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Ring Opening of Cyclopropylketones Induced by Photochemical Electron Transfer

Janine Cossy*, Nathalie Furet, Samir BouzBouz

Laboratoire de Chimie Organique, Associé au CNRS, ESPCI, 10 rue Vauquelin

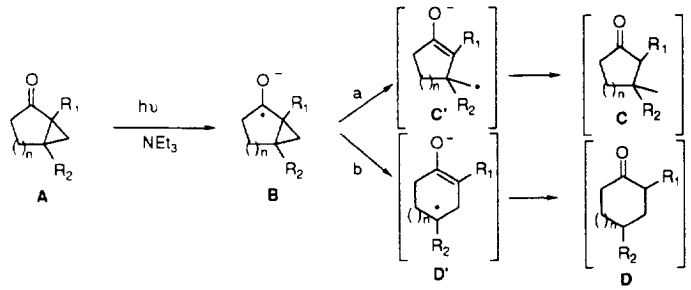
75231-Paris Cedex 05 France

Abstract: Depending on the substitution pattern of cyclopropylketones, the photochemically induced electron transfer of tertiary amines to cyclopropylketones leads either to the formation of 3-substituted cycloalkanones or to ring expanded products.

Radical ring closure has been intensively investigated as a method for the construction of organic compounds. Synthetic applications of the reverse process, radical ring opening, have received less attention. The physical organic chemistry of radical ring opening has been studied in details, particularly for carbocyclic system. Most of the reported measurements involve small rings, such as cyclopropylcarbinyl systems. The rate constant for ring opening of methylcyclopropylcarbinyl radical is about 10^8 s^{-1} at 25°C and the rate for the reverse process is about 10^4 s^{-1}. [1] The cleavage of a cyclopropane conjugated to a ketone has been of considerable interest. This cleavage has been achieved by using electrolysis, [2] samarium iodide, [3] alkali metal. [4]

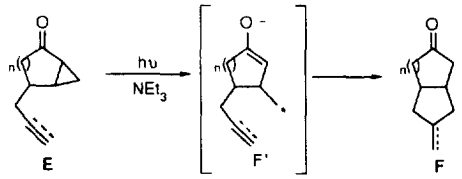
As part of our interest in the development of useful sequences featuring the cyclopropylcarbinyl radical rearrangement, we have examined the photochemically induced electron transfer of tertiary amines to cyclopropylketones with the aim of obtaining 3-substituted cycloalkanones (path a) and/or ring expanded products (path b) under very mild conditions according to the mechanism outlined in Scheme I.

Scheme I: ring opening of cyclopropylketones

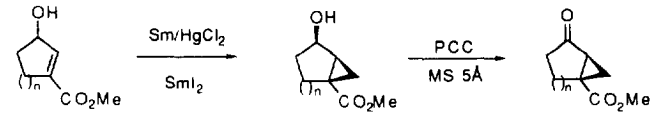


Secondly, we would like to report a further extension of the reaction of the photochemical electron transfer which can induce a fragmentation and a cyclization from

bicyclo[n.1.0]alkanones bearing an unsaturated alkyl side chain at C-4, able to produce bicyclic systems such as **F**.



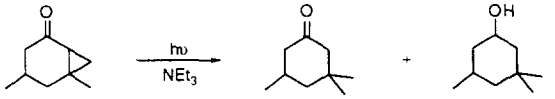
Various bicyclo[n.1.0]alkanones **1-3**, [5] **4-5**, [27] **8-10**, [5] **26-28** [5] were prepared according to literature procedures. Compounds **6** and **7** were synthesized by treatment of the corresponding allylic alcohol [6] with diiodomethane in the presence of samarium-mercury chloride. [7] The obtained alcohols were then oxidized with PCC in the presence of molecular sieves. [8]



n = 1 **6"** **6'** **6** (58%)

n = 2 **7"** **7'** (80%) **7** (60%)

Initially we chose to examine the irradiation of the bicyclo[4.1.0]heptanone **1** at 254 nm in acetonitrile (5 x 10^{-2} M) in the presence of triethylamine (10 equivalents). Under these conditions two products were formed in low yields *i.e.* the expected ketone **11** (10 %) and the alcohol **11'** [9] (15 %).

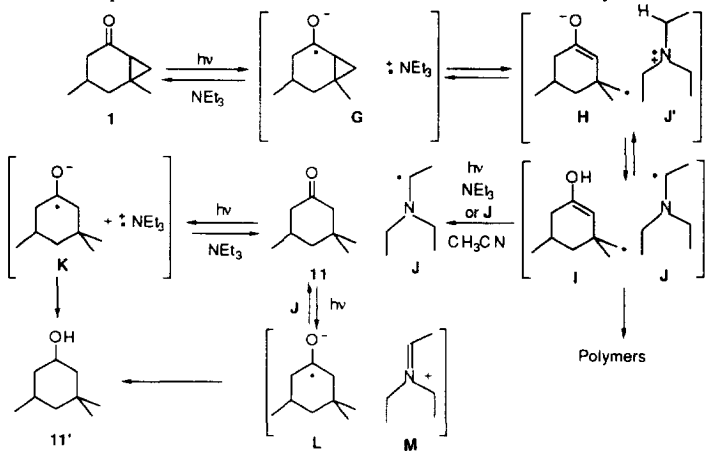


In order to improve the yield of **11**, the reaction conditions and the presence of additives were screened in some details. The addition of $LiClO_4$ was found to be quite beneficial. [10] In the presence of 1 equivalent of $LiClO_4$, and 10 equivalents of NEt3, the yield of ketone **11** was increased to 55 % and alcohol **11'** was no longer detected [11]. The effect of $LiClO_4$ can be explained as follows.

