Rhodium Carbenoid Mediated Cyclisations. Part 3.[1] Synthesis of Cyclic Ethers from Lactones

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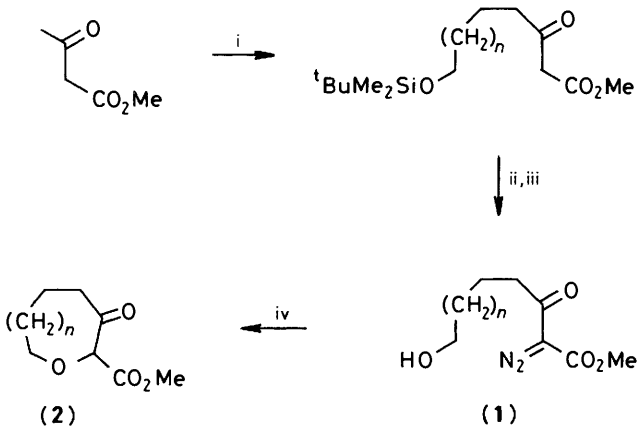
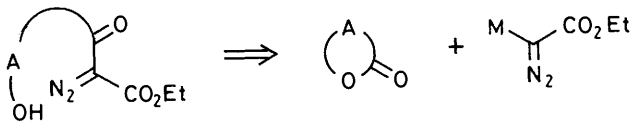
Ethyl lithiodiazoacetate ring opens lactones, *N*-Boc lactams, and cyclic anhydrides and carbonates to give ω-functionalised α-diazo-β-keto esters in varying yield (Tables 1 and 2). Thus simple 5-, 6-, 7-, and 8-membered lactones react to give α,ω-diazo alcohols, and benzo-fused lactones give diazo phenols. The corresponding reaction with *N*-Boc lactams gives Boc-amino diazo compounds, and cyclic anhydrides give α,ω-diazo carboxylic acids. Treatment of the diazo compounds derived from 5-, 6-, and 7-membered lactones with a catalytic amount of rhodium(II) acetate resulted in rhodium carbenoid mediated cyclisation to give 6-, 7-, and 8-membered cyclic ethers (Table 3). Attempted preparation of larger rings, however, resulted in formation of cyclopentanones by competing C–H insertion reactions. Similarly, the Boc-protected amino diazo compounds only gave the products of C–H insertion on treatment with rhodium(II) acetate.

We have recently described a new route to 7- and 8-membered ring cyclic ethers.[1] The reaction, which involves a formal insertion of a carbene or metallocarbenoid into an O–H bond, is based on the rhodium(II) acetate mediated cyclisation of α-diazo-ω-hydroxy-β-keto esters. The substrates for cyclisation, for example the diazo alcohols (**1**; n = 1, 2), were prepared in 3 steps from the dianion of methyl acetoacetate as shown in Scheme 1, and were cyclised to the ethers (**2**), by treatment with a catalytic amount of rhodium(II) acetate in boiling benzene.



Scheme 1. *Reagents:* i, NaH, THF; BuLi; $Bu^tMe_2SiOCH_2(CH_2)_nCH_2I$; ii, TsN_3; iii, H^+; iv, $Rh_2(OAc)_4$

Although this route (Scheme 1) gives acceptable overall yields of diazo alcohols (**1**) using a range of simple silyl protected α,ω-halogeno alcohols, we encountered problems at the dianion alkylation step when more complex halides were used.[2] In looking for an alternative route to circumvent these problems, we were attracted by the possibility of acylating an organometallic derivative of a diazo compound with a lactone to give the required diazo alcohols in a *single* step as shown retrosynthetically in Scheme 2. Various organometallic derivatives of diazo compounds are known,[3] and ethyl diazoacetate, in particular, is easily metallated. The organolithium, ethyl lithiodiazoacetate, is stable in solution at low temperature, and is reported to react with electrophiles such as



Scheme 2. A = linking chain, M = metal

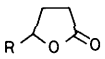
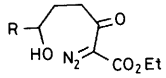
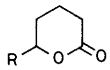
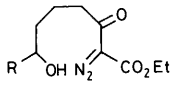
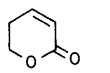
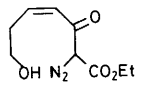
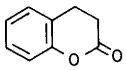
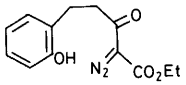
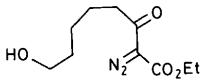
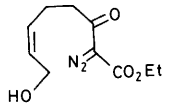
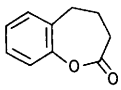
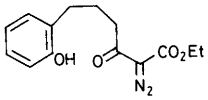
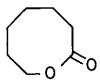
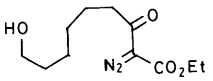
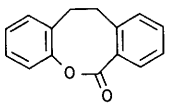
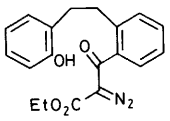
alkyl halides, acid chlorides, and ketones,[3] and therefore seemed an ideal candidate with which to attempt the acylation reaction with lactones. The results of this investigation, together with related work are reported in detail herein.[4]

Results and Discussion

Ring Opening of Lactones with Ethyl Lithiodiazoacetate.— Commercially available ethyl diazoacetate (EDA) was metallated by addition to a solution of lithium di-isopropylamide (LDA) in tetrahydrofuran (THF) at −90 °C. The resulting orange solution was treated with γ-butyrolactone, and then allowed to warm to −75 °C. The reaction mixture was quenched by addition of acetic acid at −75 °C, followed by warming to 0 °C and standard aqueous work-up. Chromatography gave the required diazo-alcohol (**3a**) in 47% yield. γ-Valerolactone reacted similarly to give the diazo alcohol (**3b**) (51%). However, with other lactones, this 'normal addition' procedure was less satisfactory than the alternative 'inverse addition'. In this, a solution of LDA was added to a mixture of EDA and the lactone in THF, the temperature being kept below −70 °C. Using this procedure, several lactones were ring opened, and a range of diazo alcohols (**4**)—(**11**) were prepared (Table 1).

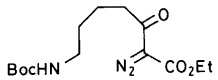
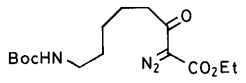
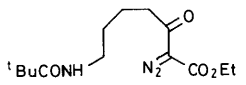
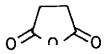
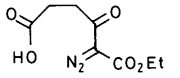
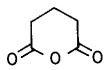
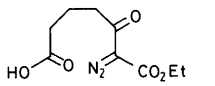
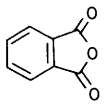
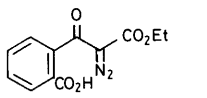
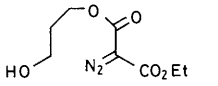
Simple 5-, 6-, 7-, and 8-membered ring lactones react readily with ethyl lithiodiazoacetate to give the expected diazo alcohol in moderate to good yield. Benzo fused lactones are also ring opened, but the reaction is slower, and the dibenzo-fused 8-membered lactone gives a very poor yield of the diazo phenol (**11**). The diazo alcohol (**6**) was also formed in low yield from the α,β-unsaturated lactone, 5,6-dihydropyran-2-one. Lactones which did not give ω-hydroxy-α-diazo-β-keto esters under either set of reaction conditions included β-lactones such as β-butyrolactone and diketene, phthalide, isochroman-3-one, coumarin, and tetramethyl-1,5-gluconolactone.

Table 1. Ring opening of lactones with ethyl lithiodiazoacetate

Lactone	Addition[a]	Diazo alcohol	Yield (%)
	**a**, R = H N **b**, R = Me N	 (**3**)	47 51
	**a**, R = H I(N) **b**, R = C_6H_{13} I(N)	 (**4**)	81 (32) 99 (95)
	I	 (**5**)	6
	I	 (**6**)	80
	I(N)	 (**7**)	63 (65)
	I	 (**8**)	58
	I	 (**9**)	56
	I	 (**10**)	65
	I	 (**11**)	8

[a] N = normal addition; I = inverse addition.

Table 2. Ring opening of lactams, cyclic anhydrides, and carbonates with ethyl lithiodiazoacetate

Substrate	Addition[a]	Diazo compound	Yield (%)
	I	 (**12**)	60
	I(N)	 (**13**)	73 (45)
	N	 (**14**)	18[b]
	I(N)	 (**15**)	25 (43)
	I	 (**16**)	36
	I	 (**17**)	26
	N	 (**18**)	41

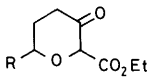
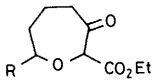
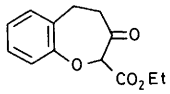
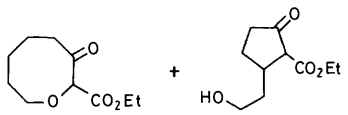
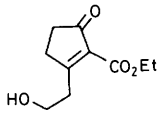
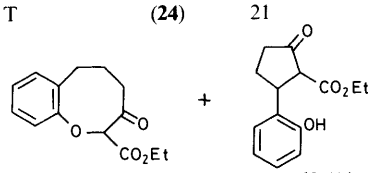
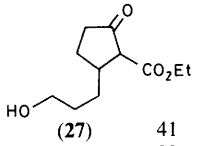
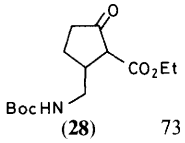
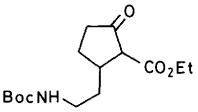
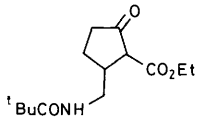
[a] N = normal addition; I = inverse addition; [b] +starting material (25%).

Ring Opening of Lactams, Cyclic Anhydrides, and Carbonates with Ethyl Lithiodiazoacetate.—The anion reaction was also extended to the ring opening of lactams, cyclic anhydrides, and cyclic carbonates. Initial attempts with *N*-methyl γ-, δ-, and ε-lactams were unsuccessful, so an electron-withdrawing group was introduced onto the lactam nitrogen to stabilise the *N*-anion which would result from the ring opening reaction. Since it was important to avoid attack on the nitrogen substituent itself, the bulky t-butoxycarbonyl (Boc) group was chosen. This proved successful, and addition of LDA to a mixture of EDA and *N*-Boc-δ-valerolactam or *N*-Boc-ε-caprolactam resulted in smooth ring opening and formation of the Boc-protected ω-amino-α-diazo-β-ketoesters (**12**) and (**13**) in good yield (Table 2). The use of the pivaloyl group as a bulky electron-withdrawing substituent on the lactam nitrogen was less satisfactory. Imides, such as *N*-methylphthalimide were not ring opened by ethyl lithiodiazoacetate.

The cyclic carboxylic acid anhydrides, succinic, glutaric and phthalic, also underwent attack by ethyl lithiodiazoacetate to give the ω-carboxy-α-diazo-β-keto esters (**15**), (**16**), and (**17**) in modest yield (Table 2). Finally, cyclic carbonates were subjected to the ring opening reaction. 1,3-Dioxan-2-one gave the diazo alcohol (**18**) (41%), and although the five-membered ring carbonate, 4-methyl-1,3-dioxolan-2-one, was also ring opened, it gave an inseparable mixture of isomeric diazo alcohols.

