Diazo transfer reactions of tosyl azide with carbocyclic β-keto esters: production and decomposition of ring-opened *N*-tosylcarbamoyl-substituted α-diazo esters

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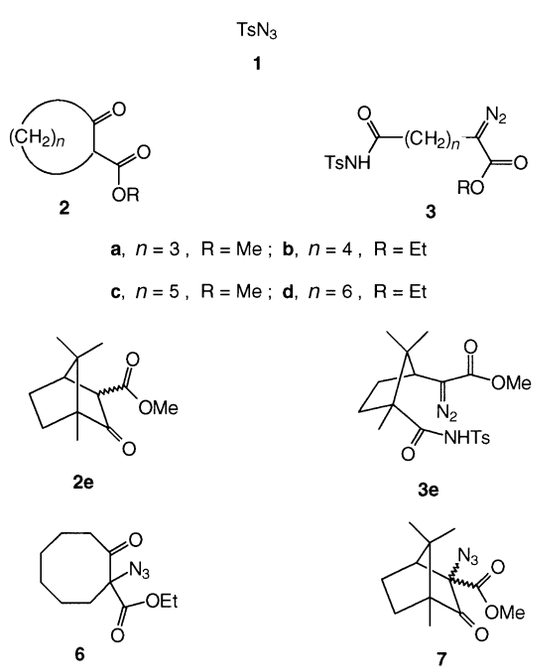
The diazo transfer reaction of tosyl azide 1 with methyl 2-oxocyclopentanecarboxylate 2a, ethyl 2-oxocyclohexanecarboxylate 2b and methyl 2-oxocycloheptanecarboxylate 2c, in the presence of triethylamine, gives ring-opened diazo amido esters 3a–c in fairly high yields. Similar reaction with ethyl 2-oxocyclooctanecarboxylate 2d and methyl camphor-3-carboxylate 2e also leads to the respective diazo esters 3d,e but accompanied by the corresponding azido transfer products 6, 7 to a significant (or major) extent. The thermal, photochemical and rhodium(II) acetate-catalysed decomposition of the novel diazocarbonyl compounds 3a–e has been examined. The results show that intramolecular cyclization onto the *N*-tosylcarbamoyl substituent can smoothly take place provided that it gives rise to a six-membered ring ylide or diazonium betaine intermediate. Otherwise, β-hydride elimination by an intermediate carbene or rhodium-carbenoid becomes the preferred, if not exclusive, decomposition mode. However, unusual behaviour is encountered with the diazo amido ester 3d in that its rhodium(II)-induced decomposition results in the preferential formation of the α-hydroxy ester 19.

α-Diazocarbonyl compounds have a long history of useful applications in organic chemistry since they can undergo a wide variety of chemical transformations under very mild conditions.[1,2] In recent years diazo group transfer from a suitable azide reagent (often a sulfonyl azide) to the α-methylene of an ester or ketone has become a popular source of α-diazocarbonyl compounds.[1,3–5] Diazo transfer to the active methylene of a β-dicarbonyl compound normally works well, but it usually fails when the methylene group is linked to a single carbonyl group only. In such cases, however, the diazo transfer can be successfully achieved by employing an indirect deacylating diazo transfer strategy involving prior activation of the monocarbonyl compound by formylation, trifluoroacylation[6] or benzoylation[7] and subsequent elimination of the activating acyl group in the course of the actual diazo transfer.

In recent work[8] we showed that the reaction of toluene-4-sulfonyl (tosyl) azide **1** with 2-methyl- and 2-phenyl-indane-1,3-dione, in the presence of triethylamine, smoothly leads to the corresponding ring-opened *o*-*N*-tosylcarbamoyl-substituted α-diazoacetophenones, thus providing the first example of deacylating diazo transfer with cyclic β-diones. These diazoacetophenones proved to be useful synthetic intermediates undergoing various intramolecular cyclizations to give *N*-tosyl-substituted isoquinoline-1,3-diones, isoquinoline-1,4-diones and/or isoindolones according to the decomposition conditions employed.

In the light of our previous results with the above indanediones, we were prompted to investigate analogous reactions of the azide **1** with carbocyclic β-keto esters with the expectation that these might similarly undergo a deacylating diazo transfer process to give *N*-tosylcarbamoyl-substituted α-diazo esters. As far as we know, there is no earlier record of attempted diazo transfer to these β-keto esters. The feasibility of such a process seemed of special interest to us in view of the ready availability of carbo- (and hetero-)cyclic β-keto esters, which are normally prepared by direct acylation of the corresponding ketones as well as by the Dieckmann condensation.[9] In principle, a wide variety of diazo amido esters might be constructed from mono- (and poly-)cyclic ketone precursors, including those occurring in nature. Herein, we report our results of a study of the reaction of the tosyl azide **1** with the monocyclic five-, six-, seven- and eight-membered β-keto esters **2a–d**, all commercially available, as well as with the bicyclic compound **2e**, which was prepared by methylation of the commercial carboxylic acid.

