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A short protocol for the synthesis of spirocyclic tetrahydrofurans via intramolecular O–H insertion

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Abstract—The conversion of cyclic ketones to functionalised spirocyclic tetrahydrofurans via a three-step sequence of acetoacetate ester dianion–aldol reaction, diazo-transfer and carbene O–H insertion is described.

The spirocyclic ether unit is found in a wide variety of natural products. In particular, the 2,2-spirocyclic tetrahydrofuran moiety is found in simple natural products such as theaspirone **1** isolated from tea[1] as well as in more complex natural products such as kuroyurinidine **2**, isolated from a Japanese plant (Fig. 1).[2]

The synthesis of the oxaspirodecane system found in each of these natural products has received attention from a number of chemists. One of the earliest approaches utilised the acid-catalysed addition of an alcohol to a cyclohexene double bond in the first synthesis of theaspirone.[3] This was followed some years later by the conceptually similar acid-catalysed cyclisation of a 1,5-diol.[4] An alternative approach to the oxaspirodecane skeleton of theaspirone involved an oxidative cyclisation of an alcohol via lead(IV) acetate-mediated oxidation of the tertiary, allylic hydrogen.[5] A more recent approach reported by Simpkins involved the conjugate addition of an alkyl radical derived from the phenylselenyl compound **3** to an enone system to generate a range of spirocyclic ethers **4** of differing ring sizes (Scheme 1).[6]

The use of the rhodium(II)-catalysed decomposition of α-diazocarbonyl compounds has found widespread use in the synthesis of cyclic compounds[7] in particular oxygen

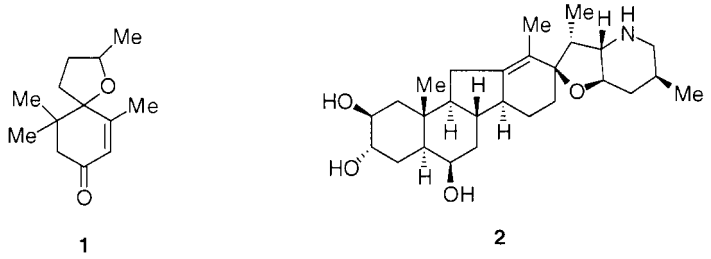
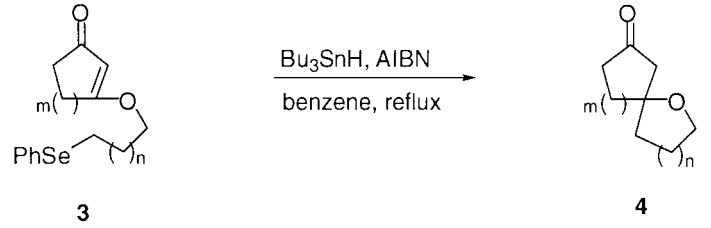


Figure 1.



Scheme 1.

Keywords: cyclic ketones; spirocyclic tetrahydrofurans; diazo-transfer; carbenes.
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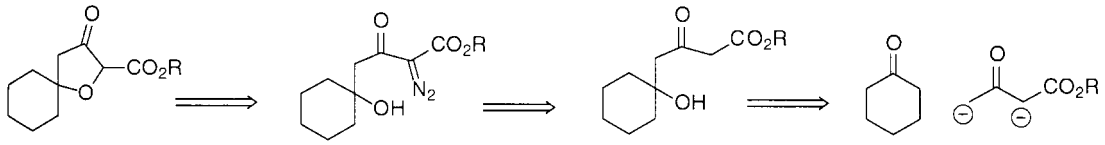