Rhodium Carbenoid Mediated Cyclisation Reactions.—The functionalised diazo compounds that were obtained in good yield were then subjected to normal conditions for the rhodium carbenoid cyclisation reaction. On treatment with a catalytic amount of rhodium(II) acetate in boiling benzene or at room temperature in dichloromethane, the diazo alcohols (**3a**), (**3b**), (**4a**), (**4b**), and (**6**) cyclised to the corresponding 6- and 7-membered cyclic ethers (**19a**) (unstable), (**19b**), (**20a**), (**20b**), and (**21**) in good yield (Table 3), after filtration of the mixture to remove the catalyst, evaporation of the solvent, and distillation of the residue. Purification by chromatography was less satisfactory owing to the instability of the products on silica gel. A range of other catalysts was used in the formation of the oxepane (**20a**), although rhodium(II) acetate gave the best yield in this case, and was generally the most useful (Table 3). When

Table 3. Cyclisation reactions of diazo compounds

Diazo	Catalyst	Solvent[a]	Product	Yield (%)
				
(**3a**)	$Rh_2(OAc_4$	B (D)	(**19a**)	57 (59)
(**3b**)	$Rh_2(OAc)_4$	B (D)	(**19b**)	80 (64)
				
(**4a**)	$Rh_2(OAc)_4$	B (D)	(**20a**)	64 (58)
(**4a**)	$Rh_2(OCOCF_3)_4$	B	(**20a**)	57
(**4a**)	$Cu(OAc)_2$	B	(**20a**)	28
(**4a**)	$Cu(OCOCF_3)_2$	B	(**20a**)	46
(**4a**)	$Cu(OSO_2CF_3)_2$	B	(**20a**)	59
(**4b**)	$Rh_2(OAc)_4$	B (D)	(**20b**)	77 (68)
				
(**6**)	$Rh_2(OAc)_4$	B (D)	(**21**)	80 (59)
(**6**)	$Rh_2(OCOCF_3)_4$	D	(**21**)	63
				
(**7**)	$Rh_2(OAc)_4$	B (D)	(**22**)	(**23**) 31 + 5 (18 + 30)
				
(**8**)	$Pd(OAc)_2$	T	(**24**)	21
				
(**9**)	$Rh_2(OAc)_4$	B (D)	(**25**)	(**26**) 12 + 69 (11 + 62)
(**9**)	$Rh_2(OCOCF_3)_4$	D	(**25**)	(**26**) 32 + 34
(**9**)	$Cu(acac)_2$	B	only (**26**)	54
				
(**10**)	$Rh_2(OAc)_4$	D	(**27**)	41
(**10**)	$Rh_2(OCOCF_3)_4$	D	(**27**)	39
				
(**12**)	$Rh_2(OAc)_4$	D	(**28**)	73
				
(**13**)	$Rh_2(OCOCF_3)_4$	D	(**29**)	76
(**13**)	$Rh_2(OAc)_4$	D	(**29**)	63
				
(**14**)	$Rh_2(OAc)_4$	B	(**30**)	19

[a] B = benzene; D = dichloromethane; T = toluene.

the O–H group of the diazo alcohol (**4a**) was silylated with a t-butyldimethylsilyl group, only C–H insertion occurred, although the yield was poor possibly owing to steric effects.

As before,[1] the yield of 8-membered ring ethers was lower, the oxecane (**22**) being formed in 31% yield when the diazo compound (**7**) was decomposed in boiling benzene, together with the cyclopentanone ester (**23**) (5%), formed by competing C–H insertion,[5] although the ratio of oxecane to cyclopentanone was different when the reaction was carried out in dichloromethane (Table 3). In an attempt to favour the formation of oxecanes, the diazo compound (**8**) containing a *Z*-double band was prepared. However, on treatment with rhodium(II) acetate, the diazo alcohol (**8**) gave a complex mixture of products, although with palladium(II) acetate as catalyst, the cyclopentenone (**24**) was formed in low yield, presumably *via* a palladium complex.[6]

Decomposition of the diazo phenol (**9**) also gave a mixture of 8- and 5-membered ring products: the benzoxecane (**25**) (12%) and the cyclopentanone (**26**) (69%). However the yield of the benzoxecane (**25**) could be improved to 32% at the expense of the cyclopentanone (**26**) (34%) by using rhodium(II) trifluoroacetate as the catalyst in dichloromethane. With copper(II) bis(acetonylacetone) as catalyst, the cyclopentanone (**26**) was the only product isolated. The dependence of the cyclisation reaction on the nature of the catalyst probably reflects the difference in reactivity of the metallocarbenoid intermediates. Rhodium catalysts are known to be more effective than copper catalysts in formal O–H insertion reactions.[7]

The diazo alcohol (**10**) gave only the C–H insertion product, the cyclopentanone (**27**) on treatment with rhodium(II) acetate, the formation of the 9-membered ring ether presumably being too unfavourable on entropic grounds. The Boc- and pivaloylamino diazo compounds (**12**), (**13**), and (**14**) also gave only the corresponding cyclopentanones (**28**), (**29**), and (**30**) (Table 3), the products of C–H insertion. In these cases it is probably the fact that the Boc- or pivaloyl-protected nitrogen is too hindered and non-nucleophilic to intercept the electrophilic rhodium carbenoid that results in exclusive C–H insertion. The formation of 4-, 5-, and 6-membered rings by rhodium carbenoid insertion into N–H bonds has been reported,[8,9] although competing C–H insertion has also been noted.[9] Attempts to remove the Boc group from the diazo compound (**12**) before cyclisation using trifluoroacetic acid in dichloromethane were unsuccessful.

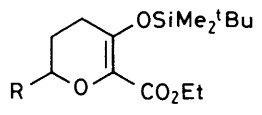
Although diazocarbonyl compounds are more stable to acids than simple diazoalkanes, they can be decomposed by carboxylic acids, particularly in the presence of catalysts.[10] Therefore compounds (**15**) and (**16**) with a terminal carboxylic acid group were expected to undergo intramolecular reaction with the diazo group to give lactones on treatment with rhodium(II) acetate. However, this proved not to be the case, and no characterisable products were isolated from the rhodium (or copper) catalysed decomposition of the diazo acids (**15**) and (**16**), even in the presence of base. However, we were able to effect a cyclisation of a rhodium carbenoid to a carboxylic acid in a different system. The diazo acid (**31**), prepared by ring opening of diazodimedone with hydroxide ion,[11] cyclised to the keto lactone (**32**) (67%) on treatment with rhodium(II) acetate or with boron trifluoride–diethyl ether.[12] The successful cyclisation of the diazo acid (**31**), which contrasts with the failure of the diazo acid (**16**) to cyclise under similar conditions, is possibly due to either the influence of the gem-dimethyl group,[13] or the modified nature of the rhodium carbenoid intermediate which lacks the ester group.

Finally, we attempted to cyclise the diazo alcohol (**18**), derived by ring opening of propylene carbonate. No simple 7-membered ring compound, derived by O–H insertion, was isolated. Instead, a complex mixture was formed which

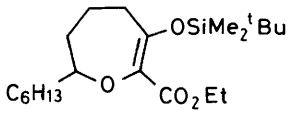
(31) (32)

contained two unknown compounds derived by attack on the benzene solvent, and by dimerisation of the 'carbene'.

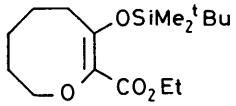
As before,[1] the spectral analysis of the cyclic β-keto esters was complicated by the presence of both keto and enol forms. However, the spectra of the corresponding silyl derivatives were considerably simplified. Thus the cyclic ethers (**19a**), (**19b**), (**20b**), (**22**), and (**25**) were converted into the silyl derivatives (**33a**), (**33b**), (**34**), (**35**), and (**36**) by reaction with t-butyldimethylsilyl trifluoromethanesulphonate (TBDMSOTf). The cyclopentanones (**26**) and (**28**) were also silylated to give silyl enol ethers (**37**) and (**38**); in addition, the cyclopentanone (**26**) readily lactonised on treatment with camphorsulphonic acid in benzene to give the tricyclic lactone (**39**).



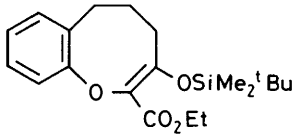
(33a) R = H
(33b) R = Me



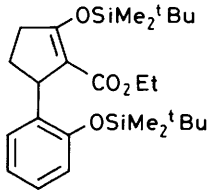
(34)



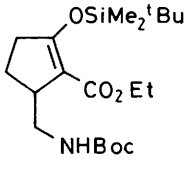
(35)



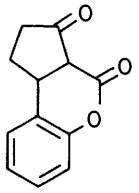
(36)



(37)



(38)



(39)

Conclusions.—The reaction of ethyl lithiodiazoacetate with lactones, lactams, and cyclic anhydrides and carbonates provides a simple one step route to a range of ω-functionalised α-diazo-β-keto esters. The subsequent rhodium carbenoid mediated cyclisation reactions of the diazo compounds derived from lactones gives 6-, 7-, and 8-membered cyclic ethers, and hence the overall reaction represents a 2-step procedure for the ring expansion of lactones by 'insertion' of the $CHCO_2Et$ unit into the lactone O–CO bond. Not surprisingly the yield of cyclisation to 8-membered rings is lower and attempts to form larger rings were thwarted by competing C–H insertion reactions to give cyclopentanones. Cyclopentanones are also formed when the terminal nucleophilic group is bulky and non-nucleophilic.

Experimental

270 MHz ^1H N.m.r. spectra were run on a JEOL GSX270 spectrometer. Internal reaction temperatures were measured with a Comark digital temperature probe. Distillations were carried out in a Kugelrohr apparatus, and the temperatures quoted refer to the oven temperature. For other general points, see ref. 1.

In quoting the ^1H n.m.r. spectroscopic data for compounds that exist as keto/enol mixtures, the 'theoretical' integral is given for signals corresponding to the individual keto and enol forms; the observed integral is the theoretical value multiplied by the percentage of keto or enol form present.

Lithium Di-isopropylamide (LDA).—Solutions of LDA in THF were prepared in the normal way by addition of butyllithium (in hexane) to a stirred solution of dry di-isopropylamine in dry THF, with cooling if necessary. All LDA solutions were used within 30 min of their preparation.

Preparation of Starting Materials. Lactones.—γ-Butyrolactone, γ-valerolactone, δ-valerolactone, undecanoic acid δ-lactone, ε-caprolactone, and dihydrocoumarin are commercially available. 5,6-Dihydropyran-2-one[14] and 2,3,4,7-tetrahydrooxepin-2-one[15] were prepared by the literature methods. Heptanolactone[16] and 2,3,4,5-tetrahydrobenz[*b*]oxepin-2-one[17] were prepared by Baeyer-Villiger oxidation of the corresponding ketones with 3-chloroperbenzoic acid.

5,6-*Dihydrobenz*[b]*oxecin-2-one.* A mixture of 10,11-dihydrodibenzo[*a,d*]cyclohepten-5-one (5.0 g, 24 mmol) and 3-chloroperbenzoic acid (6.2 g, 1.5 equiv.) was heated at reflux in chloroform (45 ml) for 48 h. The organic phase was washed successively with sodium metabisulphite (10%) and saturated sodium hydrogen carbonate, dried, and evaporated. Chromatography of the residue gave the *title compound* (1.90 g, 35%), m.p. 112.5–114.5 °C (Found: C, 80.2; H, 5.2. $C_{15}H_{12}O_2$ requires C, 80.3; H, 5.4%); $\nu_{max.}$(Nujol) 1 734 and 1 066 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 3.10—3.26 (4 H, m), 6.96—7.15 (6 H, m), and 7.19—7.34 (2 H, m); *m/z* (120 °C) 224 (M^+, 100%), 206 (52), 118 (66), and 90 (32).

Lactams.—*N*-Boc Lactams were prepared according to the following general procedure. Di-t-butyl dicarbonate (Boc_2O) (11 mol) was added to a solution of the lactam (10 mmol) in acetonitrile (6 ml). 4-Dimethylaminopyridine (DMAP) (1 mmol) was added and the reaction mixture was stirred at room temperature overnight (*ca.* 18 h). The acetonitrile was evaporated and the residue purified by filtration through a pad of silica, eluting with ether–light petroleum, to give the product as a clear oil. The product could be further purified by distillation.

N-*t-Butoxycarbonyl-δ-valerolactam.* DMAP (140 mg) was added to a solution of δ-valerolactam (1.00 g, 10.2 mmol) and Boc_2O (2.45 g, 11.2 mmol) in acetonitrile (10 ml). After 24 h, the reaction mixture was concentrated and the residue purified by chromatography and distillation to give the *title compound* (1.49 g, 74%) as a low melting solid, b.p. 110 °C at 0.1 mmHg (Found: C, 60.5; H, 8.7; N, 7.0. $C_{10}H_{17}NO_3$ requires C, 60.3; H, 8.6; N, 7.0%); $\nu_{max.}$(film) 1 718br, 1 288, 1 249, 1 158, and 1 138 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.47 (9 H, s, Bu^t), 1.68—1.84 (4 H, m, CH_2CH_2), 2.44 (2 H, t, *J* 7.5 Hz, CH_2CO), and 3.59 (2 H, t, *J* 7.5 Hz, CH_2N); *m/z* (150 °C) 199 (M^+, 1%), 184 (1), 144 (39), 126 (16), 99 (36), and 57 (100).