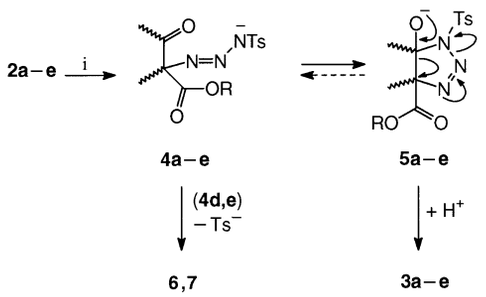


Methyl 2-oxocyclopentanecarboxylate **2a** was treated, at room temperature, with tosyl azide **1** (1 equiv.) and triethylamine (1 equiv.) in anhydrous tetrahydrofuran over 4 h. After this time, complete absence of starting material was monitored by TLC. Column chromatography of the crude reaction mixture led to the isolation of the expected diazo ester **3a** in high yield (Table 1). Evidently, the azide **1** was capable of reacting smoothly with the enolate of the cyclic dione **2a** to give a triazenyl anion **4a**[3,8] and then a fused triazoline **5a**[3,8] whose fragmentation eventually furnished the observed product **3a**

Table 1 Reaction of tosyl azide **1** with the cyclic keto esters **2a–e** in the presence of Et_3N at 20 °C

Entry	Keto ester	Time (h)	Diazo ester, yield[a] (%)	Azido ester, yield[a] (%)
1	**2a**	4	**3a**, 90	—
2	**2b**	118	**3b**, 71	—
3	**2c**	95	**3c**, 85	—
4	**2d**	140	**3d**, 20	**6**, 74
5	**2e**	190	**3e**, 56	**7**, 20

[a] Yield isolated by column chromatography.



Scheme 1 *Reagents and conditions:* i, TsN_3, Et_3N, 20 °C

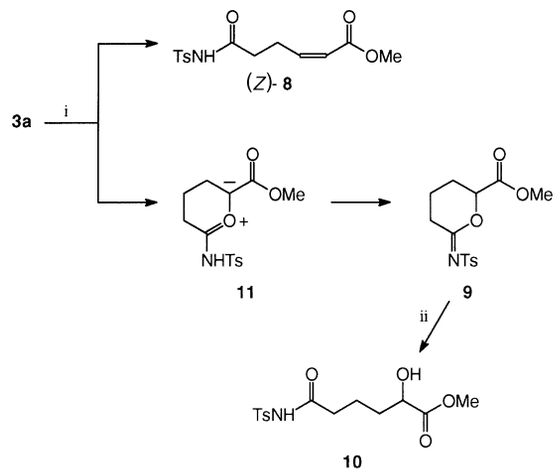
(Scheme 1). Similar results were obtained with the higher keto esters homologues **2b** and **2c** that were also converted into the corresponding diazo amido esters **3b,c** in fairly high yield, though over much longer reactions times (Table 1 and Scheme 1).

Instead, after comparatively long times, the keto esters **2d** and **2e** unexpectedly furnished the azido transfer products **6** and **7** to a major and minor extent respectively, in addition to the desired diazo transfer products **3d,e** (Table 1 and Scheme 1). Azido group transfer reactions of sulfonyl azides, including the tosyl azide **1**, with aliphatic carbanions having no α-hydrogen have been shown to occur, although to a limited extent.[3,10] Azido transfer to aromatic and heteroaromatic anions is known to be a fairly general process, especially employed in the preparation of five-membered heteroaromatic azides.[11] However, no example of such a type of reaction with anions having a ketone (or aldehyde) α-carbonyl group appears to have been encountered.[12]

The above findings provided by the keto esters **2d,e** suggest that unfavourable steric and/or strain factors can seriously discourage cyclization of the initially formed triazenyl anions **4d,e** to triazolines **5d,e**, thus favouring the competing fragmentation of the former intermediates into toluene-*p*-sulfinate and the azides **6**, **7** (Scheme 1). Hence, our present study clearly established that, as was expected, tosyl azide **1** can actually perform deacylating diazo transfer to cyclic β-keto esters, but seemingly in a fashion strictly dependent upon structural features of the dione substrate.

In the present work the thermal, photochemical and rhodium(II) acetate-catalysed behaviour of the novel diazo amido esters **3a–e** was also briefly examined.

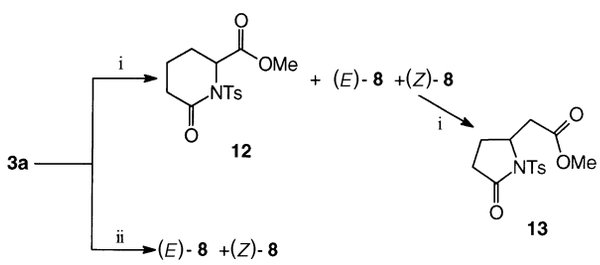
Treatment of the diazo amido ester **3a** with rhodium(II) acetate at 20 °C in methylene dichloride for several minutes afforded the imino lactone **9** accompanied by minor amounts of the *Z*-alkene *Z*-**8**, as was monitored by ^{1}H NMR analysis of the crude reaction mixture. Subsequent column chromatography led to the isolation of the *Z*-alkene *Z*-**8** and the ring-cleaved hydroxy ester **10**, which was the hydrolytic product of the initial lactone **9** (Scheme 2). Compound **9** is fairly consistent with rapid cyclization of an intermediate rhodium-carbenoid onto the neighbouring carbonyl group to give the six-membered carbonyl ylide **11**, which undergoes a subsequent proton transfer. Intramolecular cyclizations of rhodium-carbenoids onto an adjacent carbonyl function are well documented.[1,2] Moreover, intramolecular proton transfers are characteristic of carbonyl ylides



Scheme 2 *Reagents and conditions:* i, $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C; ii, SiO_2, H_2O

derived from the reaction of diazoalkanes with carbonyl compounds.[2,12] The *Z*-alkene *Z*-**8** is ascribable to competing β-hydride elimination of the metallocarbenoid. Rhodium-carbenoids derived from α-diazocarbonyl compounds are known to undergo β-hydride elimination in a highly stereoselective fashion.[13]

