Dirhodium(II)-catalysed intramolecular carbon–hydrogen insertion reaction of α-diazo ketones: stereoselective synthesis of 2,3-*cis*-2-alkyl-5-oxo-3-silyloxycyclopentanecarboxylates

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Methyl 5-(*tert*-butyldimethylsilyloxy)-2-diazo-3-oxoheptanoate 2a, upon treatment with 1 mol% of dirhodium(II) tetraacetate in dichloromethane under reflux, gives a mixture of methyl (1*R,2*R**,3*S**)-3-(*tert*-butyldimethylsilyloxy)-2-methyl-5-oxocyclopentanecarboxylate 3a and its (1*S**,2*S**,3*S**) isomer 4a in a ratio of 79:21 and 87% combined yield. Similarly, 5-(*tert*-butyldimethylsilyloxy)-2-diazo-3-oxoalkanoates 2c–g give 2,3-*cis*-2-alkyl- (or 2-phenyl)-3-(*tert*-butyldimethylsilyloxy)cyclopentanecarboxylates 3c–g as the major products. The presence of both the keto and ester groups in the precursors was found to be essential for this site- and stereo-selective C–H insertion to take place. A possible interpretation for the observed stereoselectivity is presented.**

Introduction

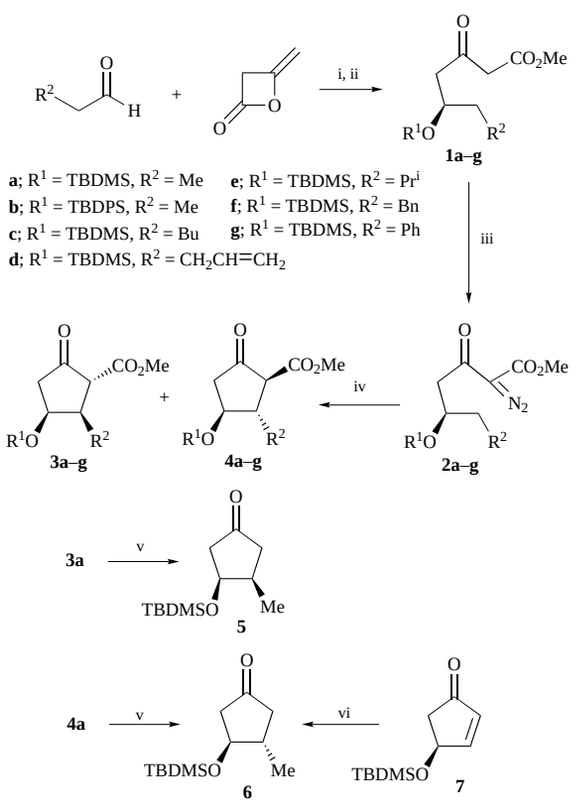
Of a number of syntheses of the cyclopentane ring,[1] the dirhodium(II)-catalysed intramolecular C–H insertion reaction of α-diazo carbonyl compounds has proved to be one of the most effective and versatile for the construction of such functionalised compounds.[2] This reaction is believed to proceed through a metal carbenoid, a species which can undergo, in addition to C–H insertion, a wide range of synthetic transformations such as X–H insertion (X = heteroatom), cyclopropanation, ylide formation and β-elimination. Therefore, in order to use the C–H insertion reaction for the synthesis of the cyclopentane ring, the efficient and predictable control of site selectivity is required. A growing number of examples govern this selectivity by steric,[3,4] conformational[3] and electronic factors.[3,5]

The Rh^{II}-catalysed reactions of α-diazo ketones having oxygen substituents near the site of insertion usually give oxonium ylides[6] or the products derived by insertion into the C–H bond adjacent to the oxygen atom.[7] Recently, we reported the site selective synthesis of 7-(*tert*-butyldimethylsilyloxy)-octahydrobenzo[*b*]furan-2-ones† *via* the dirhodium(II)-catalysed C–H insertion reaction of 2-TBDMSoxycyclohexyl diazoacetoacetates.[8] This result is attributed, at least in part, to the reduction of the reactivities of the oxygen atom and its adjacent C–H bond by the steric bulkiness of the TBDMSoxy group. As an extension of this TBDMSoxy group-controlled site selective reaction, we have now examined the reactions of 5-silyloxy-2-diazo-3-oxoalkanoates **2a**–**g** and found that the 5-TBDMSoxy derivatives **2a**,**c**–**g** gave the 2,3-*cis*-2-alkyl- (or 2-phenyl)-3-TBDMSoxy-5-oxocyclopentanecarboxylates **3a**,**c**–**g** with high site- and stereo-selectivity.[9]

Results and discussion

The precursors **2a**–**g** were easily prepared by the diazo transfer reaction of the β-keto esters **1a**–**g**, which, in turn, were synthesised by the reaction of an appropriate aldehyde and diketene in the presence of titanium(IV) chloride[10] followed by *O*-silylation of the resulting 5-hydroxy-3-oxoalkanoates.

A solution of **2a** in dichloromethane was heated with 1 mol% of $Rh_2(OAc)_4$ under reflux for 15 min. After evaporation of the solvent, the crude material was chromatographed on silica gel to give the 2-oxocyclopentanecarboxylates **3a** and **4a** in 87% combined yield and in a ratio of 79:21 (determined by ^1H NMR spectroscopy). Careful chromatography on silica gel gave pure samples of **3a** and **4a**. The structure and stereochemistry of **3a** and **4a** were confirmed by a combination of spectroscopic and chemical evidence. The large *J* value between H-1 and H-2 in both isomers (12.2 Hz for **3a** and 11.9 Hz for **4a**) showed the *trans* relationship.[3,11] Treatment of both **3a** and **4a** with 4-dimethylaminopyridine (DMAP) in toluene in the presence



Scheme 1 *Reagents and conditions*: i, $TiCl_4$, CH_2Cl_2, −78 °C, then MeOH, −20 to −10 °C; ii, TBDMSCl or TBDPSCl, imidazole, DMF, room temp.; iii, TsN_3, Et_3N, CH_3CN, room temp.; iv, 1 mol% of $Rh_2(OAc)_4$, CH_2Cl_2, reflux; v, DMAP, toluene–H_2O, 90 °C; vi, Me_2Cu-Li, Et_2O, −70 °C

† *tert*-butyldimethylsilyloxy = TBDMS.

Table 1 Dirhodium(II)-catalysed intramolecular C–H insertion reactions of **2a**–**g**

Entry	Starting material	Solvent	Reaction temp.	Reaction time (min)	Yield (%) of **3** and **4**[a]
1	**2a**	CH_2Cl_2	Reflux	15	87 (79:21)[b]
2	**2a**	CH_2Cl_2	RT	90	76 (75:25)
3	**2a**	CH_2Cl_2	−20 °C	Overnight	48 (79:21)
4	**2a**	benzene	RT	6.5 h	15 (73:27)
5	**2b**	CH_2Cl_2	Reflux	15	83 (57:43)
6	**2c**	CH_2Cl_2	Reflux	15	74 (78:22)
7	**2d**	CH_2Cl_2	Reflux	15	74 (80:20)
8	**2e**	CH_2Cl_2	Reflux	15	75 (90:10)
9	**2f**	CH_2Cl_2	Reflux	15	39 (83:17)
10	**2g**	CH_2Cl_2	Reflux	15	36 (70:30)

[a] The values in parentheses refer to the ratio of **3** and **4**. [b] Determined by ^{1}H NMR spectroscopy.

of water at 90 °C[12] gave the cyclopentanones **5** (66%) and **6** (62%), respectively. The *trans*-stereochemistry of **6** was confirmed by direct comparison with an authentic sample prepared by the stereoselective methylation[13] of 4-(TBDMSoxy)-cyclopent-2-enone **7**[14] with lithium dimethylcuprate, thereby confirming the stereochemistry of **3a** and **4a** to be 1,2-*trans*-2,3-*cis* and 1,2-*trans*-2,3-*trans*, respectively.

When the reaction of **2a** was carried out at room temperature or at −20 °C, the yield decreased to 76 and 48%, respectively (entries 2 and 3). Replacement of the solvent with benzene gave a poor yield (15%) of **3a** and **4a** (entry 4). The more bulky *tert*-butyldiphenylsilyloxy congener **2b** afforded **3b** and **4b** in satisfactory yield (83% combined yield) but poor stereoselectivity (57:43) (entry 5). The derivatives having other protecting groups such as trimethylsilyloxy, ethoxyethyloxy, and pivaloyloxy groups instead of the TBDMSoxy group of **2a** gave complex mixtures.