N-*t-Butoxycarbonyl-ε-caprolactam.* DMAP (120 mg) was added to a solution of ε-caprolactam (1.00 g, 8.8 mmol) and Boc_2O (2.12 g, 9.7 mmol) in acetonitrile (6 ml). After 18 h, the solvent was evaporated and the residue chromatographed to give the *title compound* (1.27 g, 67%) as a clear oil, b.p. 120 °C at 0.03 mmHg (Found: C, 61.9; H, 9.2; N, 6.3. $C_{11}H_{19}NO_3$ requires

C, 61.9; H, 9.0; N, 6.6%); $\nu_{max.}$(film) 1 769, 1 714, and 1 153 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.51 (9 H, s, Bu^t), 1.60—1.83 (6 H, m, CH_2CH_2), 2.63 (2 H, m, CH_2CO), and 3.74 (2 H, m, CH_2N); *m/z* (170 °C) 213 (M^+, 1%), 198 (1), 158 (36), 140 (16), 114 (24), 85 (41), and 57 (100).

N-t-Butylcarbonyl-δ-valerolactam. A solution of δ-valerolactam (0.90 g, 9.08 mmol) and triethylamine (1.6 ml, 11 mmol) in THF (10 ml) was cooled to 0 °C, and pivaloyl chloride (1.3 ml, 10.5 mmol) added dropwise; a white solid was immediately precipitated. The suspension was stirred for 18 h at room temperature, filtered through Celite, and the Celite washed with cold ether. The filtrate and washings were evaporated to give a crude product which was purified by chromatography to give the *title compound* (1.595 g, 96%) as a low melting solid, b.p. 90 °C at 0.2 mmHg (Found: C, 65.5; H, 9.5; N, 7.8. $C_{10}H_{17}NO_2$ requires C, 65.5; H, 9.4; N, 7.6%); $\nu_{max.}$(film) 1 685br, 1 290, and 1 167 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.19 (9 H, s, Bu^t), 1.69—1.83 (4 H, m, CH_2CH_2), 2.37 (2 H, m, CH_2CO), and 3.41 (2 H, m, CH_2N); *m/z* (100 °C) 183 (M^+, 6%), 168 (4), 128 (29), 99 (92), and 57 (100).

General Procedures for the Preparation of the Diazo Compounds.—(a) *Normal addition.* Ethyl diazoacetate (EDA) (3.3 mmol) was added dropwise over *ca.* 5 min to a cold solution of LDA (3.3 mmol) in THF (20 ml), under an atmosphere of nitrogen, the temperature being maintained at −90 °C. The orange-brown solution was stirred at −90 °C for 10—15 min and this was followed by dropwise addition of a lactone (3.0 mmol) at −90 °C. The solution was stirred for 1 h at −90 °C, allowed to warm to −75 °C, and finally stirred for 1 h at −75 °C before dropwise addition of acetic acid (10 mmol). The reaction mixture was allowed to warm to 0 °C, water (10 ml) was added, and the contents transferred to a separating funnel. The solution was acidified to pH 5 with dilute hydrochloric acid, if required, and then extracted with dichloromethane (×3). The combined organic extracts were washed successively with water, brine, dried ($MgSO_4$), and evaporated and the crude product was purified by flash chromatography on silica gel.

(b) *Inverse addition.* A solution of LDA (3.3 mmol) in THF (10 ml) was added dropwise to a solution of ethyl diazoacetate (3.3 mmol) and a lactone (3.0 mmol) in THF (15 ml) over a period of 10—60 min the temperature being maintained below −72 °C. The solution was stirred for 3 h at −75 °C and the acetic acid (6 mmol) added dropwise. The product was extracted and purified as described as above.

Ethyl 2-Diazo-6-hydroxy-3-oxohexanoate (**3a**).—EDA (0.67 ml, 6.39 mmol) was added dropwise to a solution of LDA (6.39 mmol) in THF (25 ml) at −91 °C. The solution was stirred for 15 min, and then γ-butyrolactone (0.45 ml, 5.81 mmol) was added dropwise over 8 min. The temperature was maintained at −90 °C for 0.5 h, and then warmed to −75 °C for 1.5 h before dropwise addition of acetic acid (0.44 ml). Work-up and chromatography gave the *title compound* (**3a**) (544 mg, 47%) as a pale yellow oil (Found: C, 48.1; H, 6.2; N, 13.9. $C_8H_{12}N_2O_4$ requires C, 48.0; H, 6.0; N, 14.0%); $\nu_{max.}$(film) 3 425, 2 137, 1 718, 1 655, and 1 304 cm^{-1}; δ_H(90 MHz; $CDCl_3$) 1.35 (3 H, t, *J* 7 Hz, CH_2Me), 1.92 (2 H, quin, *J* 6.5 Hz, CH_2CH_2OH), 2.65 (1 H, br, OH), 2.99 (2 H, t, *J* 6.5 Hz, CH_2CO), 3.70 (2 H, t, *J* 6.5 Hz, CH_2OH), and 4.34 (2 H, q, *J* 7 Hz, CH_2Me); *m/z* (f.a.b.; $CHCl_3$–glycerol) 201 (MH^+, 100%), 183 (49), and 127 (67); *m/z* (60 °C) 172 ($M^+ - N_2$, 1%).

Ethyl 2-Diazo-6-hydroxy-3-oxoheptanoate (**3b**).—EDA (0.87 ml, 8.24 mmol) was added dropwise to a solution of LDA (8.24 mmol) in THF (40 ml) at −91 °C. The solution was stirred for 10 min and then γ-valerolactone (0.71 ml, 7.49 mmol) was added dropwise over 10 min. The temperature was maintained at −90 °C for 1 h and then kept at −75 °C for 3 h before the addition of acetic acid (0.65 ml). Work-up and chromatography gave the *title compound* (**3b**) (811 mg, 51%) as a pale yellow oil, which solidified at 4 °C (Found: C, 50.4; H, 6.8; N,13.2. $C_9H_{14}N_2O_4$ requires C, 50.5; H, 6.6; N, 13.1%); $\nu_{max.}$(film) 3 426, 2 137, 1 719, 1 656, and 1 305 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.19 (3 H, d, *J* 6.1 Hz, $CHMe$), 1.32 (3 H, t, *J* 6.9 Hz, CH_2Me), 1.77 (2 H, m, $CHCH_2$), 2.40 (1 H, br, OH), 2.96 (2 H, t, *J* 7.2 Hz, CH_2CO), 3.78 (1 H, sextet, *J* 6.1 Hz, $CHOH$), and 4.30 (2 H, q, *J* 6.9 Hz, CH_2Me); *m/z* (f.a.b.; thiodiethanol) 215 (MH^+, 100%), 197 (69), 127 (96), and 99 (68); *m/z* (60 °C) 197 (M^+ − OH, 4%) and 186 ($M^+ - N_2$, 3).

Ethyl 2-Diazo-7-hydroxy-3-oxoheptanoate (**4a**).—A solution of LDA (7.34 mmol) in THF (10 ml) was added dropwise to a solution of EDA (838 mg, 7.34 mmol) and δ-valerolactone (700 mg, 6.99 mmol) in THF (35 ml) over 0.75 h at −90 °C. The solution was allowed to warm to −75 °C over 1 h and then stirred for 1.25 h before acetic acid (0.46 ml) was added. Work-up and chromatography gave the *title compound* (**4a**) (1.18 g, 81%) as a pale yellow oil, b.p. 110 °C at 0.2 mmHg (decomp.) (Found: C, 50.6; H, 6.8; N, 13.0, $C_9H_{14}N_2O_4$ requires C, 50.5; H, 6.6; N, 13.1%); *m/z* 196.0844 ($M - H_2O$ requires 196.0848); $\nu_{max.}$(film) 3 426, 2 136, 1 718, 1 656, and 1 305 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7.0 Hz, CH_2Me), 1.41—1.78 (4 H, m, CH_2CH_2), 2.05 (1 H, br, OH), 2.86 (2 H, t, *J* 6.7 Hz, CH_2CO), 3.61 (2 H, t, *J* 6.7 Hz, CH_2OH), and 4.28 (2 H, q, *J* 7.0 Hz, CH_2Me); δ_C (62.9 MHz; $CDCl_3$) 192.1, 160.9, 75.3, 61.5, 60.9, 39.2, 31.7, 20.3, and 13.7; *m/z* (90 °C) 215 (MH^+, 2%), 196 (5), 184 (1), 169 (1), 156 (15), 130 (27), and 101 (31).

Ethyl 2-Diazo-7-hydroxy-3-oxotridecanoate (**4b**).—A solution of LDA (1.50 mmol) in THF (5 ml) was added dropwise to a solution of EDA (171 mg, 1.50 mmol) and undecanoic δ-lactone (184 mg, 1.00 mmol) in THF (7.5 ml) over a period of 15 min at −75 °C. The solution was stirred for 4 h after which acetic acid (0.1 ml) was added. Work-up and chromatography gave the *title compound* (**4b**) (295 mg, 99%) as a pale yellow oil which solidified at 4 °C (Found: C, 60.4; H, 8.9; N, 9.2. $C_{15}H_{26}N_2O_4$ requires C, 60.4; H, 8.8; N, 9.4%); *m/z* 270.1831 ($M - N_2$ requires 270.1831); $\nu_{max.}$(film) 3 449, 2 134, 1 720, 1 657, and 1 303 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.87 (3 H, m, CH_2CH_2Me), 1.32 (3 H, t, *J* 7.1 Hz, CH_2Me), 1.20—1.54 (12 H, m), 1.63—1.84 (2 H, m), 1.87 (1 H, br, OH), 2.73—2.97 (2 H, m, CH_2CO), 3.52—3.63 (1 H, m, $CHOH$), and 4.27 (2 H, q, *J* 7.1 Hz, CH_2Me); δ_C(62.9 MHz; $CDCl_3$) 192.5, 161.1, 75.5, 70.9, 61.1, 39.8, 37.3, 36.6, 31.6, 29.1, 25.4, 22.3, 20.2, 14.0, and 13.7; *m/z* (f.a.b.; glycerol) 299 (MH^+, 100%) and 281 (75); *m/z* (90 °C) 280 ($M^+ - H_2O$, 2%), 270 ($M^+ - N_2$, 21), 252 (11), 224 (3), 213 (13), 185 (33), 166 (29), and 99 (100).

(Z)-Ethyl 2-Diazo-7-hydroxy-3-oxohept-4-enoate (**5**).—A solution of LDA (5.33 mmol) in THF (7.5 ml) was added dropwise to a solution of EDA (608 mg, 5.33 mmol) and 5,6-dihydropyran-2-one (350 mg, 3.55 mmol) in THF (10 ml) over 25 min at −74 °C. The solution was stirred for 3.25 h after which acetic acid (0.45 ml) was added. Work-up and chromatography gave the *title compound* (**5**) (66 mg, 6%) as a yellow oil (Found: M^+, 212.0793. $C_9H_{12}N_2O_4$ requires *M*, 212.0797); $\nu_{max.}$(film) 3 443, 2 138, 1 718, 1 653, 1 611, and 1 303 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.33 (3 H, t, *J* 7.1 Hz, CH_2Me), 1.69 (1 H, br, OH), 2.81 (2 H, dq, *J* 6.2, 1.3 Hz, $=CHCH_2$), 3.80 (2 H, t, *J* 5.9 Hz, CH_2OH), 4.30 (2 H, q, *J* 7.1 Hz, CH_2Me), 6.31 (1 H, dt, *J* 11.9, 8.1 Hz, $=CH$), and 7.19 (1 H, dt, *J* 11.7, 1.3 Hz, $=CH$); *m/z* (90 °C) 212 (M^+, 22%), 182 (65), 125 (21), 108 (58), and 99 (74).