Thermolysis of the same compound **3a** in benzene at 100 °C resulted in the formation of the pyridone **12** (35%) and pyrrolidone **13** (15%) along with a mixture of *E*- and *Z*-**8** in a 7 : 1 ratio (17%) (Scheme 3). A control experiment established that the



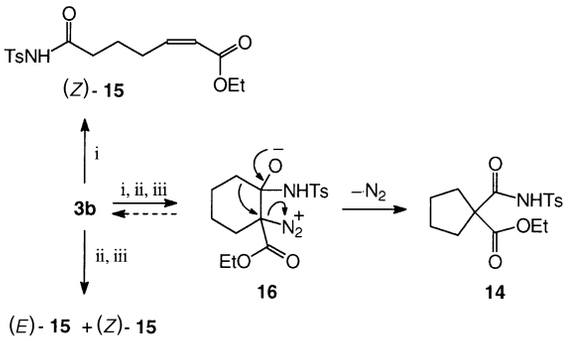
Scheme 3 *Conditions:* i, benzene, 100 °C; ii, *hv*, 20 °C

pyrrolidone **13** was produced by cyclization of the *Z*-isomer *Z*-**8** under the thermal reaction conditions. Hence, under these circumstances the derived carbene, besides β-hydride elimination, preferred to undergo intramolecular attack by the carbamoyl nitrogen, probably as a consequence of less electrophilic power of the ensuing 'free' carbene with respect to the corresponding rhodium-carbenoid. Moreover, photolysis of compound **3a** in benzene furnished mainly a *ca.* 1 : 1 *E*/*Z* mixture of the alkene **8** (Scheme 3).

The rhodium(II)-catalysed decomposition of the diazo homologue **3b** gave the cyclopentane **14** (70%) along with the *Z*-alkene *Z*-**15**, to some extent (Scheme 4). Comparable results were obtained from its thermal and photochemical decomposition, but in these cases the alkene **15** was formed to a much greater extent and in non-stereospecific fashion (Scheme 4).

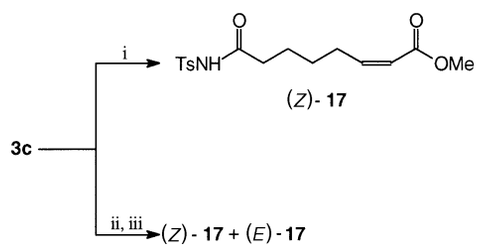
Compound **3b** therefore showed a marked tendency to decompose *via* the six-membered ring diazonium betaine **16** that might result from intramolecular attack of the diazo carbon onto the carbamoyl carbon. In fact, ring contraction of the betaine **16** with concomitant loss of nitrogen can conceivably afford the observed cyclopentane product **14** (Scheme 4).

Moreover, the carbene/metallocarbenoid derived from **3b** showed a definite preference for β-hydride elimination rather than intramolecular seven-membered cyclization, which is expected to be somewhat discouraged by unfavourable entropic factors.[2,12]

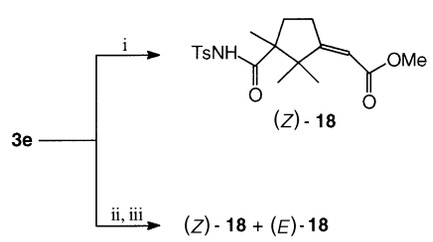


Scheme 4 *Reagents and conditions:* i, $Rh_2(OAc)_2$, CH_2Cl_2, 20 °C; ii, benzene, 100 °C; iii, *hv*, benzene, 20 °C

In behaviour similar to that of the diazo ester **3b**, under all the reaction conditions tried in the present work, the acyclic and cyclic analogues **3c** and **3e** failed to exhibit any intramolecular cyclization product onto the carbamoyl group and instead gave mainly the corresponding β-elimination products **17** and **18** (Schemes 5 and 6).

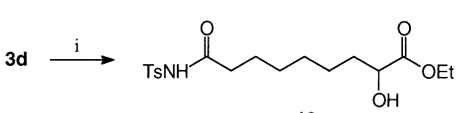


Scheme 5 *Reagents and conditions:* i, $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C; ii, benzene, 100 °C; iii, benzene, *hv*, 20 °C



Scheme 6 *Reagents and conditions:* i, $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C; ii, benzene, 100 °C; iii, benzene, *hv*, 20 °C

Instead, unusual behaviour was exhibited by the higher homologue **3d** in that, upon decomposition in the presence of rhodium(II) acetate, it surprisingly afforded the α-hydroxy ester **19** in fairly high yield (Scheme 7).



Scheme 7 *Reagents and conditions:* i, $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C

Unclear formation of α-hydroxycarbonyl products from analogous decompositions of α-diazocarbonyl compounds tethered to an ester group has been previously encountered, but in rare cases,[14] and is believed to possibly occur by hydrolysis of a cyclized carbonyl ylide. In the present case, the possible route responsible for the ester **19** remains quite obscure.

In conclusion, we have first shown that the reaction of the tosyl azide **1** with carbocyclic β-keto esters, in the presence of triethylamine, can successfully afford ring-opened *N*-tosylcarbamoyl-substituted α-diazo esters. However, our deacylating diazo transfer reactions proved to be normally slow and, in two instances, limited by competing occurrence of azido transfer processes. Since the rate and outcome of diazo transfer to a dicarbonyl compound are often greatly affected by the nature of the diazo donor, base and/or solvent, it is hoped that further studies will allow a quite effective and general protocol for the useful conversion of cyclic β-keto esters into diazo amido esters.

