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Stereoselective Baeyer–Villiger oxidation of some bridged bicyclic diketones

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The regioselectivity of the Baeyer–Villiger oxidation of bicyclo[3.3.1]nonane and bicyclo[2.2.2]octane ketones **1**–**7** with carbonyl groups located at different positions and bearing other substituents in the bicyclic ring is studied. The impact of the formation of the tetrahedral intermediate and the ring-bond migratory aptitude are considered as major factors governing the reaction's regioselectivity. The distortion from sp^2-hybridization of the valence angle of the C-9 carbonyl group is found to be considerably greater than that at the C-2 carbonyl in bicyclo[3.3.1]nonane-2,9-dione structures according to semiempirical calculations. Highly regioselective oxygen insertion leading to the functionalized oxabicyclic keto lactones is accounted for by kinetic and stereoelectronic factors.

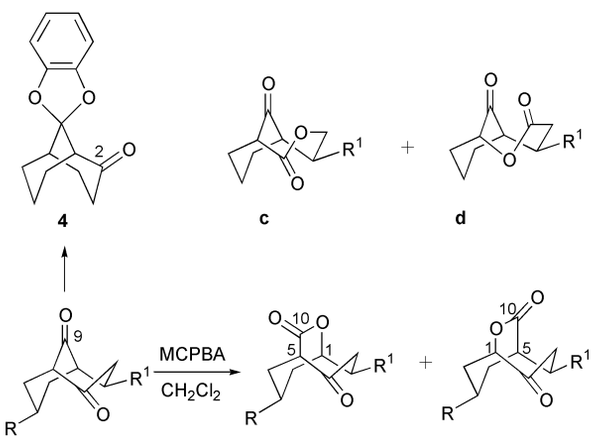
The transformation of cyclic ketones into lactones by the Baeyer–Villiger reaction has been widely employed for the synthesis of many natural and other valuable products.[1] As a result, much research has been devoted to developing a variety of methods and conditions for the reaction.[2] In recent years the Baeyer–Villiger reaction has been used rather frequently for oxidation of bicyclic and polycyclic ketones[3] since many cyclic lactone structures are found in natural products or are the key steps in their synthesis.[4] The reaction involves migration of one of the groups flanking the carbonyl to the adjacent electron-deficient oxygen atom *via* the generally accepted Criegee two-step mechanism.[5] Isolation or formation of oxocarbenium ions during the reaction has been evidenced recently.[6] Stereoelectronic effects in the oxidation suggested by Noyori[7] have gained further experimental support.[8] The group that migrates does so from a position antiperiplanar to the dissociating oxygen–oxygen bond of the peroxide.[8b,9] The migratory aptitude appears to be related to the ability of the migrating group to support the developing positive charge in the transition state and this determines the regioselectivity of the reaction.

Thus, the stereochemical outcome in Baeyer–Villiger oxidation is mainly governed by the nature of the α-substituent in the ketone molecule and by steric and conformational effects. Obviously the problem is much more complex when applying the Baeyer–Villiger oxidation to diketones of bicyclic structure. The question of stereoselectivity arises when performing this reaction with conformationally labile bicyclic molecules containing non-equivalent carbonyl groups.

Therefore, investigation of suitable model structures could add to our knowledge of the Baeyer–Villiger reaction mechanism and provide potential utility toward the selective synthesis of functionalized lactones. Bicyclo[3.3.1]nonane and bicyclo[2.2.2]octane diketones appeared to be appropriate structures to study stereoselectivity combined with regioselective Baeyer–Villiger oxidation. In addition, this transformation can afford potential precursors for synthesis of natural products, as the bridged bicyclic lactones of the frameworks considered are important synthons for the synthesis of specifically substituted rings.

Results and discussion

Herein we study the Baeyer–Villiger oxidation of bicyclononane and bicyclooctane diketones **1**–**7** with carbonyl groups located at different positions and, in addition, having substituents in the bicyclic ring (Scheme 1). The bicyclic diketones used in this work were synthesized according to the procedures described previously (see Experimental section) and subjected to oxidation with 75% *m*-chloroperbenzoic acid (MCPBA).



