Molecules **1996**, *1*, 175 – 180

Regioselectivity of the Michael Addition of Nitromethane on α,β-Unsaturated Acid Esters

Lubomír Floch[1,*], Juraj Kubán[1], Andrea Gogová[1], Peter Zálupsky[1], Tibor Jakubík[2], Nada Prónayová[2]

[1]Department of Organic Chemistry

[2]Central Research Laboratories, Faculty of Chemical Technology, Slovak Technical University, Radlinskeho 9, SK-812 37 Bratislava, Slovakia, Fax: +42–7368560 (floch@chelin.chtf.stuba.sk)

Received: 24 October 1996 / Accepted: 17 January 1997 / Published: 7 February 1997

Abstract

Triton B catalyzed Michael addition of nitromethane on esters of α,β-unsaturated acids **1** has been studied. The course and regioselectivity of the reaction is discussed in the view of structure of products **2a-g, 3a-g, 4g, f, 5g, f,** assessed by GC/MS, NMR and IR spectroscopy and by MOPAC 6 (AM1) calculations, respectively.

Keywords: Michael Addition, α,β-unsaturated acid esters, reactivity modelling

Introduction

Ethyl 4-isothiocyanatobutanoate is the most potent isothiocyanate tested so far on the antiproliferative activity of HeLa cells and produces a significant inhibition of the growth of transplanted sarcoma cells B77-RF in rats [1]. With the aim of obtaining a set of 3-substituted 4-isothiocyanatobutanoic acid esters for biological tests and QSAR study, we have synthesised 3-substituted 4-nitrobutanoic acid esters **2** as necessary intermediates [2]. The key step for their synthesis was Michael addition, catalyzed by Triton B [3] of nitromethane on esters of α,β-unsaturated acids **1**.

* *To whom correspondence should be addressed*

† *Presented at the Joint 12th Symposium on the Chemistry of Heterocyclic Compounds (SCHHC) and the 6th Blue Danube Symposium on Heterocyclic Chemistry (BDSHC), Brno, Czech Republic, September 1–4, 1996.*

Results and discussion

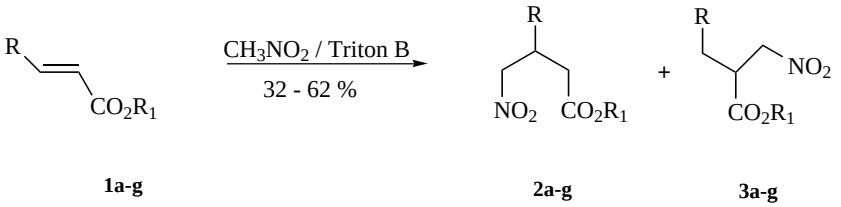
The Michael addition of nitromethane onto the unsaturated acid esters under alkaline condition was expected to produce solely adducts **2** as a result of a regioselective attack at the β-position of the α,β-unsaturated ester moiety. Contrary to this simple scenario, the reaction mixture contained, in addition to the expected products **2,** also the isomeric compounds **3,** in addition to other unexpected products. Although the reaction failed as an easy regioselective approach to the desired compounds, the lack of literature data [2–5] on regioselectivity of Michael addition prompted us to examine the reaction in more detail.

The experimental data of Triton B catalyzed Michael addition of nitromethane to α,β-unsaturated esters are summarized in Table 1. All the described compounds **2** have already been described in the literature, compounds **2f,g** being the only exception. Compounds **3** are up to now unknown. The comparison of known data with our spectra of

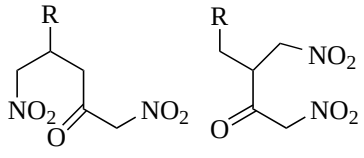
Table 1. *Regioselectivity of the Michael addition of nitromethane on α,β -unsaturated acid esters.*