Moreover, our present findings for the thermal, photochemical and rhodium(II)-catalysed decomposition of the novel diazo compounds **3a–e** have established that intramolecular attack of diazo carbon or derived carbene/metallocarbenoid onto a neighbouring carbamoyl substituent can smoothly occur provided that it results in a six-membered cyclic intermediate. Otherwise, β-hydride elimination of transient carbene or metallocarbenoid can become the preferred, if not exclusive, decomposition mode. However, for unknown reasons, the diazo amido ester **3e** was found to be converted largely into the α-hydroxy ester **19** in the presence of the rhodium catalyst.

Experimental

Methyl 2-oxocyclopentanecarboxylate **2a**, ethyl 2-oxocyclohexanecarboxylate **2b**, methyl 2-oxocycloheptanecarboxylate **2c** and ethyl 2-oxocyclooctanecarboxylate **2d** were commercial Aldrich products. Methyl (±)-camphor-3-carboxylate **2e** was prepared by methylation of the corresponding carboxylic acid (purchased from Fluka). Tosyl azide **1** was prepared according to a literature method.[15]

All solvents were distilled before use. Diethyl ether and benzene were distilled over sodium wire; THF was distilled from sodium–benzophenone and CH_2Cl_2 from calcium hydride. All mps (Kofler melting point apparatus) are uncorrected. ^1H and ^{13}C NMR spectra were performed in $CDCl_3$ with Me_4Si as internal standard and recorded on a Varian Gemini 200 or 300 instrument. IR spectra were performed in $CHCl_3$ and recorded on a Perkin-Elmer 257 spectrometer. Mass spectra were determined by the electron impact method (70 eV) on a VG 7070E instrument. Column chromatography was carried out on ICN silica gel 63–200 60A by gradual elution with light petroleum (bp 40–70 °C)–diethyl ether and final elution with dichloromethane.

Reactions of tosyl azide 1 with the keto esters 2a–e: general procedure

A solution of tosyl azide **1** (8 mmol) and the appropriate keto ester **2a–e** (8 mmol) in dry diethyl ether (10 cm^3) (or THF, in the case of compound **2a**) was treated with freshly distilled triethylamine (8 mmol). The resulting mixture was stirred at room temperature until the starting reagents had disappeared (monitored by TLC), after which the excess of solvent was evaporated off and the residue chromatographed. Approximate reaction times and isolated product yields are given in Table 1.

The following new diazo esters **3a–e** and azides **6**, **7** were thus obtained.

(i) Methyl 2-diazo-5-(*N*-tosylcarbamoyl)pentanoate 3a. Mp 103–104 °C (decomp.) (Found: C, 49.60; H, 5.04; N, 12.45; S, 9.48. $C_{14}H_{17}N_3O_5S$ requires C, 49.55; H, 5.05; N, 12.38; S, 9.45%); ν_{max}/cm^{-1} 3380 (NH), 2080 (C=N_2), 1730 (C=O) and 1680 (C=O); δ_H(200 MHz) 1.72–1.87 (2 H, m), 2.25–2.4 (4 H, m), 2.48 (3 H, s, ArMe), 3.79 (3 H, s, OMe), 7.42 (2 H, d, *J* 8.4, ArH), 7.98 (2 H, d, *J* 8.4, ArH) and 9.35 (1 H, br s, NH); *m/z* 311 (M^+ − 28, 7%), 247 (28), 155 (35), 108 (67) and 91 (100).

(ii) Ethyl 2-diazo-6-(*N*-tosylcarbamoyl)hexanoate 3b. A yellow oil (Found: C, 52.45; H, 5.80; N, 11.50; S, 8.80. $C_{16}H_{21}N_3O_5S$ requires C, 52.30; H, 5.76; N, 11.44; S, 8.73%); ν_{max}/cm^{-1} 3380 (NH), 2080 (C=N_2), 1730 (C=O) and 1680 (C=O); δ_H(200 MHz) 1.29 (3 H, t, *J* 6.9, CH_3CH_2O), 1.43–1.79 (4 H, m), 2.07–2.39 (4 H, m), 2.43 (3 H, s, ArMe), 4.15 (0.6 H, q, *J* 6.9) and 4.25 (1.4 H, q, *J* 6.9) [two different kinds of CH_3CH_2O

owing to restricted rotation about the C(O)–C(N_2) bond], 7.32 (2 H, d, *J* 8.4, ArH), 7.93 (2 H, d, *J* 8.4, ArH) and 9.02 (1 H, br s, NH); *m/z* 367 (M^+, 0.1%), 339 ($M^+ - 28$, 6), 184 (7), 155 (39), 108 (100) and 91 (90).

(iii) Methyl 2-diazo-7-(*N*-tosylcarbamoyl)heptanoate 3c. A yellow oil (Found: C, 52.47; H, 5.78; N, 11.49; S, 8.79. $C_{16}H_{21}N_3O_5S$ requires C, 52.30; H, 5.76; N, 11.44; S, 8.73%); ν_{max}/cm^{-1} 3380 (NH), 2080 (C=N_2), 1740 (C=O) and 1680 (C=O); δ_H(200 MHz) 1.23–1.71 (6 H, m, CH_2), 2.27 (2 H, t, *J* 7, CH_2), 2.29 (2 H, t, *J* 6.9, CH_2), 2.47 (3 H, s, ArMe), 3.83 (3 H, s, OMe), 7.43 (2 H, d, *J* 8.4, ArH), 8.04 (2 H, d, *J* 8.4, ArH) and 9.1 (1 H, br s, NH); *m/z* 339 ($M^+ - 28$, 3%), 168 (8), 155 (21), 108 (100) and 91 (55).