Scheme 1

Oxidation of 2,9-diketone **1** and 7-methyl diketone **2** with MCPBA afforded a mixture of keto lactones in the ratio 92 : 8. The main reaction products were keto lactone **1a** and the corresponding 7-*exo*-methyl keto lactone **2a**, and the minor products **1b** and **2b** (Scheme 1). The ratio of the two regioisomeric pairs of keto lactones was determined by GC-MS. The obtained mixtures were separated by flash chromatography and fully characterized by analytical methods. The signals of the bridgehead protons at C-1 and C-5 are well separated in the ^1H NMR spectra. The chemical shift of the proton at C-1 in compounds **1a** and **2a** is observed downfield compared with the doublet of doublets of the proton signal at C-5. An interchanged order of resonance signals is observed for minor keto lactones **1b** and **2b**, *i.e.* the doublet of doublets for 1-H is observed at lower field compared with the multiplet for the proton at C-5 (Table 1).

Analogous highly regioselective oxidation was observed for ethyl 4,9-dioxobicyclo[3.3.1]nonane-2-carboxylate **3** (Scheme 1).

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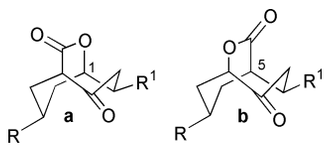
Table 1 ^{1}H NMR data of keto lactones **1**–**3a**,**b**

Compound	δ, ppm (multiplicity)	
	H-C1	H-C5
1a	5.00–4.94 (m)	3.66–3.64 (dd)
1b	4.73–4.71 (dd)	3.48–3.43 (m)
2a	4.97–4.92 (m)	3.66–3.63 (dd)
2b	4.72–4.70 (dd)	3.45–3.41 (m)
3a	5.28–5.26 (t)	3.70–3.68 (dd)
3b	4.76–4.74 (dd)	3.74–3.72 (m)



The electron-withdrawing group CO_2Et in a β-position to both carbonyl groups of this 1,3-diketone should diminish the propensity of the bonds to migrate. Indeed, it took much longer to complete the oxidation reaction of **3** compared with ketones **1** and **2**. Stirring overnight was required to finish the oxidation. Again two keto lactones, namely **3a** and **3b**, of a possible four were formed in the ratio 85 : 15. Flash chromatography afforded only the major isomer, *i.e.* ethyl 4,10-dioxo-9-oxabicyclo[3.3.2]decane-2-carboxylate **3a**, since both compounds had the same R_f-value under various conditions investigated. In the ^{1}H NMR spectrum analogous chemical shifts for a CH-OC(=O)CH fragment were observed as in the case of compounds **1a** and **2a**: a triplet at δ 5.28–5.26 due to the dihedral angle H–C^1–C^2–H of close to 90° (101.2°, AM1 method) corresponds to C*H*–OC(=O)CH; the other bridgehead proton is observed as a doublet of doublets at δ 3.70–3.68. The reversed order of signals is observed for the minor keto lactone **3b**, *i.e.* a doublet of doublets at δ 4.74–4.76 for the proton at C-1, and a multiplet at δ 3.74–3.72 for the proton at C-5.

The obtained results indicate a highly regioselective oxidation of the bridged carbonyl group in our studied 1,3-diketones and selective oxygen insertion into that position in compounds **1**–**3**. The regioselectivity of the C-9 oxidation could be explained by thermodynamic or kinetic factors, as shielding effects of both carbonyl groups in this bicyclic skeleton are analogous. The heat of formation of the most stable conformers of all keto lactones **1**–**3a**–**d** was calculated by semi-empirical methods (AM1, PM3, and MNDO).[10] Calculations gave rather similar results, and those obtained by the AM1 method are presented in Table 2, though it should be noted that these data should be compared very cautiously and with the assumption that the reaction proceeds through analogous mechanistic pathways.