We next investigated the reaction of the other α-diazo-β-keto esters **2c**–**g**. The results are summarised in Table 1. Compounds **2c**–**g**, upon treatment with $Rh_2(OAc)_4$ in dichloromethane under reflux, gave also the corresponding 2,3-*cis* isomers **3c**–**g** as the major products (entries 6–10), although the yields of **3f**,**g** were relatively low (entries 9 and 10). The stereochemistries of the major isomers **3c**–**g** were determined by a comparison of the coupling constants of H-1 and H-3 ($J_{1,2}$ 11.3–12.7 and $J_{3,4}$ 2.9–3.9 Hz) in the ^{1}H NMR spectra with those of **3a** ($J_{1,2}$ 12.2 and $J_{3,4}$ 3.9 Hz).

In order to determine the role played by the two carbonyl groups of α-diazo-β-keto esters **2a**,**c**–**g** in the stereoselective formation of the cyclopentanones, the diazo ketone **8** and the diazo ester **9** were prepared and treated with $Rh_2(OAc)_4$ in dichloromethane. Compound **8** gave the corresponding C–H insertion products **5** and **6** in lower yield (66%) and poor stereoselectivity (*cis*:*trans* = 56:44), while compound **9** gave the (*Z*)-α,β-unsaturated ester **10** in 62% yield. The *Z*-stereochemistry of the double bond in **10** was assigned on the basis of the coupling constant (*J* 11.5 Hz) between the two olefinic protons in the ^{1}H NMR spectrum. The formation of **10** is rationalised in terms of β-elimination from the rhodium carbenoid intermediate.[5e,15] These results clearly indicate that the presence of both the keto and ester groups are essential for the stereoselective cyclopentanone formation.

Based on a documented example of the reaction of methyl 2-diazo-4-benzyloxy-3-oxobutanoate with $Rh_2(OAc)_4$ which produces the less stable 1,2-*cis*-5-oxo-2-phenyl-3-oxolanecarboxylate as a single isomer,[16] it was suggested that the 1,2-*trans* isomer **3a** could be formed by isomerisation of the initially formed 1,2-*cis* isomer during silica gel chromatography. To confirm this possibility, we examined the ^{1}H NMR spectrum of the crude reaction products of **2a** before treatment with silica gel. The ^{1}H NMR spectrum revealed a new doublet (*J* 9.0 Hz) due to H-1 at δ 3.22 in addition to two doublets for **3a** and **4a** at

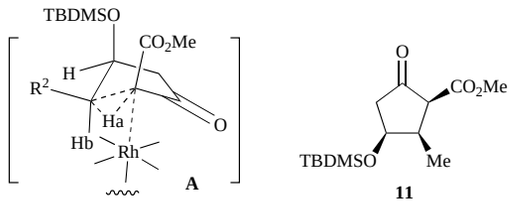
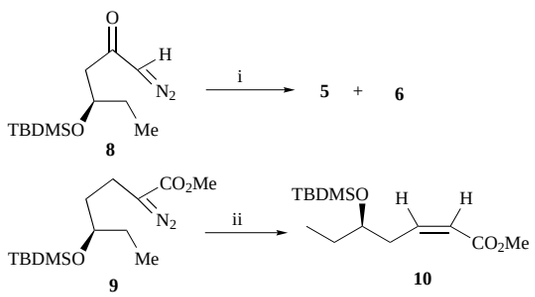


Fig. 1



Scheme 2 *Reagents and conditions*: i, 1 mol% of $Rh_2(OAc)_4$, CH_2Cl_2, reflux; ii, 1 mol% of $Rh_2(OAc)_4$, CH_2Cl_2, room temp.

δ 3.13 (*J* 12.0 Hz) and δ 2.84 (*J* 12.0 Hz), respectively, in a ratio of 52:23:25. After passage of the product through a silica gel column, the signal at δ 3.22 completely disappeared. The spatial relationship between the substituents at C-1 and C-2 of the new isomer was assigned as *cis* on the basis of its smaller *J* value compared with the corresponding values for **3a** and **4a**. These observations revealed that the major reaction pathway for the formation of **3a** would involve the initial formation of the 1,2-*cis*-2,3-*cis* isomer **11** which undergoes isomerisation to the 1,2-*trans*-2,3-*cis* isomer **3a** on silica gel.

The preference for the *cis*-insertion products with a pendent silyloxy group is striking. Clearly, the C–H insertion which leads to the *cis* product is more favourable than the diastereotopic C–H insertion which leads to the *trans* product. Considering the observation of Taber and Ruckle[3,17] that the Rh^{II}-catalysed cyclisation of methyl 2-diazo-3-oxo-5-phenylheptanoate gives predominantly methyl 1,2-*trans*-2,3-*trans*-2-methyl-5-oxo-3-phenylcyclopentanecarboxylate, this is not a steric influence from the pendent silyloxy group, but may likely be electronic in nature. One possible rationalisation would involve the formation of a cyclic transition state **A**,[5d,18] in which both bulky dirhodium complex and the R^2 group occupy pseudoequatorial positions and the TBDMSoxy and ester groups pseudoaxial positions. Such axial preference of the silyloxy group has been reported in 3- and 4-oxygen substituted cyclohexanones and cyclohexane.[19] It is likely that the transition state **A** is further stabilised by a favourable electronic interaction between the pseudoaxial ether oxygen atom and pseudoaxial ester carbonyl groups. In this transition state that leads to the all-*cis* product, the C–OTBDMS bond and C–H_a are orthogonal, minimising the electron-withdrawing effect of the oxygen and making H_a more reactive than H_b in which there can be good overlap with the electron-withdrawing oxygen. Isomerisation of the 1,2-*cis* isomer **11** on silica gel leads to the more stable 1,2-*trans* isomer **3a**.

In summary, this study shows that dirhodium(II)-catalysed intramolecular C–H insertion of the 5-(TBDMSoxy)-2-diazo-3-oxoalkanoates **2a**,**c**–**g** gives the 1,2-*trans*-2,3-*cis*-2-alkyl- (or 2-phenyl)-3-(TBDMSoxy)-5-oxocyclopentanecarboxylates **3a**, **c**–**g** as the major products. The presence of both the keto and ester groups in the precursors was essential for this site- and stereo-selective C–H insertion reaction to take place. It was suggested that the major reaction course would involve the initial formation of the all-*cis* isomers, which undergo isomerisation to the more stable 1,2-*trans* isomers on silica gel.

Experimental

Mps are uncorrected. IR spectra were recorded on a JASCO IR-1 spectrophotometer for solutions in CCl_4. ^1H NMR spectra (300 MHz) and ^{13}C NMR spectra (75.4 MHz) were determined with a Varian XL-300 spectrometer for solutions in $CDCl_3$. δ Values quoted are relative to tetramethylsilane, and J values are given in Hz. All ^{13}C NMR spectra were determined with complete proton decoupling. Exact mass determinations were obtained on a JEOL JMS-SX 102A instrument at 20 eV. Column chromatography was performed on silica gel 60 PF_{254} (Nacalai Tesque, Inc.) under pressure.

General procedure for the preparation of methyl 5-silyloxy-3-oxoalkanoates 1a–g

Following the method reported by Izawa and Mukaiyama,[10] titanium(IV) chloride (3 mol cm^{-3} solution in dichloromethane; 8 cm^3, 24 mmol) was added to a solution of an appropriate aldehyde (20 mmol) and diketene (3.36 g, 40 mmol) in dichloromethane (45 cm^3) at −78 °C under a nitrogen atmosphere, and the reaction mixture was stirred for 5 min. After this, absolute methanol (20 cm^3) was added to the mixture which, after being stirred for 30 min at −20 to −10 °C, was poured into ice-cooled 45% aq. K_2CO_3 (12 cm^3). The precipitated inorganic material was filtered off and the organic layer was separated. The aqueous layer was further extracted with diethyl ether after which the combined organic layer and extracts were washed with sat. aq. $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (3:1)] to give crude methyl 5-hydroxy-3-oxoalkanoate as a colourless oil, which was treated with *tert*-butyldimethylchlorosilane (1.43 g, 9.47 mmol) (for **1a**,**c**–**g**) or *tert*-butyldiphenylchlorosilane (2.60 g, 9.47 mmol) (for **1b**) and imidazole (1.34 g, 19.7 mmol) in dimethylformamide (40 cm^3) at room temperature. The mixture was stirred overnight and then diluted with water (30 cm^3) and extracted with diethyl ether. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (50:1)]. The following compounds were thus obtained as a mixture of the keto and enol forms.

