Rhodium(II)-carbenoid C–H insertion reactions in the synthesis of α,β′-dioxospirane systems

Pompiliu S. Aburel, Christian Rømming and Kjell Undheim *

Department of Chemistry, University of Oslo, N-0315, Oslo, Norway

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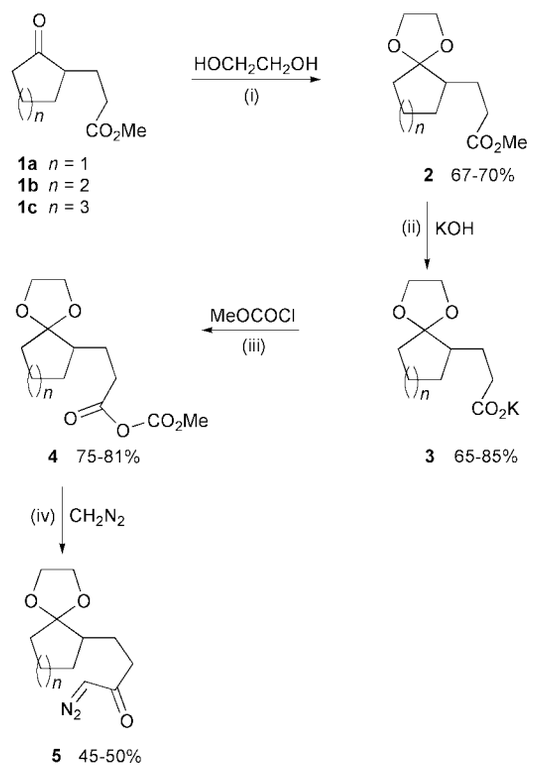
Spiro[4.4]nonane-, spiro[4.5]decane- and spiro[4.6]undecane-α,β′-diones have been prepared from 1-diazo-4-(2,2-ethylenedioxycycloalkan-1-yl)butan-2-one intermediates by $Rh_2(OAc)_4$- and $Rh_2(TPA)_4$-catalyzed C–H insertions. Competitive insertions also gave *trans*-bicyclic derivatives. The relative stereochemistry in bicyclic derivatives has been determined by single crystal X-ray analyses.

Introduction

From continued studies on the synthesis and carbosubstitution reactions in spiranes we report results from the work on the construction of α,β′-dioxospiranes.[1–3] Our most recent report described methodology for the preparation of β,β′-dioxospiranes by dirhodium(II) carbenoid C–H insertion.[1] The spiranes are of special interest because the rigidity of such systems provides a stiff framework for the attachment of pharmacophoric active groups, or for attachment of metal coordination functions in the construction of catalyst systems. For additional modifications of the groups attached to the framework, we have also studied substitution reactions in spiranes with α,α′-dioxospiranes as initial substrates.[2,3] The present report describes results from the preparation of α,β′-dioxospiranes using Rh(II)-carbenoids for cyclopentane spiroannulation.

The usual order of reactivity with dirhodium tetraacetate-catalyzed C–H insertion is methine > methylene > methyl. The C–H insertion is normally site selective in that five-membered ring formation is greatly favoured.[4–6] On the other hand, heteroatoms such as the oxygen in an ether can activate an adjacent C–H bond for insertion. This activation will often take precedence over the normally preferred five-membered ring formation.[7] The opposite effect in insertion reactions is experienced in the presence of electron-withdrawing groups because of the electrophilic nature of the carbenoid function.[8] Therefore the carbonyl group in the cycloalkanone was converted into an acetal function (Scheme 1). C–H insertion at the α-carbon in an acetal function was to be expected by analogy to the activation by an ether oxygen. On the other hand, increased steric interactions from the acetal function would be unfavourable for C–H insertion at the acetal α-carbon. The β′-oxo group in the second spirane ring, which is formed by the spiroannulation, is a stabilizing part of the Rh(II) carbenoid moiety for the C–H insertion reaction.



Scheme 1 (i) Benzene, reflux, 6 h; (ii) MeOH, reflux, 7 h; (iii) THF, 20 °C, 10 h; (iv) Et_2O, O °C, 15 h.

Results and discussion

The substrates were five-, six- and seven-membered ring derivatives of 3-(2-oxocycloalkan-1-yl)propionates which were available from the corresponding cycloalkanones by a Michael addition reaction with acrylate.[9] Ethylene glycol was used for the acetalization. In the preparation of the diazoketones **5**, the initial step was a hydrolytic reaction of the propionic esters **1** under alkaline conditions. The potassium salts **3** were converted into mixed anhydrides **4** using methyl chloroformate, and the anhydrides reacted further with diazomethane in diethyl ether solution at 0 °C to furnish the diazoketones **5**. The carbenoid insertion was effected using 5 mol% dirhodium tetraacetate in dichloromethane at ambient temperature. The reactions required 12 h to go to completion and were run under an atmosphere of argon. Previously, the Rh(II)-catalyzed synthesis of β,β′-dioxospiranes was effected under a purified nitrogen atmosphere.[1] Subsequently we discovered that the yields in these reactions were increased by some 10–20% on changing the gas from nitrogen to argon. This was also true in the present work. The product ratios were essentially unaffected by the nature of the gas atmosphere (*vide infra*).

The product from the five-membered substrate **5a** was the spiroannulated structure **6a** in 70% yield (Scheme 2). From the six-membered homologue **5b** both the spirane **6b** and the β-decalone **7b** were formed in 21% and 48% yield, respectively. From the seven-membered ring substrate **5c**, the spiro product

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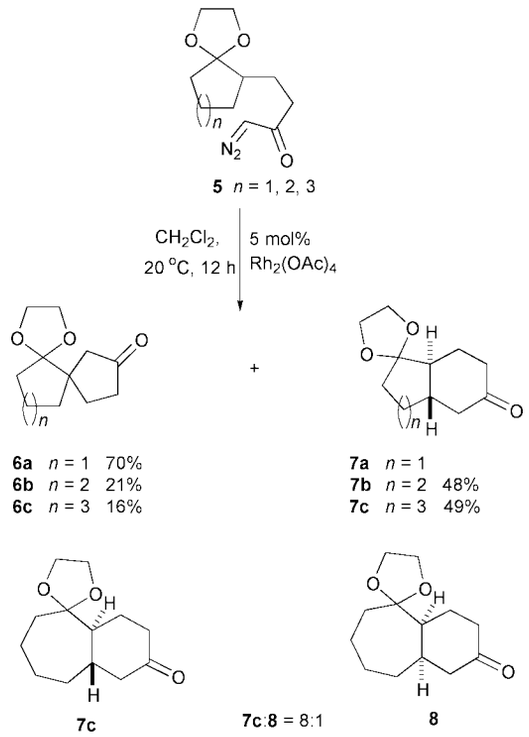


Scheme 2

6c and bicyclo[5.4.0]undecanone products were formed in 16% and 49% yield, respectively (Scheme 2). The vicinal annulation of a cyclohexane ring in the formation of the products **7** requires that C–H insertion takes place into a non-activated methylene group. The regiochemistry preferences may in part be rationalized as due to repulsive steric interactions with the vicinal acetal function. Exclusive *trans* stereochemistry at the ring junction was found for the bicyclo[4.4.0]decanone product **7b** from the six-membered ring substrate **5b**. The bicyclo-[5.4.0]undecanone product from the more flexible seven-membered ring substrate **5c** was a mixture of the *trans*- and *cis*-isomers **7c** and **8** in the ratio 8 : 1 (*vide infra*).