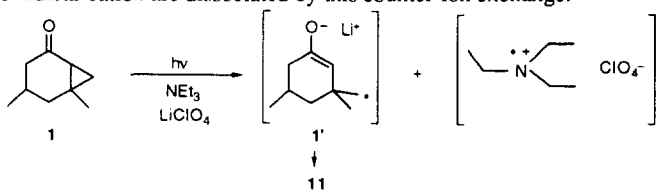
On irradiating ketone **1** in the presence of triethylamine without $LiClO_4$, a fast electron transfer from the amine to the ketone takes place and leads to the formation of a contact ion radical pair **G** in acetonitrile [12]. This electron transfer is followed by the ring cleavage of the cyclopropane ring which produces the ion pair **H-J'**. The radical-anion **H** most probably has a Pk_a in the range of ~ 10 and the triethylamine radical-cation a Pk_a of ~8 in water. [13] Therefore the radical-anion **H** is basic enough to deprotonate the amine radical-cation. The proton tranfer can take place if a contact ion pair is previously formed. [14] Radical **I** can then abstract an hydrogen atom from the solvent or from triethylamine to produce ketone **11**. Ketone **11** can be reduced to the alcohol **11'** by a second electron transfer either from the amino-radical **J** or from

a second molecule of triethylamine. We have to point out that without $LiClO_4$ unindentified polymers were formed which are probably initiated by radicals **I** and/or **J** and propagated at the expense of **11**.

Scheme II: photoinduced electron transfer between **1** and triethylamine

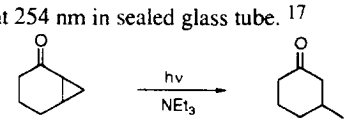


When $LiClO_4$ is present, the ketyl radical-anion counter ion $Et_3N^{+\bullet}$ is exchanged by Li^+, producing a very tight ion pair **1'**. [15] The proton transfer is delayed as the radical-anion and the amine radical-cation are dissociated by this counter-ion exchange.



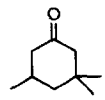
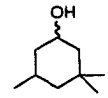
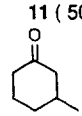
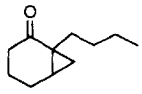
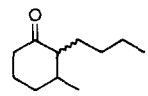
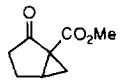
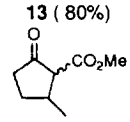
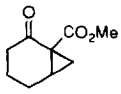
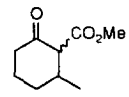
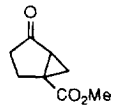
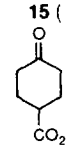
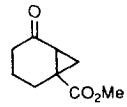
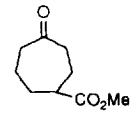
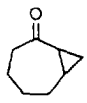
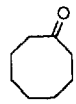
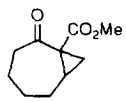
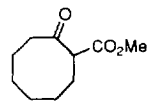
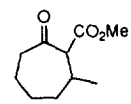
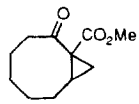
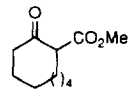
Irradiation of ketones **2-10** at 254 nm in acetonitrile, in the presence of 10 equivalents of triethylamine and 1 equivalent of $LiClO_4$ in acetonitrile led to the results reported in Table I.

The bicyclo[4.1.0]heptanone **2** led exclusively to the formation of the corresponding 3-methylcyclohexanone **12** with a yield of 70 % at 70 % conversion. We have to point out that the photochemical electron transfer is possible either by exciting the ketone at 300 nm or by exciting the donor molecule (triethylamine) at 254 nm. [16] However, lower yieds in **12** were obtained when the irradiation of **2** was performed with triethylamine in ethanol at 254 nm or 300nm, [16] or in acetonitrile at 254 nm in sealed glass tube. [17]



Solvent	additive	NEt3	Conc	λ nm	Duration	Yield in %
EtOH	0	20 %	2 x 10^{-2} M	300	4 h	55 % [16]
CH_3CN	0	5 %	5 x 10^{-2} M	254	10 h	40 % [17]
CH_3CN	$LiClO_4$	10 %	5 x 10^{-2} M	254	2 h	70 % [11]

TABLE I: Irradiation of bicyclo[n.1.0]alkanones in the presence of $LiClO_4$

Starting Material	Conversion	Products (Yield%)	
 **1**	100%	 **11** (50%)	 **11'** (0%)
 **2**	70%	 **12** (70%)	
 **3**	60%	 **13** (80%)	
 **4**	75%	 **14** (60 %)	
 **5**	80%	 **15** (60%)	
 **6**	90%	 **16** (50%)	
 **7**	100%	 **17** (65%)	
 **8**	100%	 **18** (60%)	 **19** (trace)
 **9**	100%	 **20** (80%)	 **21** (trace)
 **10**	100%	 **22** (55%)	

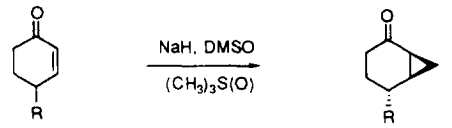
Thus, the irradiation of **3**, in the presence of 10 equivalents of triethylamine and 1 equivalent of $LiClO_4$, led to the formation of **13** as a mixture of two isomers *trans/cis* in a ratio 1.8/1 with a yield of 80% at 60% conversion. When compounds **4** and **5** were irradiated, the corresponding 3-methylcycloalkanones **14** (*trans/cis* = 10/1) [18] and **15** (*trans/cis* = 5.7/1), [18] respectively, were isolated with a yield of 60 %.