Methyl 5-(*tert*-butyldimethylsilyloxy)-3-oxoheptanoate 1a. Yield 22% from propanal, as an *oil* (Found: C, 58.3; H, 10.0. $C_{14}H_{28}O_4Si$ requires C, 58.3; H, 9.8%); ν_{max}/cm^{-1} 1740, 1720, 1650 and 1630; δ_H 0.01 (1/6 × 3 H, s, SiMe of enol form), 0.03 (5/6 × 3H, s, SiMe of keto form), 0.04 (1/6 × 3 H, s, SiMe of enol form), 0.06 (5/6 × 3 H, s, SiMe of keto form), 0.86 (1/6 × 9 H, s, $SiCMe_3$ of enol form), 0.87 (5/6 × 9 H, s, $SiCMe_3$ of keto form), 0.88 (3 H, t, J 7.4, Me), 1.43–1.58 (2 H, m, 6-H_2), 2.25–2.32 (1/6 × 2 H, m, 4-H_2 of enol form), 2.59 (5/6 × 1 H, dd, J 15.3 and 5.0, one of 4-H_2 of keto form), 2.70 (5/6 × 1 H, dd, J 15.3 and 7.0, one of 4-H_2 of keto form), 3.48 and 3.52 (5/6 × 1 H each, ABq, J 15.8, 2-H_2 of keto form), 3.73 (1/6 × 3 H, s, OMe of enol form), 3.74 (5/6 × 3 H, s, OMe of keto form), 3.93–4.02 (1/6 × 1 H, m, 5-H of enol form), 4.05–4.15 (5/6 × 1 H, m, 5-H of keto form) and 5.02 (1/5 × 1 H, s, 2-H of enol form).

Methyl 5-(*tert*-butyldiphenylsilyloxy)-3-oxoheptanoate 1b. Yield 22% from propanal, as an *oil* (Found: M + H^+, 413.2157. $C_{24}H_{33}O_4Si$ requires M, 413.2148); ν_{max}/cm^{-1} 1750, 1720, 1660 and 1630; δ_H for the keto form 0.77 (3 H, t, J 7.4, Me), 1.03 (9 H, s, $SiCMe_3$), 1.40–1.55 (2 H, m, 6-H_2), 2.64 (2 H, d, J 5.9, 4-H_2) 3.29 and 3.35 (1 H each, ABq. J 15.7, 2-H_2), 3.68 (3 H, s, OMe), 4.12–4.21 (1 H, m, 5-H), 7.30–7.45 (6 H, m, ArH) and 7.65–7.75 (4 H, m, ArH).

Methyl 5-(*tert*-butyldimethylsilyloxy)-3-oxodecanoate 1c. Yield 11% from hexanal, as an *oil* (Found: C, 61.7; H, 10.5. $C_{17}H_{34}O_4Si$ requires C, 61.8; H, 10.4%); ν_{max}/cm^{-1} 1740, 1720, 1650 and 1630; δ_H for the keto form 0.03 (3 H, s, SiMe), 0.06 (3 H, s, SiMe), 0.86 (9 H, s, $SiCMe_3$), 0.88 (3 H, t, J 6.4, Me), 1.20–1.50 (8 H, m, 4 × CH_2), 2.58 (1 H, dd, J 15.3 and 4.9, one of 4-H_2), 2.69 (1 H, dd, J 15.3 and 7.0, one of 4-H_2), 3.45 and 3.52 (1 H each, ABq, J 15.7, 2-H_2), 3.73 (3 H, OMe) and 4.09–4.19 (1 H, m, 5-H).

Methyl 5-(*tert*-butyldimethylsilyloxy)-3-oxonon-8-enoate 1d. Yield 16% from pent-4-enal, as an *oil* (Found: C, 61.5; H, 9.9. $C_{16}H_{30}O_4Si$ requires C, 61.1; H, 9.6%); ν_{max}/cm^{-1} 1750, 1720, 1660 and 1630; δ_H for the keto form 0.03 (3 H, s, SiMe), 0.07 (3 H, s, SiMe), 0.87 (9 H, s, $SiCMe_3$), 1.52–1.65 (2 H, m, 6-H_2), 2.03–2.15 (2 H, m, 7-H_2), 2.62 (1 H, dd, J 15.6 and 5.2, one of 4-H_2), 2.72 (1 H, dd, J 15.6 and 6.7, one of 4-H_2), 3.45 and 3.52 (1 H each, ABq, J 15.1, 2-H_2), 3.74 (3 H, s, OMe), 4.19 (1 H, quintet, J 6.0, 5-H), 4.93–5.06 (2 H, m, CH=CH_2) and 5.72–5.88 (1 H, m, CH=CH_2).

Methyl 5-(*tert*-butyldimethylsilyloxy)-7-methyl-3-oxooctanoate 1e. Yield 25% from 3-methylbutanal, as an *oil* (Found: C, 60.6; H, 10.3. $C_{16}H_{32}O_4Si$ requires C, 60.7; H, 10.2%); ν_{max}/cm^{-1} 1750, 1720, 1660 and 1630; δ_H for the keto form 0.03 (3 H, s, SiMe), 0.06 (3 H, s, SiMe), 0.86 (9 H, s, $SiCMe_3$), 0.87 (3 H, t, J 6.6, Me), 0.89 (3 H, t, J 6.6, Me), 1.22–1.43 (2 H, m, 6-H_2), 1.54–1.73 (1 H, m, 7-H), 2.60 (1 H, dd, J 15.8 and 5.4, one of 4-H_2), 2.67 (1 H, dd, J 15.8 and 6.3, one of 4-H_2), 3.46 and 3.51 (1 H each, ABq, J 15.1, 2-H_2), 3.73 (3 H, s, OMe) and 4.14–4.24 (1 H, m, 5-H).

Methyl 5-(*tert*-butyldimethylsilyloxy)-3-oxo-7-phenylheptanoate 1f. Yield 22% from 3-phenylpropanal, as an *oil* (Found: M + H^+ 365.2154. $C_{20}H_{33}O_4Si$ requires M, 365.2148); ν_{max}/cm^{-1} 1740, 1730, 1660 and 1630; δ_H for the keto form 0.03 (3 H, s, SiMe), 0.08 (3 H, s, SiMe), 0.89 (9 H, s, $SiCMe_3$), 1.70–1.90 (2 H, m, 6-H_2), 2.60–2.82 (4 H, m, 4-H_2 and 7-H_2), 3.45 and 3.51 (1 H each, ABq, J 15.7, 2-H_2), 3.73 (3 H, s, OMe), 4.19–4.27 (1 H, m, 5-H) and 7.15–7.42 (5 H, m, ArH).

Methyl 5-(*tert*-butyldimethylsilyloxy)-3-oxo-6-phenylhexanoate 1g. Yield 11% from phenylacetaldehyde, as an *oil* (Found: M + H^+ 351.2001. $C_{19}H_{31}O_4Si$ requires M, 351.1991); ν_{max}/cm^{-1} 1750, 1720, 1660 and 1630; δ_H for the keto form −0.10 (3 H, s, SiMe), −0.02 (3 H, s, SiMe), 0.85 (9 H, s, $SiCMe_3$), 2.56 (1 H, dd, J 15.9 and 5.4, one of 4-H_2), 2.67 (1 H, dd, J 15.9 and 6.5, one of 4-H_2), 2.75–2.80 (2 H, m, 6-H_2), 3.44 (2 H, s, 2-H_2), 3.71 (3 H, s, OMe), 4.31–4.41 (1 H, m, 5-H) and 7.15–7.35 (5 H, m, ArH).

General procedure for the preparation of methyl 5-(*tert*-butyldimethylsilyloxy)-2-diazo-3-oxoalkanoates 2a–g

A solution of **1** (4.22 mmol), triethylamine (854 mg, 8.44 mmol), and toluene-*p*-sulfonyl azide (997 mg, 5.06 mmol) in acetonitrile (40 cm^3) was stirred at room temperature for 5 h and then diluted with diethyl ether (50 cm^3). The mixture was then washed with 9% aq. KOH (10 cm^3) and brine, dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (50:1)]. The following compounds were thus obtained.

