A New Synthesis of *exo*-Methylene Butyrolactones from Nitroalkanes

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Abstract: A versatile route to *exo*-methylene butyrolactones was developed by employing a three step reaction sequence consisting of Michael addition of primary nitroalkanes **1** to ethyl (2-bromomethyl)acrylate (**2**), then Nef conversion of the nitro derivatives **3**, and subsequent lactonization of the obtained keto esters **4**. The method is chemoselective for important functionalities such as ester, C=C double bond and hydroxyl.

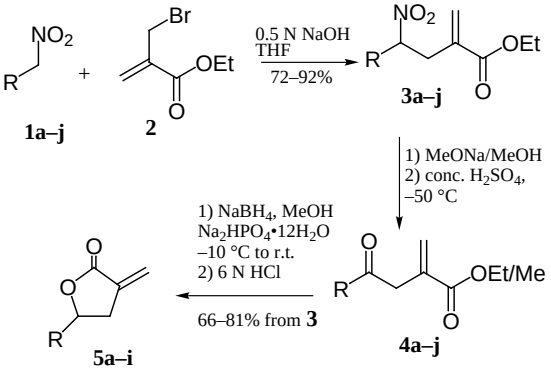
Key words: nitro compounds, Michael addition, lactones, Nef reaction, elimination

The lactone functionality is present in a large variety of natural products and biologically active compounds.[1] They are also largely used as starting material for the preparation of butenolides, furans, cyclopentenones, alkaloids, macrocyclic antibiotics, pheromones, antileukemics, flavor compounds, etc.[2]

exo-Methylene butyrolactones constitute a very important part of this class of compounds,[3] mainly due to their presence as the major structural feature in many biologically active natural products.[4] Their occurrence coupled with their pharmacophoric activity have spurred the development of numerous procedures for their preparation,[5] but these methods suffer from certain drawbacks such as restricted generality, the need for tedious procedures, and expensive chemicals. Much attention has been focused on the synthesis of α-methylene unit from α-phosphono-γ-butyrolactones,[6] but their synthesis required a multi-step sequence, high temperature, and α-halo-γ-lactones as starting material, some of which are not easily available.[7]

Recently, we reported the synthesis of α-(alkylmethylene)butyrolactone derivatives[8] by conjugate addition of nitroalkanes to methyl *trans*-4-oxo-2-pentenoate, followed by in situ elimination of nitrous acid from the Michael adduct, then lactonization by sodium borohydride reduction or by Grignard reagents in the presence of dry cerium(III) chloride.

As part of our study on the synthetic potential of aliphatic nitrocompounds,[9] we wish to report here an efficient method for the preparation of functionalised *exo*-methylene butyrolactones **5** starting from primary nitroalkanes **1** and, commercially available, ethyl (2-bromomethyl)acrylate (**2**) (Scheme 1).



Scheme 1

Thus, conjugate addition of the nitro compounds **1** to **2**, performed using 0.5 N sodium hydroxide in THF, afforded nitro adducts **3** (72–92%) through tandem nucleophilic addition-elimination reaction. Successive conversion of the nitro group to carbonyl (Nef reaction, **3** to **5**) by formation of the nitronate anion (MeONa, 1.2 equivalents), followed by its addition, at –50 °C, to concentrated sulphuric acid[10] allowed the formation of the keto derivatives **4** as a mixture of ethyl and methyl esters, due to the partial transesterification. Thus, both the unsaturated keto esters are prone to lactonization by reduction of the

Table 1 Synthesis of Adduct **3a–j** and Lactones **5a–j**

Entry	R	Yield (%)[a] of **3**	Yield (%)[a] of **5** from **3**
a	$CH_3(CH_2)_3$	76	66
b	$CH_3(CH_2)_4$	75	77
c	$CH_3(CH_2)_2$	77	70
d	$CH_3OCO(CH_2)_4$	72	71
e	$HO(CH_2)_5$	78	80
f	$CH_3(CH_2)_8$	88	75
g	$CH_3OCO(CH_2)_{10}$	86	81
h	$CH_2=CH(CH_2)_8$	88	80
i	$PhCH_2$	92	78
j	$CH_3CO(CH_2)_2$	75	75[b,c]

[a] Yield of isolated, purified product.
[b] The alkyl group (R) for **5j** is $CH_3CH(OH)(CH_2)_2$.
[c] As diastereomeric mixture (0.55:0.45).