Thus, according to AM1 calculations the relative stability of isomeric keto lactones **1**–**3** decreases in the order **c** > **a** > **b** >> **d**, and the **c** isomers were also found to be the most stable by other methods as well. Consequently, under thermodynamic reaction control the main reaction product should be lactones **1**–**3c** after oxidation of the C-2 carbonyl group. However, the observed experimental results do not correspond to the calculated relative stability of the lactones, therefore the regioselectivity could be governed by reaction kinetic control. If this assumption is correct, the energy of formation of the tetrahedral intermediate at C-9 should be lower compared with that at the C-2 carbonyl group due to the larger relief of torsional strain. The distortion from sp^2-hybridization of the valence angle of the C-9 carbonyl group is considerably greater compared with that at the C-2 carbonyl according to semiempirical calculations (Table 3). Therefore the addition of the peracid to the latter should release the excess of strain in the molecule, when the tetrahedral intermediate is

Table 2 Relative stability of keto lactones **1**–**3a**–**d**, calculated by the AM1 method

Compound	Rel. energy/kcal mol^{-1}			
	a	**b**	**c**	**d**
1	0.65	0.73	0 (−131.32)[a]	2.47
2	0.92	1.0	0 (−136.41)	2.45
3	0.81	1.23	0 (−216.45)	2.87

[a] Heat of formation of the most stable isomer in kcal mol^{-1}. 1 cal = 4.184 J.

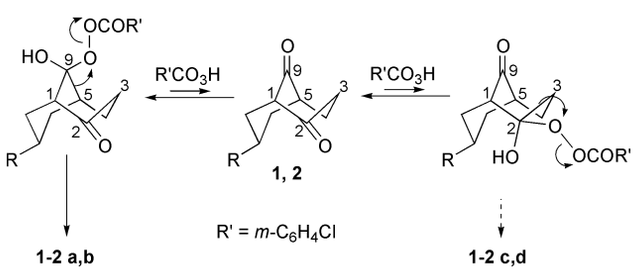
Table 3 Valence angles of ketones **1**–**3** calculated by the PM3[a] method

Ketone	Valence angle/deg	
	C^1–C^9–C^5	C^1–C^2–C^3
1	112.05 (112.16)[b]	115.67 (117.32)
2	111.97 (112.06)	115.69 (117.49)
3	112.07 (112.3)	115.58 (117.47)[c,d]

[a] AM1 and MNDO methods gave similar results. [b] Values in parenthesis correspond to the less stable chair–chair conformers of **1**–**3**. [c] X-Ray data of methyl ester chair–boat conformer: angle C^1–C^9–C^5 is 112.0(3)° and C^3–C^4–C^5 −116.2(3)°.[16] [d] This angle corresponds to C^3–C^4–C^5 for **3**.

formed. Since the addition of peracid is a reversible reaction, the kinetic control should lead to addition at C-9.

The migratory preferences of the ring carbons also play a significant role in the regioselectivity of the reaction.[11] Due to the electron-withdrawing effect both carbonyl groups significantly diminish the propensity of the C^1–C^2 and C^1–C^9 bonds to migrate though migratory preferences are apparently equivalent in the bicyclo[3.3.1]nonane structures **1**, **2**. However, the migration of bridgehead bond C^5–C^9 *vs.* the C^2–C^3 bond is obviously preferable. The two alternative reaction pathways in an equilibrium mixture are presented in Scheme 2, showing two

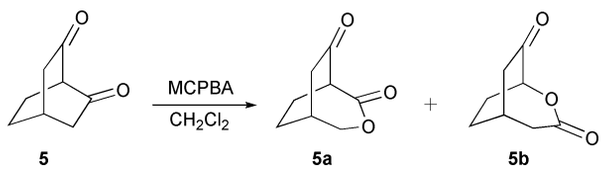


Scheme 2

of the four conceivable Criegee intermediates. The conformation and configuration of the latter are given tentatively. Arrows indicate the two most likely migrations according to the migratory preferences of the respective groups. Carbon atom C-1 in structure **3** is more nucleophilic since the CO_2Et group is rendered equivalent with respect to both C^1–C^9 and C^3–C^4 bonds. Therefore, the oxidation of the C-9 carbonyl group should proceed by preferentially encountering migratory aptitudes of bridgehead carbon atoms. Due to the electron-withdrawing effect of the CO_2Et group oxygen insertion is less stereoselective for compound **3**. It is difficult to judge which one of the two effects, *i.e.* formation of the tetrahedral intermediate or migratory aptitude, has a decisive influence on the regioselectivity of oxidation of the C-9 carbonyl group. Commonly the migratory propensity has more profound effect, which is in a concord with earlier observations.[3] However, considering each effect separately one could explain either the formation of the minor lactones **1**–**3b** encountering strain release during the reaction, or the third keto lactone **1**–**3c** by considering only the stereoelectronic effects (Scheme 1).