Methyl 5-(*tert*-butyldimethylsilyloxy)-2-diazo-3-oxoheptanoate 2a. Yield 100%, as a pale yellow *oil* (Found: C, 53.7; H, 8.4; N, 9.1. $C_{14}H_{26}N_2O_4Si$ requires C, 53.5; H, 8.3; N, 8.9%); ν_{max}/cm^{-1} 2140, 1720 and 1660; δ_H −0.01 (3 H, s, SiMe), 0.03 (3 H, s, SiMe), 0.84 (9 H, s, $SiCMe_3$), 0.89 (3 H, t, J 7.4, Me), 1.45–1.58 (2 H, m, 6-H_2), 2.83 (1 H, dd, J 15.0 and 5.0, one of 4-H_2), 3.15 (1 H, dd, J 15.0 and 7.6, one of 4-H_2), 3.82 (3 H, s, OMe) and 4.18 (1 H, dq, J 8.9 and 5.1, 5-H).

Methyl 5-(*tert*-butyldiphenylsilyloxy)-2-diazo-3-oxoheptanoate 2b. Yield 91%, as a pale yellow *oil* (Found: M + H^+ 439.2068. $C_{24}H_{31}N_2O_4Si$ requires M, 439.2053); ν_{max}/cm^{-1} 2140, 1725 and 1660; δ_H 0.81 (3 H, t, J 7.4, Me), 1.02 (9 H, s, $SiCMe_3$), 1.46–1.58 (2 H, m, 6-H_2), 2.90 (1 H, dd, J 15.3 and 4.7, one of 4-H_2), 3.13 (1 H, dd, J 15.3 and 7.7, one of 4-H_2), 3.77 (3 H, s, OMe), 4.24–4.34 (1 H, m, 5-H), 7.31–7.45 (6 H, m, ArH) and 7.63–7.74 (4 H, m, ArH).

Methyl 5-(*tert*-butyldimethylsilyloxy)-2-diazo-3-oxodecanoate 2c. Yield 100%, as a pale yellow *oil* (Found: C, 57.5; H, 9.2; N, 7.9. $C_{17}H_{32}N_2O_4Si$ requires C, 57.3; H, 9.05; N, 7.9%); ν_{max}/cm^{-1}

2130, 1720 and 1660; δ_H −0.01 (3 H, s, SiMe), 0.04 (3 H, s, SiMe), 0.84 (9 H, s, $SiCMe_3$), 0.88 (3 H, t, *J* 6.6, Me), 1.20–1.55 (8 H, m, 4 × CH_2), 2.84 (1 H, dd, *J* 15.0 and 5.0, one of 4-H_2), 3.15 (1 H, dd, *J* 15.0 and 7.5, one of 4-H_2), 3.83 (3 H, s, OMe) and 4.16–4.26 (1 H, m, 5-H).

Methyl 5-(*tert*-butyldimethylsilyloxy)-2-diazo-3-oxonon-8-enoate 2d. Yield 100%, as a pale yellow *oil* (Found: M + H^+, 341.1902. $C_{16}H_{29}N_2O_4Si$ requires *M*, 341.1896); ν_{max}/cm^{-1} 2130, 1720 and 1650; δ_H 0.01 (3 H, s, SiMe), 0.06 (3 H, s, SiMe), 0.85 (9 H, s, $SiCMe_3$), 1.54–1.68 (2 H, m, CH_2), 2.07–2.19 (2 H, m, CH_2), 2.88 (1 H, dd, *J* 15.2 and 5.3, one of 4-H_2), 3.18 (1 H, dd, *J* 15.2 and 7.3, one of 4-H_2), 3.84 (3 H, s, OMe), 4.26 (1 H, dq, *J* 7.3 and 5.5, 5-H), 4.92–5.07 (2 H, m, CH=CH_2) and 5.74–5.89 (1 H, m, C*H*=CH_2).

Methyl 5-(*tert*-butyldimethylsilyloxy)-2-diazo-7-methyl-3-oxooctanoate 2e. Yield 100%, as a pale yellow *oil* (Found: C, 55.7; H, 8.9; N, 8.4. $C_{16}H_{30}N_2O_4Si$ requires C, 56.1; H, 8.8; N, 8.2%); ν_{max}/cm^{-1} 2100, 1700 and 1640; δ_H 0.01 (3 H, s, SiMe), 0.06 (3 H, s, SiMe), 0.85 (9 H, s, $SiCMe_3$), 0.91 (6 H, d, *J* 6.6, 2 × Me), 1.20–1.47 (2 H, m, 6-H_2), 1.60–1.75 (1 H, m, 7-H), 2.88 (1 H, dd, *J* 15.2 and 5.1, one of 4-H_2), 3.14 (1 H, dd, *J* 15.2 and 7.3, one of 4-H_2), 3.84 (3 H, s, OMe) and 4.23–4.33 (1 H, m, 5-H).

Methyl 5-(*tert*-butyldimethylsilyloxy)-2-diazo-3-oxo-7-phenylheptanoate 2f. Yield 97%, as a pale yellow *oil* (Found: C, 61.5; H, 7.9; N, 7.3. $C_{20}H_{30}N_2O_4Si$ requires C, 61.5; H, 7.7; N, 7.2%); ν_{max}/cm^{-1} 2125, 1715 and 1650; δ_H 0.02 (3 H, s, SiMe), 0.07 (3 H, s, SiMe), 0.88 (9 H, s, $SiCMe_3$), 1.72–1.93 (2 H, m, CH_2), 2.59–2.78 (2 H, m, CH_2), 2.95 (1 H, dd, *J* 15.3 and 5.5, one of 4-H_2), 3.23 (1 H, dd, *J* 15.3 and 7.1, one of 4-H_2), 3.83 (3 H, s, OMe), 4.27–4.37 (1 H, m, 5-H) and 7.15–7.30 (5 H, m, ArH).

Methyl 5-(*tert*-butyldimethylsilyloxy)-2-diazo-3-oxo-6-phenylhexanoate 2g. Yield 96%, as a pale yellow *oil* (Found: C, 60.5, H, 7.6; N, 7.4. $C_{19}H_{28}N_2O_4Si$ requires C, 60.6; H, 7.5; N, 7.4%); ν_{max}/cm^{-1} 2150, 1720 and 1650; δ_H −0.17 (3 H, s, SiMe), −0.06 (3 H, s, SiMe), 0.82 (9 H, s, $SiCMe_3$), 2.81 (2 H, d, *J* 6.4, 6-H_2), 2.89 (1 H, dd, *J* 15.7 and 5.5, one of 4-H_2), 3.14 (1 H, dd, *J* 15.7 and 6.9, one of 4-H_2), 3.81 (3 H, s, OMe), 4.39–4.49 (1 H, m, 5-H) and 7.17–7.30 (5 H, m, ArH).