Steric interactions are known to affect the site of C–H insertion as in the case of competitive γ- and δ-lactone spiro-annulations in an appropriately functionalized bicyclo[3.3.0]-octan-3-one ethylene acetal.[10] In another case the preference was for cyclobutanone spiroannulation rather than for cyclo-pentanone bicyclic annulation into cyclopentane substrates including derivatives with an adjacent ethylene acetal function.[11] In the latter case, when the ethylenediol in the acetal was changed to a butane-2,3-diol, the additional steric interaction from the methyl groups prevented spiroannulation at the α-carbon.[11] In constrained ethers steric factors may become more important than the α-CH ether activation for the regiochemistry for the insertion.[12]

The bulky dirhodium(II) tetrakis(triphenylacetate) (Rh_2-$(TPA)_4$) was used to gain some additional information of steric interactions in reactions of the substrates **5**. A higher regio-control with less spirane annulation was to be expected.[11] Comparative results from studies with $Rh_2(OAc)_4$ and $Rh_2(TPA)_4$ are given in Scheme 3. The $Rh_2(TPA)_4$ catalyst was available from dirhodium tetraacetate by an acid exchange reaction.[13] The reactions catalyzed by $Rh_2(TPA)_4$ were faster than for $Rh_2(OAc)_4$. In the former case the starting material was consumed after 1.5 h at 0 °C and for $Rh_2(OAc)_4$ catalysis the reaction time was 12 h at ambient temperature. The expected increase in the relative amount of the bicyclic products **7b** and **7c** was observed (Scheme 3). In the case of the five-membered ring substrate **5a**, the product composition goes from exclusive spiroannulation with the rhodium acetate catalyst to the ratio **6a** : **7a** 14 : 86 in favour of the ring annulated cyclohexanone **7a**

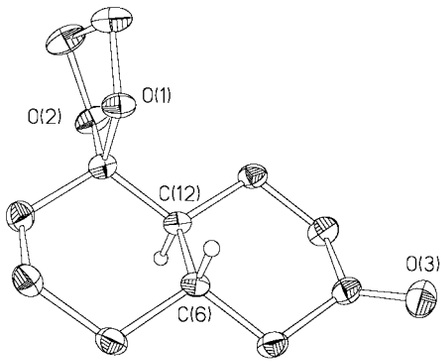
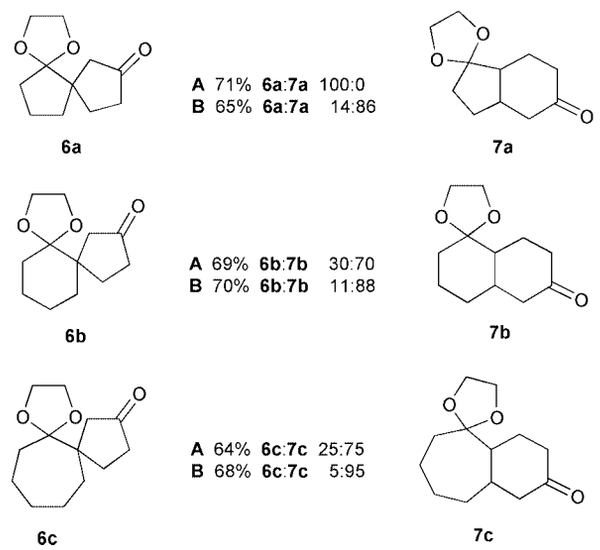


Fig. 1 The ORTEP plot of compound **7b**. Ellipsoids are shown at 50% probability. For clarity only hydrogens at C(6) and C(12) are shown.



Scheme 3 **A** 5 mol% $Rh_2(OAc)_4$, CH_2Cl_2, 20 °C, 12 h; **B** 5 mol%, $Rh_2(TPA)_4$, CH_2Cl_2, 0 °C, 1.5 h. TPAH = Ph_3CCO_2H.

with the triphenylacetate catalyst. The bicyclo[4.3.0]nonane product has been assigned the *trans* structure **7a** by analogy to *trans* stereochemistry found in the higher homologues in the series, *viz*. the products **7b** and **7c**. In a related cyclopentanone annulation to a cyclohexane system under the influence of $Rh_2(TPA)_4$ *trans*-bicyclo[4.3.0]nonane was the almost exclusive product whereas the same annulation to a cyclopentane system gave the *cis*-bicyclo[3.3.0]octane. In the former case with the $Rh_2(OAc)_4$-catalyst, a mixture of *trans*- and *cis*-isomers resulted.[11]

The stereochemistry at the ring junction in the annulated cyclohexanone derivatives **7b** and **7c** has been established by single crystal X-ray determinations. The β-decalone **7b** was a crystalline material. The X-ray analysis led to the assignment of the *trans*-configuration shown in Fig. 1. The seven-membered ring product was a 8 : 1 mixture of the isomers **7c** and **8** which we failed to separate by chromatography. Instead the keto group was reduced with $LiAlH(tBuO)_3$ in an attempt to effect stereoselective reduction of the major isomer to the corresponding alcohol. The yield of a single alcohol isomer was 60% from the mixture of the *trans* and *cis* ketones **7c** and **8** after chromatography. Another 20% of a stereoisomeric mixture of alcohols was isolated after chromatography. Chromic acid reoxidation of this isolate gave the *trans* and *cis* ketones **7c** and **8** in a 1 : 1 ratio confirming the hydroxy nature of the reduction products.

The major alcohol isomer **9** was converted into a crystalline *p*-nitrobenzoate ester (Scheme 4) which was used for the single crystal X-ray analysis. Its structure **10** is shown in Fig. 2. The ring junction has *trans* stereochemistry.