Ethyl 2-Diazo-5-(2-hydroxyphenyl)-3-oxopentanoate (**6**).—A solution of LDA (5.25 mmol) in THF (15 ml) was added

dropwise to a solution of EDA (608 mg, 5.25 mmol) and dihydrocoumarin (520 mg, 3.50 mmol) in THF (10 ml) at −72 °C over 8 min. The solution was stirred at −75 °C for 5 h after which a solution of acetic acid (1.0 ml) in ether (4 ml) was added. Work-up and chromatography gave the *title compound* (**6**) (740 mg, 80%) as a pale yellow solid, m.p. 85—87 °C (from ether) (Found: C, 59.7; H, 5.4; N, 10.6. $C_{13}H_{14}N_2O_4$ requires C, 59.5; H, 5.4; N, 10.7%); $\nu_{max.}$(Nujol) 3 200, 2 140, 1 712, and 1 627 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.33 (3 H, t, *J* 7.1 Hz, CH_2*Me*), 2.92 (2 H, t, *J* 6.4 Hz, CH_2CO), 3.22 (2 H, t, *J* 6.4 Hz, CH_2Ar), 4.30 (2 H, q, *J* 7.1 Hz, CH_2Me), 6.81—6.92 (2 H, m, ArH), 7.06—7.16 (2 H, m, ArH), and 7.80 (1 H, br, OH); *m/z* (130 °C) 262 (M^+, 28%), 234 (3), 177 (16), 160 (14), 120 (45), and 107 (100).

Ethyl 2-*Diazo*-8-*hydroxy*-3-*oxo*-*octanoate* (**7**).—A solution of LDA (1.20 mmol) in THF (5 ml) was added dropwise to a solution of EDA (171 mg, 1.20 mmol) and ε-caprolactone (114 mg, 1.00 mmol) in THF (5 ml) over a period of 0.5 h at −67 °C. The solution was stirred for 3.5 h after which water (1.5 ml) was added. Work-up and chromatography gave the *title compound* (**7**) (143 mg, 63%) as a pale yellow oil (Found: C, 52.8; H, 7.4; N, 12.3. $C_{10}H_{16}N_2O_4$ requires C, 52.6; H, 7.1; N, 12.3%); *m/z* 228.1114 (*M* requires 228.1110); $\nu_{max.}$(film) 3 423, 2 136, 1 718, 1 655, and 1 304 cm^{-1}; δ_H(90 MHz; $CDCl_3$) 1.32 (3 H, t, *J* 7 Hz, CH_2*Me*), 1.20—1.90 (6 H, m), 2.70 (1 H, br, OH), 2.85 (2 H, t, *J* 6.5 Hz, CH_2CO), 3.62 (2 H, t, *J* 6.5 Hz, CH_2OH), and 4.34 (2 H, q, *J* 7 Hz, CH_2Me); *m/z* (80 °C) 228 (M^+, 1%), 200 (2), 183 (1), 156 (100), 115 (21), and 99 (40).

(Z)-*Ethyl* 2-*Diazo*-8-*hydroxy*-3-*oxo*-*oct*-6-*enoate* (**8**).—A solution of LDA (4.91 mmol) in THF (15 ml) was added dropwise to a solution of EDA (560 mg, 4.91 mmol) and 2,3,4,7-tetrahydro-oxepin-2-one (500 mg, 4.46 mmol) in THF (15 ml) over 25 min at −73 °C. The solution was stirred at −75 °C for 4 h, after which saturated aqueous ammonium chloride (4 ml) was added. Work-up and chromatography gave the *title compound* (**8**) (588 mg, 58%) as a pale yellow oil (Found: C, 53.0; H, 6.4; N, 12.3. $C_{10}H_{14}N_2O_4$ requires C, 53.1; H, 6.2; N, 12.44%); $\nu_{max.}$(film) 3 420, 2 140, 1 720, 1 655, and 1 303 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.31 (3 H, t, *J* 7.3 Hz, CH_2*Me*), 2.29 (1 H, br, OH), 2.42 (2 H, m, =CHCH_2), 2.93 (2 H, t, *J* 6.6 Hz, CH_2CO), 4.17 (2 H, dd, *J* 6.8, 0.8 Hz, CH_2OH), 4.27 (2 H, q, *J* 7.3 Hz, CH_2Me), 5.46 (1 H, dtt, *J* 10.6, 7.6, 1.0 Hz, CH_2CH_2C*H*=), and 5.66 (1 H, dtt, *J* 10.9, 6.8, 1.3 Hz, =C*H*CH_2OH); *m/z* (f.a.b.; glycerol) 227 (MH^+).

Ethyl 2-*Diazo*-6-(2-*hydroxyphenyl*)-3-*oxohexanoate* (**9**).—A solution of LDA (3.99 mmol) in THF (10 ml) was added dropwise to a solution of EDA (455 mg, 3.99 mmol) and 2,3,4,5-tetrahydrobenz[*b*]oxepin-2-one (432 mg, 2.66 mmol) in THF (10 ml) at −70 °C over 8 min. The solution was stirred for 3 h at −75 °C after which water (1.0 ml) was added. Work-up and chromatography gave the *title compound* (**9**) (414 mg, 56%) as a cream solid, m.p. 94—95 °C (from ether) (Found: C, 61.1; H, 6.0; N, 9.9. $C_{14}H_{16}N_2O_4$ requires C, 60.9; H, 5.8; N, 10.1%) $\nu_{max.}$(Nujol) 3 380, 2 142, 1 680, and 1 650 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.32 (3 H, t, *J* 7.1 Hz, CH_2Me), 1.82—1.96 (2 H, m, CH_2CH_2Ar), 2.58 (2 H, t, *J* 7.9 Hz, CH_2Ar), 2.94 (2 H, t, *J* 6.2 Hz, CH_2CO), 4.29 (2 H, q, *J* 7.1 Hz, CH_2Me), 6.80 (1 H, dt, *J* 7.1, 1.1 Hz), 6.86 (1 H, dd, *J* 8.3, 0.9 Hz), 7.03—7.14 (2 H, m), and 7.18 (1 H, s, OH); *m/z* (100 °C) 276 (M^+, 50%), 248 (6), 203 (6), 174 (22), 169 (62), 147 (34), 120 (52), and 107 (100).

Ethyl 2-*Diazo*-9-*hydroxy*-3-*oxononanoate* (**10**).—A solution of LDA (3.58 mmol) in THF (20 ml) was added dropwise to a solution of EDA (449 mg, 3.94 mmol) and heptanolactone (459 mg, 3.58 mmol) in THF (30 ml) over 10 min. The solution was stirred for 3 h at −75 °C after which acetic acid (0.35 ml) was added. Work-up and chromatography gave the *title compound* (**10**) (563 mg, 65%) as a pale yellow oil (Found: C, 54.4; H, 7.7; N, 11.6. $C_{11}H_{18}N_2O_4$ requires C, 54.5; H, 7.5; N, 11.6%); $\nu_{max.}$(film) 3 423, 2 136, 1 718, 1 656, and 1 304 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7.1 Hz, CH_2*Me*), 1.20—1.67 (8 H, m), 1.78 (1 H, br, OH), 2.80 (2 H, t, *J* 7.4 Hz, CH_2CO), 3.58 (2 H, t, *J* 6.4 Hz, CH_2OH), and 4.24 (2 H, q, *J* 7.1 Hz, CH_2Me); *m/z* (f.a.b.; neat) 243 (MH^+).

Ethyl 2-*Diazo*-3-[(2-*hydroxyphenyl*)*ethyl*]*phenyl*-3-*oxopropanoate* (**11**).—A solution of LDA (3.23 mmol) in THF (10 ml) was added to a solution of EDA (0.34 ml, 3.23 mmol) and 5,6-dihydrodibenzo[*b*;*f*]oxecin-2-one (482 mg, 2.15 mmol) over 35 min at −75 °C. The solution was stirred for 3 h before acetic acid (0.2 ml) was added. Work-up and chromatography gave (i) the lactone substrate (68 mg, 14%) and (ii) the *title compound* (**11**) (60 mg, 8%) as a viscous yellow oil (Found: M^+, 338.1267. $C_{19}H_{18}N_2O_4$ requires *M*, 338.1267); $\nu_{max.}$(film) 3 427, 2 147, 1 727, 1 709, 1 631, 1 610, and 1 314 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.20 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 2.75—2.97 (4 H, m), 4.20 (2 H, q, *J* 7.0 Hz, CH_2Me), and 6.95–-7.55 (9 H, m, ArH and OH); *m/z* (150 °C) 338 (M^+, 12%), 310 (16), 294 (10), 264 (28), 220 (46), and 107 (100).

Ethyl 7-(*t*-*Butoxycarbonylamino*)-2-*diazo*-3-*oxoheptanoate* (**12**).—A solution of LDA (2.45 mmol) in THF (10 ml) was added dropwise to a solution of EDA (284 mg, 2.45 mmol) and *N*-t-butoxycarbonyl-δ-valerolactam (450 mg, 2.26 mmol) in THF (10 ml) at −71 °C over 26 min. The solution was stirred for 3 h at −70 °C after which saturated aqueous ammonium chloride (3.5 ml) was added. Work-up and chromatography gave the *title compound* (**12**) (425 mg, 60%) as a low-melting yellow solid, m.p. 33—36 °C (from hexane-ether) (Found: C, 54.0; H, 7.4; N, 13.3. $C_{14}H_{23}N_3O_5$ requires C, 53.7; H, 7.4; N, 13.4%); $\nu_{max.}$(melt) 3 351, 2 150, 1 713, 1 683, 1 659, and 1 171 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.1 Hz, CH_2*Me*), 1.39 (9 H, s, Bu^t), 1.30—1.70 (4 H, m), 2.80 (2 H, t, *J* 7.3 Hz, CH_2CO), 3.08 (2 H, q, *J* 6.4 Hz, CH_2N), 4.24 (2 H, q, *J* 7.1 Hz, CH_2Me), and 4.65 (1 H, br, NH); *m/z* (f.a.b.; glycerol) 314 (MH^+), 258 (29), 214 (12), 140 (37), and 57 (100).

Ethyl 8-(*t*-*Butoxycarbonylamino*)-2-*diazo*-3-*oxo*-*octanoate* (**13**).—A solution of LDA (2.49 mmol) in THF (10 ml) was added dropwise to a solution of EDA (284 mg, 2.49 mmol) and *N*-t-butoxycarbonyl-ε-caprolactam (482 mg, 2.26 mmol) over 20 min at −72 °C. The solution was stirred for 3 h at −75 °C and after which acetic acid (0.2 ml) was added. Work-up and chromatography gave the *title compound* (**13**) (543 mg, 73%) as a viscous yellow oil (Found: M^+, 254.1140. $C_{15}H_{25}N_3O_5 - C_4H_9O$ requires *M*, 254.1141); $\nu_{max.}$(film) 3 388, 2 135, 1 717, 1 655, and 1 175 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7.1 Hz, CH_2*Me*), 1.40 (9 H, s, Bu^t), 120—1.52 (4 H, m), 1.61 (2 H, quin, *J* 7.3 Hz, CH_2CH_2N), 2.81 (2 H, t, *J* 7.1 Hz, CH_2CO), 3.08 (2 H, t, *J* 6.5 Hz, CH_2N), 4.26 (2 H, q, *J* 7.1 Hz, CH_2Me), and 4.52 (1 H, br, NH); *m/z* (70 °C) 271 (M^+ − Bu^t, 1%), 254 (7), 243 (2), 226 (6), 158 (11), 140 (12), and 57 (100).

Ethyl 7-(*t*-*Butylcarbonylamino*)-2-*diazo*-3-*oxoheptanoate* (**14**).—EDA (0.37 ml, 3.51 mmol) was added dropwise to a solution of LDA (3.51 mmol) in THF (25 ml) over 2 min at −92 °C. The solution was stirred for 15 min after which a solution of *N*-t-butylcarbonyl-δ-valerolactam (585 mg, 2.19 mmol) in THF (3 ml) was added over 8 min. The temperature was maintained at −90 °C for 1 h, increased to −75 °C for 2 h, and finally raised to −25 °C over 5 min, before acetic acid (0.25 ml) was added. Work-up and chromatography gave (i) the δ-lactam substrated (145 mg, 25%) and (ii) the *title compound* (**14**) (174 mg, 18%) as a yellow oil (Found: M^+, 297.1691.

$C_{14}H_{23}N_3O_4$ requires *M*, 297.1689); $\nu_{max.}$(film) 3 351, 2 134, 1 719, 1 646, 1 531, and 1 303 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.16 (9 H, s, Bu^t), 1.30 (3 H, t *J* 6.7 Hz, CH_2*Me*), 1.42—1.70 (4 H, m), 2.83 (2 H, t, *J* 7.0 Hz, CH_2CO), 3.22 (2 H, q, *J* 6.1 Hz, CH_2N), 4.25 (2 H, q, *J* 6.7 Hz, CH_2Me), and 5.93 (1 H, br, NH); *m/z* (f.a.b.; glycerol) 298 (MH^+), 270 (16), 140 (18), 100 (14), and 57 (100).