Intramolecular C–H insertion reaction of compound 2a

General procedure. A solution of **2a** (157 mg, 0.5 mmol) in dichloromethane (4 cm^3) was added to a boiling solution of $Rh_2(OAc)_4$ (2 mg, 0.005 mmol) in dichloromethane (26 cm^3) and the mixture was refluxed for 15 min. After this, the mixture was evaporated and the crude product was chromatographed on silica gel [hexane–AcOEt (7:1)] to give a mixture of **3a** and **4a** (total 125 mg, 87%) as a colourless oil. The ratio of **3a** and **4a** was estimated to be 79:21 by integration of the intensities of the peak heights of the signals due to the methine proton at the 1-position: these appeared at δ 3.13 (d) and 2.82 (d), respectively. The mixture was re-chromatographed on silica gel [hexane–AcOEt (50:1)]. The first fraction gave *methyl* (1S*,2S*,3S*)-3-(tert-*butyldimethylsilyloxy*)-2-*methyl*-5-*oxocyclopentanecarboxylate* **4a** as a colourless oil (Found: M + H^+ 287.1694. $C_{14}H_{27}O_4Si$ requires *M*, 287.1679); ν_{max}/cm^{-1} 1760 and 1735; δ_H 0.05 (3 H, s, SiMe), 0.08 (3 H, s, SiMe), 0.89 (9 H, s, $SiCMe_3$), 1.18 (3 H, d, *J* 6.5, 2-Me), 2.34 (1 H, dd, *J* 18.5 and 8.9, one of 4-H_2), 2.50–2.65 (1 H, m, 2-H), 2.65 (1 H, ddd, *J* 18.3, 7.0 and 1.0, one of 4-H_2), 2.82 (1 H, d, *J* 11.9, 1-H), 3.75 (3 H, s, OMe) and 3.89 (1 H, td, *J* 8.6 and 7.0, 3-H); δ_C −4.9 (SiMe), −4.6 (SiMe), 16.3 (2-Me), 17.9 (quaternary C), 25.7(3) (Bu^t), 44.1 (2-C), 47.6 (4-C), 52.5 (OMe), 61.8 (1-C), 73.8 (3-C), 168.7 (ester C=O) and 207.3 (C=O). The second fraction gave *methyl* (1R*,2R*,3S*)-3-(tert-*butyldimethylsilyloxy*)-2-*methyl*-5-*oxocyclopentanecarboxylate* **3a**, mp 46.5–48 °C (from pentane) (Found: C, 58.5; H, 9.3. $C_{14}H_{26}O_4Si$ requires C, 58.7; H, 9.15%); ν_{max}/cm^{-1} 1760 and 1735; δ_H 0.05 (3 H, s, SiMe), 0.08 (3 H, s, SiMe), 0.87 (9 H, s, $SiCMe_3$), 1.15 (3 H, d, *J* 6.6, 2-Me), 2.37 (1 H, d, *J* 18.1, one of 4-H_2), 2.52 (1 H, dd, *J* 18.1 and 4.2, one of 4-H_2), 2.62 (1 H, dqd, *J* 12.0, 6.6 and 3.6, 2-H), 3.13 (1 H, d, *J* 12.2, 1-H), 3.77 (3 H, s, OMe) and 4.33 (1 H, t, *J* 3.9, 3-H); δ_C −5.0 (SiMe), −4.7 (SiMe), 14.0 (2-Me), 18.0 (quaternary C), 25.7(3) (Bu^t), 42.0 (2-C), 49.3 (4-C), 52.4 (OMe), 58.6 (1-C), 71.0 (3-C), 169.8 (ester C=O) and 210.2 (C=O).

3,4-*cis*-3-(*tert*-Butyldimethylsilyloxy)-4-methylcyclopentanone 5. Following the method reported by Taber and his coworkers,[12] a mixture of **3a** (40 mg, 0.14 mmol) and DMAP (7 mg, 0.06 mmol) in toluene (1 cm^3) and 1 mol dm^{-3} phosphate buffer (pH 7; 1 cm^3) was stirred at 90 °C for 21 h, and then partitioned between aq. NH_4Cl and AcOEt. The organic layer was separated, dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (20:1)] to give **5** (21 mg, 66%) as a colourless oil (Found: M + H^+, 229.1639. $C_{12}H_{25}O_2Si$ requires *M*, 229.1624); ν_{max}/cm^{-1} 1750; δ_H 0.05 (3 H, s, SiMe), 0.07 (3 H, s, SiMe), 0.88 (9 H, s, $SiCMe_3$), 1.10 (3 H, d, *J* 6.3, 4-Me), 2.01–2.41 (5 H, m, 2-H_2, 4-H, and 5-H_2) and 4.30–4.34 (1 H, m, 3-H).

3,4-*trans*-3-(*tert*-Butyldimethylsilyloxy)-4-methylcyclopentanone 6. (i) According to the reported method,[13a] a solution of methyllithium in diethyl ether (1.03 mol dm^{-3}; 0.93 cm^3, 0.96 mmol) was added to a solution of copper(II) iodide (91 mg, 0.48 mmol) in diethyl ether (1 cm^3) at −70 °C under a nitrogen atmosphere and the mixture was stirred at the same temperature for 2 h. A solution of 4-(*tert*-butyldimethylsilyloxy)-2-cyclopentenone **7**[14] (50 mg, 0.24 mmol) in diethyl ether (1.5 cm^3) was added to this mixture after which it was stirred for a further 30 min, and then treated with aq. NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layer and extracts were washed with brine, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (20:1)] to give **6** (32 mg, 59%) as a colourless oil (Found: M + H^+, 229.1633); ν_{max}/cm^{-1} 1750; δ_H 0.06 (3 H, s, SiMe), 0.09 (3 H, s, SiMe), 0.89 (9 H, s, $SiCMe_3$), 1.09 (3 H, d, *J* 6.9, 4-Me), 1.76–1.88 (1 H, m, 4-H), 2.12–2.29 (2 H, m), 2.46–2.61 (2 H, m) and 3.98 (1 H, q, *J* 6.0, 3-H).

(ii) Following a procedure similar to that described above for the preparation of **5**, compound **6** (13 mg, 62%) was obtained from **4a** (26 mg, 0.09 mmol) and DMAP (5 mg, 0.04 mmol) as a colourless oil, the spectral data for which were identical with those of an authentic sample obtained from **7**.

Intramolecular C–H insertion reaction of compound 2b

Following the general procedure, compound **2b** (244 mg, 0.56 mmol) was treated with $Rh_2(OAc)_4$ (3 mg, 0.006 mmol), and the crude material was chromatographed on silica gel [hexane–AcOEt (7:1)] to give an oily mixture of *methyl* (1R*,2R*,3S*)-3-(tert-*butyldiphenylsilyloxy*)-2-*methyl*-5-*oxocyclopentanecarboxylate* **3b** and *methyl* (1S*,2S*,3S*)-3-(tert-*butyldiphenylsilyloxy*)-2-*methyl*-5-*oxocyclopentanecarboxylate* **4b** (total 190 mg, 83%) (Found: M + H^+, 411.2003. $C_{24}H_{31}O_4Si$ requires *M*, 411.1991); ν_{max}/cm^{-1} 1760 and 1725; δ_H (for **3b**) 1.07 (9 H, s, $SiCMe_3$), 1.20 (3 H, d, *J* 6.7, 2-Me), 2.25 (2 H, d, *J* 2.5, 4-H_2), 2.51–2.64 (1 H, m, 2-H), 3.28 (1 H, d, *J* 12.2, 1-H), 3.76 (3 H, s, OMe), 4.44 (1 H, q, *J* 2.9, 3-H), 7.34–7.49 (6 H, m, ArH) and 7.56–7.67 (4 H, m, ArH); δ_C (for **3b**) 14.3 (2-Me), 19.4 (quaternary C), 26.9(3) (Bu^t), 42.2 (2-C), 48.8 (4-C), 52.5 (OMe), 59.0 (1-C), 72.2 (3-C), 127.7(3) (Ar), 127.9 (Ar), 130.0(2) (Ar), 132.9 (Ar), 133.5 (Ar), 135.8(2) (Ar), 135.9(2) (Ar), 169.6 (ester C=O) and 210.0 (C=O). The ratio of **3b** and **4b** was estimated to be 57:43 from integration of the intensities of the peak heights of the signals due to the methine proton at the 3-position which appeared at δ 4.44 (q) and 3.85–4.00 (m), respectively.

Intramolecular C–H insertion reaction of compound 2c

Following the general procedure, compound **2c** (125 mg, 0.35 mmol) was treated with $Rh_2(OAc)_4$ (2 mg, 0.004 mmol), and the crude material was chromatographed on silica gel [hexane–

