_2CO_2), 2.02 and 1.93 (2H, 2d, *J* 7.7, cyclopropyl H)	166.5 (C=O), 140.6, 139.4 (s), 129.1, 128.8, 128.5, 127.7, 127.2, 127.0 (d), 68.0 (s), 42.2 (t), 35.8 (s), 21.7 (t)

Ethyl *trans*-1-methyl-5-oxo-4-oxaspiro[2.3]hexane-1-carboxylate 4c

Ethyl 2-diazopropionate[7] **2c** (2.0 g, 15.6 mmol) in benzene was added dropwise to a stirred mixture of $Rh_2(OAc)_4$ (6 mg, 0.14 mmol) and diketene (15.0 g, 0.178 mol) over 2 h at 70 °C. The mixture was stirred for a further hour and then allowed to cool. After filtering through a short column of silica gel the excess diketene was removed (25 °C, 0.1 mmHg) to give a red oil. The title compound was obtained as a colourless oil after chromatography (0.32 g, 32%). Physical and spectroscopic data for **4c** are given in Tables 4 and 5.

Ethyl *cis*-1-ethyl-5-oxo-4-oxaspiro[2.3]hexanecarboxylate 3d and ethyl *trans*-1-ethyl-5-oxo-4-oxaspiro[2.3]hexanecarboxylate 4d

A solution of ethyl 2-diazobutyrate[8] (**2d**, 1.4 g, 0.1 mol), diketene (10.0 g, 0.12 mol) and benzophenone (1.8 g, 0.1 mol) in acetonitrile (50 cm^3) was placed in a Rayonet reactor and was irradiated for 18 h. The acetonitrile and excess diketene was removed by distillation at room temperature under water and oil pump vacuum, respectively, to give a yellow oil. Chromatography of this oil (ether–petroleum ether, 3 : 7) gave in order of elution, **4d** (0.27 g, 13%) and **3d** (0.36 g, 17%). Physical and spectroscopic data for the title compounds are given in Tables 4 and 5.

Ethyl *cis*-1-(methylethyl)-5-oxo-4-oxaspiro[2.3]hexanecarboxylate 3e and ethyl *trans*-1-(methylethyl)-5-oxo-4-oxaspiro[2.3]-hexanecarboxylate 4e

A solution of ethyl 2-diazoisovalerate[8] (**2e**, 1.6 g, 0.1 mol), diketene (10.0 g, 0.12 mol) and benzophenone (1.8 g, 0.1 mol) in acetonitrile (50 cm^3) was placed in a Rayonet reactor and was irradiated for 18 h. The acetonitrile and excess diketene was removed by distillation at room temperature under water and oil pump vacuum, respectively, to give a yellow oil. Chromatography of this oil (ether–petroleum ether, 3 : 7) gave in order of elution, **4e** (0.50 g, 26%) and **3e** (0.36 g, 18%). Physical and spectroscopic data for the title compounds are given in Tables 4 and 5.

trans-1-Heptanoyl-5-oxo-4-oxaspiro[2.3]hexane 4f[17]

A solution of 1-diazooctan-2-one[9] **2f** (2.3 g, 0.015 mol) in

benzene (10 cm^3), was added dropwise over 2 h at 70 °C to a stirred mixture of $Rh_2(OAc)_4$ (6 mg, 0.14 mmol) and diketene (10.0 g, 0.12 mol). After cooling the mixture was filtered through a short bed of silica and the excess solvent and diketene were removed (25 °C, 0.1 mmHg). Chromatography of the residue (ether–petroleum ether, gradient) gave in order of elution, **4f** (0.88 g, 28%) and a 2:5 mixture of **4f** and **3f** (0.44 g, 14%).[17] Physical and spectroscopic data were in excellent agreement with those previously reported.[17]

Dispiro[fluorene-9,1′-cyclopropane-2′,2″-oxetan]-4″-one 12a

A solution of diazofluorene[11] **11a** (3 g, 0.016 mol) in ether was added dropwise over 2 h to a stirred solution of diketene (6.7 g, 0.08 mol) and $Rh_2(OAc)_4$ (2 mg, 6.5×10^{-5} mol) at room temperature. The formation of a white precipitate was observed as the addition progressed and on completion the mixture was cooled for 1 h in ice. Filtering, washing with cold petroleum ether (50 cm^3) and drying under suction gave **12a** (Tables 4 and 5, 2.8 g, 71%) as a white solid. A further portion of the title compound was obtained (0.35 g, 14%) by concentration of the filtrate and chromatography (ether–petroleum ether gradient).