The bicycloalkanone **6** and **7** that are substituted by an electron-withdrawing group at C-4 led to the formation of ring expanded cycloalkanone **16** (50 %) and **17** (65 %), respectively. Similarly, cyclooctanone **18** (60 %) was obtained by irradiation of the bicyclo[5.1.0]octanone **8** together with a trace of the 3-methylcycloheptanone **19** that was detected by GC/MS. [19] With compounds **9** and **10** the corresponding ring expanded β-ketoester **20** (80 %) and **22**(55 %) were isolated.

The preferred regioselectivity of the ring opening depends on the substitution pattern of the bicycloalkanones and on its ring size. [20] (Scheme I)

The radical-enolate intermediates of type **D'** arising from the cleavage of bond C(1)-C(n+2) (ring enlargement process) are more stable (3-4 kcal/mol if R_2 = H and 11-14 kcal/mole if R = CO_2Me) [21] than the corresponding intermediate **C'**. The former is a secondary radical either substituted or not by an ester moiety, the latter is a primary radical. The ring enlargement can be explained by the fact that the C(1)-C(n+2) bond of the bicyclo[n.1.0]alkan-2-ones is weaker than that of bond C(1)-C(n+3). In the case of **1**, **2**, **3**, **4** and **5**, the C(1)-C(n+3) bond is cleaved preferentially due to stereoelectronic factor, the latter bond being better aligned with the π-system of the ketone radical-anion than bond C(1)-C(n+2). In the case of compound **6** and **7** the kinetic stereoelectronic factor does not compete with the highly favorable factor which makes the ring enlarged radical-anion intermediates highly stabilized by the carbonyl group. In compounds **8** and **9**, the flexibility of the bicyclic carbon skeleton makes both the C(1)-C(7) and C(1)-C(8) bond capable of proper alignment with the π-system of the ketone radical-anion, thus leading to mixture of the corresponding methylcycloheptanones and ring-enlarged cyclooctanones.

The intramolecular trapping of the radical **C'** induced by the PET fragmentation of the bicyclo[n.1.0]alkanones was achieved through irradiation of the bicycloalkanones **26**, **27** and **28**. These compounds were synthesized by cyclopropanation of the 4-alkylcyclohexen-2-ones [22] according to Corey's method using trimethylsulfoxonium iodide. [5] The cyclopropanation of the 4-alkylcyclohexen-2-ones **23**, **24** and **25** produced one major isomer in a ratio 95/5 (GC). Due to a Michael type addition of the trimethylsulfoxonium iodide on the ketone, the unsaturated alkyl side chain at C-4 and the cyclopropane group are in a *trans* relationship in the major isomer.



23 R = $CH_2CH=CH_2$ **26** (54%)

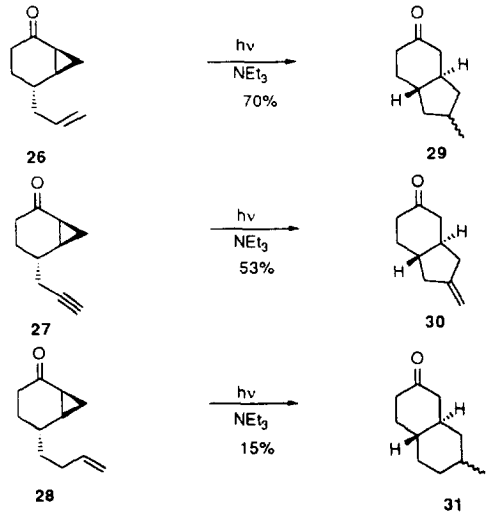
24 R = $CH_2C\equiv CH$ **27** (50%)

25 R = $(CH_2)_2CH=CH_2$ **28** (56%)

The irradiation of compounds **26**, **27** and **28** in the presence of triethylamine (10 eq) and $LiClO_4$ (1 eq) in acetonitrile led to the formation of **29** (70%), **30** (53%) and **31** (15 %), respectively (Table II). The formation of these bicyclic compounds showed, as expected, only the cleavage of the exocyclic cyclopropyl bond.

We have to point out that the irradiation of compound **26** at 300 nm in the presence of 4 equivalents of triethylamine, with or without $LiClO_4$ (1 eq) produced compound **29** with a yield of 28 %. [23]

Table II: irradiation of 5-alkylbicyclo[4.1.0]alkanones



Since the configuration at C-4 and C-5 in compounds **26**, **27** and **28** is not affected during the course of the reaction, the relative configuration at the ring jonction is *trans* in compounds **29**, **30** and **31**.

The photoreductive cyclopropane ring opening of bicyclo[n.1.0]alkanones reveals that this reaction can be controlled by stereoelectronic factors and by the relative stabilities of the radical enolate anion intermediates **C'** and **D'** generated by the cleavage of bond C(1)-C(n+3) and C(1)-C(n+2) respectively. The latter factor depends on the ring size (n value) and on the

substitution pattern. Furthermore, the intermediate radical can be trapped intramolecularly by an unsaturation.

Presently, we are investigating application of the cyclopropane fragmentation process, disclosed here, to the synthesis of natural products.

Experimental part

General methods

All experiments were run under an Ar atmosphere. ^1H NMR and ^{13}C-NMR spectra were obtained with a Bruker AC 300 instrument at 300 MHz and 75 MHz respectively, in $CDCl_3$ (Me_4Si as internal standard). IR spectra were recorded on a Perkin-Elmer Infracord 137 spectrometer. Mass spectra were run on a Hewlett-Packard (EI mode at 70 eV).