AcOEt (7:1)] to give an oily mixture of **3c** and **4c** (total 85 mg, 74%). The ratio of **3c** and **4c** was estimated to be 78:22 by integration of the intensities of the peak heights of the signals due to the methine proton at the 1-position which appeared at δ 3.15 (d) and 2.88 (d), respectively. The mixture was rechromatographed on silica gel [hexane–AcOEt (50:1)]. The first fraction gave *methyl* (1S*,2S*,3S*)-3-(tert-*butyldimethylsilyloxy*)-2-*butyl*-5-*oxocyclopentanecarboxylate* **4c**, as an oil (Found: M + H$^+$, 329.2158. $C_{17}H_{33}O_4Si$ requires *M*, 329.2148); ν_{max}/cm^{-1} 1760 and 1730; δ_H 0.05 (3 H, s, SiMe), 0.08 (3 H, s, SiMe), 0.88 (3 H, t, *J* 5.2, Me), 0.89 (9 H, s, $SiCMe_3$), 1.22–1.42 (6 H, m, 3 × CH_2), 2.37 (1 H, dd, *J* 18.3 and 8.3, one of 4-H_2), 2.53–2.70 (1 H, m, 2-H), 2.64 (1 H, ddd, *J* 18.3, 6.8 and 1.0, one of 4-H_2), 2.88 (1 H, d, *J* 10.7, 1-H), 3.75 (3 H, s, OMe) and 3.99 (1 H, td, *J* 8.1 and 6.8, 3-H); δ_C −4.9 (SiMe), −4.5 (SiMe), 13.9 (CH_3), 17.9 (quaternary C), 22.7 (CH_2), 25.7(3) (Bu^t), 29.1 (CH_2), 31.7 (CH_2), 47.7 (2-C), 49.0 (4-C), 52.5 (OMe), 60.4 (1-C), 72.7 (3-C), 169.4 (ester C=O) and 208.1 (C=O). The second fraction gave *methyl* (1R*,2R*,3S*)-3-(tert-*butyldimethylsilyloxy*)-2-*butyl*-5-*oxocyclopentanecarboxylate* **3c**, as an oil (Found: M + H$^+$, 329.2155); ν_{max}/cm^{-1} 1760 and 1725; δ_H 0.05 (3 H, s, SiMe), 0.08 (3 H, s, SiMe), 0.86 (9 H, s, $SiCMe_3$), 0.90 (3 H, t, *J* 6.9, Me), 1.20–1.70 (6 H, m, 3 × CH_2), 2.37 (1 H, d, *J* 18.0, one of 4-H_2), 2.50 (1 H, dd, *J* 18.0 and 4.0, one of 4-H_2), 2.48–2.58 (1 H, m, 2-H), 3.15 (1 H, d, *J* 11.8, 1-H), 3.76 (3 H, s, OMe) and 4.43 (1 H, t, *J* 3.7, 3-H); δ_C −5.1 (SiMe), −4.5 (SiMe), 14.0 (CH_3), 17.9 (quaternary C), 22.8 (CH_2), 25.6(3) (Bu^t), 28.7 (CH_2), 29.2 (CH_2), 47.5 (2-C), 49.2 (4-C), 52.4 (OMe), 57.9 (1-C), 69.3 (3-C), 170.3 (ester C=O) and 210.3 (C=O).

Intramolecular C–H insertion reaction of compound 2d

Following the general procedure, compound **2d** (170 mg, 0.50 mmol) was treated with $Rh_2(OAc)_4$ (2 mg, 0.005 mmol), after which the crude product was chromatographed on silica gel [hexane–AcOEt (7:1)] to give an oily mixture of **3d** and **4d** (total 116 mg, 74%). The ratio of **3d** and **4d** was estimated to be 80:20 by integration of the intensities of the peak heights of the signals due to the methine proton at the 1-position which appeared at δ 3.15 (d) and 2.93 (d), respectively. The mixture was re-chromatographed on silica gel [hexane–AcOEt (50:1)]. The first fraction gave *methyl* (1S*,2S*,3S*)-3-(tert-*butyldimethylsilyloxy*)-5-*oxo*-2-(*prop*-2-*enyl*)*cyclopentanecarboxylate* **4d**, as an oil (Found: M + H$^+$, 313.1844. $C_{16}H_{29}O_4Si$ requires *M*, 313.1835); ν_{max}/cm^{-1} 1760 and 1725; δ_H 0.06 (3 H, s, SiMe), 0.09 (3 H, s, SiMe), 0.90 (9 H, s, $SiCMe_3$), 2.09–2.24 (1 H, m, one of CH_2CH=), 2.36 (1 H, dd, *J* 18.4 and 8.4, one of 4-H_2), 2.45–2.56 (1 H, m, one of CH_2CH=), 2.61–2.77 (2 H, m, 2-H and one of 4-H_2), 2.93 (1 H, d, *J* 11.2, 1-H), 3.73 (3 H, s, OMe), 4.03 (1 H, td, *J* 8.2 and 6.9, 3-H), 5.00–5.12 (2 H, m, CH=CH_2) and 5.67–5.83 (1 H, m, C*H*=CH_2); δ_C −4.9 (SiMe), −4.5 (SiMe), 17.9 (quaternary C), 25.7(3) (Bu^t), 35.2 (CH_2), 47.5 (2-C), 48.5 (4-C), 52.5 (OMe), 59.4 (1-C), 71.4 (3-C), 117.9 (=CH_2), 134.6 (=CH), 168.9 (ester C=O) and 207.5 (C=O). The second fraction gave *methyl* (1R*,2R*,3S*)-3-(tert-*butyldimethylsilyloxy*)-5-*oxo*-2-(*prop*-2-*enyl*)*cyclopentanecarboxylate* **3d**, as an oil (Found: M + H$^+$, 313.1853); ν_{max}/cm^{-1} 1760 and 1730; δ_H 0.04 (3 H, s, SiMe), 0.06 (3 H, s, SiMe), 0.86 (9 H, s, $SiCMe_3$), 2.18–2.44 (2 H, m, CH_2CH=), 2.37 (1 H, d, *J* 18.0, one of 4-H_2), 2.50 (1 H, dd, *J* 18.0 and 4.0, one of 4-H_2), 2.58–2.70 (1 H, m, 2-H), 3.15 (1 H, d, *J* 12.0, 1-H), 3.72 (3 H, s, OMe), 4.43 (1 H, t, *J* 3.7, 3-H), 4.97–5.13 (2 H, m, CH=CH_2) and 5.68–5.84 (1 H, m, C*H*=CH_2); δ_C −5.1 (SiMe), −4.5 (SiMe), 17.9 (quaternary C), 25.7(3) (Bu^t), 33.5 (CH_2), 47.1 (2-C), 49.1 (4-C), 52.4 (OMe), 57.5 (1-C), 69.5 (3-C), 116.7 (=CH_2), 135.5 (=CH−), 170.3 (ester C=O) and 210.3 (C=O).

Intramolecular C–H insertion reaction of compound 2e

Following the general procedure, compound **2e** (171 mg, 0.50 mmol) was treated with $Rh_2(OAc)_4$ (2 mg, 0.005 mmol), after which the crude product was chromatographed on silica gel [hexane–AcOEt (7:1)] to give an oily mixture of **3e** and **4e** (total 118 mg, 75%). The ratio of **3e** and **4e** was estimated to be 90:10 by integration of the intensities of the peak heights of the signals due to the methine proton at the 1-position which appeared at δ 3.16 (d) and 2.98 (d), respectively. The mixture was re-chromatographed on silica gel [hexane–AcOEt (50:1)] to give pure *methyl* (1R*,2R*,3S*)-3-(tert-*butyldimethylsilyloxy*)-2-(1-*methylethyl*)-5-*oxocyclopentanecarboxylate* **3e** and a mixture of **3e** and *methyl* (1S*,2S*,3S*)-3-(tert-*butyldimethylsilyloxy*)-2-(1-*methylethyl*)-5-*oxocyclopentanecarboxylate* **4e**. Compound **3e** was an oil (Found: C, 61.0; H, 9.8. $C_{16}H_{30}O_4Si$ requires C, 61.1; H, 9.6%); ν_{max}/cm^{-1} 1740 and 1710; δ_H 0.04 (3 H, s, SiMe), 0.07 (3 H, s, SiMe), 0.84 (9 H, s, $SiCMe_3$), 0.86 (3 H, d, *J* 7.0, Me), 0.99 (3 H, d, *J* 6.5, Me), 1.85–2.00 (1 H, m, C*H*Me_2), 2.26 (1 H, ddd, *J* 11.4, 10.4 and 3.4, 2-H), 2.38 (1 H, d, *J* 17.7, one of 4-H_2), 2.49 (1 H, dd, *J* 17.7 and 3.7, one of 4-H_2), 3.16 (1 H, d, *J* 11.5, 1-H), 3.73 (3 H, s, OMe) and 4.51 (1 H, t, *J* 3.5, 3-H); δ_C −5.1 (SiMe), −4.3 (SiMe), 17.9 (quaternary C), 20.6 (CH_3), 20.9 (CH_3), 25.6(3) (Bu^t), 27.8 (CH), 49.5 (4-C), 52.5 (OMe), 54.9 (2-C), 57.3 (1-C), 69.1 (3-C), 171.0 (ester C=O) and 210.6 (C=O).