9,10-Dihydrodispiro[anthracene-10,1′-cyclopropane-2′,2″-oxetane]-4″,10-dione 12b

Diazoanthrone[12] **11b** (6.6 g, 0.03 mol) was dissolved in benzene (400 cm^3) and the mixture was degassed by bubbling N_2 through it for 1 h. A solution of diketene (25 g, 0.34 mol) in benzene (30 cm^3) was similarly degassed. $Rh_2(OAc)_4$ (5 mg, 1×10^{-5}mol) was added to the stirred diketene solution and the diazoanthrone solution was then added dropwise over 4 h. Stirring was continued (1 h) until the red colour of diazoanthrone had completely disappeared. The reaction mixture was filtered and concentrated using a rotary evaporator without applying any heat. As the volume of the solution decreased, the crude spiro-β-lactone **12b** (~ 90% pure) was obtained as a yellow solid (3.9 g) which was filtered off. Further concentration of the filtrate gave additional solid (1.0 g) and the combined solids were washed with cold petroleum ether to remove diketene. Silica gel chromatography (dichloromethane–petroleum ether gradient) of the solid (1.4 g) gave two fractions. The first compound was identified as anthraquinone (0.1 g, 4%). The second product was **12b** (0.45 g, 15%) which was further purified by recrystallisation from ethanol; spectroscopic and physical data are given in Tables 4 and 5.

1-Oxadispiro[3.0.4.1]deca-6,8-dien-2-one 12c

Diazocyclopentadiene[13] **11c** (1.0 g, 11 mmol) in benzene was added dropwise to a mixture of diketene (5.0 g, 60 mmol) and $Rh_2(OAc)_4$ (3 mg, 0.007 mmol) and benzene (2 cm^3) at 80 °C for 3 h. Benzene was then removed on a rotary evaporator and excess diketene was removed using an oil pump vacuum at room temperature. Chromatography (petroleum ether elution) gave 1,1′-bi[cyclopentadienylidene][26] **13c** (0.28 g, 41%). Further elution with ether–petroleum ether (1:10) gave **12c** (0.56 g, 37%) as a colourless oil. Physical and spectroscopic data for **12c** are given in Tables 4 and 5.

Dispiro[indene-1,1′-cyclopropane-2′,2″-oxetan]-4″-one 12e

Diazoindene[14] **11e** (2.0 g, 14 mmol) in benzene (10 cm^3) was added to a mixture of diketene and $Rh_2(OAc)_4$ (3 mg, 0.007 mmol) in benzene (10 cm^3) at 80 °C and the mixture was heated for 18 h. Benzene and diketene were removed as usual and the oil obtained was chromatographed (ether–petroleum ether gradient) and gave two fractions. The first fraction was the title compound (physical and spectroscopic data are given in Tables 4 and 5, 0.74 g, 26%). The second fraction was impure 3-methyl-2,5-dihydrospiro[furan-2,1′-indan]-5-one **15** (0.27 g, 10%) which decomposed on standing at room temperature; δ_H 7.35–7.08 (4H, m, Ar H), 6.90 (1H, d, *J* 5.5, ArCH=C*H*), 6.58 (1H, br s, C*H*=CCH_3), 6.25 (1H, d, *J* 5.5, ArC*H*=CH), 2.41 (3H, br s, CH_3); ν_{max} (film/cm^{-1}) 1793 (C=O).

