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Synthesis of novel functionalized olefins *via* fragmentation of $S_{RN}1$ products with a cyclanone β-ester subunit

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Summary – Base-promoted fragmentation of products resulting from $S_{RN}1$ reactions between *gem* halonitro alkanes and cyclanone β-esters as nucleophiles gives rise to di- or trifunctionalized olefins. These olefins carry a chain whose length is determined by the size of the ring in the cyclic nucleophile.

cyclanone β-ester / fragmentation / NO_2^- extrusion / trifunctionalized olefins / difunctionalized olefin

Introduction

In the preceding article [1] we reported $S_{RN}1$ reactions between functionalized *gem* halonitro alkane derivatives as substrates and anions derived from malonic esters or linear β-keto esters as nucleophiles (scheme 1). Depending upon the structure of the nucleophile, olefins resulted from spontaneous ionic NO_2H elimination on the primary $S_{RN}1$ product (**P1**) (eq 1), while products **P2** were readily isolated when such an elimination was structurally unfeasible (eq 2).

In order to extend the study to cyclic derivatives **P3**, $S_{RN}1$ reactions involving nucleophiles derived from cyclanone β-esters (n = 2, 3 or 4) were planned. The desired products were obtained in this way except for the n = 2 product which resulted from reaction with the cyclobutanone ester anion as a nucleophile. This unexpected result prompted further investigations into the chemical behavior of **P3**, which eventually led to a novel synthesis of functionalized olefins.

Results

A test $S_{RN}1$ reaction was first carried out with the substrate **1a** (table I) and the cyclobutanone ester derived enolate **2a** (entry 1). GC/MS monitoring of the reaction course did not indicate formation of the expected product **3a** (M^+ 255), but that of another product (M^+ 226) which had unexpectedly lost the nitro function. In contrast, the reaction between **1a** and the anion generated from cyclopentanone ester **2b** as a nucleophile afforded **3b** (entry 2). Similarly, the homologous **3c** was obtained, although in a lower yield, from the reaction between **1a** and **2c** (entry 3).

Considering the results of these reactions, we assumed that the product **3a** was also formed in the reaction between **1a** and **2a**, but had subsequently lost nitrogen in the alkaline medium of the $S_{RN}1$ reaction in which **3b** (or **3c**) was stable. After several trials, we found that alkaline conditions (KOH, EtOH, rt) converted **3b** (or **3c**) quantitatively into diester olefins **4b** (entry 2) or **4c** (entry 3). Hence, structure **4a** was tentatively assigned to an acid ester product (M^+ 226) generated *via* **3a** in the first reaction (entry 1).

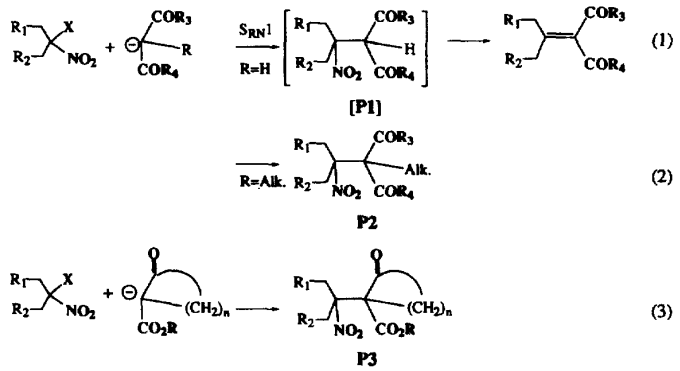
An olefin synthesis based upon heat-promoted elimination of NO_2 and a carboxyl group from $S_{RN}1$ products similar to **3b,c** was reported by Ono *et al* [2]. There is a large number of examples of this, and the one depicted in scheme 2 (eq 4), where the nucleophile is derived from **2b**, is relevant to our work.

We therefore prepared **3d** and treated it under our alkaline conditions (eq 5). In contrast to the thermal elimination of NO_2 and CO_2Et from **3d** giving the α-isopropylidene cyclopentanone, NO_2 elimination and *fragmentation of the cyclopentanone* led to the olefin **4d** (entry 4), which retains all the carbon atoms of the parent $S_{RN}1$ product. The homologous olefin **4e** was obtained similarly from the $S_{RN}1$ reaction product **3e** treated under alkaline conditions (entry 5).