Intramolecular C–H insertion reaction of compound 2f

Following the general procedure, compound **2f** (170 mg, 0.44 mmol) was treated with $Rh_2(OAc)_4$ (2 mg, 0.004 mmol), after which the crude product was chromatographed on silica gel [hexane–AcOEt (7:1)] to give an oily mixture of *methyl* (1R*,2R*,3S*)-3-(tert-*butyldimethylsilyloxy*)-5-*oxo*-2-*benzylcyclopentanecarboxylate* **3f** and *methyl* (1S*,2S*,3S*)-3-(tert-*butyldimethylsilyloxy*)-5-*oxo*-2-*benzylcyclopentanecarboxylate* **4f** (total 61 mg, 39%) (Found: M + H$^+$ 363.2009. $C_{20}H_{31}O_4Si$ requires *M*, 363.1992); ν_{max}/cm^{-1} 1760 and 1730; δ_H (for **3f**) 0.05 (6 H, s, 2 × SiMe), 0.91 (9 H, s, $SiCMe_3$), 2.40 (1 H, d, *J* 18.0, one of 4-H_2), 2.52 (1 H, dd, *J* 18.1 and 3.9, one of 4-H_2), 2.75–3.01 (3 H, m, 2-H and CH_2Ph), 3.25 (1 H, d, *J* 11.3, 1-H), 3.46 (3 H, s, OMe), 4.43 (1 H, t, *J* 3.4, 3-H) and 7.18–7.32 (5 H, m, ArH); δ_C (for **3f**) −5.0 (SiMe), −4.4 (SiMe), 18.0 (quaternary C), 25.8(3) (Bu^t), 35.5 (CH_2), 49.1 (2-C), 49.2 (4-C), 52.5 (OMe), 57.6 (1-C), 69.7 (3-C), 126.4 (Ar), 128.3(2) (Ar), 129.0(2) (Ar), 138.9 (Ar), 169.6 (ester C=O) and 209.8 (C=O). The ratio of **3f** and **4f** was estimated to be 83:17 by integration of the intensities of the peak heights of the signals due to the methine proton at the 3-position which appeared at δ 4.43 (t) and 4.00–4.10 (m), respectively.

Intramolecular C–H insertion reaction of compound 2g

Following the general procedure, compound **2g** (127 mg, 0.34 mmol) was treated with $Rh_2(OAc)_4$ (1 mg, 0.003 mmol), after which the crude product was chromatographed on silica gel [hexane–AcOEt (7:1)] to give an oily mixture of **3g** and **4g** (total 42 mg, 36%). The ratio of **3g** and **4g** was estimated to be 70:30 by integration of the intensities of the peak heights of the signals due to the methine proton at the 3-position which appeared at δ 4.52 (t) and 4.29 (td), respectively. The mixture was re-chromatographed on silica gel [hexane–AcOEt (50:1)]. The first fraction gave *methyl* (1S*,2R*,3S*)-3-(tert-*butyldimethylsilyloxy*)-5-*oxo*-2-*phenylcyclopentanecarboxylate* **4g**, mp 81.5–83 °C (from hexane) (Found: C, 65.2; H, 8.3. $C_{19}H_{28}O_4Si$ requires C, 65.5; H, 8.1%); ν_{max}/cm^{-1} 1760 and 1740; δ_H −0.34 (3 H, s, SiMe), −0.18 (3 H, s, SiMe), 0.76 (9 H, s, $SiCMe_3$), 2.52 (1 H, dd, *J* 18.6 and 9.0, one of 4-H_2), 2.83 (1 H, ddd, *J* 18.1, 7.2 and 1.0, one of 4-H_2), 3.52 (1 H, d, *J* 12.5, 1-H), 3.69 (3 H, s, OMe), 3.71 (1 H, dd, *J* 12.6 and 8.9, 2-H), 4.29 (1 H, td, *J* 9.0 and 7.2, 3-H) and 7.25–7.40 (5 H, m, ArH); δ_C −5.4 (SiMe), −5.2 (SiMe), 17.9 (quaternary C), 25.6(3) (Bu^t), 47.7 (4-C), 52.7 (OMe), 54.7 (2-C), 61.4 (1-C), 74.3 (3-C), 127.5 (Ar), 127.8(2) (Ar), 128.7(2) (Ar), 138.5 (Ar), 168.1 (ester C=O) and 206.4 (C=O). The second fraction gave *methyl* (1R*,2S*,3S*)-3-(tert-*butyldimethylsilyloxy*)-5-*oxo*-2-*phenylcyclopentanecarb-*

oxylate **3g**, as an oil (Found: M + H^+, 349.1852. $C_{19}H_{29}O_4Si$ requires *M*, 349.1835); ν_{max}/cm^{-1} 1760 and 1730; δ_H −0.45 (3 H, s, SiMe), −0.22 (3 H, s, SiMe), 0.71 (9 H, s, $SiCMe_3$), 2.52 (1 H, d, *J* 18.1, one of 4-H_2), 2.72 (1 H, dd, *J* 18.1 and 4.2, one of 4-H_2), 3.70 (3 H, s, OMe), 3.86 (1 H, dd, *J* 12.7 and 3.2, 2-H), 3.97 (1 H, d, *J* 12.7, 1-H), 4.52 (1 H, t, *J* 3.8, 3-H) and 7.25–7.38 (5 H, m, ArH); δ_C −5.7 (SiMe), −5.5 (SiMe), 17.9 (quaternary C), 25.6(3) (Bu^t), 49.4 (4-C), 52.5 (OMe), 52.6 (2-C), 55.8 (1-C), 72.0 (3-C), 127.3 (Ar), 128.3(2) (Ar), 128.4(2) (Ar), 136.8 (Ar), 169.3 (ester C=O) and 209.5 (C=O).

Methyl 3-(*tert*-butyldimethylsilyloxy)pentanoate

A mixture of commercially available methyl 3-hydroxypentanoate (800 mg, 6.05 mmol), *tert*-butyldimethylchlorosilane (1.55 g, 10.3 mmol) and imidazole (1.48 g, 21.8 mmol) in dimethylformamide (25 cm^3) was stirred overnight at room temperature, and then poured into water (30 cm^3) and extracted with diethyl ether. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (50:1)] to give the title compound (1.49 g, 100%) as a colourless oil (Found: M + H^+, 247.1734. $C_{12}H_{27}O_3Si$ requires *M*, 247.1730); ν_{max}/cm^{-1} 1715; δ_H 0.03 (3 H, s, SiMe), 0.06 (3 H, s, SiMe), 0.87 (9 H, s, $SiCMe_3$), 0.89 (3 H, t, *J* 7.4, Me), 1.47–1.58 (2 H, m, 4-H_2), 2.41 (1 H, dd, *J* 14.7 and 5.7, one of 2-H_2), 2.46 (1 H, dd, *J* 14.7 and 7.0, one of 2-H_2), 3.67 (3 H, s, OMe) and 4.04–4.14 (1 H, m, 3-H).

4-(*tert*-Butyldimethylsilyloxy)-1-diazohexan-2-one 8

Aqueous LiOH (1.5 mol dm^{-3}; 4.1 cm^3, 6.1 mmol) was added to a solution of methyl 3-(*tert*-butyldimethylsilyloxy)pentanoate (300 mg, 1.2 mmol) in methanol (10 cm^3) at room temperature. The mixture was stirred overnight and then neutralised with 10% aq. HCl and extracted with diethyl ether. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated to give crude carboxylic acid (251 mg). To a solution of the carboxylic acid (251 mg, 1.08 mmol) in benzene (10 cm^3) were added pyridine (85 mg, 1.08 mmol) and oxalyl chloride (411 mg, 3.24 mmol) at 0 °C. The mixture was stirred at room temperature for 13 h after which the precipitate was filtered off. The filtrate was concentrated to afford the crude acid choloride (216 mg). The acid chloride in diethyl ether (5 cm^3) was treated with a solution of diazomethane in diethyl ether at 0 °C. After the mixture had been stirred for 2 h the excess diazomethane was decomposed by addition of acetic acid. The resulting mixture was diluted with diethyl ether and washed with sat. aq. $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (10:1)] to give **8** [136 mg, 49% from methyl 3-(*tert*-butyldimethylsilyloxy)pentanoate] as a colourless oil (Found: M + H^+, 257.1694. $C_{12}H_{25}N_2O_2Si$ requires *M*, 257.1686); ν_{max}/cm^{-1} 2100 and 1640; δ_H 0.03 (3 H, s, SiMe), 0.06 (3 H, s, SiMe), 0.88 (9 H, s, $SiCMe_3$), 0.89 (3 H, t, *J* 7.4, Me), 1.46–1.61 (2 H, m, 5-H_2), 2.33–2.53 (2 H, m, 3-H_2), 4.01–4.14 (1 H, m, 4-H) and 5.32 (1 H, br s, CHN_2).