1-*Ethyl* 6-*Hydrogen* 2-*Diazo*-3-*oxohexanedioate* (**15**).—EDA (0.58 ml, 5.50 mmol) was added dropwise to a solution of LDA (5.50 mmol) in THF (20 ml) at −95 °C. After 15 min a solution of succinic anhydride (500 mg, 5.00 mmol) in a mixture of THF (4 ml) and 1,3-dimethyltetrahydropyrimidin-3-one (1 ml) was added over a period of 10 min at −90 °C. The solution was stirred for 1 h at −90 °C and then 0.5 h at −75 °C, after which water was added. The aqueous phase was saturated with sodium hydrogencarbonate and extracted with dichloromethane. The aqueous phase was acidified with hydrochloric acid (2M) and extracted with dichloromethane (×3). The organic phase was washed with water and brine, dried ($MgSO_4$) and evaporated. Chromatography of the residue gave the *title compound* (**15**) (459 mg, 43%) as a pale yellow solid, m.p. 71—74 °C (from hexane–ether) (Found: C, 45.1; H, 4.7; N, 12.8. $C_8H_{10}N_2O_5$ requires C, 44.9; H, 4.7; N, 13.1%); $\nu_{max.}$(melt) 3 100br, 2 141, 1 718br, 1 656, and 1 310 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.34 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 2.70 (2 H, t, *J* 6.5 Hz, CH_2CO), 3.17 (2 H, t, *J* 6.5 Hz, CH_2CO_2H), and 4.30 (2 H, q, *J* 7.0 Hz, CH_2Me); CO_2H not observed; *m/z* (90 °C) 214 (M^+, 7%), 197 (5), 187 (17), 169 (3), 112 (32), and 101 (100); *m/z* (f.a.b.; glycerol) 215 (MH^+, 100%).

1-*Ethyl* 6-*Hydrogen* 2-*Diazo*-3-*oxoheptanedioate* (**16**).—A solution of LDA (3.30 mmol) in THF (10 ml) was added dropwise to a solution of EDA (0.35 ml, 3.30 mmol) and glutaric anhydride (342 mg, 3.00 mmol) at −75 °C over a period of 25 min. The solution was stirred for 2 h after which acetic acid (0.21 ml) was added. Work-up and chromatography gave the *title compound* (**16**) (244 mg, 36%) as a yellow solid, m.p. 48—50 °C (from hexane–ether) (Found: C, 47.3; H, 5.3; N, 12.1. $C_9H_{12}N_2O_5$ requires C, 47.4; H, 5.3; N, 12.3%); $\nu_{max.}$(melt) 3 000br, 2 144, 1 707, 1 659, and 1 313 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.26 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 1.90 (2 H, quin, *J* 7.2 Hz, CH_2CH_2CO), 2.36 (2 H, t, *J* 7.2 Hz, CH_2CO), 2.86 (2 H, t, *J* 7.2 Hz, CH_2CO_2H), 4.23 (2 H, q, *J* 7.0 Hz, CH_2Me), and 11.10 (1 H, br, CO_2H); *m/z* (80 °C) 228 (M^+, 14%), 200 (1), 183 (1), 156 (58), 115 (100), and 87 (56).

Ethyl 3-(2-*Carboxyphenyl*)-2-*diazo*-3-*oxopropanoate* (**17**).—A solution of LDA (4.10 mmol in THF (12 ml) was added dropwise to a solution of EDA (470 mg, 4.10 mmol) and phthalic anhydride (551 mg, 3.72 mmol) in THF (15 ml) at −75 °C over 15 min. After 2 h at −75 °C, acetic acid (0.26 ml) was added. Work-up and chromatography gave the *title compound* (**17**) (251 mg, 26%) as a viscous oil (Found: M^+, 234.0531. $C_{12}H_{10}N_2O_5$–N_2 requires *M*, 234.0528); $\nu_{max.}$(film) 3 300, 2 147, 1 725, 1 640, and 1 305 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 1.10 (3 H, t, *J* 7 Hz, CH_2*Me*), 4.10 (2 H, q, *J* 7 Hz, CH_2Me), 7.2—8.3 (4 H, m, ArH), and 10.2 (1 H, br, CO_2H); *m/z* (70 °C) 234 ($M^+ - N_2$, 2%), 228 (22), and 149 (100).

Ethyl 3-*Hydroxypropyl Diazomalonate* (**18**).—EDA (472 mg, 4.14 mmol) was added dropwise to a solution of LDA (4.14 mmol) in THF (20 ml) at 93 °C over 10 min. The mixture was stirred for 15 min after which a solution of 1,3-dioxan-2-one (422 mg, 4.14 mmol) in THF (14 ml) was added to it over 10 min. It was then stirred at −90 °C for 1 h, and then at −75 °C for 2 h, before the addition of acetic acid (0.24 ml). Work-up and extraction give the *title compound* (**18**) (364 mg, 41%) as a yellow oil (Found: M^+, 186.0652. $C_8H_{12}N_2O_5$–CH_2O requires *M*, 186.0641); $\nu_{max.}$(film) 3 510, 2 144, 1 740, 1 697, and 1 323 cm^{-1}; δ_H(250 mHz; $CDCl_3$) 1.26 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 1.90 (2 H, quin, *J* 5.9 Hz, CH_2CH_2OH), 2.80 (1 H, br, OH), 3.70 (2 H, t, *J* 5.3 Hz, CH_2OH), 4.25 (2 H, q, 7.0 Hz, CH_2Me), and 4.36 (2 H, t, *J* 6.1 Hz, CH_2OCO); *m/z* (f.a.b.; glycerol) 217 (MH^+); *m/z* (120 °C) 216 (M^+, 1%), 186 (22), 159 (32), and 59 (18).

General Procedures for the Dirhodium Tetra-acetate Catalysed Decomposition of the Diazo Compounds.—(*a*) A solution of the diazo compound (0.6 mmol) in benzene (10 ml) was added dropwise over 5—60 min, to a rapidly stirred suspension of dirhodium tetra-acetate (2 mg) in refluxing benzene (15 ml) under a nitrogen atmosphere. The suspension was maintained at reflux for a period of 5—30 min after which it was allowed to cool and then filtered through a pad of Celite. Evaporation of the solvent, and distillation or flash chromatography of the residue gave the required product.

(*b*) Dirhodium tetra-acetate (2 mg) was added in one portion to a solution of the diazo compound (0.6 mmol) in dichloromethane (25 ml) at room temperature and the mixture stirred for 0.5—3 h to give a green solution. This was evaporated and the residue either directly purified by chromatography or triturated with light petroleum–ether, filtered through Celite, evaporated, and then distilled.

Ethyl 3-*Oxotetrahydropyran*-2-*carboxylate* (**19a**).—A solution of the diazo compound (**3a**) (185 mg, 0.924 mmol) in benzene (10 ml) was added over 35 min to a suspension of dirhodium tetra-acetate (3.8 mg, 0.9 mol %) in benzene (12 ml) at reflux; the mixture was then maintained at reflux for 1 h. Work-up and distillation gave the *title compound* (**19a**) (91 mg, 57%) as a pale oil, b.p. 90—95 °C at 0.3 mmHg (Found: M^+ 172.0737. $C_8H_{12}O_4$ requires *M*, 172.0736), $\nu_{max.}$(film) 3 440, 1 733, 1 665, 1 626, 1 467, 1 418, 1 309, 1 235, 1 207, and 1 089 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.29 (3 H, t, CH_2*Me*), keto), 1.35 (3 H, t, CH_2*Me*, enol), 1.94 (2 H, m, CH_2CH_2O, enol), 2.07—2.20 (2 H, m, CH_2CH_2O, keto), 2.36 (2 H, t, *J* 6.2 Hz, CH_2CO, enol), 2.58 (2 H, t, *J* 6.2 Hz, CH_2CO, keto), 3.88 (1 H, m, CHHO, keto), 3.93 (2 H, t, *J* 4.8 Hz, CH_2O, enol), 4.14 (1 H, ddd, *J* 11.0, 6.0, 4.0 Hz, CHHO, keto), 4.26 (2 H, q, CH_2Me, keto), 4.30 (2 H, q, CH_2Me, enol), 4.54 (1 H, s, $CHCO_2Et$, keto), and 10.30 (1 H, s, OH, enol); *ca.* 75% enol form; *m/z* (120 °C) 172 (M^+, 6%), 144 (3), 126 (14), 115 (31), 91 (28), 87 (90), and 42 (100).

Ethyl 6-*Methyl*-3-*oxotetrahydropyran*-2-*carboxylate* (**19b**).—A solution of the diazo compound (**3b**) (200 mg, 0.934 mmol) in benzene (9 ml) was added over 12 min to a suspension of dirhodium tetra-acetate (4 mg) in benzene (10 ml) at reflux. Reflux was continued for 5 min. Work-up and distillation gave the *title compound* (**19b**) (139 mg, 80%) as a clear oil, b.p. 90—100 °C at 0.25 mmHg (Found: C, 58.0; H, 7.8. $C_9H_{14}O_4$ requires C, 58.1; H, 7.6%); $\nu_{max.}$(film) 3 428, 1 741, 1 664, 1 626, 1 312, 1 239, 1 208, and 1 052 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.1, CH_2*Me*, keto), 1.30 (3 H, d, *J* 5.8 Hz, Me, keto/enol), 1.33 (3 H, t, *J* 7.1, CH_2*Me*, enol), 1.58—1.74 (1 H, m, CHHCH$_2$O, enol), 1.88 (ddt, *J* 13.2, 7.1, 2.6 Hz, CHHCH$_2$O, enol), 1.95—2.10 (2 H, m, CH_2CH_2O, keto), 2.29 (1 H, ddd, *J* 18.4, 6.6, 2.9 Hz, CHHCO, enol), 2.43 (1 H, ddd, *J* 17.6, 10.3, 7.1 Hz, CHHCO, enol), 2.54 (2 H, m, CH_2CO, keto), 3.77—3.91 (1 H, m, CHMe, enol), 4.15—4.25 (1 H, m, CHMe, keto), 4.28 (2 H, q, *J* 7.1, CH_2Me, keto/enol), 4.56 (1 H, s, $CHCO_2Et$, keto), and 10.39 (1 H, s, OH, enol); *ca.* 80% enol form; *m/z* (140 °C) 186 (M^+, 1%), 158 (4), 140 (2), 129 (26), 101 (57), 83 (27), and 56 (100).

Ethyl 3-*Oxo*-*oxepane*-2-*carboxylate* (**20a**).—A solution of the diazo compound (**4a**) (103 mg, 0.481 mmol) in benzene (13 ml) was added to a suspension of dirhodium tetra-acetate (4.9 mg)

in benzene (14 ml) at room temperature over 20 min. After 5 h the mixture was filtered, concentrated, and distilled to give the *title compound* (**20a**) (57 mg, 64%) as a clear oil, b.p. 90 °C at 0.2 mmHg (Found: C, 57.9; H, 7.8. $C_9H_{14}O_4$ requires C, 58.1; H, 7.6%) $\nu_{max.}$(film) 3 475, 1 748, 1 718, 1 654, 1 618, 1 320, 1 272, 1 182, and 1 132 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.24 (3 H, t, *J* 7.1 Hz, CH_2*Me*, keto), 1.27 (3 H, t, *J* 7.1 Hz, CH_2*Me*, enol), 1.40—2.00 (4 H, m, CH_2CH_2, keto/enol), 2.42—2.52 (2 + 1 H, m, CH_2CO, enol and C*H*HCO, keto), 2.84 (1 H, dt, *J* 11.9, 2.8 Hz, C*H*HCO keto), 3.42 (1 H, ddd, *J* 12.8, 10.0, 2.3 Hz, C*H*HO, keto), 3.73 (2 H, t, *J* 5.0 Hz, CH_2O, enol), 4.10—4.32 (2 + 1 H, m, CH_2Me, keto/enol + C*H*HO, keto), 4.42 (1 H, C*H*CO_2Et, keto), and 10.87 (1 H, s, OH, enol); *ca.* 20% enol form; *ca.* 20% enol form; δ_C (62.9 MHz; $CDCl_3$) 207.9, 166.3, 86.3, 73.3, 72.8, 61.6, 60.6, 41.7, 33.2, 31.9, 30.8, 23.6, 22.7, 13.9, and 13.7; *m/z* (100 °C) 186 (M^+, 66%), 158 (17), 140 (66), 129 (77), 113 (31), 101 (47), 84 (42), 55 (100), and 41 (71).