The $Rh_2(OAc)_4$ catalysed reaction of 3-diazo-2-phenyl-3*H*-indole 11d with diketene

3-Diazo-2-phenyl-3*H*-indole[15] **11d** (3.0 g, 0.015 mol) in benzene (10 cm^3) was added dropwise to a stirred mixture of $Rh_2(OAc)_4$ (6 mg, 0.14 mmol) and diketene (10.0 g, 0.12 mol) over 2 h at room temperature. The excess solvent and diketene were removed (25 °C, 0.1 mmHg). Chromatography of the residue (ether–petroleum ether, gradient) gave 2,2′-diphenyl-3,3′-azinodi-3*H*-indole; mp 256–258 °C (lit.,[18] 260 °C).

1,1-Diphenyl-4-oxaspiro[2.3]hexan-5-one 12f

A solution of diphenyldiazomethane[10] **11a** (2 g, 0.01 mol) and diketene (8.4 g, 0.1 mol) was irradiated in a Rayonet reactor in acetonitrile (50 cm^3) for 40 h. The solution was cooled overnight and the white precipitate of benzophenone azine[27] **14f** (0.5 g) which formed was removed by filtration. The filtrate was concentrated giving a yellow oil (2.9 g) which was chromatographed. Elution with ether–petroleum ether (1:20) gave further benzophenone azine (0.4 g). Further elution with ether–petroleum ether (1:10) gave the title compound as an oil (0.36 g, 14%), which was crystallised from ether–petroleum ether giving a white solid (0.28 g, 11%). Physical and spectroscopic data for **12f** are given in Tables 4 and 5.

General procedure for sealed tube reactions

Borosilicate glass tubes were cleaned (water–detergent and acetone) and dried before use. The spiro-β-lactone (0.3–0.5 mmol) was added to a tube and this was then sealed. The tube was placed vertically in an oven at 170–190 °C for 50 min. The products were isolated from the reaction mixture by distillation, recrystallisation or chromatography. A summary of results is given in Table 2.

General procedure for metal catalysed rearrangement of spiro-β-lactones to furanones

A typical procedure involved heating the spiro-β-lactone (1.0–5.0 mmol) in refluxing toluene (5–20 cm^3) in the presence of $Cu(acac)_2$ (20–100 mg, 0.008–0.04 mmol). The reactions were monitored by TLC, GC or IR. After completion, the product was dissolved in ether and was passed through a short column of silica (5 g) eluting with ether (100 cm^3). The residue obtained after removal of ether was chromatographed (ether–petroleum ether gradient) to give the individual products. The physical and spectroscopic data of the products are given in Tables 6 and 7. A summary of the results is given in Table 3.

Sealed tube pyrolysis of ethyl *cis*-5-oxo-4-oxaspiro[2.3]hexane-1-carboxylate 3b and ethyl *trans*-5-oxo-4-oxaspiro[2.3]hexane-1-carboxylate 4b

The spirolactone **4b** was treated as described above and the crude products from a number of sealed tubes were combined (0.3 g). Rapid distillation (50 °C, 0.1 mmHg) gave an oil which was identified as ethyl 4-oxopentanoate (ethyl levulinate) **18b** (0.05 g, 17%) by comparison of its spectroscopic data with those of an authentic sample. The residue was chromatographed (chloroform–petroleum ether gradient) giving two fractions.

The first fraction was obtained as an oil (0.03 g, 10%), which was further purified by distillation (70–80 °C, 0.1 mmHg) and was identified as diethyl 3-oxohexane-1,6-dioate[5] **19b**; δ_H 4.15 (2H, q, *J* 7.1, CH_2CH_3), 4.12 (2H, q, *J* 7.1, CH_2CH_3), 3.48 (2H, s, CO_2CH_2CO), 2.84 (2H, t, *J* 6.6, $CH_2COCH_2CH_2$), 2.59 (2H,