The two-step sequence leading to these novel *difunctionalized* olefins was extended to the synthesis of *trifunctionalized* olefins. The $S_{RN}1$ reaction between the monofunctionalized substrate **1c** (R^1 = OMOM) and the four-membered β-keto ester derived enolate **2a** (entry 6) afforded an olefin which was fully characterized as the acid ester olefin **4f** analogous to the olefin **4a** detected in the first reaction (entry 1). Reactions between **1d** and **2d** (entry 7) or **1d** and **2c** (entry 8) afforded

† Dedicated to the memory of André Lechevallier (1951-1991)

* Correspondence and reprints

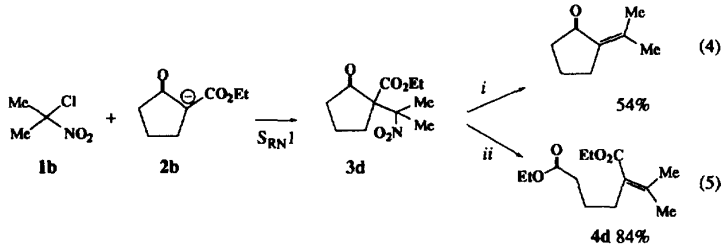


Scheme 1. $S_{RN}1$ reactions leading to products **P1**, **P2**, **P3**.

Table I. Synthesis of olefins **4a-h** from $S_{RN}1$ products **P3**.

	Substrates		Nucleophiles		$S_{RN}1$ Products P3		Olefins	
Entry		R^1 R^2		n R		yield (%)		R' yield (%)[b,c]
1	**1a**	$-(CH_2)_3-$	**2a**[a]	2 CH_3	[3a]		**4a**	H
2	**1a**	$-(CH_2)_3-$	**2b**	3 C_2H_5	**3b**	87	**4b**	C_2H_5 86 (74.8)
3	**1a**	$-(CH_2)_3-$	**2c**	4 C_2H_5	**3c**	47	**4c**	C_2H_5 99 (46.5)
4	**1b**	H H	**2b**	3 C_2H_5	**3d**	57	**4d**	C_2H_5 84 (47.8)
5	**1b**	H H	**2c**	4 C_2H_5	**3e**	23	**4e**	C_2H_5 99 (22.7)
6	**1c**	OMOM H	**2a**	2 CH_3	[3f]		**4f**[e]	H 30
7	**1d**	OTHP H	**2b**	3 C_2H_5	**3g**[d]	70	**4g**[e]	C_2H_5 75 (52.5)
8	**1d**	OTHP H	**2c**	4 C_2H_5	**3h**[d]	67	**4h**[e]	C_2H_5 48 (32)

a) Prepared according to reference 5; b) pure isolated product; c) in parentheses overall yield of pure isolated product calculated upon the corresponding product **P3**; d) (1:1) mixture of *Er/Thr* isomers (reference 1); e) (1:1) mixture of *Z/E* isomers.



Reagents and conditions : *i)* Δ, DMSO, 4 h (reference 2). *ii)* KOH (1.2 equiv)/EtOH (10 mL), rt.

Scheme 2. Comparison of thermal with ionic elimination from alicyclic compound **3d**.

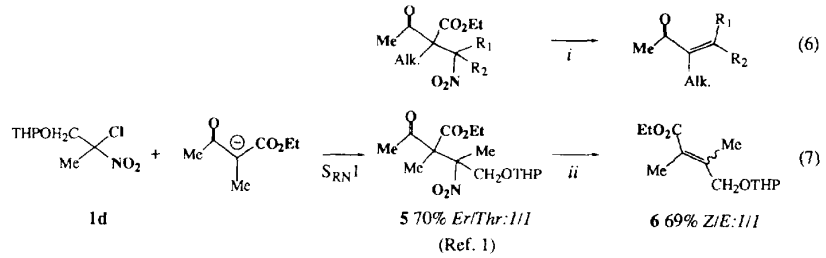
the primary $S_{RN}1$ products **3g** or **3h**, the precursors of the desired olefins **4g** or **4h**, respectively.

The large majority of thermally induced elimination reactions reported by Ono *et al* [2] belong to the aliphatic series (eq 6). The **P2** aliphatic $S_{RN}1$ product **5** treated under alkaline conditions (eq 7) gave olefin **6** resulting from the loss of NO_2 and COMe. The carbonyl fragment was thus eliminated from the parent molecule **5** while it remained attached as the $(CH_2)_nCO_2R$ substituent in olefins **4a-h** generated from **P3** products encompassing a cyclanone β-ester subunit.