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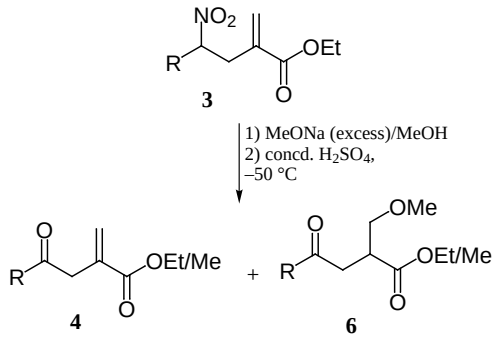
crude compounds **4** at –10 °C to room temperature with sodium borohydride in the presence of a catalytic amount of sodium hydrogenophosphate dodecahydrate (Na_2HPO_4•$12H_2O$), so that, the title compounds **5** are obtained in good yields (66–81%, Table 1), directly from **3**. The spectroscopic data for compounds **3** and **5** are given in Tables 2 and 3, respectively.

The amount of MeONa (1.2 equivalents) employed in the formation of the nitronate form is very important, since, increasing the base equivalents favours the formation of compound **6** as a by-product (Scheme 2).

It should be emphasized that other important functionalities such as ester, C=C double bond and hydroxyl are preserved, however, when a third carbonyl moiety is enclosed in the alkyl structure **4j**, its conversion to a hydroxy group (**4j** to **5j**, Scheme 3) is observed.

In conclusion, this method demonstrates that the title compounds **5** can be conveniently prepared in two steps starting from easily available nitroalkanes **1** and ethyl (2-bromomethyl)acrylate (**2**) through a simple chemical procedure, and is further evidence of the great versatility of the aliphatic nitro compounds in organic synthesis.



Scheme 2

All reactions were monitored by TLC and gas chromatographic analyses, performed on a Carlo Erba Fractovap 4160 using a capil-

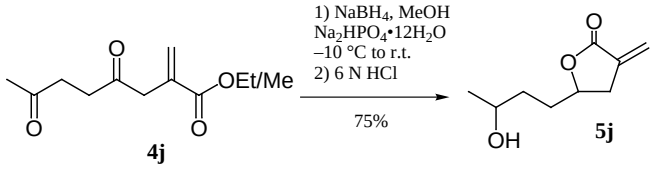
Table 2 Spectroscopic Data for Adducts **3a–j**