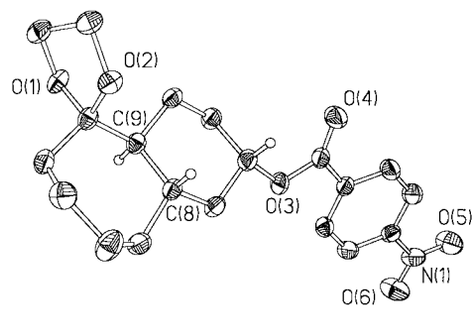
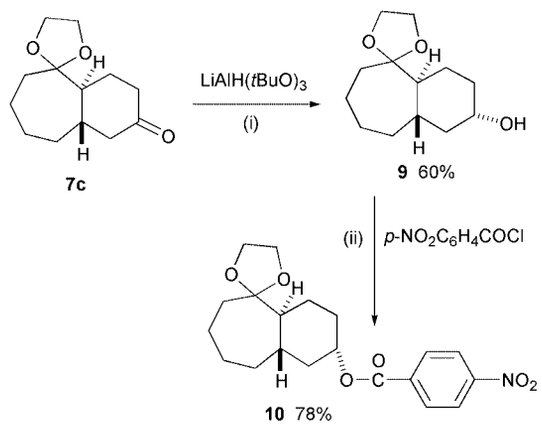
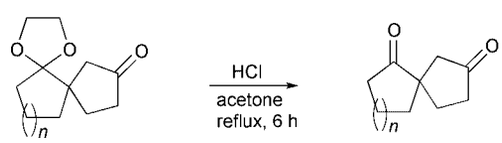


Fig. 2 The ORTEP plot of compound **10.** Ellipsoids are shown at 50% probability. For clarity only hydrogens at C(8), C(9) and at C(12) are shown.



Scheme 4 (i) THF, 0 °C to rt, 3 h; (ii) DMAP, CH_2Cl_2, rt, 3 h.

Cleavage of the acetal function in the spiranes **7** was effected under acidic conditions to furnish the α,β′-dioxospiranes **11** (Scheme 5).



Scheme 5

In conclusion, we have described a method for the preparation of spiro[4.4]nonane-2,6-dione and higher homologues together with their α,α-ethylenedioxy monoacetalized derivatives. The Rh(II)-carbenoid insertion also provides α,α-ethylenedioxy monoacetalized derivatives of bicyclo[4.3.0]-nonan-3-one and higher homologues.

Experimental

The ^{1}NMR spectra were recorded at 200 MHz or 300 MHz, and the ^{13}C NMR spectra at 50 MHz or 75 MHz unless otherwise specified. *J* Values are given in Hz. The mass spectra under electron impact conditions were recorded at 70 eV (EI). The spectra are presented as *m*/*z* (% rel. int.).

Dry THF was distilled from sodium and benzophenone. Dry dichloromethane was distilled from calcium hydride. Diethyl ether–diazomethane solution was prepared from Diazald.[14]

X-Ray crystallographic analysis for compounds 7b and 10

X-Ray data were collected on a Siemens SMART CCD diffractometer[15] using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data collection method: ω-scan, range 0.6°, crystal to detector distance 5 cm. Data reduction and cell determination were carried out with the SAINT and XPREP programs.[15] Absorption corrections were applied by the use of the SADABS program.[16] The structure was determined and refined using the SHELXTL program package.[17] The non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen positions in **7b** were found from difference Fourier maps and refined with isotropic thermal parameters, for **10** the hydrogen positions were calculated and not refined.

Crystal data for **7b**,† $C_{12}H_{18}O_3$, $M = 210.26$, triclinic, *P*-1, $a = 5.602(1)$, $b = 9.071(1)$, $c = 11.238(1)$ Å, $\alpha = 100.20(1)$, $\beta = 99.78(1)$, $\gamma = 99.32(1)°$, $V = 542.9(1)$ Å^3, $Z = 2$, $D_x = 1.286$ Mg m^{-3}, $\mu = 0.091$ mm^{-1}, $T = 150(2)$ K, measured 9220 reflections in the 2θ range 4.7–72.2°, $R_{int} = 0.012$. 208 Parameters refined against 4640 F^2, $R = 0.039$ for $I_o > 2\sigma(I_o)$ and 0.043 for all data.

Crystal data for **10**,† $C_{20}H_{25}NO_6$ $M = 375.41$, orthorhombic, $P2_12_12_1$, $a = 5.461(1)$, $b = 16.035(1)$, $c = 20.772(1)$ Å, $V = 1819.1(5)$ Å^3, $Z = 4$, $D_x = 1.371$ Mg m^{-3}, $\mu = 0.101$ mm^{-1}, $T = 150(2)$ K, measured 22780 reflections in the 2θ range 3.2–49.4°, $R_{int} = 0.088$. 244 Parameters refined against 3726 F^2, $R = 0.042$ for $I_o > 2\sigma(I_o)$ and 0.066 for all data.

Methyl 3-(2,2-ethylenedioxycyclopentan-1-yl)propionate 2a

A solution of the methyl 3-(2-oxocyclopentan-2-yl)propionate (**1a**)[9] (39 g, 0.23 mol), ethylene glycol (30 ml) and toluene-*p*-sulfonic acid (2.0 g) in benzene (250 ml) was heated under reflux for 8–10 h using a Dean–Stark trap. Most of the solvent was then distilled off, the residual material poured into 10% NH_4OH (150 ml) and the mixture extracted with diethyl ether (3 × 100 ml). The combined ethereal extracts were dried ($MgSO_4$), the ether distilled off and the residual oil isolated after distillation to give a colourless liquid (34.0 g, 70%), bp 90 °C/0.5 mmHg. HRMS: M 214.1206. $C_{11}H_{18}O_4$ requires 214.1205; ν_{max}(film)/cm^{-1} 2910, 2880 (C–H), 1720 (CO); δ_H($CDCl_3$) 1.20–1.86 (9 H, m, 4 × CH_2, CH), 2.23–2.32 (2 H, m, CH_2CO_2Me), 3.60 (3 H, s, OCH_3), 3.8–3.92 (4 H, m, OCH_2CH_2O); δ_C($CDCl_3$) 20.4 (CH_2), 24.2 (CH_2), 29.1 (CH_2), 32.6 (CH_2), 45.3 (CH), 51.6 (OCH_3), 64.3 and 64.4 (OCH_2CH_2O), 117.8 (2-C), 174.1 (CO_2Me); *m*/*z* (EI) 214 (M$^+$, 7%), 185 (16), 171 (6), 141 (18), 113 (10), 99 (100).