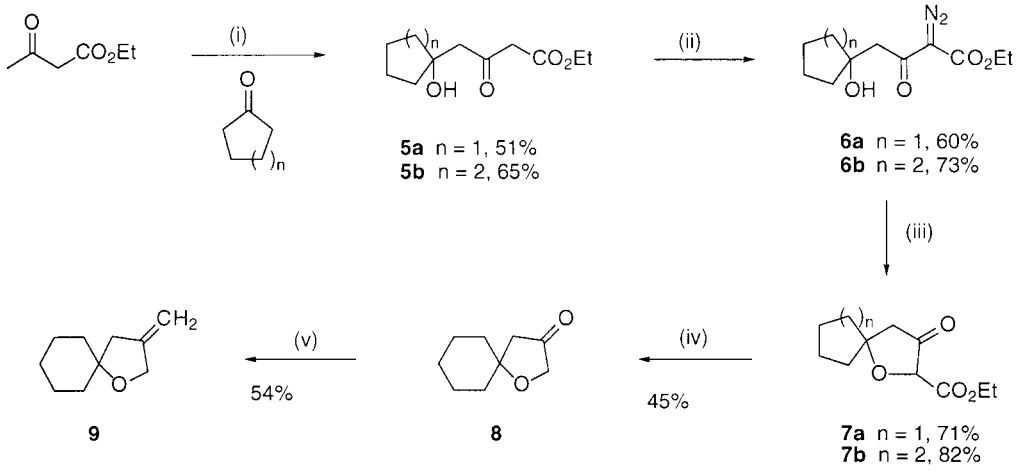
Scheme 2.

heterocycles.[8] The putative metallocarbenes generated under these conditions undergo both C–H and O–H bond insertion and examples of both these processes in the creation of tetrahydrofurans and derivatives have been reported. The C–H insertion reaction has been reported by Doyle as a method for the synthesis of 4,4-spirocyclic butyrolactones.[9] The O–H insertion reaction was first reported by Rapoport[10] and has been extensively explored by Moody.[11] As part of this work, Moody has examined the role of the catalyst, the nature of the precursor diazocarbonyl compound and the intervention of competing C–H insertion reactions.[11d] However, the main preparative focus of this work was on the synthesis of oxepanes[11b,c,e] and not spirocyclic ethers.

Our strategy was to use carbene chemistry to create the spirocyclic tetrahydrofuran system found in theaspirone and kuroyurinidine in a simple three-step procedure shown retrosynthetically in Scheme 2. Insertion of the carbene derived from the α-diazo-β-ketoester into the O–H bond of the tertiary alcohol is the key step leading to a spirocyclic system carrying useful functionality for further elaboration. The α-diazo-β-ketoester is readily available by diazo-transfer reaction of the β-ketoester. The second key disconnection involves the reaction of the dianion of the acetoacetate ester with a cyclic ketone to create the tertiary alcohol.[12]

The recent report of an aldol-cyclisation sequence involving the reaction of the enolate of an α-diazo-β-ketoester with an aldehyde followed by O–H insertion to prepare monocyclic tetrahydrofurans[13] and deoxy-C-nucleosides[14] prompts us to report the successful realisation of the sequence shown in Scheme 2.

Generation of the bis-enolate of ethyl acetoactate was achieved using 2 mol equiv. of lithium diisopropylamide (LDA) at −78°C in an adaptation of a procedure first reported by Weiler.[15] This was then reacted at this temperature with 1 mol equiv. of cyclopentanone to give **5a** in 51% yield. Similar reaction of the bis-enolate with cyclohexanone gave **5b** in 65% yield. The regioselectivity of reaction of the dianion with electrophiles is well-precedented and the slightly lower yield for the reaction of cyclopentanone may simply reflect a slightly increased propensity for proton transfer in cyclopentanones compared to cyclohexanones.[12] Both **5a** and **5b** exist almost exclusively in their keto-form (>95%) with a small singlet peak in their ^{1}H NMR spectra at δ 5.03 being attributable to the alkene proton of the enol-form. The most commonly used reagent for diazo-transfer reactions is tosyl azide used in conjunction with triethylamine as base.[16] Problems with incomplete reaction prompted us to use the conditions of Koskinen involving acetonitrile as solvent and powdered potassium carbonate as base.[17] Precipitation of the toluene sulfonamide by-product facilitated purification of the resultant α-diazo-β-ketoesters **6** but chromatography was still necessary to give pure products. As a consequence, the yields of **6a** and **6b** were 60 and 73%, respectively in spite of the reactions appearing to be much higher yielding by TLC. Alternatives such as polymer-bound azides[18] and the less stable mesyl azide[19] were not explored. The α-diazo-β-ketoesters **6** were characterised by the usual methods but it should be noted that no resonance for the diazo-carbon was observed in the ^{13}C NMR spectrum presumably owing to slow relaxation of this carbon signal.[20] The O–H insertion reaction was carried out using the readily available rhodium(II) acetate as catalyst. Addition of ca. 3 mol% rhodium(II) acetate to a refluxing solution of α-diazo-β-ketoesters **6** in toluene led to