Product	IR (film) ν (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm), *J* (Hz)	MS: *m/z*
3a	1713, 1630, 1557	0.90 (t, 3 H, *J* = 6.7), 1.32 (t, 3 H, *J* = 7.1), 1.30–1.50 (m, 4 H), 1.70–2.10 (m, 2 H), 2.82 (d, 2 H, *J* = 9.0), 4.23 (q, 2 H, *J* = 7.1), 4.70–4.80 (m, 1 H), 5.65 (s, 1 H), 6.25 (s, 1 H)	184, 153, 137, 109 (100), 95, 81, 67, 55, 41, 29
3b	1710, 1631, 1551	0.90 (t, 3 H, *J* = 6.4), 1.32 (t, 3 H, *J* = 7.1), 1.20–1.40 (m, 6 H), 1.60–2.00 (m, 2 H), 2.82 (t, 2 H, *J* = 7.6), 4.23 (q, 2 H, *J* = 7.1), 4.70–4.80 (m, 1 H), 5.64 (s, 1 H), 6.25 (s, 1 H)	198, 197, 123 (100), 95, 81, 67, 55, 41, 29
3c	1714, 1632, 1551	0.94 (t, 3 H, *J* = 7.3), 1.30 (t, 3 H, *J* = 7.1), 1.20–1.40 (m, 2 H), 1.60–2.00 (m, 2 H), 2.81 (d, 2 H, *J* = 7.5), 4.22 (q, 2 H, *J* = 7.1), 4.70–4.90 (m, 1 H), 5.63 (s, 1 H), 6.23 (s, 1 H)	170, 169, 139, 123, 95 (100), 67, 55, 41, 29
3d	1737, 1713, 1631, 1551	1.30 (t, 3 H, *J* = 7.1), 1.20–1.40 (m, 2 H), 1.60–1.70 (m, 2 H), 1.90–2.10 (m, 2 H), 2.32 (t, 2 H, *J* = 7.3), 2.80 (d, 2 H, *J* = 7.5), 3.67 (s, 3 H), 4.22 (q, 2 H, *J* = 7.1), 4.70–4.80 (m, 1 H), 5.64 (s, 1 H), 6.24 (s, 1 H)	256, 241, 209, 179, 163 (100), 153, 107, 93, 79, 55
3e	3403, 1708, 1631, 1549	1.31 (t, 3 H, *J* = 7.1), 1.30–1.50 (m, 2 H), 1.50–1.70 (m, 2 H), 1.70–1.90 (m, 2 H), 1.90–2.10 (m, 2 H), 2.80 (d, 2 H, *J* = 7.6), 3.64 (t, 2 H, *J* = 6.3), 4.23 (q, 2 H, *J* = 7.1), 4.70–4.80 (m, 1 H), 5.64 (s, 1 H), 6.24 (s, 1 H)	213, 167, 149, 121, 107, 93, 79 (100), 67, 55
3f	1719, 1630, 1551	0.98 (t, 3 H, *J* = 6.4), 1.30 (t, 3 H, *J* = 7.1), 1.30–2.10 (m, 16 H), 2.80 (d, 2 H, *J* = 7.0), 4.23 (q, 2 H, *J* = 7.1), 4.70–4.80 (m, 1 H), 5.64 (s, 1 H), 6.24 (s, 1 H)	253, 179, 135, 123, 109, 95 (100), 81, 67, 55
3g	1736, 1716, 1631, 1551	1.20–1.70 (m, 18 H), 1.30 (t, 3 H, *J* = 7.1), 2.30 (t, 2 H, *J* = 7.5), 2.80 (d, 2 H, *J* = 7.6), 3.65 (s, 3 H), 4.22 (q, 2 H, *J* = 7.1), 4.70–4.80 (m, 1 H), 5.64 (s, 1 H), 6.26 (s, 1 H)	280, 123, 109, 95, 81, 67, 55 (100)
3h	1714, 1638, 1552	1.30–1.40 (m, 11 H), 1.50–2.10 (m, 8 H), 2.81 (d, 2 H, *J* = 8.8), 4.22 (q, 2 H, *J* = 7.1), 4.70–4.80 (m, 1 H), 4.90–5.10 (m, 2 H), 5.64 (s, 1 H), 5.70–5.90 (m, 1 H), 6.24 (s, 1 H)	265, 189, 109, 95, 81, 67, 55 (100)
3i	1718, 1629, 1550	1.29 (t, 3 H, *J* = 7.1), 2.10–2.20 (m, 1 H), 2.80–2.90 (m, 1 H), 3.10 (dd, 1 H, *J* = 5.8, 14.2), 3.29 (dd, 1 H, *J* = 8.7, 14.2), 4.21 (q, 2 H, *J* = 7.1), 5.00–5.10 (m, 1 H), 5.64 (s, 1 H), 6.27 (m, 1 H), 7.20–7.40 (m, 5 H)	216, 171, 143, 128, 115, 91 (100), 65
3j	1715, 1709, 1630, 1546	1.30 (t, 3 H, *J* = 7.1), 2.10–2.20 (m, 2 H), 2.16 (s, 3 H), 2.52 (t, 2 H, *J* = 7.1), 2.82 (d, 2 H, *J* = 6.3), 4.25 (q, 2 H, *J* = 7.1), 4.70–4.90 (m, 1 H), 5.64 (s, 1 H), 6.27 (s, 1 H)	197, 167, 151 (100), 123, 109, 97, 91, 79, 67