Moreover, the C-2 carbonyl group proved to be unreactive in benzenediol ketal **4** derived from the C-9 carbonyl in diketone **1** (Scheme 1) with MCPBA. Oxidation of **4** with the stronger trifluoroperacetic acid gave a complex mixture according to GC-MS analysis. Probably deprotection of the benzenediol group takes place in strong acid with subsequent oxidation, hydrolysis and ring reopening.[12]

Bicyclo[2.2.2]octane-2,6-dione **5** is a structural analogue of 2,9-diketone **1** with a plane of symmetry (Scheme 3). Oxidation



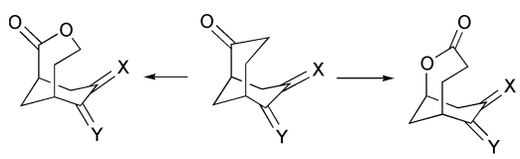
5 **5a** **5b**

Scheme 3

of **5** was completely regioselective to furnish exclusively keto lactone **5a**. The reaction was rather slow and only *ca.* one-third of initial diketone **5** had reacted after 48 h.

Keto lactone **5a** was separated from starting diketone by flash chromatography. The signal due to CH_2–OC(=O)CH in the lactone **5a** appears as a multiplet at δ 4.66–4.55 and 4.43–4.31, and the signal due to CH_2–OC(=O)C*H* is a doublet of doublets at δ 3.66–3.58. Regioselective formation of **5a** is determined by the dominant electronic effect of the bridgehead C-1 atom, which has an electron-withdrawing α-carbonyl group and is less nucleophilic, compared with the methylene group.

Bicyclo[3.3.1]nonane-2,7-dione **6** with MCPBA gave exclusively 3-oxabicyclo[4.3.1]decane-2,8-dione **6a** (Scheme 4). The



6a X = O, Y = H_2 **6** X = O, Y = H_2 **6b** X = O, Y = H_2
7a X = H_2, Y = O **7** X = H_2, Y = O **7b** X = H_2, Y = O

Scheme 4

multiplets for the C-4 methylene group at δ 4.18 and the C-1 proton at δ 3.66–3.62 in the ^{1}H NMR spectrum confirmed the proposed structure. The characteristic signals for the carbons of the lactone carbonyl group and for the OCH_2 fragment for the secondary carbon atom adjacent to the lactone oxygen atom are observed at δ_C 176.2 and 64.8, respectively, in the ^{13}C NMR spectrum.

The inactivity of the carbonyl group at the C-3 position has been manifested in earlier work and explained by the hindrance effect caused by the *endo*-proton at C-7.[13] However, in the molecule of diketone **6** this steric interaction is lessened due to distortion of the six-membered ring bearing a second carbonyl group at C-2. The regioselective formation of **6a** could be accounted for by electronic factors since a carbonyl group in a β-position might significantly reduce migration of the bridgehead carbon atom. It should be noted that the isolated yield of **6a** was rather low due to hydrolysis of the latter during the reaction.

Oxidation of bicyclo[3.3.1]nonane-2,6-dione **7** was also highly regioselective giving lactones **7b** : **7a** in the ratio 98 : 2 (Scheme 4). However, only the major keto lactone **7b** was isolated by flash chromatography, in 29% yield. The migratory propensity of the bond involving the bridgehead carbon is in accord with earlier observations for diketones **1**–**3**. The lactones formed in this reaction are very unstable and easily undergo hydrolysis when exposed to air to give 3-(5-hydroxy-2-oxocyclohexyl)propanoic acid.

In conclusion, the Baeyer–Villiger oxidation of bicyclo[3.3.1]nonane and bicyclo[2.2.2]octane diketones **1**–**7** with carbonyl groups located at different positions, and with some structures bearing additional substituents in the bicyclic ring, has shown a highly regioselective oxygen insertion. The regioselectivity of the reaction leading to oxabicyclic structures was accounted for by kinetic and stereoelectronic factors. These factors operate simultaneously in the oxidation of bicyclo[3.3.1]nonane-2,9-dione derivatives. The obtained functionalized bicyclic keto lactones could be used as synthons in the synthesis of natural products.