Scheme 3. *Reagents and conditions*: (i) 2 equiv. LDA, THF, −78°C, 40 min, then cyclopentanone or cyclohexanone, −78°C, 70 min; (ii) tosyl azide, potassium carbonate, acetonitrile, room temperature, 30 min; (iii) 3 mol% $Rh_2(OAc)_4$, toluene, reflux, 10 h; (iv) aqueous NaOH, room temperature, 10 h, then excess sulfuric acid; (v) methyltriphenylphosphonium bromide, *n*-BuLi, ether, room temperature, then **8**.

evolution of nitrogen and, after chromatography, spirocycles **7a** and **7b** were isolated in 71% and 82% yield, respectively. Interestingly, the ^{13}C NMR spectra of both **7a** and **7b** showed that the methylene carbons adjacent to the spirocentre are clearly non-equivalent. This loss of symmetry in the spirocyclic system is caused by the stereogenic centre in the tetrahydrofuranone ring. However, the methylene carbons β- to the spirocentre resonate at the same chemical shift. There was no evidence in the NMR spectra of either **7a** or **7b** of any measurable enol content (Scheme 3).

As expected, no product was isolated from the potentially competing C–H insertion reaction. This is in accord with the results reported by Moody which clearly demonstrated that O–H insertion to give seven-membered rings was faster than C–H insertion in non-activated systems and was ascribed to the electronic nature of the metallocarbenes generated from α-diazo-β-ketoesters.[11b] In order to demonstrate the subsequent synthetic possibilities of the functionalised spirocycles **7**, the oxaspirodecane **7b** was saponified with aqueous sodium hydroxide and then immediately treated with sulfuric acid to induce decarboxylation. This led to the spirocyclic ketone **8** in 45% yield after chromatography. The relatively low yield of **8** could be attributed to its volatility. Wittig reaction of ketone **8** with the yield derived from methyltriphenylphosphonium bromide gave alkene **9** in 54% yield after chromatography. Again volatility presented a practical problem in the isolation and handling of this product.

In conclusion, we have shown that the three-step strategy of dianion aldol reaction, diazo-transfer and carbene O–H insertion provides a rapid route to functionalised spirocyclic tetrahydrofurans. The application of this protocol to the synthesis of more complex systems and exploration of aspects of relative and absolute stereochemistry need to be addressed.

1. Experimental

1.1. General details

All reactions were carried out under argon and solutions dried with magnesium sulfate. Diethyl ether, tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl immediately before use. Acetonitrile was dried over potassium carbonate and distilled. Column chromatography was performed with silica gel (Merck 7734) using the flash chromatography technique. Thin layer chromatographic analysis was performed using plastic-backed silica plates (Merck 5735). Components were visualised by either UV or phosphomolybdic acid dip. Infrared spectra were recorded on a Perkin–Elmer 1605 FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM360 spectrometer operating at 360 MHz for proton and 90 MHz for carbon. Tetramethylsilane (TMS) was adopted as the internal standard for ^1H NMR spectra and the solvent peaks for ^{13}C NMR spectra. Chemical shifts (δ_H and δ_C) values are reported as parts per million (ppm). The multiplicity of an ^1H NMR signal is designated by one of the following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, br=broad and m=multiplet. Coupling constants are reported in Hz. High resolution mass spectra were performed at the Mass Spectrometry Centre, Chemistry Department, King's College London.