Table 3 Spectroscopic Data for Methylene Lactones **5a–j**

Product	IR (film) ν (cm^{-1})	^1H NMR (200 MHz, $CDCl_3$) δ ppm, *J* (Hz)	^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm)	MS: *m/z*
5a	1763, 1685	0.90 (t, 3 H, *J* = 7.0), 1.20–1.40 (m, 4 H), 1.50–1.70 (m, 2 H), 2.57 (ddt, 1 H, *J* = 3.0, 6.1, 17.1), 3.06 (ddt, 1 H, *J* = 2.5, 7.6, 17.0), 4.40–4.60 (m, 1 H), 5.62 (t, 1 H, *J* = 2.5), 6.22 (t, 1 H, *J* = 2.9)	170.80, 135.26, 122.38, 77.50, 36.46, 34.05, 27.45, 22.89, 14.40	154 (M^+), 125, 108, 97 (100), 69, 55, 41
5b	1765, 1666	0.90 (t, 3 H, *J* = 6.5), 1.30–1.80 (m, 8 H), 2.57 (ddt, 1 H, *J* = 3.0, 6.1, 17.1), 3.05 (ddt, 1 H, *J* = 2.5, 7.6, 17.1), 4.50–4.60 (m, 1 H), 5.62 (t, 1 H, *J* = 2.5), 6.22 (t, 1 H, *J* = 2.9)	170.89, 135.26, 122.38, 78.09, 36.73, 34.04, 31.94, 25.02, 22.97, 14.44	168 (M^+), 139, 122, 97 (100), 69, 41
5c	1762, 1667	0.95 (t, 3 H, *J* = 7.3), 1.20–1.70 (m, 4 H), 2.56 (ddt, 1 H, *J* = 3.0, 6.1, 17.0), 3.10 (ddt, 1 H, *J* = 2.5, 7.6, 17.0), 4.50–4.60 (m, 1 H), 5.62 (t, 1 H, *J* = 2.5), 6.22 (t, 1 H, *J* = 3.0)	170.34, 134.77, 121.83, 77.32, 38.35, 33.57, 18.20, 13.83	140 (M^+), 111, 97 (100), 69, 55, 41, 27
5d	1760, 1735, 1667	1.50–1.70 (m, 6 H), 2.33 (t, 2 H, *J* = 7.2), 2.56 (ddt, 1 H, *J* = 3.0, 6.1, 17.0), 3.06 (ddt, 1 H, *J* = 2.5, 7.6, 17.0), 3.67 (s, 3H), 4.40–4.60 (m, 1 H), 5.62 (t, 1 H, *J* = 2.5), 6.22 (t, 1 H, *J* = 3.0)	173.79, 170.21, 134.55, 122.07, 77.19, 51.54, 35.95, 33.77, 33.52, 24.53, 24.50	194, 162, 135, 97 (100), 69, 55, 41
5e	3401, 1759, 1667	1.40–1.80 (m, 8 H), 2.57 (ddt, 1 H, *J* = 3.0, 6.1, 17.0), 3.06 (ddt, 1 H, *J* = 2.5, 7.6, 17.0), 3.65 (t, 2 H, *J* = 6.3), 4.40–4.60 (m, 1 H), 5.62 (t, 1 H, *J* = 2.5), 6.22 (t, 1 H, *J* = 2.8)	170.39, 134.63, 122.08, 77.04, 62.69, 36.27, 33.56, 32.49, 25.48, 24.75	166, 148, 111, 97 (100), 81, 69, 41
5f	1763, 1664	0.87 (t, 3 H, *J* = 6.9), 1.20–1.80 (m, 14 H), 1.50–1.60 (m, 1 H), 1.70–1.80 (m, 1 H), 2.55 (ddt, 1 H, *J* = 3.0, 6.1, 16.9), 3.03 (ddt, 1 H, *J* = 2.5, 7.6, 16.9), 4.40–4.50 (m, 1 H), 5.60 (t, 1 H, *J* = 2.5), 6.20 (t, 1 H, *J* = 2.9)	170.87, 135.28, 122.37, 77.50, 36.78, 34.06, 32.34, 29.95, 29.76, 25.35, 23.15, 14.59	224 (M^+), 140, 97 (100), 83, 69, 55, 41
5g	1764, 1736, 1667	1.20–1.70 (m, 18 H), 2.30 (t, 2 H, *J* = 7.4), 2.57 (ddt, 1 H, *J* = 2.9, 6.1, 17.0), 3.06 (ddt, 1 H, *J* = 2.5, 7.6, 17.0), 3.37 (s, 3 H), 4.40–4.60 (m, 1 H), 5.62 (t, 1 H, *J* = 2.5), 6.22 (t, 1 H, *J* = 2.9)	174.34, 170.39, 134.77, 121.90, 77.03, 51.46, 36.29, 34.11, 33.57, 29.41, 29.36, 29.27, 29.22, 29.12, 24.94, 24.86	278, 264, 112, 97 (100), 81, 69, 55, 41
5h	1765, 1664, 1639	1.20–1.70 (m, 14 H), 2.04 (q, 2 H, *J* = 6.9), 2.57 (ddt, 1 H, *J* = 3.0, 6.1, 17.0), 3.06 (ddt, 1 H, *J* = 2.5, 7.6, 17.0), 4.40–4.60 (m, 1 H), 4.90–5.10 (m, 2 H), 5.62 (t, 1 H, *J* = 2.5), 5.70–5.90 (m, 1 H), 6.22 (t, 1 H, *J* = 2.8)	170.30, 139.16, 134.76, 121.91, 114.15, 77.02, 36.29, 33.78, 33.57, 29.39, 29.34, 29.28, 29.06, 28.89, 24.86	236 (M^+), 151, 109, 97 (100), 81, 68, 55, 41
5i	1759, 1666	2.68 (ddt, 1 H, *J* = 3.0, 6.0, 17.1), 2.92 (dd, 1 H, *J* = 3.4, 14.0), 2.98 (ddt, 1 H, *J* = 2.5, 7.6, 17.1), 3.13 (dd, 1 H, *J* = 3.0, 14.0), 4.70–4.80 (m, 1 H), 5.58 (t, 1 H, *J* = 2.5), 6.20 (t, 1 H, *J* = 2.9), 7.20–7.40 (m, 5 H)	170.12, 135.5, 134.34, 129.52, 128.67, 127.04, 122.12, 77.45, 41.86, 32.72	188 (M^+), 143, 97 (100), 91, 69, 41
5j	3435, 1759	1.09 (d, 3 H, *J* = 6.0), 1.50–1.80 (m, 4 H), 2.56 (ddt, 1 H, *J* = 2.9, 9.1, 17.0), 3.05 (ddt, 1 H, *J* = 2.4, 7.6, 17.0), 3.80–3.90 (m, 1 H), 4.50–4.60 (m, 1 H), 5.61 (t, 1 H, *J* = 2.6), 6.21 (t, 1 H, *J* = 2.9)	(diastereomeric mixture, 0.55:0.45): 170.31 (2C), 134.58, 134.54, 122.16 (2C), 77.03 (2C), 67.68, 67.32, 34.57, 34.05, 33.64, 33.50, 32.83, 32.32, 23.81, 23.74	155, 126, 111, 97 (100), 81, 69, 45, 39