No	R	R_1	Formula M.w.	Reaction time [h]	B.p. [torr]/°C] Yield [%]	R.t. **2** [min]	%**2**	R.t. **3** [min]	%**3**	%**3**/%**2**
2a	Me	Et	$C_7H_{13}NO_4$	18	114/10	10.34	96	9.11	4	1/24
3a			175.2		62[a,b]					
2b	2-Furyl	Et	$C_{10}H_{13}NO_5$	18	122–123/0.5	15.12	66.5	14.13	33.5	1/2
3b			227.2		62[a,c]					
2c	3-Thienyl	Et	$C_{10}H_{13}NO_4S$	18	130–131/0.15	17.53	88.6	16.59	13.4	1/6.5
3c			243.3		60[a,d]					
2d	2-Pyridyl	Et	$C_{11}H_{14}NO_4$	18	76–80/0.03		82.6		17.3	
3d			238.2		61[a,e]	17.48		16.52		1/4.8
				36[f]	117–118/0.02		20.0		33.1	
					66[i,g]					1.6/1
2e	3-Pyridyl	Et	$C_{11}H_{14}NO_4$	2[h,i]	—	18.50	89	—	—	—
3e			238.2	16[h,j]	—	18.50	99	—	—	—
				18	136/0.05	18.50	87.2	17.55	10.4	1/8.4
					60[a,e]					
2f	4-Pyridyl	Et	$C_{11}H_{14}NO_4$	18[h,k]	—	18.46	89	—	—	—
3f			238.2	36 [f]	80/0.05	18.46	25	17.57	1	1/25
					32[l]					
2g	4-Pyridyl	Me	$C_{10}H_{12}NO_4$	18	48–50/0.04	14.09	73.9	13.23	14.9	1/4.9
3g			224.2		50					

R.t.[min.$^{-1}$] - retention time
[a] satisfactory elemental analysis %C 0.25, H% 0.11, %N 0.15 obtained
[b] lit. 2: 113 °C/9 torr
[c] lit. 3: 172–175 °C/11 torr
[d] lit. 3 150–152 °C/0,2 torr
[e] lit. 4: bp are omitted
[f] after 18 hours 100% excess of Triton B was added
*[g] further compounds detected: R.t. (%) 14.27 (2.7), **4d**, 13.24 (17.3), **5d**, 18.10 (20), **6** unknown comp.*
[h] crude reaction mixtures were analysed
*[i] starting **1e** detected, R.t. 14.33 (10%)*
*[j] no **1e,** detected*
*[k] R.t. (%): 13.12 (14.6), **1f***
*[l] further two compounds were identified, R.t. (%): 15.12 (52.7), **4f**, 14.19 (21.3), **5f**.*



1a-g **2a-g** **3a-g**



4d,f **5d,f**

R: a) Me, b) 2-Furyl-, c) 3-Thienyl-, d-f) 2-, 3-, 4-Pyridyl-, R_1 = Et

g) R_1 = Me, R = 4-Pyridyl

Scheme 1. *Preparation of Alkyl 3R-substituted 4-nitro butanoates **2** and Alkyl 2R-substituted 3-nitro propanoates **3**.*

Table 2. *Mass spectral data of ethyl 4-nitro-3R-subst. butanoates* ***2a–g****.and ethyl 3-nitro-2R-methylene subst. propanoates* ***3a–g****.*

No	M	M-61 *m/z* (%)	M-60 *m/z* (%)	M-47 *m/z* (%)	M-46 *m/z* (%)	M-45 *m/z* (%)	*m/z*100% %
2a		(2)	(2)	(11)	(4)	(100)	130
	175	114	115	128	129	130	
3a		(19)	(9)	(-)	(-)	(85)	59
2b		(2)	(1)	(62)	(12)	(8)	108
	227	166	167	180	181	182	
3b		(89)	(13)	(-)	(-)	(7)	108
2c		(2)	(-)	(75)	(21)	(28)	123
	243	187	183	196	197	198	
3c		(93)	(20)	(-)	(-)	(18)	123
2d		(-)	(12)	(8)	(70)	(44)	118
	238	177	178	191	192	193	
3d		(9)	(75)	(-)	(-)	(15)	118
2e		(1)	(1)	(44)	(59)	(41)	118
	238	177	178	191	192	193	
3e		(87)	(55)	(-)	(-)	(21)	118
2f		(1)	(1)	(28)	(44)	(32)	118
	238	177	178	191	192	193	
3f		(78)	(61)	(-)	(-)	(26)	118