Flash chromatography was accomplished with Merck silicagel 0.043-0.063 nm.

Preparative irradiations were conducted in a merry-go-round type system equipped with 12 low pressure mercury Philips TUV 15 lamps (254 nm), using 10 mm 0.d. quartz tubes. Acetonitrile and triethylamine were distilled from CaH_2.

Cyclopropanation of cycloalken-2-ones. Synthesis of bicyclo[n.1.0]alkanones

To a suspension of sodium hydride (1.6 g, 67.6 mmol, 1.3 eq) in DMSO (90 mL) was added trimethylsulfoxonium iodide (14.9 g, 67.6 mmol, 1.3 eq). After 15 mn, a solution of enone (52.0 mmol, 1.0 eq) in DMSO (15 mL) was added dropwise and the reaction mixture was stirred at r. t. for 2 h and at 50°C for 1 h. Water was then added (150 mL). The reaction mixture was extracted with ether (3 x 10 mL). The organic phases were combined, dried over $MgSO_4$ and evaporated *in vacuo*. The bicyclo[n.1.0]alkanones were purified by distillation or by flash chromatography.

4, 6-Dimethylbicyclo[4.1.0]heptan-2-one **1** [24]

R_f: 0.32 (Pentane-Et_2O: 80/20). Yield: 40 %. IR: 1685; 1295; 1243 cm^{-1}. ^1H NMR: δ 0.88 (dd, 1H, J = 10.0 Hz, J = 5.0 Hz); 0.94 (d, 3H, J = 6.0 Hz); 1.20 (s, 3H); 1.34 (m, 1H); 1.40 (d, 1H, J = 12.5 Hz); 1.50-1.90 (m, 3H); 1.97 (dd, 1H, J = 13.1 Hz, J = 3.5 Hz); 2.35-2.40 (dd, 1H, J = 13.0 Hz, J = 3.5 Hz). ^{13}C NMR: δ 17.9 (t); 21.9 (q); 23.4 (s); 24.5 (d); 24.8 (q); 33.5 (d); 37.2 (t); 44.8 (t); 208.8 (s). MS (CI, NH_3): *m/z* 156 (MNH_4^+, 72); 139 (MH^+,100).

Bicyclo[4.1.0]heptan-2-one **2** [24]

B.p.: 43°C (0.2 mm Hg). Yield: 80 %. IR: 1693, 1350, 1244 cm^{-1}. ^1H NMR: δ 0.84 (m, 1H); 0.93-1.03 (m, 1H); 1.29-1.53 (m, 4H); 1.68-1.87 (m, 3H); 1.96-2.10 (m, 1H).

^{13}C NMR: δ 10.0 (t); 17.2 (d); 17.6 (t); 21.4 (t); 25.6 (d); 36.6 (t); 209.1 (s). MS: *m/z* 110 (M^+, 84); 95 (58); 82 (44); 67 (92); 55 (84); 54 (100).

2-Butylbicyclo[4.1.0]heptanone 3

R_f: 0.4 (Hexane/AcOEt: 90/10). Yield: 90%. IR: 1690, 1465, 1360 cm^{-1}. ^1H NMR: δ 0.92-0.75 (m, 5H); 1.15-1.33 (m, 5H); 1.42-1.50 (m, 1H); 1.55-1.70 (m, 2H); 1.85-2.12 (m, 4H); 2.18-2.30 (m, 1H). ^{13}C NMR: δ 13.9 (q); 16.9 (t); 18.8 (t); 21.9 (t); 22.6 (t); 24.0 (q); 29.2 (t); 34.0 (t); 37.2 (t); 209.6 (s). MS: *m/z* 166 (M^+, 8); 151 (100); 137 (43); 123 (56); 95 (90); 67 (98); 55 (70).

Bicyclo[5.1.0]octan-2-one 8 [25]

R_f: 0.36 (Hexane/AcOEt: 80/20). Yield: 40%. IR: 1665, 1360 cm^{-1}. ^1H NMR: δ 1.05 (m, 1H); 1.13-1.30 (m, 2H); 1.85-2.03 (m, 7H); 2.30-2.45 (m, 2H). ^{13}C NMR: δ 12.3 (t); 18.6 (d); 23.5 (t); 25.0 (t); 27.6 (t); 30.3 (d); 41.4 (t); 211.4 (s). MS: *m/z* 124 (M^+, 67); 95 (39); 80 (100); 67 (60).

Methyl 2-oxobicyclo[5.1.0]octane-1-carboxylate 9

Prepared from the corresponding enone [26]

R_f: 0.30 (Hexane/AcOEt: 80/20). Yield: 50 %. IR: 1755, 1715, 1320, 1300 cm^{-1}. ^1H NMR: δ 0.50-0.70 (m, 1H); 1.20-1.30 (m, 1H); 1.30-1.50 (m, 2H); 1.50-1.60 (m, 1H); 1.70-2.00 (m, 3H); 2.35-2.50 (m, 1H); 2.50-2.60 (m, 1H); 2.80-3.00 (m, 1H); 3.70 (s, 3H). ^{13}C NMR: δ 22.3 (t); 25.3 (d); 25.8 (t); 26.2 (t); 30.4 (t); 39.6 (s); 43.9 (t); 52.5 (q); 171.9 (s); 205.2 (s). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found : C, 65.97; H, 7.69.

Methyl 2-oxobicyclo[6.1.0]nonane-1-carboxylate 10

Prepared from the corresponding enone [26].