Table 6 Physical and IR data for the furanones

Furanone (molecular formula)	Mp/°C (solvent)	Found (%) [Requires (%)] C	H	ν_{max}/cm^{-1} Lactone C=O	Other C=O	C=C
6a ($C_{12}H_{10}O_3$)	121–123 (petroleum ether)	71.3 [71.3]	5.0 [5.0]	1754	1680	1644
8a ($C_{12}H_{10}O_3$)	78–80 (Et_2O–petroleum ether)	71.5 [71.3]	5.2 [5.0]	1790	1684	1665
6b	Oil[2]	—		1770	1730	—
7b	Oil[2]	—		1780	1730	—
7c ($C_9H_{12}O_4$)	Oil	58.6 [59.0]	6.8 [6.5]	1782	1748	—
7d ($C_{10}H_{14}O_4$)	Oil	60.3 [60.6]	7.0 [7.1]	1781	1748	—
21a ($C_{17}H_{12}O_2$)	133–134 (Et_2O–petroleum ether)	82.1 [82.2]	4.7 [4.9]	1756	—	1640
22a ($C_{17}H_{12}O_2$)	>250 ($CHCl_3$)	81.9 [82.2]	4.8 [4.9]	1778	—	1665
21f ($C_{17}H_{14}O_2$)	91–93 (Et_2O)	81.2 [81.6]	5.4 [5.6]	1748	—	1640
24 ($C_{18}H_{12}O_3$)	126–128 (Et_2O–petroleum ether)	78.2 [78.3]	4.4 [4.4]	1754	1665	1643

Table 7 NMR spectroscopic data for furanones

Furanone	δ_H	δ_C
6a	8.02–7.39 (5H, m, Ar H), 6.04 (1H, br s, C=C*H*), 4.96 (2H, br s, CH_2O), 4.21 (2H, br s, CH_2Bz)	193.7 (C=O), 173.2 (C=O), 162.2, 135.7 (s), 134.1, 128.9, 128.3, 119.1 (d), 73.3 and 38.2 (t)
8a	7.95–7.46 (5H, m, Ar H), 6.25 (1H, br s, OC*H*Bz), 5.21 (1H, br s, C*H*(H)=C), 5.11 (1H, br s, CH(*H*)=C), 3.25 and 3.30 (2H, 2d, *J* 21.3, CH_2CO_2)	192.8 (C=O), 174.1 (C=O), 137.3 (s), 134.4 (d), 133.5 (s), 129.2 (d), 112.6 (t), 81.8 (d) and 33.3 (t)
6b	6.06 (1H, br s, C=C*H*), 4.91 (2H, br s, CH_2O), 4.21 (2H, q, *J* 7.2, CH_2CH$_3$), 3.52 (2H, br s, O_2CCH_2), 1.30 (3H, t, *J* 7.2, CH_2CH_3)	173.3 (C=O), 167.8 (C=O), 161.6 (s), 118.3 (d), 73.0, 61.5, 34.1 (t) and 13.8 (q)
7b	5.91 (1H, br s, C=CH), 5.26 (1H, br s, CHOCO), 4.28 (2H, q, *J* 7.2, CH_2CH_3), 2.16 (3H, br s, CH_3C=C), 1.32 (3H, t, *J* 7.2, CH_2CH_3)	170.2 (C=O), 167.2 (C=O), 160.8 (s), 117.6, 92.1 (d), 61.5 (t) and 13.7 (q)
7c	5.88 (1H, br s, C=CH), 4.23 (2H, q, *J* 7.1, CH_2CH$_3$), 2.12 (3H, br s, CH_3C=C), 1.70 (3H, CH_3), 1.29 (3H, t, *J* 7.1, CH_2CH_3)	171.0 (C=O), 167.5 (C=O), 167.4 (s), 116.7 (d), 87.6 (s), 62.0 (t), 20.3, 13.5 and 12.6 (q)
7d	5.86 (1H, br s, C=CH), 4.25 (2H, m, OCH_2CH$_3$), 2.26 and 1.91 (each m, CH_2CCO_2), 2.06 (3H, br s, CH_3C=C), 1.32 (3H, t, *J* 7.3, OCH_2CH_3), 0.91 (3H, t, *J* 7.0, $CH_3CH_2CCO_2$)	171.8 (C=O), 167.9 (C=O), 166.2 (s), 118.1 (d), 91.3 (s), 62.4, 27.1 (t), 13.9, 13.2 and 7.1 (q)
21f	7.37–7.25 (10H, m, Ar H), 5.95 (1H, q, *J* 1.4, CH), 2.09 (3H, d, *J* 1.4, CH_3)	171.9 (C=O), 170.8 (s), 138.46 (s), 128.7, 128.5, 127.5, 117.6 (d), 94.1 (s), 15.1 (q)
21a	7.79–7.19 (8H, m, Ar H), 6.12 (1H, q, *J* 1.4, CH), 1.55 (3H, d, *J* 1.4, CH_3)	173.2 (C=O), 169.2, 140.6, 140.0 (s), 130.7, 128.8, 123.7, 121.2, 115.0 (d), 94.1 (s), 12.0 (q)
22a	7.78–7.32 (8H, m, Ar H), 5.55 (2H, br s, CH_2O), 3.84 (2H, br s, CH_2C=O)	[a]
24	8.41–7.35 (8H, m, Ar H), 6.02 (1H, q, *J* 1.5, CH), 1.52 (3H, d, *J* 1.5, CH_3)	182.9 (C=O), 173.4 (C=O), 172.6, 137.2 (s), 134.2 (d), 131.4 (s), 129.8, 127.9, 125.3, 115.0 (d), 85.9 (s), 12.8 (q)