Methyl 3-(2,2-ethylenedioxycyclohexan-1-yl)propionate 2b

Compound **2b** was obtained as above from methyl 3-(2-oxocyclohexan-1-yl)propionate[4] (**1b**) as a colourless liquid (69%) with bp 96–98 °C/0.2 mmHg. HRMS: M 228.1372. $C_{12}H_{20}O_4$ requires 228.1371; ν_{max}(film)/cm^{-1} 2910, 2860 (C–H), 1740 (CO); δ_H($CDCl_3$) 1.15–1.8 (10 H, m, 5 × CH_2), 1.83–2.1 (1 H, m, CH), 2.2–2.45 (2 H, m, CH_2CO_2Me), 3.68 (3 H, s, OCH_3), 3.87–3.92 (4 H, m, OCH_2CH_2O); δ_C($CDCl_3$) 23.7 (CH_2), 23.8 (CH_2), 24.4 (CH_2), 29.0 (CH_2), 32.4 (CH_2), 34.5 (CH_2), 44.0 (CH), 51.4 (OCH_3), 64.5 and 64.7 (OCH_2CH_2O), 110.6 (2-C), 174.5 (CO_2Me); *m*/*z* (EI) 228 (M$^+$, 15%), 197 (6), 185 (34), 155 (19), 113 (12), 99 (100), 86 (15).

Methyl 3-(2,2-ethylenedioxycycloheptan-1-yl)propionate 2c

Compound **2c** was obtained as above from methyl 3-(2-oxocycloheptan-1-yl)propionate[9] (**1c**) as a colourless oil (67%) with bp 102 °C/0.5 mmHg. HRMS: M 242.1517. $C_{13}H_{22}O_4$ requires 242.1518; ν_{max}(film)/cm^{-1} 2910, 2860 (C–H), 1740 (CO); δ_H($CDCl_3$) 1.35–1.92 (13 H, m, 6 × CH_2, 1 H, CH), 2.15–2.46 (2 H, m, CH_2CO_2Me), 3.61 (3 H, s, OCH_3), 3.83–3.92 (4 H, m, OCH_2CH_2O); δ_C($CDCl_3$) 22.2 (CH_2), 25.7 (CH_2), 27.4 (CH_2), 27.8 (CH_2), 29.1 (CH_2), 33.2 (CH_2), 37.3 (CH_2), 47.2 (CH), 51.8 (OCH_3), 64.0, 65.1 (OCH_2CH_2O), 113.50 (2-C), 173.5 (CO_2Me); *m*/*z* (EI) 242 (M$^+$, 17%), 211 (11), 199 (16), 185 (65), 169 (35), 155 (17), 127 (7), 113 (21), 99 (100), 86 (8).

† CCDC reference numbers 156270 and 156271. See http://www.rsc.org/suppdata/p1/b1/b100179p for crystallographic files in.cif or other electronic format.

Potassium 3-(2,2-ethylenedioxycyclopentan-1-yl)propionate 3a

A solution of methyl 3-(2,2-ethylenedioxycyclopentan-1-yl)-propionate (**2a**) (10.2 g, 43 mmol) and KOH (2.64 g, 44 mmol) in methanol (15 ml) was heated under reflux for 7 h before the solvent was distilled off. The residue was triturated with THF before being used in the subsequent reaction; white solid (6.52 g, 67%) with mp 188–189 °C. ν_{max}(KBr)/cm^{-1} 2940, 2830 (C–H), 1550 (CO), 1400, 1310; δ_H(D_2O) 1.16–2.09 (11 H, m, 5 × CH_2, CH), 3.84 (4 H, m, OCH_2CH_2O); δ_C(D_2O) 22.8 (CH_2), 28.3 (CH_2), 31.4 (CH_2), 37.8 (CH_2), 39.0 (CH_2), 48.1 (CH), 66.89, 67.10 (OCH_2CH_2O), 121.48 (2-CH), 186.4 (CO_2^-).

Potassium 3-(2,2-ethylenedioxycyclohexan-1-yl)propionate 3b

Compound **3b** was obtained as above from methyl 3-(2,2-ethylenedioxycyclohexan-1-yl)propionate **2b** as a white solid (85%) with mp 205–206 °C. ν_{max}(KBr)/cm^{-1} 2905, 2860 (C–H), 1580 (CO), 1380, 1150; δ_H(D_2O) 1.09–2.11 (13 H, m, 6 × CH_2, CH), 3.85 (4 H, s, OCH_2CH_2O); δ_C(D_2O) 26.2 (CH_2), 26.5 (CH_2), 31.3 (CH_2), 36.8 (CH_2), 38.5 (CH_2), 46.4 (CH), 67.13, 67.29 (OCH_2CH_2O), 114.4 (2-C), 186.7 (CO_2^-).

Potassium 3-(2,2-ethylenedioxycycloheptan-1-yl)propionate 3c

Compound **3c** was obtained as above from methyl 3-(2,2-ethylenedioxycycloheptan-1-yl)propionate **2c** as a white solid (65%) with mp 192.5–194 °C. ν_{max}(KBr)/cm^{-1} 2910, 2880 (C–H), 1580 (CO), 1378, 1150; δ_H(D_2O) 1.21–2.20 (15 H, m, 7 × CH_2, 1 H, CH), 3.77–3.85 (4 H, m, OCH_2CH_2O); δ_C(D_2O) 25.1 (CH_2), 29.8 (CH_2), 30.4 (CH_2), 30.8 (CH_2), 32.3 (CH_2), 39.7 (CH_2), 40.4 (CH_2), 50.2 (CH), 66.9, 68.1 (OCH_2CH_2O), 117.89 (2-C), 185.8 (CO_2^-).

3-(2,2-Ethylenedioxycyclopentan-1-yl)propionic (methyl carbonic) anhydride 4a

Methyl chloroformate (3.1 g, 33 mmol) in THF (10 ml) was added to a rapidly stirred suspension of potassium 3-(2,2-ethylenedioxycyclopentan-1-yl)propionate (**3a**) (7.14 g, 30 mmol) in dry THF (200 ml). The mixture was stirred at ambient temperature for 6 h when the precipitated salt was removed by filtration. Evaporation of the filtrate and flash chromatography using hexane–EtOAc 6 : 1 (R_f 0.40) gave the product as a colourless liquid (6.13 g, 80%). HRMS: M 258.1104. $C_{12}H_{18}O_6$ requires 258.1103; ν_{max}($CHCl_3$)/cm^{-1} 2940, 2860 (C–H), 1800 and 1750 (2 × CO); δ_H($CHCl_3$) 1.2–1.90 (9 H, m, 4 × CH_2, CH), 2.38–2.43 (2 H, m, CH_2CO), 3.83 (3 H, s, OCH_3), 3.84–3.87 (4 H, m, OCH_2CH_2O); δ_C($CHCl_3$) 20.5 (CH_2), 23.5 (CH_2), 29.2 (CH_2), 32.8 (CH_2), 35.5 (CH_2), 45.0 (CH), 55.8 (OCH_3), 64.3, 64.4 (OCH_2CH_2O), 117.7 (2-C), 167.9 and 169.6 (2 × CO); *m*/*z* (EI) 258 (M^+, 5%), 229 (7), 183 (22), 141 (37), 113 (6), 99 (100).