R_f: 0.24 (Hexane/AcOEt: 85/15). IR: 1760, 1720, 1375, 1320 cm^{-1}. ^1H NMR: δ 0.50-0.75 (m, 1H); 1.20-1.35 (m, 1H); 1.35-2.15 (m, 9H); 2.30-2.45 (m, 1H); 3.10-3.30 (m, 1H); 3.75 (s, 3H). ^{13}C NMR: δ 19.0 (t); 24.9 (t); 26.6 (t); 27.4 (t); 28.5 (t); 30.6 (d); 39.5 (s); 45.0 (t); 52.9 (q); 171.7 (s); 207.0 (s). MS: *m/z* 196 (M^+, 30); 166 (65); 137 (60); 81 (70); 55 (100).

5-(Prop-2-enyl)bicyclo[4.1.0]heptan-2-one 26

R_f: 0.31 (Hexane/AcOEt: 65/35). Yield: 54 %. IR: 1675, 1430, 1400 cm-1. ^1H NMR: δ 1.00-1.25 (m, 2H); 1.45-1.90 (m, 4H); 1.90-2.30 (m, 5H); 4.90-5.15 (m, 2H); 5.65-5.95 (m, 1H). ^{13}C NMR: δ 12.5 (t); 23.5 (t); 23.8 (d); 25.4 (d); 31.4 (d); 32.8 (t); 38.9 (t); 116.6 (t); 136.4 (d); 209.4 (s). MS: *m/z* 150 (M^+, 15); 122 (22); 109 (95); 91 (22); 81 (100); 79 (61); 67 (75); 55 (42). Exact Mass Calcd for $C_{10}H_{14}O$: 150.10446. Found: 150.10445.

5-(Prop-2-ynyl)bicyclo[4.1.0]heptan-2-one **27**

R_f: 0.36 (Hexane/AcOEt: 50/50). Yield: 50 %. IR: 1685, 1350 cm^{-1}. ^1H NMR: δ 1.10-1.28 (m, 2H); 1.67-1.90 (m, 4H); 2.09 (t, 1H, J = 2.4 Hz); 2.11-2.22 (m, 2H); 2.24-2.43 (m, 3H). ^{13}C NMR: δ 12.2 (t); 23.1 (d); 24.2 (t); 24.7 (t); 25.3 (d); 31.2 (d); 32.4 (t); 69.8 (d); 82.0 (s); 208.5 (s). MS (CI, NH_3): *m/z* 166 (MNH_4^+, 20); 149 (MH^+, 100); 109 (15); 91 (20). Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.06; H, 8.19.

5-(But-3-enyl)bicyclo[4.1.0]heptan-2-one **28**

R_f: 0.35 (Hexane/AcOEt: 75/25). Yield: 56 %. IR: 1685, 1630, 1440 cm^{-1}. ^1H NMR: δ 1.10-1.35 (m, 2H); 140-1.70 (m, 4H); 1.70-1.90 (m, 2H); 1.95-2.10 (m, 2H); 2.10-2.30 (m, 3H); 4.85-5.15 (m, 2H); 5.70-5.95 (m, 1H). ^{13}C NMR: δ 13.4 (t); 24.7 (t); 24.9 (d); 26.2 (d); 32.2 (d); 33.3 (t); 33.8 (t); 34.4 (t); 115.6 (t); 138.9 (d); 209.8 (s). MS: *m/z* 164 (M^+, 3); 149 (10); 136 (13); 122 (18); 109 (24); 94 (61). Anal. Calcd. for $C_{11}H_{16}O$: C, 80.43 ; H, 9.82. Found: C, 80.55; H,9.78.

Cyclopropanation of methyl 3-hydroxycycloalk-1-ene-1-carboxylate

To a solution of mercuric chloride (0.4 g, 1.4 mmol. 1.0 eq) in THF (30 mL) is added metallic samarium (2.1 g, 13.8 mmol, 10.0 eq) in THF (30 mL). After 10 mn, methyl 3-hydroxycycloalk-1-ene-1-carboxylate (3.5 mmol, 2.5 eq) is added. The reaction mixture is cooled to -78°C and diiodomethane (3.7 g, 13.8 mmol, 10.0 eq) is added dropwise. After 2 h at r. t., an aqueous solution of K_2CO_3 is added (10 mL) followed by the addition of ether (3 x 10 mL). The organic phases were combined and dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue is purified by flash chromatography.

Methyl 4-hydroxybicyclo[3.1.0]hexane-1-carboxylate **6'**

As the product was difficult to purify, it was oxidized directly.

Methyl 4-hydroxybicyclo[4.1.0]heptane-1-carboxylate **7'**

R_f: 0.39 (Hexane/AcOEt: 50/50). Yield: 80 %. IR: 1715, 1745, 1295 cm^{-1}. ^1H NMR: δ 0.93 (m, 1H); 1.02-2.57 (m, 9H); 3.66 (s, 3H); 4.18-4.29 (m, 1H). ^{13}C NMR: δ 17.4 (t); 19.6 (t); 23.6 (t); 25.7 (s); 28.0 (d); 29.3 (t); 52.1 (q); 65.7 (d); 175.0 (s). MS: *m/z* 170 (M^+, 2); 152 (4); 138 (60); 127 (16); 110 (100); 93 (36); 82 (66).