Ethyl 7-Hexyl-3-oxo-oxepane-2-carboxylate (**20b**).—A solution of the diazo compound (**4b**) (163 mg, 0.547 mmol) in benzene (5 ml) was added dropwise over 4 min to a suspension of dirhodium tetra-acetate (2.8 mg, 1.2 mol %) in benzene (15 ml) at reflux. After 3 min at reflux the suspension was cooled, filtered, concentrated, and distilled to give the *title compound* (**20b**) (113 mg, 76.5%) as a viscous oil, b.p. 170—180 °C at 0.02 mmHg (Found: C, 66.7; H, 9.8. $C_{15}H_{26}O_4$ requires C, 66.6; H, 9.7%); $\nu_{max.}$(film) 1 753, 1 720, 1 690, 1 657, 1 619, 1 319, 1 276, 1 247, and 1 184 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.76—0.90 (3 H, m, $(CH_2)_5$*Me*, keto/enol), 1.29 (3 H, t, *J* 7.1 Hz, CH_2*Me*, keto/enol), 1.15—2.02 (14 H, m, keto/enol), 2.28 (1 H, dd, *J* 14.3, 6.2 Hz, C*H*HCO, enol), 2.46 (1 H, dd, *J* 12.4, 5.7 Hz, C*H*HCO, keto), 2.71 (1 H, ddd, *J* 14.7, 11.4, 1.4 Hz, C*H*HCO, enol), 2.97 (1 H, dt, *J* 12.3, 2.4 Hz, C*H*HCO, keto), 3.27 (1 H, dt, *J* 9.5, 1.9 Hz, CHO, enol), 3.78—3.95 (1 H, m, CHO, keto), 4.13—4.36 (2 H, m, CH_2Me, keto/enol), 4.42 and 4.69 (1 H, s, C*H*CO_2Et, keto), and 10.92 (1 H, s, OH, enol); *ca.* 75% enol form; *m/z* (100 °C) 270 (M^+, 100%), 224 (7), 213 (30), 197 (14), 167 (46), 149 (52), 104 (35), 84 (69), and 55 (54).

Ethyl 3-Oxo-2,3,4,5-tetrahydrobenzoxepin-2-carboxylate (**21**).—A solution of the diazo compound (**6**) (69.5 mg, 0.265 mmol) in benzene (7.5 ml) was added dropwise over 45 min to a suspension of dirhodium tetra-acetate (2.3 mg) in benzene (7.5 ml). The mixture was heated under reflux for 1 h. Work-up and distillation gave the title compound (**21**) as a clear oil (49.5 mg, 80%), b.p. 135 °C at 0.1 mmHg (lit.,[18] 123 °C at 0.1 mmHg); $\nu_{max.}$(film) 3 440, 1 740, 1 722, and 1 442 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.1 Hz, CH_2*Me*, keto), 1.39 (3 H, t, *J* 7.1 Hz, CH_2*Me*, enol), 2.71 (2 H, q, *J* 6.9 Hz, CH_2CO, enol), 2.73 (1 H, dd, *J* 14.4, 7.0 Hz, HC*H*CO, keto), 2.93—3.34 (2 + 1 H, m, ArCH_2, keto/enol and HC*H*CO, keto), 4.27 (2 H, q, *J* 7.1 Hz, CH_2Me, keto), 4.31 (2 H, q, *J* 7.1 Hz, CH_2Me, enol), 4.95 (1 H, s, C*H*CO_2Et, keto), 6.97—7.25 (4 H, m, ArH), and 11.02 (1 H, s, OH, enol); *ca.* 35% enol form; *m/z* (170 °C) 234 (M^+, 10%), 188 (3), 161 (9), 149 (17), 133 (8), and 120 (20).

Ethyl 3-Oxo-oxecane-2-carboxylate (**22**) *and Ethyl 5-(2-Hydroxyethyl)-2-oxocyclopentanecarboxylate* (**23**).—A solution of the diazo compound (**7**) (200 mg, 1.00 mmol) in benzene (10 ml) was added dropwise over 5 min to a suspension of dirhodium tetra-acetate (3 mg) in benzene (10 ml) at reflux. After a further 5 min, the mixture was cooled, filtered, concentrated, and distilled to give the *oxecane* (**22**) (54 mg, 31%) as a clear oil, b.p. 100 °C at 0.4 mmHg (Found: C, 59.7; H, 8.2. $C_{10}H_{16}O_4$ requires C, 60.0; H, 8.1%); $\nu_{max.}$(film) 1 738br, 1 659, 1 621, 1 324, 1 238, and 1 186 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.0 Hz, CH_2*Me*, keto), 1.29 (3 H, t, *J* 7.1 Hz, CH_2*Me*, enol), 1.50—2.26 [6 H, m, $(CH_2)_3CH_2O$, keto/enol], 2.41 (2 H, t, *J* 5.6 Hz, CH_2CO enol), 2.54—2.65 (1 H, m, C*H*HCO, keto), 2.99 (1 H, dt, *J* 11.4, 3.1, C*H*HCO, keto), 3.67 (1 H, ddd, *J* 12.0, 4.5, 1.9 Hz, C*H*HO, keto), 3.84 (2 H, t, *J* 4.8 Hz, CH_2O, enol), 3.99 (1 H, dt, *J* 12.3, 3.7 Hz, C*H*HO, keto), 4.10 (1 H, s, C*H*CO_2Et, keto), 4.13—4.26 (2 H, m, CH_2Me), keto), 4.24 (2 H, q, *J* 7.0 Hz, CH_2Me, enol), and 10.92 (1 H, s, OH, enol); *ca.* 55% enol form; *m/z* (170 °C) 200 M^+, 100%, 154 (38), 143 (66), 126 (22), 115 (29), 97 (48), 69 (97), and 55 (88).

Purification of the distillation residue by chromatography gave the *cyclopentanone* (**23**) (9 mg, 5%) as a viscous oil, b.p. 120 °C at 0.002 mmHg (Found: C, 60.0; H, 8.4. $C_{10}H_{16}O_4$ requires C, 60.0; H, 8.1%); $\nu_{max.}$(fllm) 3 450, 1 752, 1 724, 1 655, 1 193, and 1 127 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 1.41—1.90 (4 H, m, CH_2CH_2), 2.15—2.50 (2 H, m, CH_2), 2.63—2.82 (1 H, m, C*H*CHCO_2Et), 2.86 (1 H, d, *J* 11.3 Hz, C*H*CO_2Et), 3.57—3.74 (2 H, m, CH_2OH), and 4.21 (2 H, q, *J* 7.0 Hz, CH_2Me); *m/z* (120 °C) 200 (M^+, 11%), 182 (2), 171 (18), 155 (73), 127 (72), 109 (55), and 99 (100).

Ethyl 2-(2-Hydroxyethyl)-5-oxocyclopentenecarboxylate (**24**).—A solution of the diazo compound (**8**) (122 mg, 0.539 mmol) in toluene (6.5 ml) was added over 7 min to a solution of palladium(II) acetate (8 mg) in toluene (6.5 ml) at reflux. After a further 5 min, the mixture was cooled, filtered, concentrated, and distilled (*ca.* 220 °C at 0.1 mmHg; partial decomp.). Chromatographic purification of the distillate gave the *title compound* (**24**) (22 mg, 21%) as a viscous oil (Found: M^+, 198.0895. $C_{10}H_{14}O_4$ requires *M*, 198.0892); $\nu_{max.}$(film) 3 451, 1 738, 1 710, 1 621, 1 375, 1 299, and 1 034 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.30 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 2.41—2.49 (2 H, m, CH_2CO), 2.52 (1 H, br, OH), 2.67—2.77 (2 H, m, CH_2C=), 2.95 (2 H, t, *J* 6.0 Hz, CH_2CH_2OH), 3.87 (2 H, t, *J* 6.0 Hz, CH_2OH), and 4.26 (2 H, q, *J* 7.0 Hz, CH_2Me); δ_C(62.9 MHz; $CDCl_3$) 202.6, 183.6, 163.9, 134.7, 61.0, 60.5, 35.8, 35.1, 31.0, and 14.1; *m/z* (190 °C) 198 (M^+, 2%), 180 (3), 168 (45), 153 (31), 152 (34), 122 (100), and 94 (18).

Ethyl 3-Oxo-3,4,5,6-tetrahydrobenzoxocine-2-carboxylate (**25**) *and Ethyl 5-(2-Hydroxyphenyl)-2-oxocyclopentanecarboxylate* (**26**).—(*a*) A solution of the diazo compound (**9**) (121 mg, 0.438 mmol) in benzene (7.5 ml) was added dropwise over 35 min to a suspension of dirhodium tetra-acetate (1.0 mg) in benzene (7.5 ml) at reflux. After 2 h at reflux the suspension was cooled, filtered, concentrated, and the residue chromatographed to give (*i*) the *benzoxocin* (**25**) (13 mg, 12%) as a clear oil, b.p. 150 °C at 0.1 mmHg, and m.p. 37—40 °C (Found: C, 67.6; H, 6.8. $C_{14}H_{16}O_4$ requires C, 67.7; H, 6.5%); $\nu_{max.}$(film) 1 760, 1 740, 1 724, 1 656, 1 491, 1 223, 1 186, and 1 097 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.32 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 1.60 (1 H, m, C*H*HCH_2CO), 2.11—2.25 (1 H, m, C*H*HCH_2CO), 2.38 (1 H, ddd, *J* 10.5, 6.8, 3.8, C*H*HCO), 2.62 (1 H, ddd, *J* 13.5, 6.0, 2.4 Hz, C*H*HAr), 3.00 (1 H, ddd, *J* 11.6, 10.4, 3.9 Hz, C*H*HCO), 3.17 (1 H, ddd, *J* 13.5, 12.0, 3.7 Hz, C*H*HAr), 4.31 (2 H, q, *J* 7.0 Hz, CH_2Me), 4.71 (1 H, s, C*H*CO_2Et), and 7.00—7.26 (4 H, m, ArH); *ca.* 100% keto form; *m/z* (100 °C) 248 (M^+, 71%), 202 (27), 193 (19), 174 (17), 160 (46), 147 (24), 133 (30), 107 (86), and 91 (47); and (*ii*) the *cyclopentanone* (**26**) (75 mg, 69%), b.p. 145 °C at 0.02 mmHg (Found: C, 67.5; H, 6.8. $C_{14}H_{16}O_4$ requires C, 67.7; H, 6.5%); $\nu_{max.}$(film) 3 418, 1 751, 1 723, 1 457, 1 232, 1 118, and 756 cm^{-1}; δ_H(250 MHz; $CDCl_3$ 1.22 (3 H, t, *J* 7.1 Hz, CH_2*Me*), 2.10—2.40 (2 H, m, CH_2CH_2CO), 2.40—2.78 (2 H, m, CH_2CO), 3.56 (1 H, d, *J* 11.4 Hz, C*H*CO_2Et), 3.93 (1 H, dt, *J* 11.6, 6.0 Hz, C*H*Ar), 4.06—4.25 (2 H, m, CH_2Me), 6.78—6.96 (3 H, m, ArH and OH), 7.11 (1 H, dt, *J*, 7.5, 1.5 Hz, ArH), and 7.17 (1 H, dd, *J* 7.5, 1.5 Hz, ArH); *m/z* (100 °C) 248 (M^+, 28%), 202 (47), 173 (25), 147 (40), 107 (20), 84 (60), and 43 (73).

(*b*) Addition over 35 min of a solution of (**9**) (91.4 mg, 0.330 mmol) in dichloromethane (2.5 ml) to a solution of dirhodium

tetrakis(trifluoroacetate) (1.0 mg) in dichloromethane (7.5 ml) at reflux, followed by a further 1 h at reflux gave, upon purification, (**25**) (26 mg, 32%) and (**26**) (28 mg, 34%).

(*c*) Addition over 30 min of a solution of (**9**) (103 mg, 0.375 mmol) in benzene (9 ml) to a solution of copper(II) acetonylacetate (5.3 mg) in benzene (10 ml) at reflux, followed by a further 3.5 h at reflux gave, upon purification, solely (**26**) (50 mg, 54%).