3-(2,2-Ethylenedioxycyclohexan-1-yl)propionic (methyl carbonic) anhydride 4b

Compound **4b** was prepared as above from potassium 3-(2,2-ethylenedioxycyclohexan-1-yl)propionate (**3b**). The product was a colourless liquid (81%) (R_f 0.44). HRMS: M 272.1271. $C_{13}H_{20}O_6$ requires 272.1259; ν_{max}($CHCl_3$)/cm^{-1} 2900, 2860 (C–H), 1800 and 1740 (2 × CO); δ_H($CHCl_3$) 1.17–1.93 (11 H, m, 5 × CH_2, CH), 2.36–2.59 (2 H, m, CH_2CO), 3.81 (3 H, s, OCH_3), 3.84–3.90 (4 H, m, OCH_2CH_2O); δ_C($CHCl_3$) 23.3 (CH_2), 24.5 (CH_2), 29.3 (CH_2), 32.7 (CH_2), 33.8 (CH_2), 34.9 (CH_2), 43.7 (CH), 55.8 (OCH_3), 64.5 and 64.7 (OCH_2CH_2O), 110.49 (2-C), 168.2 and 169.9 (2 × CO); *m*/*z* (EI) 272 (M^+, 8%), 229 (15), 197 (17), 155 (36), 125 (5), 113 (10), 99 (100), 86 (15).

3-(2,2-Ethylenedioxycycloheptan-1-yl)propionic (methyl carbonic) anhydride 4c

Compound **4c** was obtained as above from potassium 3-(2,2-ethylenedioxycycloheptan-1-yl)propionate (**3c**). The product was a colourless liquid (76%) (R_f 0.38). HRMS: M 286.1422. $C_{14}H_{22}O_6$ requires 286.1416; ν_{max}($CHCl_3$)/cm^{-1} 2920, 2860 (C–H), 1810 and 1759 (2 × CO); δ_H ($CHCl_3$) 1.33–1.96 (13 H, m, 6 × CH_2, CH), 2.26–2.62 (2 H, m, CH_2CO), 3.79 (3 H, s, OCH_3), 3.82–3.90 (4 H, m, OCH_2CH_2O); δ_C($CHCl_3$) 22.1 (CH_2), 27.5 (CH_2), 28.2 (CH_2), 29.1 (CH_2), 33.5 (CH_2), 35.5 (CH_2), 37.2 (CH_2), 46.8 (CH), 56.2 (OCH_3), 64.1–65.2 (OCH_2-CH_2O), 113.4 (2-CH), 167.2 and 169.0 (2 × CO); *m*/*z* (EI) 286 (M^+, 25%), 243 (12), 229 (69), 185 (29), 169 (80), 155 (18), 127 (10), 113 (28), 99 (100), 86 (10).

1-Diazo-4-(2,2-ethylenedioxycyclopentan-1-yl)butan-2-one 5a

A solution of 3-(2,2-ethylenedioxycyclopentan-1-yl)propionic (methyl carbonic) anhydride (**4a**) (6.13 g, 23 mmol) in anhydrous diethyl ether (30 ml) was added dropwise with stirring to a solution of diazomethane (3 × 23 mmol) in anhydrous diethyl ether (250 ml) at 0 °C. The solution was stirred at this temperature for 12–14 h. Evaporation of the solvent and flash chromatography of the residual oil using hexane–EtOAc 2 : 1 (R_f 0.35) gave the product as a yellow oil (2.39 g, 45%). HRMS: ($M-N_2$) 196.1103. $C_{11}H_{16}O_3$ ($M-N_2$) requires 196.1099. ν_{max}($CHCl_3$)/cm^{-1} 2940, 2870 (C–H), 2080 (C=N_2), 1720, 1630 (CO); δ_H($CHCl_3$) 1.20–1.29 (2 H, m, CH_2), 1.44–1.88 (7 H, m, 3 × CH_2, CH), 2.24–2.33 (2 H, m, CH_2CO), 3.80–3.86 (4 H, m, OCH_2CH_2O), 5.23 (1 H, s, CHN_2); δ_C($CHCl_3$) 20.5 (CH_2), 24.1 (CH_2), 29.4 (CH_2), 32.6 (CH_2), 35.7 (CH_2), 45.4 (CH), 54.38 (CHN_2), 64.41, 64.51 (OCH_2CH_2O), 117.91 (2-CH), 195.57 (*C*OCHN_2); *m*/*z* (EI) 196 (M^+-N_2, 0.72%), 171 (6), 153 (6), 141 (22), 125 (14), 112 (8), 99 (100), 86 (12).

1-Diazo-4-(2,2-ethylenedioxycyclohexan-1-yl)butan-2-one 5b

The product obtained as above from 3-(2,2-ethylenedioxycyclohexan-1-yl)propionic (methyl carbonic) anhydride (**4b**) was a yellow oil (50%) (R_f 0.42). HRMS: ($M-N_2$) 210.1258. $C_{12}H_{18}O_3$ ($M-N_2$) requires 210.1255; ν_{max}($CHCl_3$)/cm^{-1} 2097, 2860 (C–H), 2085 (C=N_2), 1710 and 1640 (CO); δ_H($CHCl_3$) 1.12–1.92 (11 H, m, 5 × CH_2, 1 H, CH), 2.19–2.33 (2 H, m, CH_2CO), 3.80–3.89 (4 H, m, OCH_2CH_2O), 5.23 (1 H, s, CHN_2); δ_C($CHCl_3$) 23.6 (CH_2), 24.4 (CH_2), 29.1 (CH_2), 32.1 (CH_2), 34.5 (CH_2), 39.1 (CH_2), 43.9 (CH), 54.19 (CHN_2), 64.43 and 64.60 (OCH_2CH_2O), 110.43 (2-C), 195.5 (CO); *m*/*z* (EI) 210 (M^+-N_2, 2%), 171 (23), 155 (28), 125 (8), 112 (18), 99 (100), 86 (17).

1-Diazo-4-(2,2-ethylenedioxycycloheptan-1-yl)butan-2-one 5c

The product obtained as above from 3-(2,2-ethylenedioxycycloheptan-1-yl)propionic (methyl carbonic) anhydride (**4c**) was a yellow oil (47%) (R_f 0.37). HRMS: ($M-N_2$) 224.1423. $C_{13}H_{20}O_3$ ($M-N_2$) requires 224.1411; ν_{max}($CHCl_3$)/cm^{-1} 2900, 2860 (C–H), 2080 (C=N_2), 1640 (CO); δ_H($CHCl_3$) 1.18–1.87 (13 H, m, 6 × CH_2, CH), 2.22–2.36 (2 H, m, CH_2CO), 3.80–3.89 (4 H, m, OCH_2CH_2O), 5.24 (1 H, s, CHN_2); δ_C($CHCl_3$) 22.1 (CH_2), 25.7 (CH_2), 27.4 (CH_2), 27.8 (CH_2), 28.9 (CH_2), 37.1 (CH_2), 39.9 (CH_2), 47.1 (CH), 54.4 (CHN_2), 63.9, 64.9 (OCH_2-CH_2O), 113.3 (2-C), 194.1 (CO); *m*/*z* (EI) 224 (M^+-N_2, 1%), 181 (8), 169 (32), 153 (26), 125 (20), 112 (21), 99 (100), 86 (20).