Oxydation of 6' and 7'

To a suspension of molecular sieves 5 Å (0.5 g) and PCC (0.3 g, 1.5 mmol, 1.5 eq) in CH_2Cl_2 (2.5 mL) at r. t., was added rapidly a solution of the alcohol **6'** or **7'** (1.0 mmol, 1.0 eq) in CH_2Cl_2 (1.0 mL). After 24 h, the reaction mixture was diluted with ether (5 mL) and

filtered on florisil. The solvent was evaporated and the residue purified by flash chromatography.

Methyl 4-oxobicyclo[3.1.0]hexane-1-carboxylate **6**
R_f: 0.39 (Hexane/AcOEt: 70/30). Yield: 58 %. IR: 1730, 1370, 1265 cm^{-1}. ^1H NMR: δ 1.30-1.40 (m, 1H); 1.90-2.00 (m, 1H); 2.10-2.40 (m, 4H); 2.45-2.70 (m, 1H); 3.75 (s, 3H). ^{13}C NMR: δ 20.0 (t); 22.6 (t); 33.0 (t); 33.4 (s); 36.4 (d); 52.3 (q); 172.2 (s); 210.8 (s). MS: *m/z* 154 (M^+, 60); 126 (100); 123 (35); 100 (40); 98 (25). Anal. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.53. Found: C, 62.38; H, 6.59.

Methyl 5-oxobicyclo[4.1.0]heptane-1-carboxylate **7**
R_f: 0.29 (Pentane/Et_2O: 60/40). Yield: 60 %. IR: 1720, 1690, 1265 cm^{-1}. ^1H NMR: δ 1.40-1.60 (m, 2H); 1.60-1.70 (m, 1H); 1.70-1.85 (m, 1H); 1.90-2.10 (m, 1H); 2.15-2.40 (m, 4H); 3.70 (s, 3H). ^{13}C NMR: δ 16.3 (t); 17.5 (t); 21.2 (t); 25.7 (d); 35.1 (s); 38.2 (t); 53.2 (q); 170.8 (s); 202.5 (s). MS: *m/z* 168 (M^+, 33); 140 (40); 121 (18); 100 (45); 81 (65); 55 (100). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.32; H, 7.10.

Compounds **4** and **5** were prepared from methyl 2-diazo-3-oxoalkenoate [27]

Methyl 2-oxobicyclo[3.1.0]hexane-1-carboxylate **4** [27]
This compound was prepared from methyl 2-diazo-3-oxohept-6-enoate.
IR: 1760; 1730; 1380 cm^{-1}. ^1H NMR: δ 1.40-150 (m, 1H); 1.95-2.35 (m, 5H); 2.55-2.70 (m, 1H); 3.75 (s, 3H). ^{13}C NMR: δ 20.9 (t); 22.1 (t); 33.1 (d); 33.6 (t); 37.5 (s); 52.2 (q); 168.8 (s); 206.7 (s). MS: *m/z* 154 (M^+, 75); 139 (10); 126 (87); 113 (100); 98(35).

Methyl 2-oxobicyclo[4.1.0]heptane-1-carboxylate **5** [27]
This compound was prepared from methyl 2-diazo-3-oxoöct-7-enoate.
IR: 1720, 1690, 1430, 1265 cm^{-1}. ^1H NMR: δ 1.30-1.40 (m, 1H); 1.40-2.50 (m, 8H); 3.72 (s, 3H). ^{13}C NMR: δ 16.3 (t); 17.5 (t); 21.3 (t); 25.7 (d); 35.1 (s); 38.3 (t); 52.3 (q); 170.6 (s); 202.5 (s). MS: *m/z* 168 (M^+, 45); 136 (100); 108 (90); 80 (55).

Irradiation of the bicyclo[4.1.0]alkanones

A solution of bicyclo[4.1.0]alkanone (0.7 mmol, 1.0 eq) in dry acetonitrile (5×10^{-2} M) of triethylamine (10.0 eq) and lithium perchlorate (1.0 eq) was irradiated at 254 nm. After 5 h the solvent was evaporated and the residue was distilled or purified by flash chromatography.

3,3,5-Trimethylcyclohexanone ***11*** [28]

R_f: 0.32 (Pentane/Et_2O: 80/20). Yield: 50 %. IR: 1705, 1450, 1270 cm^{-1}. ^1H NMR: δ 0.89 (s, 3H); 1.02 (d, 3H, J = 7.4 Hz); 1.06 (s, 3H); 1.30 (ddd, 1H, J = 12.0 Hz, J = 13.0 Hz); 1.53-1.65 (m, 1H); 1.80-1.92 (dd, 1H, J = 13.0 Hz, J = 3.5 Hz); 2.00-2.25 (m, 2H); 2.30-2.40 (m, 2H). ^{13}C NMR: δ 22.4 (q); 25.7 (q); 29.6 (d); 32.1 (q); 35.3 (s); 47.2 (t); 49.2 (t); 54.1 (t); 211.9 (s). MS (CI, NH_3): *m/z* 158 (MNH_4^+, 100); 141 (50); 125 (30); 110 (50).

This compound has been synthesized by addition of lithium methylcuprate on 3,5-dimethylcyclohex-2-en-1-one.

3,3,5-Trimethylcyclohexanol ***11'***

R_f: 0.29 (Pentane/Et_2O: 60/40). Yield: 15 %. IR = 3400, 1210, 760 cm^{-1}. ^1H NMR: δ 0.88 (s, 3H); 0.89 (d, 3H, J = 5.7 Hz); 1.11 (s, 3H); 1.00-2.10 (m, 8H); 4.16 (m, 1H). ^{13}C NMR: δ 22.6 (q); 22.8 (q); 28.2 (d); 30.7 (s); 34.1 (q); 41.6 (t); 44.8 (t); 48.5 (t); 68.3 (d). MS: *m/z* 142 (M^+, 1.5); 124 (16); 109 (100 ; 96 (16); 91 (17); 83 (27).