Ethyl 5-(3-Hydroxypropyl)-2-oxocyclopentanecarboxylate (**27**.—Dirhodium tetra-acetate (2 mg) was added to a solution of the diazo compound (**10**) (138 mg, 0.570 mmol) in dichloromethane (20 ml). After 3 h, the catalyst was filtered off, the filtrate evaporated, and the residue chromatographed to give the *title compound* (**27**) as a viscous oil (50 mg, 41%), b.p. 140.150 °C at 0.005 mmHg (Found: C, 61.6; H, 8.6. $C_{11}H_{18}O_4$ requires C, 61.7; H, 8.5%); $\nu_{max.}$(film) 3 437, 1 758, 1 724, 1 278, 1 192, and 1 127 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.0 Hz, CH_2Me), 1.35—1.67 (5 H, m), 1.82 (1 H, br, OH), 2.12—2.45 (3 H, m), 2.47—2.63 (1 H, m, $CHCHCO_2Et$), 2.78 (1 H, d, *J* 11.1 Hz, $CHCO_2Et$), 3.52—3.65 (2 H, m, CH_2OH), and 4.16 (2 H, q, *J* 7.3 Hz, CH_2Me); δ_C(62.9 MHz; $CDCl_3$) 211.1, 169.4, 65.0, 62.7, 61.3, 41.2, 38.3, 31.4, 30.4, 27.4, and 14.2; *m/z* (130 °C) 214 (M^+, 4%), 186 (7), 168 (12), 155 (53), 113 (35), 109 (46), and 29 (100).

Ethyl 5-(N-t-Butoxycarbonyl)aminomethyl-2-oxocyclopentanecarboxylate (**28**).—To a rapidly stirred solution of the diazo compound (**12**) (247 mg, 0.788 mmol) in dichloromethane (35 ml) was added dirhodium tetra-acetate (2 mg). After 1.5 h the solvent was evaporated and the residue chromatographed to give the *title compound* (**28**) (164 mg, 73%) as a low melting solid, m.p. 50—55 °C (from ether) (Found: C, 58.8; H, 8.3; N, 5.0. $C_{14}H_{23}NO_5$ requires C, 58.9; H, 8.1; N, 4.9%); $\nu_{max.}$(film) 3 383, 1 757, 1 719br, 1 520, 1 368, 1 250, and 1 172 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.0 Hz, CH_2Me), 1.40 (9 H, s, Bu^t), 1.50—1.85 (1 H, m), 2.08—2.23 (1 H, m), 2.25—2.50 (2 H, m), 2.74 (1 H, $CHCHCO$), 2.90 (1 H, d, *J* 11.5 Hz, $CHCO_2Et$), 3.19 (1 H, dt, *J* 13.9, 6.7 Hz, $CHHN$), 3.31 (1 H, dt, *J* 13.8, 5.6 Hz, $CHHN$), 4.19 (2 H, q, *J* 7.0 Hz, CH_2Me), 4.70 (1 H, br, NH), and 10.68 (s, OH, enol); *ca.* 10% enol form; δ_C(125.8 MHz; $CDCl_3$) 210.5, 169.0, 155.8, 79.3, 61.3, 59.4, 43.8, 41.7, 38.0, 28.24, 28.18, 27.8, 24.6, and 14.0; *m/z* (140 °C) 285 (M^+, 0.1%), 228 (1), 212 (2), 199 (1), 184 (3), 168 (6), 144 (24), and 31 (100); *m/z* (CI; NH_3) 303 ($M^+ + NH_3$, 100%), 286 (75), 247 (40), 230 (17), and 186 (32).

Ethyl 5-(2-N-t-Butoxycarbonyl)aminoethyl-2-oxocyclopentanecarboxylate (**29**).—A solution of the diazo compound (**13**) (97.3 mg, 0.298 mmol) in dichloromethane (20 ml) was added to a blue solution of dirhodium tetrakis(trifluoroacetate) (2 mg) in dichloromethane (20 ml) over 2.2 h to give a green solution. After 1 h the solvent was evaporated, and the residue chromatographed to give the *title compound* (**29**) (68 mg, 76%) as a viscous oil; b.p. 130 °C at 0.003 mmHg (Found: C, 60.2; H, 8.6; N, 4.7. $C_{15}H_{25}NO_5$ requires C, 60.2; H, 8.4; N, 4.7%); $\nu_{max.}$(film) 3 380, 1 757, 1 710br, 1 515, 1 250, and 1 172 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7.0 Hz, CH_2Me), 1.42 (9 H, s, Bu^t), 1.45—1.65 (1 H, m), 1.68 (2 H, q, *J* 6.9 Hz, CH_2CH_2N), 2.14—2.49 (3 H, m), 2.60 (1 H, m, $CHCHCO$), 2.81 (1 H, d, *J* 11.3 Hz, $CHCO_2Et$), 2.98—3.30 (2 H, m, CH_2N), 4.20 (2 H, q, *J* 7.0 Hz, CH_2Me), and 4.64 (1 H, br, NH); *m/z* (120 °C) 299 (M^+, 3%), 243 (33), 226 (27), 199 (9), 182 (50), 170 (15), 155 (81), 136 (64), and 57 (100).

Ethyl 5-(N-t-Butylcarbonyl)aminomethyl-2-oxocyclopentanecarboxylate (**30**).—A solution of the diazo compound (**14**) (170 mg, 0.572 mmol) in benzene (5 ml) was added dropwise over 5 min to a suspension of dirhodium tetra-acetate (4.9 mg) in benzene (15 ml) at reflux. After 5 min the suspension was cooled, filtered, concentrated, and the residue chromatographed to give the *title compound* (**30**) (30 mg, 19%), m.p. 85—86 °C (Found: C, 62.5; H, 8.7; N, 5.2 $C_{14}H_{23}NO_4$ requires C, 62.4; H, 8.6; N, 5.2%); $\nu_{max.}$(film) 3 358, 1 755, 1 724, 1 646, 1 530, 1 206, and 1 127 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.18 (9 H, d, *J* 2.2 Hz, Bu^t), 1.30 (3 H, t, *J* 7.0 Hz, CH_2Me), 1.45—1.68 (1 H, m, $CHHCH_2CO$), 2.12—2.26 (1 H, m, $CHHCH_2CO$), 2.28—2.53 (2 H, m, CH_2CO), 2.70—2.88 (1 H, m, $CHCHCO_2Et$), 2.92 (1 H, d, *J* 11.0 Hz, $CHCO_2Et$), 3.32 (1 H, ddd, *J* 13.8, 7.5, 5.6 Hz, $CHHN$), 3.50 (1 H, dt, *J* 13.1, 5.1 Hz, $CHHN$), 4.12—4.31 (2 H, m, CH_2Me), and 5.95 (1 H, br, NH); *m/z* (140 °C) 269 (M^+, 6%), 224 (11), 212 (12), 196 (5), 184 (10), 168 (89), 155 (43), 115 (40), and 57 (100).

4,4-Dimethyl-4,5-dihydro-oxepane-2,6(3H)-dione (**32**).—6-Diazo-3,3-dimethyl-5-oxohexanoic acid (**31**) was prepared by a modification of the literature procedure;[10] 2-diazo-5,5-dimethylcyclohexane-1,3-dione (0.50 g, 3.0 mmol) was dissolved in dichloromethane (10 ml), sodium hydroxide solution (1M; 7.5—10 ml) was added, and the two phase mixture was stirred rapidly (16—18 h). The two layers were separated and the aqueous phase acidified to pH 4 with hydrochloric acid (2M) and quickly extracted with dichloromethane. The organic phase was washed with water and brine and dried ($MgSO_4$), to give a crude solution of the diazo acid.

(*a*) Boron trifluoride–diethyl ether (0.85 ml, 3 mmol) was added dropwise to a stirred solution of the crude diazo acid (**31**) in dichloromethane (100 ml) (see above), and the mixture was stirred for 12 h. Aqueous work-up and chromatography gave the *title compound* (**32**) (140 mg, 30% from 2-diazo-5,5-dimethylcyclohexane-1,3-dione) as a low melting solid, m.p. 52—56 °C (Found: C, 61.3; H, 7.9. $C_8H_{12}O_3$ requires C, 61.5; H, 7.8%); $\nu_{max.}$(film) 1 754, 1 720, 1 486, 1 432, 1 308, 1 283, and 1 077 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.17 (6 H, s, *Me*), 2.47 (2 H, s, CH_2CO), 2.59 (2 H, s, CH_2CO), and 4.50 (2 H, s, CH_2O); *m/z* (100 °C) 156 (M^+, 21%), 126 (29), 98 (7), 83 (16), 70 (61), and 56 (100).

(*b*) Alternatively, evaporation of the dichloromethane solution of (**31**) prepared from 2-diazo-5,5-dimethylcyclohexane-1,3-dione (803 mg, 4.8 mmol), gave a viscous unstable oil which was immediately subjected to partial purification by filtration through a pad of silica with ether as eluant.

The diazo acid (**31**) (462 mg, 52%) was immediately dissolved in benzene (10 ml) and added dropwise over 10 min to a suspension of dirhodium tetra-acetate (5 mg) in benzene (100 ml) at reflux. After a further 15 min the mixture was cooled and filtered through a pad of Celite. The filtrate was evaporated and the residue purified by chromatography to give (i) the title compound (**32**) (263 mg, 67%) and (ii) a second component (15 mg, 4%), a symmetrical *dimer*, m.p. 121—122 °C (hexane–ether) (Found: C, 61.6; H, 7.8. $C_{16}H_{24}O_6$ requires C, 61.5; H, 7.8%); $\nu_{max.}$(Nujol) 1 726, 1 426, 1 378, 1 250, and 1 093 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.23 (12 H, s), 2.47 (4 H, s), 2.62 (4 H, s), and 4.43 (4 H, s); *m/z* (180 °C) 312 (M^+, 7%), 254 (3), 239 (2), 212 (1), 198 (57), 183 (4), 170 (6), 156 (37), 140 (30), 115 (12), 97 (8), and 83 (100).

Decomposition of the Diazo Compound (**18**).—A solution of the diazo compound (**18**) (150 mg, 0.694 mmol) in benzene (7 ml) was added over 10 min to a suspension of dirhodium tetra-acetate (3 mg) in benzene (7 ml) at reflux. The mixture was stirred for a further 5 min, cooled, and filtered. Evaporation of the filtrate and distillation of the residue gave a liquid (27 mg, 21%), b.p. 170 °C at 0.35 mmHg which consisted of several components and a solid (6 mg), an unknown *dimer*, m.p. 105—110 °C (Found: C, 50.8; H, 6.4. $C_{16}H_{24}O_{10}$ requires C, 51.1; H, 6.4%), $\nu_{max.}$(Nujol) 1 761, 1 733, 1 462, 1 377, 1 300, 1 256, 1 219,

and 1 149 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.29 (3 H, t, *J* 7.1 Hz), 1.30 (3 H, t, *J* 7.1 Hz), 1.90—2.20 (4 H, m), 3.60—3.90 (4 H, m), 4.25 (2 H, q, *J* 7.1 Hz), 4.27 (2 H, q, *J* 7.1 Hz), 4.34—4.45 (4 H, m), 4.55 (1 H, s), and 4.58 (1 H, s); *m/z* (140 °C) 376 (M^+, 47%), 348 (6), 332 (7), 330 (11), 303 (27), 276 (64), 189 (23), 173 (100), 115 (37), and 87 (49).

Preparation of Derivatives.—General Procedure for Preparation of t-Butyldimethylsilyl Enol Ethers.—Triethylamine (1.25—2.5 equiv.) and t-butyldimethylsilyl trifluoromethanesulphonate (TBDMSOTf) (1.2—2.0 equiv.) were added in succession to a solution of the β-keto ester (0.1—0.5 mmol) in ether or THF (1 ml). The resulting suspension was stirred for 12 h at room temperature after which the volatile material was removed under high vacuum, and the residue was subjected to a neutral aqueous work-up. The crude product was distilled to give the enol silyl ether.