6,6-(Ethylenedioxy)spiro[4.4]nonan-2-one 6a

A solution of 1-diazo-4-(2,2-ethylenedioxycyclopentan-1-yl)-butan-2-one (**5a**) (2.37 g, 10.6 mmol) in dry dichloromethane (150 ml) was added dropwise over 1.5 h to a stirred suspension of $Rh_2(OAc)_4$ (0.23 g, 0.53 mmol) in dry dichloromethane (200 ml) under argon at ambient temperature. The mixture was stirred at ambient temperature for 10 h before filtration and the filtrate evaporated to dryness. The residue on flash chromatography using EtOAc–hexane 1 : 4 (R_f 0.38) gave product **6a** (1.45 g, 70%) as a colourless oil. HRMS: M 196.1107. $C_{11}H_{16}O_3$ requires 196.1099; ν_{max}($CHCl_3$)/cm^{-1} 2910, 2860 (C–H), 1740 (CO); δ_H($CHCl_3$) 1.53–1.72 (8 H, m, 4 × CH_2), 1.89–1.95 (1 H,

d, *J* 18, CH_2), 2.07–2.17 (2 H, m CH_2), 2.33–2.39 (1 H, d, *J* 18, CH_2), 3.46–3.86 (4 H, m, OCH_2CH_2O); $\delta_C(CHCl_3)$ 17.9 (CH_2), 29.1 (CH_2), 33.7 (CH_2), 35.0 (CH_2), 37.2 (CH_2), 46.1 (CH_2), 51.1 (5-C), 64.5, and 64.8 (OCH_2CH_2O), 117.9 (6-C), 218.3 (2-CO); *m*/*z* (EI) 196 (M^+, 56), 168 (7), 153 (52), 139 (11), 125 (6), 112 (19), 99 (100), 86 (30).

6,6-(Ethylenedioxy)spiro[4.4]nonan-2-one 6a and *trans*-7,7-(ethylenedioxy)bicyclo[4.3.0]nonan-3-one 7a

When the reaction was run with 5 mol% of $Rh_2(TPA)_4$ at 0 °C in CH_2Cl_2 under the above conditions, the reaction had gone to completion after 1.5 h. The reaction mixture was worked up as above to furnish the title products which were separated by flash chromatography.

Compound **6a** was obtained in 9% yield. Its physical data are given above.

7,7-(Ethylenedioxy)bicyclo[4.3.0]nonan-3-one 7a. Compound **7a** was a white crystalline material (1.17 g, 56%) (R_f 0.44) with mp 68–69 °C (sublimation at 50–55 °C/0.1 mmHg). HRMS: M 196.1104. $C_{11}H_{16}O_3$ requires 196.1099; $\nu_{max}(CHCl_3)/cm^{-1}$ 2915, 2860 (C–H), 1690 (CO); $\delta_H(CHCl_3)$ 1.20–1.59 (4 H, m, 2 × CH_2), 1.67–1.70 (2 H, m, CH_2), 1.83–1.90 (3 H, m, CH_2, CH), 2.30–2.36 (3 H, m, CH_2, CH), 3.82–3.89 (4 H, m, OCH_2CH_2O); $\delta_C(CHCl_3)$ 21.7 (CH_2), 24.6 (CH_2), 28.9 (CH_2), 34.1 (CH_2), 36.8 (CH), 44.4 (CH_2), 46.2 (CH), 62.2, and 62.3 (OCH_2CH_2O), 117.9 (7-C), 208.2 (C=O); *m*/*z* (EI) 196 (M^+, 76%), 168 (23), 154 (25), 139 (100), 125 (32), 112 (90), 99 (90), 84 (42).

6,6-(Ethylenedioxy)spiro[4.5]decan-2-one 6b and *trans*-7,7-(ethylenedioxy)bicyclo[4.4.0]decan-3-one 7b. When the reaction with 1-diazo-4-(2,2-ethylenedioxycyclohexan-1-yl)butan-2-one (**5**) (2.52 g, 10.6 mmol) was carried out as above under the conditions for $Rh_2(OAc)_4$ catalysis, the two title compounds were formed and separated by flash chromatography using EtOAc–hexane 1 : 4.

6,6-(Ethylenedioxy)spiro[4.5]decan-2-one 6b. Compound **6b** was a colourless oil (0.466 mg; 21%) (R_f 0.37). HRMS: M 210.1264. $C_{12}H_{18}O_3$ requires 210.1255; $\nu_{max}(CHCl_3)/cm^{-1}$ 2905, 2860 (C–H), 1745 (CO); $\delta_H(CHCl_3)$ 1.20–1.76 (10 H, m, 5 × CH_2), 1.88–1.94 (1 H, d, *J* 18, CH_2), 2.10–2.25 (2 H, m, CH_2), 2.40–2.46 (1 H, d, *J* 18, CH_2), 3.83–3.90 (4 H, m, OCH_2CH_2O); $\delta_C(CHCl_3)$ 20.6 (CH_2), 22.4 (CH_2), 28.0 (CH_2), 30.1 (CH_2), 34.6 (CH_2), 35.7 (CH_2), 45.7 (CH_2), 47.2 (5-C), 63.7 and 64.0 (t, OCH_2CH_2O), 110.0 (6-C), 218.6 (C=O); *m*/*z* (EI) 210 (M^+, 20%), 151 (8), 126 (7), 112 (5), 99 (100), 86 (26).

***trans*-7,7-(Ethylenedioxy)bicyclo[4.4.0]decan-3-one 7b.** Compound **7b** was a white crystalline solid (1.06 g, 48%) (R_f 0.31) mp 82–83 °C (sublimation at 65–70 °C/0.1 mmHg). HRMS: M 210.1251. $C_{12}H_{18}O_3$ requires 210.1255. $\nu_{max}(CHCl_3)/cm^{-1}$ 2910, 2860 (C–H), 1680 (CO); $\delta_H(CHCl_3)$ 1.00–1.19 (1 H, m, CH_2), 1.25–1.85 (8 H, m, 3 × CH_2, CH, 1 H from CH_2), 1.90–2.17 (2 H, m, CH_2), 2.20–2.37 (3 H, m, CH_2, CH), 3.83–3.93 (4 H, m, OCH_2CH_2O); $\delta_C(CHCl_3)$ 21.2 (CH_2), 23.3 (CH_2), 32.5 (CH_2), 34.3 (CH_2), 39.8 (CH), 42.8 (CH_2), 47.3 (CH_2), 47.5 (CH), 64.0 and 64.2 (OCH_2CH_2O), 109.5 (7-C), 210.9 (C=O); *m*/*z* (EI) 210 (M^+, 10%), 167 (51), 125 (35), 112 (51), 99 (100), 86 (30).