3-Methylcyclohexanone ***12*** [28]

R_f: 0.39 (Hexane/ACOEt: 50/50). Yield: 70 %. IR: 1715, 1450, 1270 cm^{-1}. ^1H NMR: δ 1.00 (d, 3H, J = 6.0 Hz); 1.10-2.70 (m, 9H). ^{13}C NMR: δ 22.1 (q); 25.4 (t); 33.4 (t); 34.3 (d); 41.2 (t); 50.0 (t); 211.6 (s). MS: *m/z* 112 (M^+, 72); 97 (23); 69 (100); 56 (33).

This product has been synthesized by addition of lithium methylcuprate to cyclohexenone.

2-Butyl-3-methylcyclohexanone ***13***

Rf: 0.45 (Hexane/AcOEt: 90/10). Yield: 80%. Two isomers (*trans/cis*: 65/35). ^1H NMR: Minor isomer: δ 0.75 (d, 3H, J = 6.0 Hz). Major isomer: δ 0.95 (d, 3H, J = 6.5 Hz). Both isomer δ: 0.80 (t, 3H, J = 7.0 Hz); 1.02-1.30 (m, 5H); 1.33-1.96 (m, 7H); 2.10-2.34 (m, 2H). ^{13}C NMR: Major isomer: δ 13.8 (q); 20.3 (q); 22.9 (t); 25.2 (t); 26.6 (t); 29.4 (t); 32.7 (t); 38.1 (d); 41.2 (t); 57.2 (d); 213.2 (s). MS: *m/z* 168 (M^+, 5); 125 (10); 112 (49); 97 (100).

Methyl 5-methyl-2-oxocyclopentane-1-carboxylate ***14*** [29,30]

R_f: 0.5 (Hexane/Et_2O: 90/10). Yield: 60 %. IR: 1760, 1200 cm^{-1}. ^1H NMR: δ 1.15 (d, 3H, J = 6.5 Hz); 1.40-1.60 (m, 1H); 2.10-2.70 (m, 4H); 2.80 (d, 1H, J = 11.0 Hz); 3.76 (s, 3H). ^{13}C NMR: δ 19.1 (q); 29.2 (t); 36.2 (d); 38.6 (t); 52.2 (q); 62.8 (d); 169.5 (s); 211.7 (s). MS (CI, NH_3): *m/z* 162 (MNH_4^+, 32); 145 (MH^+, 32); 125 (48); 100 (100).

Methyl 6-methyl-2-oxocyclohexane-1-carboxylate ***15*** [30]

R_f: 0.39 (Hexane/ACOEt: 70/30). Yield: 60 %. IR: 1740, 1705, 1645, 1435 cm^{-1}. ^1H NMR: δ 1.03 (d, 3H, J = 6.5 Hz); 1.05-2.50 (m, 7H); 3.05 (d, 1H, J = 12.0 Hz); 3.76 (s, 3H).

^{13}C NMR: δ 20.9 (q); 25.0 (t); 32.4 (t); 36.6 (d); 40.9 (t); 51.9 (q); 65.0 (d); 170.2 (s); 206.0 (s). MS: *m/z* 170 (M^+, 15); 155 (42); 138 (46); 123 (100).

Methyl 4-oxocyclohexane-1-carboxylate ***16***
Yield: 50 %. IR: 1735, 1715 cm^{-1}. ^1H NMR: δ 1.00-2.80 (m, 9H); 3.80 (s, 3H). MS: *m/z* 156 (50); 125 (40); 100 (100); 96 (60).

Methyl 4-oxocycloheptane-1-carboxylate ***17*** [31]
R_f: 0.21 (Hexane/AcOEt: 70/30). Yield: 65 %. IR: 1720, 1700, 1265 cm^{-1}. ^1H NMR: δ 1.40-2.40 (m, 8H); 240-2.70 (m, 3H); 3.67 (s, 3H). ^{13}C NMR: δ 23.0 (t); 26.9 (t); 29.2 (t); 42.1 (t); 44.0 (t); 46.9 (d); 52.4 (q); 176.0 (s); 214.2 (s). MS: *m/z* 170 (M^+, 45); 139 (45); 111 (89); 55 (100).

Cycloöctanone ***18***
Yield: 60 %. B.p.: 193-195°C. IR: 1685 cm^{-1}. ^1H NMR: δ 1.31-1.43 (m, 2H); 1.49-1.62 (m, 4H); 1.81-1.94 (m, 4H); 2.35-2.46 (m, 4H). ^{13}C NMR: δ 24.6 (t); 25.5 (2t); 27.0 (2t); 41.8 (2t); 217.9 (s). MS: *m/z* 216 (M^+, 20); 111 (10); 98 (10); 83 (38).
This compound was compared with an authentic sample.

3-Methylcycloheptanone ***19***
IR: 1690, 1450 cm^{-1}. ^1H NMR: δ 1.00 (d, 3H, J = 6.7 Hz); 1.20-2.00 (m, 7H); 2.30-2.60 (m, 4H). ^{13}C NMR: δ 23.4 (q); 24.1 (t); 28.4 (t); 31.1 (d); 39.1 (t); 43.9 (t); 51.6 (t); 214.2 (s). MS: *m/z* 126 (M^+, 27); 111 (11); 98 (50); 82 (74); 69 (100); 55 (49).
This product has been synthesized by addition of lithium methylcuprate to cycloheptenone.