(iv) Ethyl 2-diazo-8-(*N*-tosylcarbamoyl)octanoate 3d. A yellow oil (Found: C, 54.73; H, 6.40; N, 10.70; S, 8.13. $C_{18}H_{25}N_3O_5S$ requires C, 54.67; H, 6.37; N, 10.63; S, 8.11%); ν_{max}/cm^{-1} 3380 (NH), 2080 (C=N_2), 1740 (C=O) and 1660 (C=O); δ_H(200 MHz) 1.26 (3 H, t, *J* 6.5, OCH_2CH_3), 1.31–1.62 (8 H, m), 2.26 (4 H, m), 2.45 (3 H, s, ArMe), 4.21 (2 H, q, *J* 6.5, OCH_2CH_3), 7.31 (2 H, d, *J* 8.5, ArH), 7.92 (2 H, d, *J* 8.5, ArH) and 9.04 (1 H, br s, NH); *m/z* 367 ($M^+ - 28$, 1%), 196 (21), 170 (16), 155 (31), 108 (100) and 91 (84).

(v) Methyl [2,2,3-trimethyl-3-(*N*-tosylcarbamoyl)cyclopentyl]-diazoacetate 3e. Mp 147–148 °C (decomp.) (Found: C, 56.50; H, 6.20; N, 10.40; S, 7.90. $C_{19}H_{25}N_3O_5S$ requires C, 56.00; H, 6.18; N, 10.31; S, 7.87%); ν_{max}/cm^{-1} 3400 (NH), 2080 (C=N_2), 1700 (C=O) and 1680 (C=O); δ_H(200 MHz) 0.56 (3 H, s, Me), 1.02 (3 H, s, Me), 1.22 (3 H, s, Me), 1.49 (2 H, m), 1.97 (1 H, m), 2.35–2.55 (1 H, m), 2.44 (3 H, s, ArMe), 2.82 (1 H, t, *J* 9.3), 3.73 (3 H, s, OMe), 7.31 (2 H, d, *J* 8.4, ArH), 7.93 (2 H, d, *J* 8.4, ArH) and 8.28 (1 H, br s, NH); *m/z* 379 ($M^+ - 28$, 9%), 348 (10), 224 (10), 208 (7), 155 (29), 121 (74) and 91 (100).

(vi) Ethyl 1-azido-2-oxocyclooctanecarboxylate 6. An oil (Found: C, 55.32; H, 7.18; N, 17.60. $C_{11}H_{17}N_3O_3$ requires C, 55.22; H, 7.16; N, 17.56%); ν_{max}/cm^{-1} 2110 (N_3), 1750 (C=O) and 1720 (C=O); δ_H(200 MHz) 0.87–2.1 (9 H, m), 1.29 (3 H, t, *J* 6.6, OCH_2CH_3), 2.29–3.0 (3 H, m), 4.26 (2 H, q, *J* 6.6, OCH_2CH_3); δ_C(50 MHz) 14.45, 23.35, 24.3, 26.0, 30.2, 30.9, 38.6, 63.3, 76.55, 168.4 (C=O) and 209.1 (C=O).

(vii) Methyl 3-azidocamphor-3-carboxylate 7. Mp 82–84 °C (Found: C, 57.46; H, 6.85; N, 16.75. $C_{12}H_{17}N_3O_3$ requires C, 57.36; H, 6.82; N, 16.72%); ν_{max}/cm^{-1} 2115 (N_3), 1760 (C=O) and 1730 (C=O); δ_H(200 MHz) 0.98 (3 H, s, Me), 1.03 (3 H, s, Me), 1.08 (3 H, s, Me), 1.21–1.37 (1 H, m), 1.62–1.77 (2 H, m), 1.94–2.17 (1 H, m), 2.32 (1 H, br m) and 3.84 (3 H, s, OMe); δ_C(50 MHz) 10.0, 20.4, 21.45, 24.15, 28.8, 46.15, 50.45, 53.4, 59.2, 73.05, 169.6 (C=O) and 208.9 (C=O).

Rhodium(II) acetate-catalysed decomposition of the diazo compounds 3a–e: general procedure

To a solution of the appropriate diazo compound (4 mmol) in anhydrous dichloromethane (32 cm^3) was added a catalytic quantity of $Rh_2(OAc)_4$ (*ca*. 0.012 mmol) and the mixture was stirred at room temperature for *ca*. 30 min, after which it was filtered through Celite. After evaporation of the dichloromethane solvent the residual material was analysed by ^{1}H NMR spectroscopy and/or directly subjected to column chromatography.