1.1.1. Ethyl 4-(1-hydroxycyclopentyl)-3-oxobutanoate (5a). Ethyl acetoacetate (3.406 g, 26 mmol) in dry THF (80 mL) was added dropwise to a stirred solution of LDA in THF (2 M, 13 mL) dropwise at 0°C under argon. The resulting solution was stirred for 40 min at this temperature to ensure complete formation of the dianion and then cooled to −78°C. A solution of cyclopentanone (2.268 g, 27 mmol) in dry THF (35 mL) was added dropwise. After completion of the addition, the reaction mixture was stirred for a further 70 min at −78°C and then quenched with saturated ammonium chloride solution (100 mL) at this temperature. After warming to ambient temperature, diethyl ether was added (100 mL) and the organic layer separated. The aqueous layer was extracted with diethyl ether (2×50 mL) and the combined organic extracts washed with saturated brine, dried over magnesium sulfate and concentrated in vacuo. The residue was chromatographed (hexane/ethyl acetate, 4:1) to give alcohol **5a** (3.023 g, 51%) as a viscous, pale orange oil. R_f 0.44 (hexane/ethyl acetate, 4:1); ν_{max}/cm^{-1} 3500 (OH), 1740 (CO), 1710 (CO); $\delta_H(CDCl_3)$ 1.29 (3H, t, *J* 7, CH_3), 1.61 (4H, m, 2×cyclopentane CH_2), 1.84 (4H, m, 2×cyclopentane CH_2), 2.87 (2H, s, $CH_2C{=}O$), 3.18 (1H, s, OH), 3.47 (2H, s, $COCH_2CO$), 4.20 (2H, q, *J* 7, CH_2O); $\delta_C(CDCl_3)$ 14.2 (CH_3), 23.7 (CH_2), 39.8 (CH_2), 50.3 (CH_2), 52.5 (CH_2), 61.6 (CH_2), 79.9 (C-quaternary), 166.9 (CO), 205.0 (CO); *m/z* 214 (6%, M^+), 197 (16, M^+-OH), 185 (100, M^+-Et); Found: M^+, 214.1203. $C_{11}H_{18}O_4$ requires M^+, 214.1205.

1.1.2. Ethyl 4-(1-hydroxycyclohexyl)-3-oxobutanoate (5b). Ethyl acetoacetate (13.624 g, 104 mmol) in dry THF (320 mL) was added dropwise to a stirred solution of LDA in THF (2 M, 52 mL) dropwise at 0°C under argon. The resulting solution was stirred for 40 min at this temperature to ensure complete formation of the dianion and then cooled to −78°C. A solution of cyclohexanone (10.584 g, 108 mmol) in dry THF (140 mL) was added dropwise. After completion of the addition, the reaction mixture was stirred for a further 70 min at −78°C and then quenched with saturated ammonium chloride solution (400 mL) at this temperature. After warming to ambient temperature, diethyl ether was added (100 mL) and the organic layer separated. The aqueous layer was extracted with diethyl ether (2×50 mL) and the combined organic extracts washed with saturated brine, dried over magnesium sulfate and concentrated in vacuo. The residue was chromatographed (hexane/ethyl acetate, 4:1) to give alcohol **5b** (16.005 g, 65%) as a viscous, pale orange oil. R_f 0.37 (hexane/ethyl acetate, 4:1); ν_{max}/cm^{-1} 3440 (OH), 1740 (CO), 1710 (CO); $\delta_H(CDCl_3)$ 1.28 (3H, t, *J* 7, CH_3), 1.42 (6H, m, 3×cyclohexane CH_2), 1.64 (4H, m, 2×cyclohexane CH_2), 2.71 (2H, s, $CH_2C{=}O$), 3.25 (1H, s, OH), 3.48 (2H, s, $COCH_2CO$), 4.20 (2H, q, *J* 7, CH_2O); $\delta_C(CDCl_3)$ 14.1 (CH_3), 21.9 (CH_2), 25.6 (CH_2), 37.5 (CH_2), 50.9 (CH_2), 52.7 (CH_2), 61.5 (CH_2), 70.8 (C-quaternary), 167.0 (CO), 204.6 (CO); *m/z* 228 (20%, M^+), 211 (5, M^+-OH), 155 (100, $M^+-COOEt$); Found: M^+, 228.1356. $C_{12}H_{20}O_4$ requires M^+, 228.1361.