Thus, comparison of the experiments summarized in schemes 2 and 3 and the experiments in table I gives evidence that the KOH/EtOH-promoted fragmentation of the **P2** and **P3** products proceeds by a mechanism other than thermal elimination.

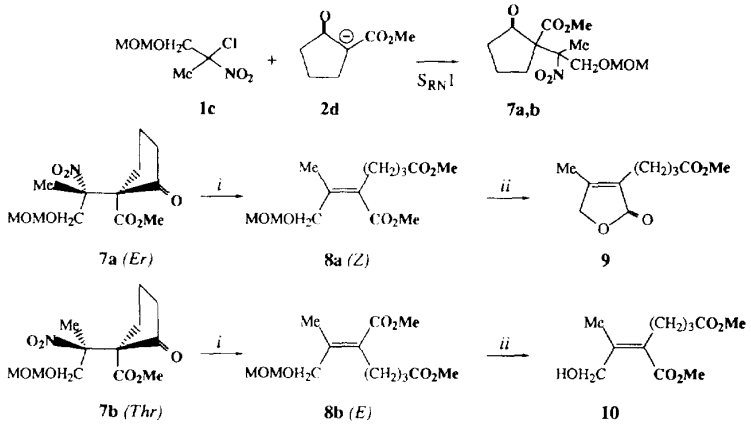
The stereoelectronic process governing the selective ionic NO_2 elimination/acyl fragmentation was also evidenced by a reaction carried out on the mixture of isomers **3g** and **3h** (*Er/Thr* = 1) yielding a mixture of olefins **4g** (entry 7) or **4h** (entry 8) in a *Z/E* ratio identical to the *Er/Thr* ratio of the precursors. This was established by reactions on pure *Er* and *Thr* $S_{RN}1$ products (scheme 4).

Pure **7a** (*Er*) and **7b** (*Thr*) were separated from the $S_{RN}1$ mixture of products **7a,b** (*Er/Thr* = 1). They were treated under identical base conditions to afford the olefin **8a** (*Z*) or **8b** (*E*) specifically. The formation



Reagents and conditions : *i)* Δ, DMSO, 4 h (reference 2). *ii)* KOH (1.2 equiv)/EtOH (10 mL), rt.

Scheme 3. Comparison of thermal with ionic elimination from aliphatic compounds.



Reagents : *i)* KOH (1.2 equiv), MeOH (10 mL), rt, 15 min; *ii)* TsOH (10% molar), MeOH (10 mL), reflux, 10 min (**8a**) and 30 min (**8b**).

Scheme 4. Stereoselective ionic elimination from pure $S_{RN}1$ products **7a** (*Er*) and **7b** (*Thr*).

of lactone **9** from **8a** and olefin alcohol **10** from **8b** under acidic conditions unambiguously establishes the (*Z*) and (*E*) geometry of their respective precursors. This result suggests that the stereospecific ionic NO_2 elimination/fragmentation occurring for products **3a-h** which have a cyclanone β-ester subunit is closely related to the Grob fragmentation [3].

Conclusion

The ionic NO_2 elimination/fragmentation reaction undergone by $S_{RN}1$ products resulting from reactions utilizing cyclanone β-esters as nucleophiles affords di- or trifunctionalized olefins bearing a $(CH_2)_nCO_2R$ chain whose length is determined by the nucleophile ring size. This novel synthesis is supplementary to syntheses involving $S_{RN}1$ products as starting materials [1, 2, 4a-c].

Experimental section

The melting points were measured on a Reichert apparatus. The IR spectra (cm^{-1}) were recorded on a Nicolet (205, FTIR) spectrometer in $CHCl_3$ or $CDCl_3$ (NMR sample) solution. The mass spectra were recorded on AEIMS-50 (MSEI) or EIMS-9 (MSCI) spectrometers (relative intensity). The proton spectra ($CDCl_3$) were recorded on a Bruker spectrometer 4.7 T (200 MHz). Chemical shifts are reported in δ units, parts per million (ppm) downfield from TMS.