Rhodium-catalysed decomposition of the diazo compound 3a. ^{1}H NMR analysis of the crude product was consistent with a 10:90 mixture of *methyl* Z-5-(N-*tosylcarbamoyl*)*pent*-2-*enoate* *Z*-**8** and *methyl* 2-(N-*tosylimino*)*tetrahydro*-2H-*pyran*-6-*carboxylate* **9** [ν_{max}/cm^{-1} 1750 (C=O), 1600 (C=N); δ_H(300 MHz) 1.72–2.27 (4 H, m), 2.39–2.79 (2 H, m), 2.43 (3 H, s, ArMe), 3.77 (3 H, s, OMe), 5.02 (1 H, t, *J* 4.6, 6-CH), 7.31 (2 H, d, *J* 8.4, ArH) and 7.9 (2 H, d, *J* 8.4, ArH); *m/z* 311 (M^+, 8%), 171 (32), 155 (43), 91 (100)]. Column chromatography gave (i) the Z-*alkene* *Z*-**8** (10%), as an oil; ν_{max}/cm^{-1} 3380 (NH), 1710 (C=O) and 1700 (C=O); δ_H(300 MHz) 2.33–2.48 (4 H, m), 2.43 (3 H, s, ArMe), 3.7 (3 H, s, OMe), 5.77 (1 H, d, *J* 11.4, olefinic), 6.18 (1 H, dt, J_d 11.4, olefinic), 7.29 (2 H, d, *J* 8.4, ArH), 7.9 (2 H, d, *J* 8.4, ArH) and 9.29 (1 H, br s, NH); *m/z* 311 (M^+, 3%), 280 (3), 155 (33), 108 (100) and 91 (55) (Found: C, 54.22; H, 5.52; N, 4.51; S, 10.35. $C_{14}H_{17}NO_5S$ requires C, 54.01; H, 5.50; N, 4.50; S, 10.30%) and (ii) *methyl* 2-*hydroxy*-5-(N-*tosylcarbamoyl*)-*pentanoate* **10** (70%), mp 114–116 °C; ν_{max}/cm^{-1} 3540 (OH), 3380 (NH) and 1730 (br, C=O); δ_H(200 MHz) 1.52–1.77 (4 H, m, CH_2), 2.27–2.40 (2 H, m, CH_2), 2.45 (3 H, s, ArMe), 3.75 (3 H, s, OMe), 4.12–4.23 (1 H, m, 2-CH), 7.35 (2 H, d, *J* 8.4, ArH) and 7.93 (2 H, d, *J* 8.4, ArH); *m/z* 311 ($M^+ - H_2O$, 0.1%), 270 ($M - CO_2Me$, 1), 171 (18), 108 (100), 99 (50) and 91 (80) (Found: C, 51.30; H, 5.83; N, 4.27; S, 9.74. $C_{14}H_{19}NO_6S$ requires C, 51.05; H, 5.81; N, 4.25; S, 9.73%).

Rhodium-catalysed decomposition of the diazo compound 3b. Column chromatography gave (i) *ethyl* 1-(N-*tosylcarbamoyl*)-*cyclopentanecarboxylate* **14** (70%), mp 81–82 °C; ν_{max}/cm^{-1} 3360 (NH), 1720 (C=O) and 1710 (C=O); δ_H(200 MHz) 1.22 (3 H, t, *J* 6.8, OCH_2CH_3), 1.65 (4 H, m), 2.14 (4 H, m), 2.45 (3 H, s, ArMe), 4.19 (2 H, q, *J* 6.8, OCH_2CH_3), 7.4 (2 H, d, *J* 8.4, ArH), 8.0 (2 H, d, *J* 8.4, ArH) and 9.46 (1 H, br s, NH); δ_C(50 MHz) 13.7, 21.55, 25.45, 34.7, 61.2, 61.25, 169 (C=O) and 174 (C=O) and aromatic C; *m/z* 339 (M^+, 0.1%), 275 ($M - CO_2Et$, 8), 155 (18), 142 (36), 108 (100) and 91 (47) (Found: C, 56.80; H, 6.25; N, 4.12; S, 9.43. $C_{16}H_{21}NO_5S$ requires C, 56.62; H, 6.24; N, 4.13; S, 9.45%) and (ii) *ethyl* Z-6-(N-*tosylcarbamoyl*)*hex*-2-*enoate* *Z*-**15** (7%) as an oil; ν_{max}/cm^{-1} 3380 (NH), 1740 (C=O) and 1720 (C=O); δ_H(200 MHz) 1.28 (3 H, t, *J* 6.8, OCH_2CH_3), 1.61–1.86 (2 H, m, CH_2), 2.28 (2 H, t, *J* 6.7, CH_2), 2.44 (3 H, s, ArMe), 2.59 (2 H, m, CH_2), 4.18 (2 H, q, *J* 6.8, OCH_2CH_3), 5.77 (1 H, d, *J* 10.3, olefinic), 6.13 (1 H, dt, J_d 10.3 and J_t 6.8, olefinic), 7.33 (2 H, d, *J* 8.5, ArH), 7.95 (2 H, d, *J* 8.5, ArH) and 9.38 (1 H, br s, NH); *m/z* 339 (M^+, 0.1%), 168 (7), 155 (19), 108 (100) and 91 (58) (Found: C, 56.82; H, 6.26; N, 4.14; S, 9.46. $C_{16}H_{21}NO_5S$ requires C, 56.62; H, 6.24; N, 4.13; S, 9.45%).

Rhodium-catalysed decomposition of the diazo compound 3c. Column chromatography gave (i) *methyl* Z-7-(N-*tosylcarbamoyl*)*hept*-2-*enoate* *Z*-**17** (75%), as an oil; ν_{max}/cm^{-1} 3380 (NH) and 1740 (C=O); δ_H(200 MHz) 1.30–1.50 (2 H, m, CH_2), 1.53–1.68 (2 H, m, CH_2), 2.30 (2 H, t, *J* 6.8, CH_2), 2.43 (3 H, s, ArMe), 2.60 (2 H, q, *J* 7.2, CH_2), 3.73 (3 H, s, OMe), 5.80 (1 H, d, *J* 11.5, olefinic), 6.20 (1 H, dt, J_d 11.5 and J_t 7.2, olefinic), 7.34 (2 H, d, *J* 8.4, ArH), 7.95 (2 H, d, *J* 8.4, ArH) and 9.0 (1 H, br s, NH); *m/z* 339 (M^+, 0.1%), 168 (6), 155 (12), 136 (29), 108 (100) and 91 (40) (Found: C, 56.85; H, 6.22; N, 4.14; S, 9.47. $C_{16}H_{21}NO_5S$ requires C, 56.62; H, 6.24; N, 4.13; S, 9.45%); and (ii) the isomeric E-*hexenoate* *E*-**17** (5%), mp 78–80 °C; ν_{max}/cm^{-1} 3380 (NH) and 1740 (C=O); δ_H(200 MHz) 1.30–1.47 (2 H, m, CH_2), 1.50–1.70 (2 H, m, CH_2), 2.14 (2 H, q, *J* 6.8, CH_2), 2.26 (2 H, t, *J* 7.1, CH_2), 2.45 (3 H, s, ArMe), 3.75 (3 H, s, OMe), 5.79 (1 H, d, *J* 16, olefinic), 6.90 (1 H, dt, J_d 16 and J_t 6.8, olefinic), 7.35 (2 H, d, *J* 8.4, ArH), 7.95 (2 H, d, *J* 8.4, ArH) and 8.7 (1 H, br s, NH); *m/z* 339 (M^+, 1%), 168 (11), 165 (23), 136 (54), 108 (100) and 91 (69) (Found: C, 56.75; H, 6.22; N, 4.13; S, 9.48. $C_{16}H_{21}NO_5S$ requires C, 56.62; H, 6.24; N, 4.13; S, 9.45%).