[a] Not sufficiently soluble in $CDCl_3$ or DMSO-d_6 to obtain the ^{13}C spectrum.

t, *J* 6.6, $CH_2CH_2CO_2Et$), 1.26 (3H, t, *J* 7.1, CH_2CH_3), 1.24 (3H, t, *J* 7.1, CH_2CH_3); δ_C 201.0 (C=O), 172.4, 167.0 (s), 61.4, 60.7, 49.3, 37.4, 28.0 (t), 14.1 (q); ν_{max} (film)/cm^{-1} 1732 (C=O).

Evaporation of solvent gave ethyl 4-{6-[2-(ethoxycarbonyl)-ethyl]-4-hydroxy-2-oxo-2*H*-pyran-3-yl}-4-oxobutanoate **20b** (0.13 g, 43%) as an oil (0.13 g, 43%) which solidified on cooling. Recrystallisation from petroleum ether gave **20b** as a white solid (0.05 g) (Found C, 56.7, H, 5.9. $C_{16}H_{20}O_8$ requires C, 56.5, H, 5.9%); δ_H 16.20 (1, s, O*H*), 6.00 (1H, s, C=C*H*), 4.17 (2H, q, *J* 7.1, CH_2CH$_3$), 4.15 (2H, q, *J* 7.1, CH_2CH$_3$), 3.41 (2H, t, *J* 6.1, HC=CCH_2), 2.68 (6H, overlapping multiplets, CH_2), 1.28 (6H, overlapping triplets, *J* 7.1, CH_2CH_3); δ_C 205.3 (C=O), 180.5 (s), 172.5 (C=O), 171.2 (C=O), 170.2 (C=O), 160.7 (s), 101.2 (d), 99.8 (s), 61.0, 60.6, 36.9, 30.4, 29.4, 27.8 (t), 14.1 (q); ν_{max} (Nujol)/cm^{-1} 1728 (C=O), 1712 (C=O), 1643 (C=C), 1615 (C=C); mp 46–47 °C. The spirolactone **3b** was pyrolysed in the same way giving only **18b** and **19b** (Table 2).