1.1.3. Ethyl 2-diazo-4-(1-hydroxycyclopentyl)-3-oxobutanoate (6a). Powdered potassium carbonate (1.567 g, 11.33 mmol) was weighed directly into an oven-dried flask. Dry acetonitrile (70 mL) was added and the mixture stirred under an argon atmosphere. Ethyl 4-(1-hydroxycyclopentyl)-3-oxobutanoate **5a** (2.364 g, 11.05 mmol) in dry acetonitrile (25 mL) was added slowly at room temperature. After complete addition, the mixture was stirred for a further 5 min and *p*-toluenesulfonyl azide (2.255 g, 11.43 mmol) in dry acetonitrile (25 mL) was added dropwise. An intense yellow colour was observed. After completion of addition, the mixture was stirred at room temperature for a further 30 min. The reaction mixture was then filtered through a small pad of celite, which was washed with diethyl ether (10 mL). The total filtrate was treated with diethyl ether (100 mL), which precipitated *p*-toluenesulfonamide. Filtration and removal of the solvent in vacuo gave a viscous orange oil which was purified by chromatography (hexane/ethyl acetate, 5:1) to give diazo-compound **6a** (1.60 g, 60%). R_f 0.56 (hexane/ethyl acetate, 4:1); ν_{max}/cm^{-1} 3520 (OH), 2140 (C=N=N), 1760 (CO), 1730 (CO); $\delta_H(CDCl_3)$ 1.33 (3H, t, *J* 7, CH_3), 1.61 (4H, m, 2×cyclopentane CH_2), 1.83 (4H, m, 2×cyclopentane CH_2), 3.17 (2H, s, CH_2C=O), 3.53 (1H, s, OH), 4.30 (2H, q, *J* 7, CH_2O); $\delta_C(CDCl_3)$ 14.3 (CH_3), 23.7 (CH_2), 39.9 (CH_2), 49.2 (CH_2), 61.7 (CH_2), 80.5 (C-quaternary), 161.4 (CO), 193.7 (CO)—*diazo carbon not observed*; *m/z* 240 (5%, M^+), 212 (20, M^+-N_2), 85 (100); Found: M^+, 240.1101. $C_{11}H_{16}N_2O_4$ requires M^+, 240.1110.

1.1.4. Ethyl 2-diazo-4-(1-hydroxycyclohexyl)-3-oxobutanoate (6b). Powdered potassium carbonate (9.402 g, 67.98 mmol) was weighed directly into an oven-dried flask. Dry acetonitrile (420 mL) was added and the mixture stirred under an argon atmosphere. β-Ketoester **5b** (15.114 g, 66.3 mmol) in dry acetonitrile (150 mL) was added slowly at room temperature. After complete addition, the mixture was stirred for a further 5 min and *p*-toluenesulfonyl azide (13.53 g, 68.58 mmol) in dry acetonitrile (150 mL) was added dropwise. An intense yellow colour was observed. After completion of addition, the mixture was stirred at room temperature for a further 30 min. The reaction mixture was then filtered through a small pad of celite, which was washed with diethyl ether (20 mL). The total filtrate was treated with diethyl ether (600 mL), which precipitated *p*-toluenesulfonamide. Filtration and removal of the solvent in vacuo gave a viscous orange oil which was purified by chromatography (hexane/ethyl acetate, 5:1) to give diazo-compound **6b** (12.294 g, 73%). R_f 0.41 (hexane/ethyl acetate, 4:1); ν_{max}/cm^{-1} 3440 (OH), 2130 (C=N=N), 1750 (CO), 1720 (CO); $\delta_H(CDCl_3)$ 1.32 (3H, t, *J* 7, CH_3), 1.45 (6H, m, 3×cyclohexane CH_2), 1.64 (4H, m, 2×cyclohexane CH_2), 2.49 (1H, s, OH), 3.05 (2H, s, CH_2C=O), 4.31 (2H, q, *J* 7, CH_2O); $\delta_C(CDCl_3)$ 14.4 (CH_3), 22.0 (CH_2), 25.7 (CH_2), 37.9 (CH_2), 49.2 (CH_2), 61.7 (CH_2), 71.6 (C-quaternary), 161.6 (CO), 193.3 (CO)—*diazo carbon not observed*; *m/z* 254 (14%, M^+), 155 (100); Found: M^+, 254.1266. $C_{12}H_{18}N_2O_4$ requires M^+, 254.1266.