Intramolecular C–H insertion reaction of compound 8

Following the general procedure, compound **8** (135 mg, 0.53 mmol) was treated with $Rh_2(OAc)_4$ (2 mg, 0.005 mmol) after which the crude product was chromatographed on silica gel [hexane–AcOEt (20:1)] to give an oily mixture of **5** and **6** (total 80 mg, 66%). The ratio of **5** and **6** was estimated to be 56:44 by integration of the intensities of the peak heights of the signals due to the methine proton at the 3-position which appeared at δ 4.30–4.34 (m) and 3.98 (q), respectively.

Methyl (*E*)-5-(*tert*-butyldimethylsilyloxy)hept-2-enoate

A solution of diisobutylaluminium hydride in hexane (0.95 mol dm^{-3}; 1.36 cm^3, 1.29 mmol) was added to a solution of methyl 3-(*tert*-butyldimethylsilyloxy)pentanoate (318 mg, 1.29 mmol) in anhydrous dichloromethane (15 cm^3) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 15 min after which it was treated with anhydrous methanol (2 cm^3) and sat. aq. NH_4Cl (2 cm^3). After the mixture had been allowed to warm to room temperature it was diluted with diethyl ether, dried ($MgSO_4$) and concentrated to give the crude aldehyde (283 mg). A mixture of the aldehyde (283 mg, 1.31 mmol) and methyl (triphenylphosphoranylidene)acetate (659 mg, 1.97 mmol) in benzene (15 cm^3) was refluxed for 17 h, and then concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (50:1)] to give the title compound [272 mg, 93% from methyl 3-(*tert*-butyldimethylsilyloxy)pentanoate] as a colourless oil (Found: M + H^+, 273.1896. $C_{14}H_{29}O_3Si$ requires *M*, 273.1886); ν_{max}/cm^{-1} 1720 and 1660; δ_H 0.04 (6 H, s, 2 × SiMe), 0.88 (3 H, t, *J* 7.4, Me), 0.89 (9 H, s, $SiCMe_3$), 1.42–1.53 (2 H, m, 6-H_2), 2.30–2.38 (2 H, m, 4-H_2), 3.66–3.76 (1 H, m, 5-H), 3.73 (3 H, s, OMe), 5.84 (1 H, dt, *J* 15.7 and 1.3, 2-H) and 6.97 (1 H, dt, *J* 15.7 and 7.6, 3-H).

Methyl 5-(*tert*-butyldimethylsilyloxy)heptanoate

Methyl (*E*)-5-(*tert*-butyldimethylsilyloxy)hept-2-enoate (318 mg, 1.17 mmol) was hydrogenated in ethanol (5 cm^3) over 10% palladium-on-carbon (32 mg) at 3 kg cm^{-2} for 15 h. After the catalyst had been filtered off, the filtrate was concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (80:1)] to give the title compound (243 mg, 76%) as a colourless oil (Found: M + H^+, 275.2054. $C_{14}H_{31}O_3Si$ requires *M*, 275.2042); ν_{max}/cm^{-1} 1740; δ_H 0.04 (6 H, s, 2 × SiMe), 0.86 (3 H, t, *J* 7.4, Me), 0.89 (9 H, s, $SiCMe_3$), 1.39–1.51 (4 H, m, 2 × CH_2), 1.54–1.75 (2 H, m, CH_2), 2.31 (2 H, t, *J* 7.4, 2-H_2), 3.59 (1 H, quintet, *J* 5.7, 5-H) and 3.67 (3 H, s, OMe).

Methyl 5-(*tert*-butyldimethylsilyloxy)-2-benzoylheptanoate

According to the method reported by Taber and co-workers,[20] methyl 5-(*tert*-butyldimethylsilyloxy)heptanoate (171 mg, 0.62 mmol) and methyl benzoate (169 mg, 1.24 mmol) were added at 0 °C to a suspension of sodium hydride (60% dispersion in mineral oil; 45 mg, 1.86 mmol) in dimethoxyethane (6 cm^3), followed by 2 drops of methanol; the mixture was then heated to reflux for 14 h. The reaction was then quenched by the addition of 10% aq. HCl. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer and extracts were then dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (30:1)] to give a 1:1 mixture of diastereoisomers of the title compound (166 mg, 71%) as a colourless oil (Found: M + H^+, 379.2315. $C_{21}H_{35}O_4Si$ requires *M*, 379.2305); ν_{max}/cm^{-1} 1740 and 1690; δ_H −0.01, 0.02 (total 3 H, both s, SiMe), 0.03 (3 H, s, SiMe), 0.80–0.90 (3 H, m, Me), 0.84, 0.87 (total 9 H, both s, $SiCMe_3$), 1.40–1.53 (4 H, m), 1.92–2.13 (2 H, m, 3-H_2), 3.55–3.70 (1 H, m, 5-H), 3.68, 3.69 (total 3 H, both s, OMe), 4.29, 4.31 (total 1 H, both q, *J* 7.8, 5-H), 7.44–7.52 (2 H, m, ArH), 7.55–7.62 (1 H, m, ArH) and 7.95–8.01 (2 H, m, ArH).

Methyl 5-(*tert*-butyldimethylsilyloxy)-2-diazoheptanoate 9

According to the method reported by Taber and co-workers,[20] 1,8-diazabicyclo[5.4.0]undec-7-ene (104 mg, 0.68 mmol) and 4-nitrobenzenesulfonyl azide (155 mg, 0.68 mmol) were added to a solution of methyl (*tert*-butyldimethylsilyloxy)-2-benzoylheptanoate (163 mg, 0.43 mmol) in dichloromethane (5 cm^3) at 0 °C. The mixture was warmed to room temperature, stirred for 1 h and then treated with 1 mol dm^{-3} phosphate buffer (pH 7, 13 cm^3). The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined extracts were dried (Na_2SO_4) and concentrated. The residue was chromatographed on silica gel [hexane–AcOEt (20:1)] to give **9** (120 mg, 93%) as a colourless oil (Found: M − N_2 + H^+, 273.1890. $C_{14}H_{29}O_3Si$ requires *M*, 273.1886); ν_{max}/cm^{-1} 2075 and 1690; δ_H 0.05 (6 H, s, 2 × SiMe), 0.87 (3 H, t, *J* 7.5, Me), 0.89 (9 H, s,

$SiCMe_3$), 1.43–1.54 (2 H, m, CH_2), 1.57–1.70 (2 H, m, CH_2), 2.25–2.45 (2 H, m, 3-H_2), 3.60–3.70 (1 H, m, 5-H) and 3.76 (3 H, s, OMe).

Rh^{II}-catalysed reaction of compound 9

A mixture of **9** (93 mg, 0.31 mmol) and $Rh_2(OAc)_4$ (1 mg, 0.003 mmol) in dichloromethane (20 cm^3) was stirred at room temperature for 30 min. After evaporation of the mixture, the crude product was chromatographed on silica gel [hexane–AcOEt (50:1)] to give *methyl* (Z)-5-(tert-*butyldimethylsilyloxy*)*hept*-2-*enoate* **10** (52 mg, 62%) as a colourless oil (Found: M + H^+, 273.1899. $C_{14}H_{29}O_3Si$ requires *M*, 273.1886); ν_{max}/cm^{-1} 1720 and 1640; δ_H 0.047 (3 H, s, SiMe), 0.051 (3 H, s, SiMe), 0.88 (3 H, t, *J* 6.8, Me), 0.89 (9 H, s, $SiCMe_3$), 1.42–1.53 (2 H, m, 6-H_2), 2.74–2.93 (2 H, m, 4-H_2), 3.67–3.78 (1 H, m, 5-H), 3.71 (3 H, s, OMe), 5.85 (1 H, dt, *J* 11.5 and 1.7, 2-H) and 6.39 (1 H, dt, *J* 11.5 and 7.6, 3-H).

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