4′-Hydroxy-9,10-dihydrospiro[anthracene-9,1′-cyclopent[3]ene)-2′,10-dione 16

The spiro-β-lactone **12b** (0.18 g, 0.65 mmol) was heated in refluxing toluene (20 cm^3) for 72 h. A precipitate formed which was filtered off and identified as the title compound (0.12 g, 66%) (Found: C, 78.5; H, 4.3. $C_{18}H_{12}O_3$ requires C, 78.3; H, 4.4%); δ_H (DMSO-d_6) 8.26–7.20 (8H, m, Ar H), 5.42 (1H, s, C=C*H*), 3.36 (2H, s, CH_2); δ_C (DMSO-d_6) 199.5 (C=O), 193.5 (s), 182.7 (C=O), 143.6 (s), 134.0 (d), 130.7 (s), 127.5, 126.5, 125.7, 103.1 (d), 54.6 (s) and 48.1 (t); ν_{max} (Nujol)/cm^{-1} 2600 (OH, broad), 1662 (C=O), 1621 (C=O), 1600 (C=C) and 1529 (C=C); mp (decomp.) 210–240 °C. The spiroanthrone **16** was also obtained (^{1}H-NMR) when **12b** was stirred in ether (20 cm^3) containing BF_3·OEt_2 (0.1 cm^3) at room temperature.

4′-Methoxy-9,10-dihydrospiro[anthracene-9,1′-cyclopent[3]-ene]-2′,10-dione 17a and 2′-methoxy-9,10-dihydrospiro-[anthracene-9,1′-cyclopent[2]ene]-4′,10-dione 17b

The spiroanthrone **16** (0.34 g, 1.2 mmol) was dissolved in methanol (3 cm^3) and trimethyl orthoformate (1 cm^3) and sulfuric acid (0.2 cm^3) were added; the mixture was stirred under reflux for 3 h. The crude product was concentrated, sodium bicarbonate was added and the product was extracted with ether (4 × 40 cm^3) and chloroform (1 × 20 cm^3). The organic layers were combined and dried over anhydrous sodium sulfate. Filtration, concentration and chromatography gave **17a** (0.08 g, 24%) which was purified further by recrystallisation from an ether–methanol mixture (Found: C, 78.2; H, 4.9. $C_{19}H_{14}O_3$ requires C, 78.6; H, 4.9%); δ_H 8.40–7.34 (8H, m, Ar H), 5.65 (1H, t, *J* 1.0, C=C*H*), 4.07 (3H, s, OCH_3), 3.38 (2H, d,

J 1.0, CH_2); δ_C (DMSO-d_6) 202.5 (C=O), 191.5 (s), 183.3 (C=O), 143.3 (s), 134.0 (d), 131.5 (s), 127.9, 125.3, 103.7 (d), 59.7 (q), 55.1 (s) and 48.1 (t); ν_{max} (Nujol)/cm^{-1} 1696 (C=O), 1661 (C=O), 1627 (C=C) and 1593 (C=C); mp (decomp.) 197–200 °C.

Treatment of **16** (0.25 g, 0.9 mmol) in ether with an ethereal solution of diazomethane (0.7 g in 50 cm^3) in the presence of BF_3·OEt_2 (1 drop) gave, after removal of solvent and chromatography a mixture of **17a** and **17b** (0.14 g, 56%) and recovered **16** (0.08 g, 33%). The presence of **17b** the mixture was supported by signals in the ^{1}H-NMR spectrum of the mixture at δ_H 5.79 (1H, s, CH), 3.70 (3H, s, CH_3O), 3.03 (2H, s, CH_2).

Ethyl methyl 3-oxohexane-1,6-dioate 23b

A 6:5 mixture of **3b** and **4b** (0.5 g) and boron trifluoride–diethyl ether (2–3 drops) was stirred in dichloromethane (10 cm^3), the reaction being monitored by GC. After 30 min complete consumption of the starting material had occurred and some ethyl 4-oxopentanoate had formed (GC). The reaction mixture was concentrated and was shown by ^{1}H-NMR and IR to contain, in addition to ethyl 4-oxopentanoate (**18b**), 6-ethyl hydrogen 3-oxoheptanoate **23a** and its enol tautomer; δ_H 10.20 (br s, O*H*), 5.45 (s, C*H*=COH), 4.16 (q, *J* 7.2, CH_2CH_3), 3.66 (s, HO_2CCH_2CO), 2.80–2.20 (m, CH_2CH_2), 1.22 (3H, t, *J* 7.2, CH_2CH_3); ν_{max} (film)/cm^{-1} 3430 (OH), 1734 (C=O) and 1645 (C=C).