$S_{RN}1$ products **3a-h, 4f** *and* **7a,b**

A 60% suspension of sodium hydride (3.1 mmol) in oil was placed in a 50 mL argon-filled flask and washed twice with 5-10 mL portions of *n*-pentane. After removing residual pentane under a stream of argon, Me_2SO (10 mL) was added. After 5 min, cyclanone β-ester **2a-c** (2.9 mmol) dissolved in Me_2SO (5 mL) was added quickly by cannula and the resulting solution was stirred for 30 min. A solution of the *gem*-chloronitro alkane **1a-d** (1.45 mmol) in Me_2SO (5 mL) was then added by cannula. Under illumination by a Hanau 100 W, the reaction system kept under argon atmosphere was stirred at room temperature. Reaction progress was followed by TLC silica gel and after consumption of the substrate (60-150 min), the reaction was quenched by pouring into iced water (50 mL). The solution was then neutralized with 5% HCl and extracted with methylene chloride (3 × 20 mL). The organic phase was washed with cold brine solution (2 × 20 mL), dried over Na_2SO_4, and then the volatiles were removed under reduced pressure. The residual oil was purified by chromatography on silica-gel column (eluent).

- *1-(1-Nitrocyclohexyl)-2-oxocyclopentane-1-carboxylic ethyl ester* **3b**

(Pentane/diethyl ether : 4:1).

87%; colorless oil.

IR ($CHCl_3$) 2 870-2 840, 1 750, 1 720, and 1 550.

^1H NMR δ 4.07 (q, 2H, *J* = 7.0 Hz), 2.80-2.04 (m, 6H), 2.00-1.05 (m, 10H), 1.10 (t, 3H, *J* = 7.0 Hz).

MS (EI) *m/e* 236 ($M^+ - HNO_2$), 208, 81, 68 (100), 66, 43.

Anal calc for $C_{14}H_{21}NO_5$: C, 59.35; H, 7.47; N, 4.94. Found : C, 59.36; H, 7.33; N, 5.08.

• *1-(1-Nitrocyclohexyl)-2-oxocyclohexane-1-carboxylic ethyl ester* **3c**

(Dichloromethane).

47%; mp 71-72°C (dichloromethane).

IR 2 900-2 800, 1 740, 1 720, 1 540.

^{1}H NMR δ 4.20 (q, 2H, J = 7.0 Hz), 2.78-2.20 (m, 6H), 1.35 (t, 3H, J = 7.0 Hz), 2.20-0.93 (m, 12H).

MS (CI) m/e 298 (MH^+), 280, 252, 251 (100), 58, 57.

Anal calc for $C_{15}H_{23}NO_5$: C, 60.59; H, 7.80; N, 4.71. Found : C, 60.30; H, 7.91; N, 4.57.

• *1-(1-Methyl-1-nitroethyl)-2-oxocyclopentane-1-carboxylic ethyl ester* **3d**

(Dichloromethane).

57%; colorless oil.

IR 2 998-2 820, 1 752, 1 717, 1 542.

^{1}H NMR δ 4.24 (q, 2H, J = 7.0 Hz), 2.67-2.28 (m, 4H), 1.73 and 1.86 (2s, 6H), 1.86-1.64 (m, 2H), 1.30 (t, 3H, J = 7.0 Hz).

MS (Ci) m/e 244 (MH^+), 215, 198, 197 (100), 157, 155.

Anal calc for $C_{11}H_{17}NO_5$: C, 54.31; H, 7.04; N, 5.76. Found : C, 54.34; H, 7.16; N, 5.92.

• *1-(1-Methyl-1-nitroethyl)-2-oxocyclohexane-1-carboxylic ethyl ester* **3e**

(Dichloromethane).

23%; colorless oil.

IR 2 990-2 840, 1 740, 1 718, 1 550.

^{1}H NMR δ 4.38 (q, 2H, J = 7.0 Hz), 2.73-2.43 (m, 4H), 1.74 and 1.69 (2s, 6H), 1.43-1.90 (m, 4H), 1.30 (t, 3H, J = 7.0 Hz).

MS (CI) m/e 258 (MH^+), 240, 212, 211 (100), 171.

Anal calc for $C_{12}H_{19}NO_5$: C, 56.02; H, 7.44; N, 5.44. Found : C, 56.10; H, 7.24; N, 5.20.

• Z *and* E *4-Methoxycarbonyl-6-(methoxymethoxy)-5-methylhex-4-enoic acid* **4f**

(Dichloromethane/methanol : 9:1).

30% yield; oil.

IR 3 630 and 3 575-3 150, 3 000, 2 930, 2 855, 1 745, 1 725, 1 620.