Rhodium-catalysed decomposition of the diazo compound 3d. Column chromatography gave (i) *ethyl* 2-*hydroxy*-8-(N-*tosylcarbamoyl*)*octanoate* **19** (61%), as an oil; ν_{max}/cm^{-1} 3540 (OH), 3380 (NH) and 1725 (br, C=O); δ_H(200 MHz) 1.15–1.67 (10 H, m, CH_2), 1.29 (3 H, t, *J* 7, OCH_2CH_3), 2.27 (2 H, t, *J* 7.5, CH_2), 2.45 (3 H, s, ArMe), 4.17–4.24 (1 H, m, 2-CH), 4.29 (2 H, q, *J* 7, OCH_2CH_3), 7.39 (2 H, d, *J* 8.4, ArH), 7.99 (2 H, d, *J* 8.4, ArH) and 9.15 (1 H, br s, NH); δ_C(50 MHz) 14.65, 22.15, 24.6, 24.95, 29.1, 29.25, 36.6, 36.7, 62.2, 70.85, 171.8 (C=O) and 175.9 (C=O) and aromatic C; *m/z* 367 ($M^+ - H_2O$, 0.2%), 312 ($M - CO_2Et$, 9), 214 (5), 141 (36), 108 (100) and 91 (43) (Found: C, 56.25; H, 7.08; N, 3.62; S, 8.30. $C_{18}H_{27}NO_6S$ requires C, 56.09; H, 7.06; N, 3.63; S, 8.32%); and (ii) unidentified material.

Rhodium-catalysed decomposition of the diazo compound 3e. Column chromatography gave (i) Z-1,2,2-*trimethyl*-3-[(*methoxycarbonyl*)*methylene*]-N-*tosylcyclopentanecarboxamide* *Z*-**18** (86%), mp 179–181 °C; ν_{max}/cm^{-1} 3400 (NH) and 1710 (C=O); δ_H(300 MHz) 0.98 (3 H, s, Me), 1.15 (3 H, s, Me), 1.34 (3 H, s, Me), 1.57 (1 H, m), 2.21 (1 H, m), 2.46 (3 H, s, ArMe), 2.61 (2 H, m), 3.66 (3 H, s, OMe), 5.75 (1 H, s, olefinic), 7.33 (2 H, d, *J* 8.4, ArH), 7.93 (2 H, d, *J* 8.4, ArH) and 8.35 (1 H, br s, NH); *m/z* 379 (M^+, 6%), 224 (9), 192 (74), 180 (74) and 91 (100) (Found: C, 60.30; H, 6.67; N, 3.68; S, 8.47. $C_{19}H_{25}NO_5S$ requires C, 60.14; H, 6.64; N, 3.69; S, 8.45%); and (ii) an unidentified compound (61 mg).

Thermolysis of the diazo compounds 3a–c,e: general procedure
A solution of the appropriate diazo compound (4 mmol) in dry benzene (32 cm^3) was heated at 100 °C in a sealed tube until starting material was completely absent (monitored by TLC; *ca*. 6–16 h). The excess of solvent was evaporated and the residue subjected to column chromatography.