lary column of duran glass (0.32 mm × 25 m), stationary phase OV1 (film thickness 0.4–0.45 nm). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 200 and 75 MHz, respectively, on a Varian Gemini 200. Chemical shifts are expressed in ppm downfield from TMS. Mass spectra were determined on a capillary GC/MS operating in the split mode with He carrier gas and fitted with a mass-selective detector (MDS). IR spectra were recorded with a Perkin–Elmer 257 spectrophotometer. All products were purified by flash chromatography on Merck silica gel using EtOAc–petroleum ether as eluent. Elemental analyses were performed using a C, H, N Analyzer Model 185 from Hewlett–Packard. Satisfactory microanalyses were obtained for each compound; the data are available as supporting information from the publisher.



Scheme 3

2-Methylene-4-Nitro Esters (3); General Procedure

To a solution of nitroalkane **1** (5 mmol) and ethyl (2-bromomethyl)acrylate (**2**, 0.97 g, 5 mmol) in THF (25 mL), NaOH (0.5 N, 16 mL, 8 mmol) was added dropwise at r.t. The resulting solution was stirred for 12 h, then extracted with Et_2O (3 × 25 mL), and the organic layer was dried ($MgSO_4$) and evaporated. The crude product was pure enough (>93% by GC), however, purification by flash chromatography (EtOAc–petroleum ether) afforded the pure compounds **3**.

exo-Methylene Butyrolactones (5); General Procedure

The nitro ester **3** (2 mmol) was added at r.t. and under a N_2 atm, to a solution of MeONa/MeOH obtained by mixing Na (552 mg, 2.4 mmol) and anhyd MeOH (6 mL). After 30 min, the formed nitronate was added dropwise to a cooled (–50 °C) solution of concd H_2SO_4 (1.2 mL) and MeOH (6 mL). After 1–6 h (see GC), H_2O (15 mL) was added and the mixture was concentrated in order to reduce the amount of MeOH. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the organic layer was dried ($MgSO_4$) and evaporated. The crude product **4** was dissolved in MeOH (15 mL) and the solution was cooled to –10 °C. Na_2HPO_4•$12H_2O$ (83 mg, 0.23 mmol) and $NaBH_4$ (83 mg, 2.2 mmol) were added and the mixture was stirred at the same temperature for 2 h, and then at r.t. for 13 h. The mixture was acidified to pH 2 with 6 N HCl, stirred for a further 1 h, extracted with CH_2Cl_2 (3 × 15 mL), dried ($MgSO_4$), and evaporated to give the lactone **5**, which was then purified by flash chromatography (EtOAc–petroleum ether).

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