^{1}H NMR δ 4.70 (s, 2H), 4.11 (2q, 2H), 4.23-4.09 (2s, 2H), 3.35 (s, 3H), 2.73-2.23 (m, 4H), 1.95 and 1.87 (2s, 3H), 1.23 (2t, 3H).

MS (EI) m/e 201 ($M^+ - CH_2OCH_3$), 197, 185, 169, 152, 123, 45.

Anal calc for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found : C, 53.30; H, 7.54.

• *1-[2-(Methoxymethoxy)-1-methyl-1-nitroethyl]-2-oxocyclopentane-1-carboxylic methyl ester* **7a, 7b**

(Dichloromethane).

72%; colorless oil.

IR (mixture of **7a,b**) 3 000, 2 955, 2 895, 1 760, 1 730, 1 555.

Erythro isomer **7a**. ^{1}H NMR δ 4.62 (s, 2H), 4.25 and 4.13 (2d, 2H, J = 11 Hz), 3.78 (s, 3H), 3.66 (s, 3H), 2.82-2.31 (m, 4H), 1.85 (s, 3H), 2.23-1.53 (m, 2H).

Threo isomer **7b**. ^{1}H NMR δ 4.46 (s, 2H), 4.35 and 3.97 (2d, 2H, J = 11 Hz), 3.63 (s, 3H), 3.17 (s, 3H), 2.56-2.12 (m, 4H), 1.62 (s, 3H), 2.06-1.63 (m, 2H).

MS (CI) (mixture of **7a,b** m/e 290 (MH^+), 259 ($MH^+ - OCH_3$), 243 ($MH^+ - HNO_2$), 228, 197, 57.

Anal calc for $C_{12}H_{19}NO_7$ (mixture of *Er* and *Thr*) : C, 49.82; H, 6.62; N, 4.84. Found : C, 49.65; H, 6.70; N, 4.80.

General procedure for fragmentation reaction

The olefin precursors (1.1 mmol) were dissolved in methanol or ethanol (10 mL). Powdered potassium hydroxide (1.2 mmol) was added and the reaction was maintained at room temperature or heated if required. The progress of the reaction was monitored by TLC (15-60 min). After entire disappearance of the substrate, the reaction mixture was poured into water (15 mL) and the solution neutralized with 5% HCl was extracted with methylene chloride (2 × 10 mL). The organic phase was dried over Na_2SO_4, concentrated, and purified (eluent).

• *2-(Cyclohexylidene)hexanedioic diethyl ester* **4b**

(Dichloromethane).

86%; colorless oil.

IR 2 860-2 800, 1 730, 1 710.

^{1}H NMR δ 4.20 (q, 2H, J = 7.0 Hz), 4.13 (q, 2H, J = 7.0 Hz), 2.43-2.17 (m, 8H), 1.68 (m, 2H), 1.57 (m, 6H), 1.27 (t, 3H, J = 70 Hz), 1.20 (t, 3H, J = 7.0 Hz).

MS (EI) m/e 281 ($M^+ - H$), 236, 235 (100), 208, 207, 163, 152, 120, 81.

Anal calc for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found : C, 68.08; H, 9.22.

• *2-(Cyclohexylidene) heptanedioic diethyl ester* **4c**

(Dichloromethane).

100%; oil.

IR 2 930-2 860, 1 740, 1 720.

^{1}H NMR δ 4.20 (q, 2H, J = 7.0 Hz), 4.11 (q, 2H, J = 7.0 Hz), 2.50-2.03 (m, 8H), 1.74-1.36 (m, 10H), 1.29 (t, 3H, J = 7.0 Hz), 1.25 (t, 3H, J = 7.0 Hz).

MS (EI) m/e 296 (M^+), 251, 250 (100), 177, 149, 91, 81.

Anal calc for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found : C, 68.84; H, 9.46.

• *2-(Isopropylidene)hexanedioic diethyl ester* **4d**

(Pentane/diethyl ether : 4:1).

84%; colorless oil.

IR 2 985-2 830, 1 730, 1 705, 1 620.

^{1}H NMR δ 4.17 (q, 2H, J = 7.0 Hz), 4.12 (q, 2H, J = 7.0 Hz), 2.32 (m, 4H), 1.98 (s, 3H), 1.85 (s, 3H), 1.70 (qu, 2H, J = 8.0 Hz), 1.34 (t, 3H, J = 7.0 Hz), 1.30 (t, 3H, J = 7.0 Hz).