The structure of **7b** has been confirmed by a single crystal X-ray analysis.

6,6-(Ethylenedioxy)spiro[4.6]undecan-2-one 6c and *trans*-2,2-(ethylenedioxy)bicyclo[5.4.0]undecan-9-one 7c and its *cis*-isomer 8

The reaction with 1-diazo-4-(2,2-ethylenedioxycycloheptan-1-yl)butan-2-one (**5c**) (2.67 g, 10.6 mmol) was carried out as above under the conditions for $Rh_2(OAc)_4$ catalysis. The spirane **6c** was separated from the bicyclic compounds **7c** and **8** by flash chromatography using EtOAc–hexane 1 : 4.

6,6-(Ethylenedioxy)spiro[4.6]undecan-2-one 6c. Compound **6c** was a colourless oil (0.37 g, 16%) (R_f 0.33). HRMS: M 224.1412. $C_{13}H_{20}O_3$ requires 224.1412; $\nu_{max}(CHCl_3)/cm^{-1}$ 2910, 2855 (C–H), 1720 (CO); $\delta_H(CHCl_3)$ 1.21–1.79 (10 H, m, 5 × CH_2), 1.89–1.95 (1 H, d, *J* 18, CH_2), 2.15–2.31 (4 H, m, 2 × CH_2), 2.46–2.52 (1 H, d, *J* 18, CH_2), 3.84–3.92 (4 H, m, OCH_2CH_2O); $\delta_C(CHCl_3)$ 25.9 (CH_2), 26.9 (CH_2), 28.2 (CH_2), 29.2 (CH_2), 33.0 (CH_2), 36.5 (CH_2), 40.8 (CH_2), 51.4 (5-C), 63.4 and 63.6 (OCH_2CH_2O), 113.8 (6-C), 219.3 (CO); *m*/*z* (EI) 224 (M^+, 40%), 196 (8), 182 (19), 167 (34), 153 (15), 139 (17), 126 (29), 99 (100), 86 (35).

***trans*-2,2-(Ethylenedioxy)bicyclo[5.4.0]undecan-9-one 7c and its *cis*-isomer 8.** The product, a mixture of the isomers **7c** and **8** in the ratio 8 : 1, was a colourless oil (1.10 g, 49%) (R_f 0.33). HRMS: M 224.1403. $C_{13}H_{20}O_3$ requires 224.1412; $\nu_{max}(CHCl_3)/cm^{-1}$ 2915, 2880 (C–H), 1700 (CO); $\delta_H(CHCl_3)$ 1.45–1.82 (10 H, m, 5 × CH_2), 2.12–2.25 (3 H, m, CH_2, CH), 2.35–2.46 (3 H, m, CH_2, CH), 3.84–3.92 (4 H, m, OCH_2CH_2O); $\delta_C(CHCl_3)$ 20.2 (CH_2), 23.2 (CH_2), 25.3 (CH_2), 34.5 (CH_2), 34.9 (CH_2), 37.1 (CH), 38.5 (CH_2), 47.7 (CH_2), 49.1 (CH), 63.3 and 65.6 (OCH_2CH_2O), 112.6 (2-C), 212.7 (CO); *m*/*z* (EI) 224 (M^+, 15), 180 (10), 167 (84), 125 (29), 112 (23), 99 (100), 86 (15).

***cis*-2,2-(Ethylenedioxy)bicyclo[5.4.0]undecan-9-one 8.** Spectroscopic data were not resolved from those of the *trans*-isomer **7c** (*vide supra*) except for partial resolution of the ^{13}C NMR data which are: $\delta_C(CHCl_3)$ 20.7 (CH_2), 22.3 (CH_2), 24.2 (CH_2), 29.3 (CH_2), 32.3 (CH_2), 35.7 (CH), 39.7 (CH_2), 46.7 (CH), 48.1 (CH_2), 63.0 and 63.2 (OCH_2CH_2O), 112.7 (C-2), 212.2 (CO).

trans-2,2-(Ethylenedioxy)bicyclo[5.4.0]undecan-9-ol 9

A solution of the above 8 : 1 mixture of *trans*- and *cis*-2,2-(ethylenedioxy)bicyclo[5.4.0]undecan-9-one (**7c** and **8**) (0.100 g, 0.44 mmol) in THF (3 ml) was added slowly (30 min) to a solution of $LiAlH(t\text{-}BuO)_3$ (0.124 g, 0.49 mmol) in THF (8 ml) under argon at 0 °C. The mixture was stirred at this temperature for 0.5 h and at ambient temperature for 3 h before the reaction was quenched by addition of saturated aq. NH_4Cl. The mixture was extracted with diethyl ether (3 × 5 ml), the combined organic extracts dried ($MgSO_4$), evaporated and the residual material subjected to flash chromatography using EtOAc–hexane 1 : 4. The first fraction eluted was a stereoisomeric mixture of hydroxy derivatives. The yield of oily product was 20 mg (20%) (R_f 0.28). HRMS: M 226.1559. $C_{13}H_{21}O_3$ requires 226.1559; $\nu_{max}(film)/cm^{-1}$ 3500 (OH), 2915, 2870 (C–H); the product was identified by a chromic acid oxidation to furnish a mixture of the *trans* and *cis* ketones **7c** and **8** in almost equimolar ratio.

(1*R,7*S**,9*R**)-*trans*-2,2-Ethylenedioxybicyclo[5.4.0]undecan-9-ol 9c.** Compound **9c** was obtained as a colourless oil 61 mg (60%) (R_f 0.23). HRMS: M 226.1559. $C_{13}H_{21}O_3$ requires 226.1560; $\nu_{max}(film)/cm^{-1}$ 3500 (OH), 2910, 2880 (C–H); $\delta_H(CHCl_3)$ 1.31–1.95 (17 H, m, 7 × CH_2, 2 × CH, CHO*H*), 3.45–3.57 (1 H, m, C*H*OH), 3.81–3.92 (4 H, m, OCH_2CH_2O); $\delta_C(CHCl_3)$ 20.2 (CH_2), 24.3 (CH_2), 24.9 (CH_2), 34.4 (CH_2), 34.5 (CH_2), 34.9 (CH_2), 38.0 (CH), 45.5 (CH_2), 52.5 (CH), 63.8 and 65.4 (OCH_2CH_2O), 70.7 (*C*HOH), 112.6 (2-C); *m*/*z* (EI) 226 (M^+, 17), 169 (100), 125 (15), 99 (73), 86 (9).