Methyl 2-oxocyclooctane-1-carboxylate ***20***
Yield: 80 %. IR: 1750, 1705, 1640 cm^{-1}. ^1H NMR: δ 1.30-2.70 (m, 12H); 3.60 (m, 1H); 3.70 (s, 3H). ^{13}C NMR: δ 23.8 (t); 25.3 (t); 26.4 (t); 28.6 (t); 32.1 (t); 41.7 (t); 51.3 (q); 56.6 (d); 170.4 (s); 211.9 (s). MS: *m/z* 184 (M^+, 60); 152 (100); 141 (15); 124 (65); 113 (67); 98 (59); 87 (100).

Methyl 7-methyl-2-oxocycloheptane-1-carboxylate ***21***
Ratio *cis/trans*: 35/65 determined by ^1H NMR. R_f: 0.4 (Hexane/AcOEt: 70/30). IR: 1740, 1705, 1635 cm^{-1}. ^1H NMR. *Cis* isomer: δ 1.02 (d, 3H, J = 6.7 Hz); 2.70-3.00 (m, 1H); 3.80 (s, 3H); *Trans* isomer: δ 1.07 (d, 3H, J = 7.1 Hz); 3.20 (d, 1H, J = 10.0 Hz,); 3.75 (s, 3H); Both isomers: δ 1.35-2.70 (m, 9H). ^{13}C NMR: δ 20.9 (q); 25.0 (t); 32.4 (t); 35.4 (t); 36.6 (d); 41.0 (t); 52.0 (q); 65.0 (d); 170.2 (s); 204.0 (s).

Methyl 2-oxocyclononane-1-carboxylate ***22***

R_f = 0.21 (Hexane/AcOEt: 70/30). Yield: 55 %. IR: 1735, 1700, 1635 cm^{-1}. ^1H NMR: δ 1.30-2.70 (m, 14H); 3.50-3.60 (m, 1H); 3.70 (s, 3H). ^{13}C NMR: δ 23.9 (t); 24.3 (t); 24.6 (t); 25.0 (t); 25.9 (t); 26.9 (t); 31.4 (t); 51.5 (q); 58.5 (d); 176.0 (s ; 211.7 (s). MS: *m/z* 198 (M^+, 28); 167 (17); 166 (16); 110 (28); 94 (45).

8-Methylbicyclo[4.3.0]nonan-3-one ***29***

R_f: 0.56 (Pentane/Et_2O: 50/50). Yield: 70 %. Two isomers in a ratio: 5.5/1 (determined by ^1H NMR). IR: 1700, 1440, 1410 cm^{-1}. ^1H NMR. Major isomer: δ 1.00 (d, 3H, J = 7.0 Hz); Minor isomer: δ 1.05 (d, 3H, J = 7.0 Hz); Both isomers: δ 1.30-1.70 (m, 6H); 2.00-2.40 (m, 6H); 2.50-2.55 (m, 1H). ^{13}C NMR. Major isomer: δ 26.8 (q); 33.3 (t); 35.8 (d); 43.4 (t); 43.7 (t); 44.6 (t); 49.1 (d); 46.5 (d); 51.1 (t); 215.8 (s). Minor isomer δ: 27.0 (q); 33.5 (t); 35.1 (d); 46.8 (d); 51.5 (t); 216.2 (s). MS: *m/z* 152 (M^+, 85); 108 (100); 95 (75); 66 (50). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.85; H, 10.63.

8-Methylenebicyclo[4.3.0]nonan-3-one ***30***

R_f: 0.61 (Pentane/Et_2O: 90/10). Yield: 53 %. IR: 1710, 1655, 1425 cm^{-1}. ^1H NMR: δ 1.40-2.70 (m, 12H); 4.85-4.95 (m, 2H). ^{13}C NMR: δ 29.3 (t); 37.8 (t); 38.4 (t); 39.4 (t); 40.8 (d); 41.2 (d); 42.7 (t); 106.6 (t); 150.2 (s); 211.8 (s). MS: *m/z* 150 (M^+, 100); 122 (17); 106 (79); 93 (68); 79 (94). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.87; H, 9.41.

9-Methylbicyclo[4.4.0]decan-3-one ***31***

R_f: 0.45 (Pentane/Et_2O: 70/30). Yield: 15 %. Two isomers in a ratio: 2/1 (determined by ^1H NMR). IR: 1705, 1445 cm^{-1}. ^1H NMR. Major isomer: δ 0.91 (d, 3H, J = 6.5 Hz). Minor isomer: δ 0.98 (d, 3H, J = 7.0 Hz). Both isomer: δ 1.20-2.50 (m, 15H). ^{13}C NMR. Major isomer: δ 22.4 (q); 31.9 (d); 32.5 (t); 33.2 (t); 34.7 (t); 41.2 (d); 41.5 (t); 42.8 (t); 43.1 (d); 48.5 (t); 211.6 (s). Minor isomer: δ 22.2 (q); 31.4 (d); 32.6 (d); 33.5 (t); 34.5 (t); 40.9 (d); 41.7 (t); 42.9 (d); 43.4 (d); 48.7 (t); 211.7 (s). Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.53; H, 10.97.

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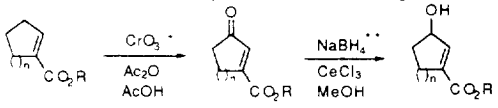

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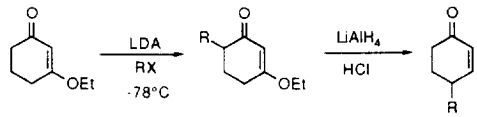

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