MS (EI) m/e 242 (M^+), 197, 196, 154, 95 (100).

Anal calc for $C_{13}H_{22}O_4$: C, 64.44; H, 9.13. Found : C, 64.51; H, 9.12.

• *2-(Isopropylidene)heptanedioic diethyl ester* **4e**

(Pentane/diethyl ether : 4:1).

84%; colorless oil.

IR 2 980-2 960, 1 735, 1 715, 1 620.

^{1}H NMR δ 4.24 (q, 2H, J = 7.0 Hz), 4.18 (q, 2H, J = 7 Hz), 2.37 (br t, 4H, J = 8 Hz), 2.03 (s, 3H), 1.89 (s, 3H), 1.71 (m, 2H), 1.47 (m, 2H), 1.35 (t, 3H, J = 7.0 Hz), 1.29 (t, 3H, J = 7.0 Hz).

MS (EI) m/e 256 (M^+), 211 (100), 210, 183, 182, 164, 137, 108, 95.

Anal calc for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found : C, 65.66; H, 9.41.

• Z *and* E-*2-{[2-(Tetrahydropyran-2-yl)oxy]-1-methylethylidene]}hexanedioic diethyl ester* **4g**

(Pentane/diethyl ether : 4:1).

75%; colorless oil.

IR 2 980-2 850, 1 730, 1 715.

^{1}H NMR δ 4.67-4.55 (m, 1H), 4.33-4.28 (2 br s, 2H), 4.20 (q, 2H, J = 7.5 Hz), 4.12 (q, 2H, J = 7.5 Hz), 3.87 and 3.53 (2m, 2H), 2.47-2.22 (m, 4H), 2.03 and 1.85 (2s, 1/1, 3H), 1.97-1.37 (m, 8H), 1.27 (t, 3H, J = 7.5 Hz), 1.20 (t, 3H, J = 7.5 Hz).

MS (CI) m/e 343 (MH^+), 260, 259 (100), 242, 241, 213.

Anal calc for $C_{18}H_{30}O_6$: C, 63.14; H, 8.83. Found : C, 62.80; H, 8.53.

• Z *and* E *2-{[2-(Tetrahydropyran-2-yl)oxy]-1-methylethylidene]}heptanedioic diethylester* **4h**

(Pentane/diethyl ether/methanol : 34:15:1).

74%; colorless oil.

IR 2 970-2 820, 1 730, 1 710.

^{1}H NMR δ 4.62 (m, 1H), 4.32 (m, 2H), 4.20 (q, 2H, J = 8.0 Hz), 4.10 (q, 2H, J = 8.0 Hz), 3.84-3.50 (m, 2H), 2.46-2.18 (m, 4H), 1.96-1.83 (2s, 2/1, 3H), 1.80-1.33 (m, 10H), 1.26 (t, 3H, J = 8.0 Hz), 1.16 (t, 3H, J = 8.0 Hz).

MS (CI) m/e 357 (MH^+), 273 (100), 255, 227, 209, 85.

Anal calc for $C_{19}H_{32}O_6$: C, 64.02; H, 9.05. Found : C, 63.97; H, 8.95.

• Z *and* E *4-[(Tetarhydropyran-2-yl)oxy]-2,3-dimethylbut-2-enoic methyl ester* **6**

(Pentane/diethyl ether : 1:1).

69%; colorless oil.

IR 2 940, 1 708, 1 630

^{1}H NMR δ 4.51 (m, 1H), 4.22 (br s, 1H), 4.10 (dd, 1H, J = 10 Hz), 3.65 (2s, 1/1, 3H), 3.82 and 3.51 (2m, 2H), 2.05-1.80 (4s, 6H), 2.08-1.20 (m, 6H).

MS (CI) m/e 229 (MH^+), 145 (100), 127, 113, 85.

Anal calc for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found : C, 63.17; H, 8.89.

• *(Z) 2-[2-(Methoxymethoxy)-1-methylethylidene] hexanedioic dimethyl ester* **8a**

(Hexane/diethyl ether/methanol : 34:15:1).

100%; colorless oil.

^{1}H NMR δ 4.62 (s, 2H), 4.26 (s, 2H), 3.75 (s, 3H), 3.68 (s, 3H), 3.38 (s, 3H), 2.47-2.28 (m, 4H), 1.88 (s, 3H), 2.00-1.56 (m, 2H).