(1*R**,7*S**,9*R**) *trans*-2,2-(Ethylenedioxy)bicyclo[5.4.0]undecan-9-yl *p*-nitrobenzoate 10

p-Nitrobenzoyl chloride (0.098 g, 0.52 mmol) was added to a solution of (1*R**,7*S**,9*R**) *trans*-2,2-(ethylenedioxy)bicyclo-

[5.4.0]undecan-9-ol (0.040 g, 0.17 mmol) and DMAP (0.064 g, 0.52 mmol) in dry dichloromethane (12 ml) and the mixture stirred at ambient temperature for 3 h. The reaction was monitored by TLC. The solvent was distilled off and the crude product purified by flash chromatography using hexane–EtOAc 5 : 1. (R_f 0.37). The product was a pale yellow crystalline material 40 mg (60%), mp 101–102 °C (Et_2O at −18 °C). HRMS: 375.1669. $C_{20}H_{25}NO_6$ requires 375.1681. ν_{max}(KBr)/cm^{-1} 2910, 2880 (C–H), 1715 (C=O), 1450 (NO_2); δ_H($CHCl_3$) 1.34–2.14 (16 H, m, 7 × CH_2, 2 × CH), 3.83–3.93 (4 H, m, OCH_2CH_2O), 4.89–4.98 (1 H, m, C*H*O$COC_6H_4NO_2$), 8.14–8.25 (4 H, m, Ph); δ_C($CHCl_3$) 20.3 (CH_2), 24.1 (CH_2), 24.9 (CH_2), 31.0 (CH_2), 34.3 (CH_2), 34.6 (CH_2), 38.0 (CH), 41.0 (CH_2), 52.4 (CH), 63.9 and 65.5 (OCH_2CH_2O), 75.0 (*C*HOCOAr), 112.2 (2-C), 123.4, and 130.6 (4 × CH, Ar), 136.2 (CNO_2), 150.4 (*C*CO_2), 164.1 (CO ester); *m*/*z* (EI) 375 (M^+, 14), 318 (7), 225 (16), 209 (29), 151 (100), 99 (67).

Spiro[4.4]nonane-2,6-dione 11a

10% HCl (2 ml) was added to a solution of 6,6-(ethylenedioxy)-spiro[4.4]nonan-2-one (**6a**) (0.196 g, 1 mmol) in acetone (5 ml) and the mixture heated under reflux for 6 h. The solution was then evaporated almost to dryness and sodium bicarbonate (30%, 20 ml) and dichloromethane (20 ml) added. The mixture was shaken and the layers separated. The organic solution was washed, dried ($MgSO_4$), evaporated and the residual material subjected to flash chromatography using CH_2Cl_2–EtOAc 6 : 1 (R_f 0.55). The product was a white crystalline solid (0.130 g, 87%) with mp 41–42 °C (sublimation at 40–50 °C/0.1 mmHg) (Found: C, 70.93; H, 8.14. $C_9H_{12}O_2$ requires C, 71.05; H, 7.89%); HRMS: M 152.0837. $C_9H_{12}O_2$ requires 152.0837; ν_{max}($CHCl_3$)/cm^{-1} 2910, 2840 (C–H), 1725 (CO); δ_H($CHCl_3$) 1.75–2.05 (6 H, m, 3 × CH_2), 2.22–2.42 (6 H, m, 3 × CH_2); δ_C($CHCl_3$) 19.1 (CH_2), 31.3 (CH_2), 35.8 (CH_2), 36.6 (CH_2), 37.0 (CH_2), 46 7 (CH_2), 52.7 (5-C), 216.5 (2-CO), 220.8 (6-CO); *m*/*z* (EI) 152 (M^+, 70%), 124 (92), 110 (30), 96 (66), 82 (56), 67 (78), 55 (45), 39 (40), 28 (100).

Spiro[4.5]decane-2,6-dione 11b

Compound **11b** was obtained as above from 6,6-(ethylenedioxy)spiro[4.5]decan-2-one (**6b**) as a white crystalline solid with mp 43.5–44 °C (sublimation at 40–50 °C/0.1 mmHg) (89%) (R_f 0.55) (Found: C, 72.43; H, 8.47. $C_{10}H_{14}O_2$ requires C, 72.28; H, 8.44%); HRMS: M 166.1000. $C_{10}H_{14}O_2$ requires 166.0994; ν_{max}($CHCl_3$)/cm^{-1} 2905, 2860 (C–H), 1740 and 1680 (CO); δ_H($CHCl_3$) 1.66–1.84 (6 H, m, 3 × CH_2), 1.86–1.92 (1 H, d, *J* 18, CH_2), 2.14– 2.45 (6 H, m, 3 × CH_2), 2.56–2.71 (1 H, d, *J* 18, CH_2); δ_C($CHCl_3$) 21.6 (CH_2), 28.8 (CH_2), 31.2 (CH_2), 36.1 (CH), 38.3 (CH_2), 47.0 (CH_2), 53.5 (5-C), 212.3 (6-CO), 216.4 (2-CO); *m*/*z* (EI) 166 (M^+, 4%), 138 (100), 110 (10), 96 (8), 82 (16), 67 (26), 55 (12).

Spiro[4.6]undecane-2,6-dione 11c

Compound **11c** was obtained as above from 6,6-(ethylenedioxy)spiro[4.6]undecan-2-one (**6c**) as a colourless oil (80%) (R_f 0.57) (Found: C, 73.35; H, 8.89. $C_{11}H_{16}O_2$ requires C, 73.33; H, 8.88%); HRMS: M 180.1154. $C_{11}H_{16}O_2$ requires 180.1150; ν_{max}($CHCl_3$)/cm^{-1} 2910, 2850 (C–H), 1730 and 1682 (CO); δ_H($CHCl_3$) 1.43–1.93 (10 H, m, 5 × CH_2), 2.15–2.48 (4 H, m, 2 × CH_2), 2.69–2.80 (2 H, m, CH_2); δ_C($CHCl_3$) 25.6 (CH_2), 26.2 (CH_2), 30.3 (CH_2), 33.0 (CH_2), 37.3 (CH_2), 40.7 (CH_2), 48.0 (CH_2), 55.9 (5-C), 215.5 (6-CO), 216.8 (5-CO); *m*/*z* (EI) 180 (M^+, 2%), 162 (12), 152 (100), 124 (17), 109 (21), 96 (36), 81 (27), 67 (30), 55 (40).

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