Experimental

Materials and general procedures

The bicyclic diketones used in this work were synthesized according to the procedures previously described by us[14] (**1**–**4**, **6**) or as reported in the literature[15] (**5**, **7**). Mps were recorded with a Koefler melting-point apparatus and are not corrected. ^{1}H NMR and ^{13}C spectra were recorded on a Bruker DRX spectrometer at 400 MHz for protons and 100.6 MHz for carbon in $CDCl_3$, and are reported in δ/ppm downfield from internal reference TMS. Mass spectra were run by GC-MS on a Varian SATURN 5 and a Hewlett-Packard 6980 instrument with mass selective detector HP 5973 using a Supelcowax capillary column (30 m × 0.25 mm), and high-resolution mass spectra were obtained on a JEOL JMS-SX 102 spectrometer. GLC analysis was carried out on a Varian 3700 instrument (FID) by using DB 23 (J & W Scientific) (carrier gas nitrogen) and SPB-5 columns (carrier gas He). IR spectra were obtained for samples in KBr on Fourier Nicolet Impact and Perkin-Elmer Spectrum BX spectrometers and data are reported in wavenumbers (cm^{-1}). Elemental analyses were performed by the analytical laboratory of the University of Vilnius.

Chromatography was performed using silica gel Kieselgel 60 (0.040–0.063 mm) for flash chromatography and Kieselgel 60 F_{254} plates for TLC. Semiempirical calculations were performed using the SPARTAN Plus program package.[10]

General procedure for oxidation with MCPBA

To a stirred solution of a bicyclic diketone (0.22–1.45 mmol) in dichloromethane (5–20 ml) was added a 1.5 molar excess of MCPBA (75%) and $NaHCO_3$ (≈4 molar excess to MCPBA). The reaction mixture was stirred at room temperature for 1.5 h. Solid sodium sulfite (0.1 g) and water (0.1 ml) were added and the mixture was stirred for 0.5 h, filtered over a layer of Na_2SO_4, dried over Na_2SO_4, and evaporated. The solid residue was purified by flash chromatography to give keto lactones.

9-Oxabicyclo[3.3.2]decane-4,10-dione 1a (51 mg, 91%) **and 9-oxabicyclo[3.3.2]decane-2,10-dione 1b** (4 mg, 7%)**.** For **1a**: R_f (3 : 1 heptane–ethyl acetate) 0.2; mp 98–100 °C (Found: C, 64.50; H, 7.16. $C_9H_{12}O_3$ requires C, 64.27; H, 7.19%); ν_{max}/cm^{-1} 1728, 1705 and 1035; δ_H 5.00–4.94 (1H, m, 1-H), 3.66–3.64 (1H, dd, J = 2.1 and 6.5 Hz, 5-H), 2.83–2.72 (1H, ddd, ^2J = 13.2, ^3J = 7.8 and 13.2 Hz, 3-H_{exo}), 2.63–2.49 (2H, m), 2.30–2.27 (1H, m), 2.12–1.58 (6 H, m); δ_C 207.39 (C=O), 173.44 (OC=O), 74.58 (O-CH), 59.65, 40.39, 34.06, 27.89, 25.35, 19.94; *m*/*z* 168 (M^+, 10%), 140 ($M^+ - CO$, 5), 124 ($M^+ - CO_2$, 74), 111 (100), 98 (50), 85 (31), 80 (12), 68 (39), 55 (96), 41 (13). For **1b**: R_f (3 : 1 heptane–ethyl acetate) 0.25; mp 138–140 °C; δ_H 4.73–4.71 (1H, dd, J = 2.5 and 5.5 Hz, 1-H), 3.48–3.43 (1H, m, 5-H), 2.97–2.88 (1H, ddd, ^2J = 13.6, ^3J = 7.8 and 13.6 Hz, 3-H_{exo}), 2.57–2.52 (1H, ddd, ^2J = 13.6, ^3J = 2.3 and 5.1 Hz, 3-H_{endo}), 2.44–2.35 (2H, m), 1.93–1.56 (6H, m); *m*/*z* 168 (M^+, 36%), 140 ($M^+ - CO$, 7), 112 (35), 97 (8), 84 (63), 68 (100), 55 (79), 41 (31); HRMS (EI) M^+, 168.0789. $C_9H_{12}O_3$ requires M, 168.0786.