MS (EI) m/e 242 (M^+ - MeOH), 213, 212, 197, 181, 165, 153, 137, 123, 109, 93, 81, 45 (100%).

• *(E) 2-[2-(Methoxymethoxy)-1-methylethylidene] hexanedioic dimethyl ester* **8b**

(Hexane/diethyl ether/methanol : 34:15:1).

100%; colorless oil.

IR 2 950, 2 895, 1 725, 1 625, 1 440.

^{1}H NMR δ 4.64 (s, 2H), 4.13 (s, 2H), 3.77 (s, 3H), 3.68 (s, 3H), 3.40 (s, 3H), 2.59-2.27 (m, 4H), 1.99 (s, 3H), 1.83-1.65 (m, 2H).

MS (EI-GC/MS) m/e 243 (M^+ - OCH_3), 242, 229, 212, 197, 181, 166, 152, 148, 139, 120°, 109, 93, 84, 45 (100%).

• *4-(4-Methyl-2-oxo-2,5-dihydrofuran-3-yl)butanoic methyl ester* **9**

Acidic treatment of **8a** in boiling methanol (15 min) and purification (hexane/diethyl ether/methanol : 34:15:1) gave **9**.

100%; colorless oil.

IR 2 950-2 855, 1 760, 1 740.

^{1}H NMR δ 4.62 (s, 2H), 3.66 (s, 3H), 2.44-2.24 (m, 4H), 2.03 (s, 3H), 1.97-1.70 (m, 2H).

MS (CI) m/e 199 (MH^+), 168, 167, 139, 138, 125.

Anal calc for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found : C, 60.39; H, 7.41.

• *2-(2-Hydroxy-1-methylethylidene)hexanedioic dimethyl ester* **10**

Acidic treatment of **8b** similar to the above (30 min) gave **10**.

100%; colorless oil.

IR 3 700 and 3 600, 2 955, 1 730 and 1 720, 1 660.

^{1}H NMR (200 MHz, $CDCl_3$) δ 4.41 (broad s, 1H), 4.25 and 4.13 (2d, 2H, J = 13 Hz), 3.75 (s, 3H), 3.65 (s, 3H), 2.03 (s, 3H), 2.50-1.80 (m, 4H), 1.83-1.60 (m, 2H).

MS (EI) m/e 212 (M^+ - H_2O), 198, 180, 166, 148, 139, 120, 109, 93, 81, 67, 59.

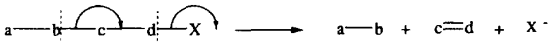
Anal calc for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found : C, 57.17; H, 7.65.

References

1 Lechevallier A, Madjadabadi Amrollah A, Benhida R, Beugelmans R, Frinault T, Gharbaoui T, Morris AD, *Bull Soc Chim Fr* (1994), 131, 1019

2 Ono N, Tamura R, Eto H, Hamamoto I, Nakatsuka T, Hayami JI, Kaji A, *J Org Chem* (1983) 48, 3678 and references therein

3 In the general formulation for fragmentation proposed by CA Grob (*Angew Chem Int Ed Engl* (1969) 8, 535; scheme 5)



Scheme 5

a-b denotes the electrofugal group (here RCO^+) and X^- a nucleofugal group which leaves with the bonding electron pair (here NO_2^-). It is known that NO_2^- is not a good nucleofugal group, but the *anti*-departure of the electrofugal group $(CH_2)_nCO^+$ is probably assisted by strain relief provided by fragmentation of the cyclic ketone as revealed by the conditions required for conversion of $S_{RN}1$ products **P3** to olefins. The cyclobutanone **3a** or **3f** reacted spontaneously in the $S_{RN}1$ medium, and conversion of the cyclopentanones **3b, 3d**, and **3g** occurred smoothly (rt, 15 min). A longer reaction time was required for the aliphatic compound **5** (rt, 60 min) and reflux temperature was necessary for efficient conversion of the cyclohexanones **3c, 3e and 3h.**

4 a) Vanelle P, Donini S, Maldonado J, Sabuco JF, Crozet M, *Tetrahedron Lett* (1994) 35, 3305
b) Crozet M, Vanelle P, Jentzer O, Donini S, Maldonado J, *Tetrahedron* (1993) 49, 11253
c) Vanelle P, Madadi N, Roubaud C, Maldonado J, Crozet M, *Tetrahedron* (1991) 47, 5173

5 Amice P, Conia JM, *Bull Soc Chim Fr* (1974) 1015