Thermolysis of the diazo compound 3a. This gave (i) an isomeric mixture (50%) of *methyl* 1-*tosyl*-2-*oxopiperidine*-6-*carboxylate* **12** and 1-*tosyl*-5-[(*methoxycarbonyl*)*methyl*]*pyrrolidin*-2-*one* **13** in *ca*. 2:1 ratio (as determined by ^{1}H NMR spectroscopy) (Found: C, 54.20; H, 5.51; N, 4.51; S, 10.32. $C_{14}H_{17}NO_5S$ requires C, 54.01; H, 5.50; N, 4.50; S, 10.30%); δ_H(*pyrrolidinone* **13**; 300 MHz) 2.0–2.64 (4 H, m), 2.41 (3 H, s, ArMe), 2.7 (1 H, dd, *J* 14.7 and 9, CH*H*CO$_2$Me), 3.12 (1 H, dd, *J* 14.7 and 2.95, C*H*HCO$_2$Me), 3.66 (3 H, s, OMe), 4.69 (1 H, m, 5-CH), 7.35 (2 H, d, *J* 8.4, ArH) and 7.95 (2 H, d, *J* 8.4, ArH); δ_C(*pyrrolidinone* **13**; 75 MHz) 22.15, 24.85, 30.7, 39.45, 53.4, 56.65, 170.4 (C=O) and 173.3 (C=O) and aromatic C. Repeated column chromatography of the above mixture gave some pure *piperidone* **12**, mp 112–113 °C; ν_{max}/cm^{-1} 1750 (C=O) and 1700 (C=O); δ_H(300 MHz) 1.57–1.96 (2 H, m), 1.96–2.25 (1 H, m), 2.25–2.64 (3 H, m), 2.47 (3 H, s, ArMe), 3.81 (3 H, s, OMe), 5.2 (1 H, dd, *J* 4.6 and 2.6, 6-CH), 7.32 (2 H, d, *J* 8.4, ArH) and 7.96 (2 H, d, *J* 8.4, ArH); δ_C(75 MHz) 17.5, 21.8, 26.7, 33.3, 53.0, 58.15, 169.5 (C=O) and 171.45 (C=O) and aromatic C; *m/z* 280 ($M^+ - 31$, 0.1%), 252 (18), 247 (25), 188 (100), 155 (47) and 91 (75); (ii) the E-*pentenoate* *E*-**8** (15%), mp 115–116 °C; ν_{max}/cm^{-1} 3380 (NH), 1720 (C=O) and 1710 (C=O); δ_H(300 MHz) 2.3–2.5 (4 H, m), 2.43 (3 H, s, ArMe), 3.69 (3 H, s, OMe), 5.75 (1 H, d, *J* 15.2, olefinic), 6.80 (1 H, dt, J_d 15.2, olefinic), 7.3 (2 H, d, *J* 8.5, ArH) and 7.88 (2 H, d, *J* 8.5, ArH); *m/z* 311 (M^+, 4%), 155 (35), 108 (100) and 91 (80) (Found: C, 54.25; H, 5.49; N, 4.49; S, 10.33. $C_{14}H_{17}NO_5S$ requires C, 54.01; H, 5.50; N, 4.50; S, 10.30%); (iii) the *Z*-pentenoate *Z*-**8** (2%); and (iv) toluene-4-sulfonamide (17%). A control experiment showed that the *Z*-alkene *Z*-**8** was largely converted into the pyrrolidinone **13** when heated in benzene at 100 °C for 4 h.

Thermolysis of the diazo compound 3b. This gave (i) the cyclopentane **14** (51%); (ii) the *Z*-alkene *Z*-**15** (17%) and (iii) the *isomer* *E*-**15** (30%), as an oil; ν_{max}/cm^{-1} 3380 (NH), 1740 (C=O) and 1720 (C=O); δ_H(200 MHz) 1.28 (3 H, t, *J* 7, OCH$_2$C*H*$_3$), 1.64–1.85 (2 H, m, CH$_2$), 2.17 (2 H, q, *J* 6.9, CH$_2$), 2.29 (2 H, t, *J* 7.1, CH$_2$), 2.46 (3 H, s, ArMe), 4.19 (2 H, q, *J* 7, OC*H*$_2$CH$_3$), 5.78 (1 H, d, *J* 16, olefinic), 6.88 (1 H, dt, J_d 16 and J_t 6.9, olefinic), 7.36 (2 H, d, *J* 8.4, ArH), 7.97 (2 H, d, *J* 8.4, ArH) and 8.97 (1 H, br s, NH); *m/z* 339 (M^+, 41%), 266 (6), 168 (11), 155 (24), 122 (47), 108 (100) and 91 (98) (Found: C, 56.79; H, 6.26; N, 4.14; S, 9.47. $C_{16}H_{21}NO_5S$ requires C, 56.62; H, 6.24; N, 4.13; S, 9.45%).

Thermolysis of the diazo compound 3c. This gave (i) the *Z*-alkene *Z*-**17** (28%); (ii) its isomer *E*-**17** (35%); (iii) toluene-4-sulfonamide (6%); (iv) an unknown compound (150 mg); and (v) tarry material.

Thermolysis of the diazo compound 3e. This gave an unresolved 25:75 mixture of the isomers *E*-**18** and *Z*-**18** in 75% yield (Found: C, 60.33; H, 6.62; N, 3.70; S, 8.48. $C_{19}H_{25}NO_5S$ requires C, 60.14; H, 6.64; N, 3.69; S, 8.45%); δ_H(*E*-**18**; 300 MHz) 0.82 (3 H, s, Me), 1.06 (3 H, s, Me), 1.13 (3 H, s, Me), 1.49 (1 H, m), 1.98 (1 H, m), 2.46 (3 H, s, ArMe), 2.87 (1 H, m), 3.03 (1 H, m), 3.69 (3 H, s, OMe), 5.63 (1 H, s, olefinic), 7.33 (2 H, d, *J* 8.4, ArH), 7.93 (2 H, d, *J* 8.4, ArH) and 8.34 (1 H, br s, NH).

Photolysis of the diazo compounds 3a–c,e. A solution of the diazo compound **3a** (1 mmol) in dry benzene (20 cm^3), in a sealed quartz tube, was irradiated at room temperature with a high-pressure mercury vapour lamp for *ca*. 5 h, after which time complete decomposition of the starting compound **3a** had occurred (TLC). Removal of the benzene solvent and column chromatography of the crude product gave a *ca*. 45:55 mixture of the isomers *Z*- and *E*-**8** in 80% yield. Similar decomposition of the diazo compound **3b** gave (i) the cyclopentane **14** (30%) and (ii) a *ca*. 35:65 mixture of the isomers *E*- and *Z*-**15** (53%). Similar decomposition of the diazo compound **3c** gave a *ca*. 50:50 mixture of the isomers *E*- and *Z*-**17** in 93% yield. Similar decomposition of the diazo compound **3e** gave a *ca*. 25:75 mixture of the isomers *Z*- and *E*-**18** in 75% yield.

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