7-Methyl-9-oxabicyclo[3.3.2]decane-4,10-dione 2a (49 mg, 90%) **and 7-methyl-9-oxabicyclo[3.3.2]decane-2,10-dione 2b** (3 mg, 5.5%)**.** For **2a**: R_f (3 : 1 heptane–ethyl acetate) 0.25; mp 76–78 °C (Found: C, 65.67; H, 7.54. $C_{10}H_{14}O_3$ requires C, 65.90; H, 7.75%); ν_{max}/cm^{-1} 1726, 1708 and 1043; δ_H 4.97–4.92 (1H, m, 1-H), 3.66–3.63 (1H, dd, J = 2 and 7.2 Hz, 5-H), 2.80–2.72 (1H, ddd, ^2J = 13.3, ^3J = 7.7 and 13.3 Hz, 3-H$_{exo}$), 2.61–2.53 (2H, m), 2.30–2.24 (1H, m), 1.97–1.72 (4H, m), 1.49–1.40 (1H, m), 0.98–0.97 (3H, d, J = 6 Hz); δ_C 206.99 (C=O), 173.14 (OC=O), 74.30 (O-CH), 59.09, 42.52, 40.17, 35.60, 26.25, 25.42, 22.40; *m*/*z* 182 (M$^+$, 9%), 154 (M$^+$ − CO, 2), 138 (M$^+$ − CO$_2$, 100), 125 (52), 111 (39), 98 (25), 85 (31), 55 (97). For **2b**: R_f (3 : 1 heptane–ethyl acetate) 0.34; mp 73–75 °C; δ_H 4.72–4.70 (1H, dd, J = 2.5 and 5.5 Hz, 1-H), 3.45–3.41 (1H, m, 5-H), 2.94–2.86 (1H, ddd, ^2J = 13.7, ^3J = 7.9 and 13.7 Hz, 3-H$_{exo}$), 2.56–2.51 (1H, ddd, ^2J = 13.7, ^3J = 2.2 and 5.1 Hz, 3-H$_{endo}$), 2.41–2.31 (2H, m), 1.87–1.67 (3H, m), 1.63–1.50 (2H, m), 0.99–0.97 (3H, d, J = 6.3 Hz); MS, *m*/*z* (rel. intensity) 182 (M$^+$, 54%), 154 (M$^+$ − CO, 3), 138 (M$^+$ − CO$_2$, 10), 126 (9), 111 (16), 98 (32), 82 (100), 68 (54), 55 (58); HRMS (ET) M^+, 182.0947. $C_{10}H_{14}O_3$ requires M, 182.0943.