1.1.5. Ethyl 1-oxa-spiro[4,4]nonan-3-one-2-carboxylate (7a). Diazoester **6a** (0.861 g, 3.59 mmol) was dissolved in dry toluene (50 mL), dirhodium tetraacetate (49 mg, 0.01 mmol) was added and the solution refluxed under an argon atmosphere for 10 h. The reaction mixture was filtered and the toluene removed in vacuo to give a pale yellow oil which was purified by chromatography (hexane/ethyl acetate, 5:1) to give the spirocyclic ether **7a** (0.54 g, 71%) as a viscous oil. R_f 0.56 (hexane/ethyl acetate, 4:1); ν_{max}/cm^{-1} 3497 (OH), 1773 (CO), 1747 (CO); $\delta_H(CDCl_3)$ 1.30 (3H, t, *J* 7, CH_3), 1.59 (4H, m, 2×cyclopentane CH_2), 1.80 (4H, m, 2×cyclopentane CH_2), 2.46 (2H, s, CH_2C=O), 4.26 (2H, q, *J* 7, CH_2O), 4.53 (1H, s, $CHCO_2Et$); $\delta_C(CDCl_3)$ 14.2 (CH_3), 24.7 (2 coincident CH_2), 38.6 (CH_2), 39.6 (CH_2), 47.1 (CH_2), 62.4 (CH_2), 87.0 (CH), 91.3 (C-quaternary), 166.4 (CO), 208.7 (CO); *m/z* 212 (100%, M^+), 139 (15, $M^+-COOEt$); Found: M^+, 212.1053. $C_{11}H_{16}O_4$ requires M^+, 212.1049.

1.1.6. Ethyl 1-oxa-spiro[4,5]decan-3-one-2-carboxylate (7b). Diazoester **6b** (10.93 g, 43.0 mmol) was dissolved in dry toluene (200 mL), dirhodium tetraacetate (410 mg, 0.09 mmol) was added and the solution refluxed under an argon atmosphere for 10 h. The reaction mixture was filtered and the toluene removed in vacuo to give a pale yellow oil which was purified by chromatography (hexane/ethyl acetate, 5:1) to give the spirocyclic ether **7b** (7.97 g, 82%) as a viscous oil. R_f 0.49 (hexane/ethyl acetate, 4:1); ν_{max}/cm^{-1} 3487 (OH), 1768 (CO), 1742 (CO); $\delta_H(CDCl_3)$ 1.29 (3H, t, *J* 7, CH_3), 1.41 (6H, m, 3×cyclohexane CH_2), 1.69 (4H, m, 2×cyclohexane CH_2), 2.45 (2H, s, CH_2C=O), 4.24 (2H, q, *J* 7, CH_2O), 4.57 (1H, s, $CHCO_2Et$); $\delta_C(CDCl_3)$ 14.2 (CH_3), 23.0 (2 coincident CH_2), 25.0 (CH_2), 36.9 (CH_2), 37.6 (CH_2), 47.6 (CH_2), 62.1 (CH_2), 79.2 (CH), 82.2 (C-quaternary), 166.6 (CO), 208.4 (CO); *m/z* 226 (100%, M^+), 153 (45, $M^+-COOEt$); Found: M^+, 226.1202. $C_{12}H_{18}O_4$ requires M^+, 226.1205.