The product was dissolved in ether and was extracted with 5% sodium carbonate (100 cm^3). The aqueous layer was then acidified with 5% hydrochloric acid and extracted with ether. The ether layer thus obtained was dried over anhydrous sodium sulfate. Filtration and concentration gave the β-ketoacid in the keto form exclusively. The product was dissolved in ether and after an ethereal solution of diazomethane (0.7 g, 0.017 mol) was added the solution was allowed to stand for 24 h. Concentration gave **23b** (0.23g) which was further purified by distillation (70–80 °C, 0.1 mmHg, 0.18 g, 37%) (Found C, 53.9; H, 7.1. $C_9H_{14}O_5$ requires C, 53.5; H, 7.0%); δ_H 4.12 (2H, q, *J* 7.2, CH_2CH_3), 3.74 (3H, s, OCH_3), 3.52 (2H, s, $CH_3O_2CCH_2$), 2.87 (2H, t, *J* 6.2, $O_2CCH_2CH_2$), 2.58 (2H, t, *J* 6.2, $O_2CCH_2CH_2$), 1.22 (3H, t, *J* 7.2, CH_2CH_3); δ_C 220.8 (C=O), 172.3, 167.3 (s), 61.3 (t), 52.2 (q), 48.9, 37.3, 27.8 (t), 14.0 (q); ν_{max} (film)/cm^{-1} 1729 (C=O).

Acknowledgements

The financial support provided by the Irish science and technology agency, Enterprise Ireland, is gratefully acknowledged.

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 N. W. A. Geraghty and P. V. Murphy, *Tetrahedron Lett.*, 1994, **35**, 6737.
5 T. Kato, N. Katagiri and R. Sato, *J. Chem. Soc.*, *Perkin Trans. 1*, 1979, 525.
6 M. S. Newman and P. Beul, *J. Am. Chem. Soc.*, 1949, **71**, 1506.
7 J. Hendrickson and W. Wolf, *J. Org. Chem.,* 1968, **33**, 3610.
8 M. Regitz and F. Menz, *Chem. Ber.*, 1968, **101**, 2622.
9 E. Wenkert, *J. Am. Chem. Soc.*, 1970, **92**, 7428–7436.
10 D. D. Keith, J. Tengi, P. Rossman, L. Todaro and M. Weigele, *Tetrahedron*, 1983, **39**, 2445.
11 R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.*, 1978, **100**, 4475.
12 M. Regitz, *Chem. Ber.*, 1964, **97**, 2742.
13 W. Von, E. Doering and C. H. Dupuy, *J. Am. Chem. Soc.*, 1953, **75**, 5400.
14 J. E. Baldwin and K. A. Black, *J. Am. Chem. Soc.*, 1984, **106**, 1029.
15 A. Gonzalez and C. Galvez, *Synthesis,* 1981, 741.
16 G. Dana, O. Convert, J. P. Girault and E. Mulliez, *Can. J. Chem.*, 1976, **54**, 1827.
17 S. Takano, T. Sugahara, M. Ishiguro and K. Ogasawara, *Heterocycles*, 1977, **6**, 1141.
18 C. Galvez, A. Gonzalez and A. Serra, *J. Chem. Res.* (*S*), 1985, 402.
19 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.
20 H. Stetter and M. Schreckenberg, *Chem. Ber.* 1974, **107**, 2453.
21 P. Dowd and S.-C. Choi, *Tetrahedron*, 1989, **45**, 1, 77.
22 J. Adams and D. M. Spero, *Tetrahedron*, 1991, **47**, 1765.
23 M. P. Doyle and D. Van Leusen, *J. Org. Chem.*, 1982, **47**, 5326.
24 A. B. Steele, A. B. Boese and M. F. Dull, *J. Org. Chem.*, 1949, **14**, 460.
25 S. Searles, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1994, vol. 7, p. 363.
26 A. G. Davies, J. R. M. Giles and J. Lusztyk, *J. Chem. Soc.*, *Perkin Trans. 2*, 1981, 747.
27 M. P. Doyle, R. L. Dorow, W. H. Tamblyn and W. E. Buhro, *Tetrahedron Lett.*, 1982, **23**, 2261.