Ethyl 4,10-dioxo-9-oxabicyclo[3.3.2]decane-2-carboxylate 3a and ethyl 2,10-dioxo-9-oxabicyclo[3.3.2]decane-4-carboxylate 3b. (Total yield 53 mg, 99%), R_f (7 : 3 heptane–ethyl acetate) 0.2. For **3a**: (11 mg, 20.5%), oil; ν_{max}/cm^{-1} 1731, 1018; δ_H 5.28–5.26 (1H, t, J = 4.1 Hz, 1-H), 4.26–4.20 (2H, q, J = 7.1 Hz, CH$_2$), 3.70–3.68 (1H, dd, J = 2 and 6.7 Hz, 5-H), 3.07–3.00 (1H, t, ^2J = 14.3 Hz, ^3J = 14.3, 3-H$_{exo}$), 2.91–2.86 (2H, m), 2.37–2.30 (1H, m), 2.19–2.07 (2H, m), 1.86–1.72 (2H, m), 1.63–1.52 (1H, m), 1.31–1.28 (3H, t, J = 7.1 Hz, CH$_3$); δ_C (62.9 MHz) 204.98 (C=O), 172.14 (OC=O), 171.36 (OC=O), 75.92 (O-CH), 62.16, 59.07, 42.77, 42.59, 33.67, 27.67, 20.16, 14.07; *m*/*z* 241 (M$^+$ + 1, 67%), 196 (M$^+$ − CO$_2$, 37), 149 (10), 128 (10), 100 (15), 68 (22), 55 (100), 39 (39). For **3b**: ^{1}H NMR δ_H 4.76–4.74 (1H, dd, J = 2.7 and 5.2 Hz, 1-H), 4.26–4.20 (2H, q, J = 7.1 Hz, CH$_2$), 3.74–3.72 (1H, m, 5-H), 3.24–3.17 (1H, t, ^2J = 13.3, ^3J = 13.3 Hz, 3-H$_{exo}$), 2.82–2.78 (1H, dd, ^2J = 13.3, ^3J = 4.9 Hz, 3-H$_{endo}$), 2.72–2.67 (1H, ddd, J = 1.2, 4.9 and 13.3 Hz, 4-H), 2.37–2.35 (1H, m), 2.19–2.05 (2H, m), 1.99–1.88 (2H, m), 1.63–1.52 (1H, m), 1.30–1.27 (3H, t, J = 7.1 Hz, CH$_3$); δ_C (62.9 MHz) 208.71 (C=O), 172.02 (OC=O), 171.80 (OC=O), 77.20 (O-CH), 65.82, 46.42, 41.47, 39.55, 30.90, 27.98, 19.96, 15.22; *m*/*z* 241 (M$^+$ + 1, 100%), 194 (33), 183 (17), 166 (47), 141 (28), 110 (14), 68 (58), 55 (68), 39 (82).

3-Oxabicyclo[3.2.2]nonane-2,7-dione 5a. (72 mg, 32%), R_f (1 : 1 heptane–ethyl acetate) 0.22; mp 180–182 °C (Found: C, 62.83; H, 6.42. $C_8H_{10}O_3$ requires C, 62.33; H 6.54); ν_{max}/cm^{-1} 1735, 1700, 1040; δ_H 4.66–4.55 and 4.43–4.31 (2H, m, 4-H$_2$), 3.66–3.58 (1H, dd, J = 1.9 and 5.3 Hz, 1-H), 2.74–2.58 (3H, m, 5-H, 6-H$_2$), 2.48–2.29 and 2.24–1.92 (4H, m); δ_C 203.92 (C=O), 167.92 (OC=O), 75.63 (O-CH$_2$), 59.08, 42.15, 30.27, 22.71, 22.33; *m*/*z* 154 (M$^+$, 8%), 126 (M$^+$ − CO, 26), 110 (M$^+$ − CO$_2$, 34,), 97 (26), 67 (22), 55 (100), 39 (17).

3-Oxabicyclo[4.3.1]decane-2,8-dione 6a. (9 mg, 16%), R_f (4 : 6 heptane–ethyl acetate) 0.28; mp 108–110 °C; ν_{max}/cm^{-1} 1720, 1707, 1065; δ_H 4.18 (2H, m, 4-H$_2$), 3.66–3.62 (1H, m, 1-H), 2.89–2.85 (1H, dd, J = 1.2 and 18.1 Hz), 2.76–2.49 (4H, m), 2.23–2.14 (3H, m), 1.99–1.94 (1H, m); δ_C 208.67 (C=O), 176.23 (OC=O), 64.80 (O-CH$_2$), 46.12, 43.29, 40.59, 35.78, 32.34, 28.57; *m*/*z* 168 (M$^+$, 11%), 140 (M$^+$ − CO, 23), 112 (74), 99 (81), 83 (38), 67 (86), 55 (100), 41 (56); HRMS (EI) M$^+$, 168.0785. $C_9H_{12}O_3$ requires M, 168.0786.

2-Oxabicyclo[4.3.1]decane-3,7-dione 7b. (16 mg, 29%), mp 84–85 °C; ν_{max}/cm^{-1} 1775, 1037; δ_H 5.05–4.7 (1H, m, 1-H), 2.85–1.65 (10H); *m*/*z* 168 (M$^+$, 50%), 140 (M$^+$ − CO, 54), 127 (25), 109 (13), 96 (13), 85 (100), 68 (23), 55 (55); HRMS (EI) M$^+$, 168.0789. $C_9H_{12}O_3$ requires M, 168.0786.

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