Ethyl 3-t-Butyldimethylsiloxy-4,5-dihydropyran-2-carboxylate (**33a**).—Triethylamine (0.12 ml, 0.85 mmol) and TBDMSOTf (0.19 ml, 0.85 mmol) were added simultaneously to a solution of ethyl 3-oxotetrahydropyran-2-carboxylate (**19a**) (120 mg, 0.70 mmol) in THF (1 ml) at −70 °C. The solution was allowed to warm to room temperature and stirred for 1.5 h before work-up. Rapid distillation of the residue gave the *title compound* (**33a**) (137 mg, 69%), b.p. 160 °C at 0.3 mmHg (Found: C, 58.6; H, 9.3. $C_{14}H_{26}O_4Si$ requires C, 58.9; H, 9.2%); $\nu_{max.}$(film) 1 719, 1 628, 1 297, 1 255, 1 223, 1 164, 1 078, 842, and 782 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 0.18 (6 H, s, SiMe), 0.95 (9 H, s, Bu^t), 1.31 (3 H, t, *J* 7.1 Hz, CH_2*Me*), 1.93 (2 H, quin, *J* 5.9 Hz, CH_2CH_2O), 2.29 (2 H, t, *J* 6.7 Hz, CH_2CO), 3.95 (2 H, t, *J* 5.1 Hz, CH_2O), and 4.25 (2 H, q, *J* 7.1 Hz, CH_2Me); *m/z* (140 °C) 286 (M^+, 1%), 271 (1), 241 (9), 229 (53), 201 (100), 189 (17), 173 (12), 147 (54), and 75 (40).

Ethyl 3-t-Butyldimethylsiloxy-4,5-dihydro-6-methylpyran-2-carboxylate (**33b**).—Triethylamine (96 μl, 0.69 mmol) and TBDMSOTf (151 μl, 0.66 mmol) were added to a solution of ethyl 6-methyl-3-oxotetrahydropyran-2-carboxylate (**19b**) (102 mg, 0.548 mmol) in ether (4 ml) at 0 °C. The solution was allowed to warm to room temperature and was stirred for 10 h before work-up. Rapid distillation of the residue gave the *title compound* (**33b**) (95 mg, 57%) as a clear oil, b.p. 135 °C at 0.5 mmHg (Found: M^+, 300.1751. $C_{15}H_{28}O_4Si$ requires *M*, 300.1757); $\nu_{max.}$(film) 1 719, 1 630, 1 224, and 1 178 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.33 (6 H, s, SiMe), 0.91 (9 H, s, Bu^t), 1.27 (3 H, t, *J* 7.1 Hz, CH_2*Me*), 1.30 (3 H, d, *J* 6.0 Hz, CH*Me*), 1.57—1.69 (1 H, m, C*H*HCHO), 1.83 (1 H, dddd, *J* 13.5, 7.0, 2.9, 2.6 Hz, C*H*HCHO), 2.18 (1 H, ddd, *J* 18.0, 6.4, 2.9 Hz, C*H*HC=), 2.34 (1 H, ddd, *J* 18.0, 10.5, 7.1 Hz, C*H*HC=), 3.83 (1 H, ddq, *J* 9.8, 6.0, 2.3 Hz, MeC*H*O), and 4.10—4.32 (2 H, m, CH_2Me); *m/z* (140 °C) 300 (M^+, 2%), 285 (1), 259 (53), 243 (57), 215 (89), and 75 (100).

Ethyl 3-t-Butyldimethylsiloxy-7-hexyl-4,5,6,7-tetrahydrooxepine-2-carboxylate (**34**).—Triethylamine (42 μl, 0.29 mmol) and TBDMSOTf (51 μl, 0.22 mmol) were added to a solution of ethyl 7-hexyl-3-oxo-oxepane-2-carboxylate (**20b**) (39.8 mg, 0.147 mmol) in THF (1 ml). After 12 h work-up and distillation of the residue gave the *title compound* (**34**) (49 mg, 86%) as a clear oil, b.p. 130—140 °C at 0.0005 mmHg (Found: C, 65.4; H, 10.5. $C_{21}H_{40}O_4Si$ requires C, 65.6; H, 10.5%), $\nu_{max.}$(film) 1 714, 1 621, 1 235, 1 177, and 833 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.15 (6 H, s, SiMe), 0.81—0.93 (3 H, m, Me), 0.93 (9 H, s, Bu^t), 1.27 (3 H, t, *J* 6.9 Hz, CH_2*Me*), 1.18—1.88 (14 H, m), 2.11 (1 H, dd, *J* 13.5, 6.0 Hz, C*H*HC=), 2.80 (1 H, ddd, *J* 14.3, 11.3, 1.7 Hz, C*H*HC=), 3.28—3.39 (1 H, m, CHRO), and 4.08—4.27 (2 H, m, CH_2Me); *m/z* 170 °C) 384 (M^+, 1%), 369 (2), 339 (3), 327 (100), 299 (6), and 73 (47).

Ethyl 3-t-Butyldimethylsiloxy-4,5,6,7-tetrahydro-oxocine-2-carboxylate (**35**).—Triethylamine (42 μl, 0.30 mmol) and TBDMSOTf (52 μl, 0.23 mmol) were added to a solution of ethyl 3-oxo-oxecane-2-carboxylate (**22**) (30.0 mg, 0.150 mmol) in THF (2 ml). After 12 h, work-up with 5% aqueous sodium carbonate and distillation of the residue gave the *title compound* (**35**) (47.1 mg, 100%) as a clear oil, b.p. 150—160 °C at 0.25 mmHg (Found: M^+, 257.1204. $C_{16}H_{30}O_4Si$—C_4H_9 requires *M*, 257.1209); $\nu_{max.}$(film) 1 717, 1 623, 1 226, and 841 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.18 (6 H, s, SiMe), 0.94 (9 H, s, Bu^t), 1.24 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 1.55—1.77 (6 H, m, $CH_2CH_2CH_2$), 2.30—2.40 (2 H, m, CH_2C=), 3.83—3.95 (2 H, m, CH_2O), and 4.20 (2 H, q, *J* 7.0 Hz, CH_2Me); *m/z* (170 °C) 314 (M^+, 1%), 299 (3), 269 (6), 257 (100), 229 (13), 173 (16), and 75 (97).

Ethyl 3-t-Butyldimethylsiloxy-5,6-dihydrobenzoxocine-2-carboxylate (**36**).—Triethylamine (22.5 μl, 0.16 mmol) and TBDMSOTf (30 μl, 0.13 mmol) were added to a solution of ethyl 3-oxo-3,4,5,6-tetrahydrobenzoxocine-2-carboxylate (**25**) (16.1 mg, 64.4 μ mol) in ether (1 ml). The mixture was stirred for 24 h, evaporated, and the residue chromatographed to give the *title compound* (**36**) (9.6 mg, 41%) as an oil (Found: M^+, 362.1913. $C_{20}H_{30}O_4Si$ requires *M*, 362.1913); $\nu_{max.}$(film) 1 718, 1 625, 1 594, 1 249, and 839 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.18 (6 H, s, SiMe), 0.93 (9 H, s, Bu^t), 1.28 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 1.95—2.15 (2 H, m, CH_2CH_2Ar), 2.61 (2 H, t, *J* 6.4 Hz, CH_2Ar), 2.85 (2 H, t, *J* 5.8 Hz, CH_2CO), 4.22 (2 H, q, *J* 7.0 Hz, CH_2Me), 6.95 (1 H, dt, *J* 7.1, 1.1 Hz), 7.03 (1 H, dd, *J* 8.0, 1.8 Hz), 7.12 (1 H, dt, *J* 7.5, 1.8 Hz), and 7.26 (1 H, dd, 8.0, 1.0 Hz); *m/z* (160 °C) 362 (M^+, 1%), 347 (2), 317 (6), 305 (100), 277 (78), and 75 (56).

Ethyl 2-t-Butyldimethylsiloxy-5-(2-t-butyldimethylsiloxyphenyl)cyclopentenoate (**37**).—Triethylamine (0.13 ml, 0.94 mmol) and TBDMSOTf (0.18 ml, 0.78 mmol) were added to a solution of ethyl 5-(2-hydroxyphenyl)-2-oxocyclopentane-2-carboxylate (**26**) (78 mg, 0.313 mmol) in DMF (2.5 ml). After 12 h, work-up and chromatography gave the *title compound* (**37**) (80 mg, 53%), m.p. 57—60 °C (Found: C, 65.6; H, 9.4. $C_{26}H_{44}O_4Si_2$ requires C, 65.5; H, 9.3%); $\nu_{max.}$(film) 1 713, 1 629, 1 487, 1 254, 1 226, and 840 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.25—0.28 (12 H, 4 × s, SiMe), 1.00 (9 H, s, Bu^t), 1.01 (9 H, s, Bu^t), 1.05 (3 H, t, *J* 7.0 Hz, CH_2*Me*), 1.52—1.67 (1 H, m, HC*H*CH_2), 2.22—2.60 (3 H, m, HC*H*CH_2), 4.02 (2 H, q, *J* 7.0 Hz, CH_2Me), 4.45 (1 H, d, *J* 7.9 Hz, C*H*Ar), 6.72—6.88 (2 H, m, ArH), and 6.95—7.09 (2 H, m, ArH); *m/z* (130 °C) 461 (M^+, − Me, 2%), 431 (4), 419 (100), 183 (32), and 73 (40).

Ethyl 5-(N-t-Butoxycarbonyl)aminomethyl-2-t-butyldimethylsiloxycyclopentenoate (**38**).—Triethylamine (26 μl, 0.19 mmol) and TBDMSOTf (40 μl, 0.17 mmol) were added to a solution of ethyl 5-(*N*-t-butoxycarbonylamino)methyl-2-oxocyclopentane-2-carboxylate (**28**) (41 mg, 0.14 mmol) in ether (1 ml). After 12 h, work-up and chromatography gave the *title compound* (**38**) (13 mg, 23%) as a low melting solid, m.p. 64—66 °C (Found: C, 60.0; H, 9.3; N, 3.4. $C_{20}H_{37}NO_5Si$ requires C, 60.1; H, 9.3; N, 3.5%); $\nu_{max.}$(film) 3 373, 1 714br, 1 622, 1 253, 1 173, and 843 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.19 (6 H, s, SiMe), 0.95 (9 H, s, Bu^tSi), 1.26 (3 H, t, *J* 7.1 Hz, CH_2*Me*), 1.41 (9 H, s, Bu^tO), 1.59—1.73 (1 H, m, HC*H*CH_2), 1.88—2.06 (1 H, m, HC*H*CH_2), 2.28 (1 H, ddd, *J* 16.8, 9.6, 3.2 Hz, C*H*HC=), 2.52 (1 H, ddt, *J* 16.8, 8.4, 1.8 Hz, C*H*HC=), 2.91—3.03 (1 H, m, C*H*CH_2N), 3.24 (2 H, t, *J* 5.7 Hz, CH_2N), 4.16 (2 H, m, CH_2Me), and 4.97 (1 H, br, NH); *m/z* (130 °C) 342 (M^+ − Bu^t, 0.1%), 326 (0.1), 297 (0.2), 285 (1), 269 (1), 212 (16), 168 (60), 155 (100), 109 (53), and 57 (89).

Lactone (**39**).—A solution of ethyl 5-(2-hydroxyphenyl)-2-oxocyclopentanecarboxylate (**26**) (29.6 mg, 0.119 mmol) and camphorsulphonic acid (CSA) (3 mg) in benzene (5 ml) was

heated to reflux. After 1 h, an extra portion of CSA (3 mg) was added to the reaction mixture and heating was continued for 2 h. The mixture was cooled, washed with water, dried ($MgSO_4$), evaporated and the residue chromatographed to give the *title compound* (**39**) (7.4 mg, 32%) as a viscous oil (Found: M^+, 202.0629. $C_{12}H_{10}O_3$ requires M, 202.0630); $\nu_{max.}$(film) 1 784, 1 737, 1 613, 1 489, 1 454, 1 218, and 760 cm^{-1}; δ_H(270 MHz; $CDCl_3$) 2.07—2.27 (1 H, m, HC*H*CH_2CO), 2.31—2.58 (3 H, m, HC*H*CH_2CO), 3.58 (1 H, d, *J* 7.0 Hz, C*H*CO), 3.90 (1 H, dd, *J* 7.0, 4.5 Hz, C*H*CHCO), and 7.05—7.37 (4 H, m, ArH); *m/z* (150 °C) 202 (M^+, 100%), 173 (33), 158 (6), 147 (57), 118 (16), 103 (24), and 91 (14).

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