1.1.7. 1-Oxa-spiro[4,5]decan-3-one (8). Ethyl 1-oxa-spiro[4,5]decan-3-one-2-carboxylate **7b** (4.0 g, 17.7 mmol) was added to an aqueous solution of sodium hydroxide (0.885 g, 22 mmol in 18 mL of water). The mixture was stirred at room temperature for 12 h after which time complete saponification of the ester was indicated by TLC. Aqueous sulfuric acid (2.5 mL, 50%) was carefully added and the mixture stirred until no further carbon dioxide was evolved. The reaction mixture was extracted with dichloromethane (5×30 mL), the combined organic extracts were dried and evaporated carefully in vacuo. Purification of the residue by chromatography (hexane/ethyl acetate, 4:1) gave the title compound (1.22 g, 45%) as a viscous, pale yellow oil. R_f 0.38 (hexane/ethyl acetate, 4:1); ν_{max}/cm^{-1} 1760 (C=O), 1180 (CO); $\delta_H(CDCl_3)$ 1.41 (6H, m, 3×cyclohexane CH_2), 1.69 (4H, m, 2×cyclohexane CH_2), 2.32 (2H, s, CH_2C=O), 3.98 (2H, s, OCH_2C=O); $\delta_C(CDCl_3)$ 22.5 (CH_2), 25.1 (CH_2), 36.2 (CH_2), 48.1 (CH_2), 69.4 (CH_2), 84.9 (C-quaternary), 215.8 (CO); *m/z* 154 (30%, M^+), 72 (100); Found: M^+, 154.1010. $C_9H_{14}O_2$ requires M^+, 154.0994.

1.1.8. 3-Methylene-1-oxa-spiro[4,5]decane (9). Methyltriphenylphosphonium bromide (2.04 g, 5.73 mmol) was dissolved in dry ether (65 mL) under an argon atmosphere at room temperature and *n*-butyllithium (2.9 mL of 2 M solution in ether) was added dropwise over 10 min. The resulting deep orange solution was stirred for a further

15 min and a solution of 1-oxa-spiro[4,5]decan-3-one **8** (0.75 g, 4.85 mmol) in dry ether (10 mL) was added dropwise over 30 min. After a further 1 h, TLC analysis showed no remaining starting material. The reaction mixture was poured into brine (50 mL), the organic layer separated and the aqueous layer extracted with ether (3×50 mL). The combined organic extracts were dried and carefully concentrated in vacuo to give an oily residue, which was purified by chromatography (hexane/ethyl acetate, 10:1) to give the title compound (0.40 g, 54%) as a pale yellow oil. R_f 0.47 (hexane/ethyl acetate, 10:1); ν_{max}/cm^{-1} 1616 (C═C), 1160 (CO); $\delta_H(CDCl_3)$ 1.43 (6H, m, 3×cyclohexane CH_2), 1.58 (4H, m, 2×cyclohexane CH_2), 2.27 (2H, s, $CH_2C{=}C$), 4.23 (2H, s, $OCH_2C{=}C$), 4.79 (1H, d, *J* 2, C═CH_2), 4.86 (1H, d, *J* 2, C═CH_2); $\delta_C(CDCl_3)$ 22.5 (CH_2), 24.8 (CH_2), 34.9 (CH_2), 42.5 (CH_2), 68.1 (CH_2), 81.8 (C-quaternary), 103.3 (CH_2), 147.9 (C-quaternary); *m/z* 152 (100%, M^+), 82 (5); Found: M^+, 152.1166. $C_{10}H_{16}O$ requires M^+, 152.1201.

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