CH_3NO_2 *m/z* 61, CH_2NO_2, *m/z* 60, HNO_2, *m/z* 47, NO_2 or C_2H_5OH, *m/z* 46, C_2H_5O, *m/z* 45

reaction mixtures allowed us to identify 3R-substituted 4-nitropropanoates **3** as well as 1,5-dinitro-4R-2-pentanones **4d,f** and 1,4-dinitro-3R-methylene-2-butanones **5d,f.** As can be seen from the Table 1, the primary products are the expected Michael adducts **2**. Only when reaction time is prolonged and temperature raised do compounds **3** arise, as is also the case when **2** are exposed to prolonged heat during vacuum distillation. Finally, only protracted treatment with excess catalyst led to the formation of compounds **4** and **5**.

Similar experiments under almost identical conditions [3] failed to detect α-addition products **3**. Since such α-products are very similar to isomeric compounds **2**, they can very well have escaped detection. Indeed, we only realised their presence after a subsequent reaction, supposed to take place on the β-addition product, gave a poor yield. Reexamination of the starting material revealed, that as much as 33% (**3b,d**) of isomeric **3** was present.

Complex reaction mixtures were assessed by the GC-MS method. None of the separated components of the mixture displayed molecular ions. Rather, principal peaks resulted from the loss of ethoxy (or ethanol) and nitroxy radicals from molecular ions, whereas compounds assigned structure **3** split off nitromethane or nitrous acid (Table 2).

In our attempt to assess the reactivity of compounds **1** towards nucleophiles by semiempirical methods [6], we envisaged only attacks to position α,β and at the ester carbonyl group. Modelling of the reactivity of compounds **1** towards nucleophilic attack revealed that reactivity decreased in going from β to α to ester carbonyl, just as one would predict. Only the primary steps of a nucleophilic addition were modelled, in which either a carbanion or an O-anion were formed. Since all these reactions had early transition states of similar polarity, even "vacuum" calculations should return correct regioselectivity.

Experimental part

All aldehydes, nitromethane, Triton B were purchased from Fluka, solvents were purified, dried and distillated prior to use.

Flash chromatography was carried out on 63–200 mm (Merck) silica gel, thin layer chromatography was carried out on aluminium backed silica plates by Merck and plates were viewed in UV254. light. IR spectra were recorded on a Philips Analytical PU spectrometer on film.

^{1}H-NMR (300 MHz) and ^{13}C-NMR (75.0 MHz) spectra were recorded on a Varian VXR 300 instrument at 293 K in $CDCl_3$. Spectra were internally referenced to TMS. Peaks are reported in ppm downfield of TMS. Multiplicities are reported as singlet (*s*), doublet (*d*), triplet (*t*), quartet (*q*), some combinations of these, broad (*br*), or multiplet (*m*).^{13}C-NMR peak assignments were made by DEPT editing of the spectra.

GC-MS measurements (scan range 30–350 Daltons) were made with a Kratos Analytical Manchester, UK, MS 25 RFA mass spectrometer equipped with a Carlo Erba (Milan, Italy) Model 5160 gas chromatograph. A Chrompack (Middelburg, Netherland) fused-silica capillary GC column (25 m × 0.32 mm I.D.) with a CP-Sil 8 CB coating (0.12 mm) was used. Helium was used as the carrier gas. The injector temperature was 250 °C. The GC oven temperature programme: 1 min at 50 °C, increased at 10 °C/min to 240 °C, then 15 min at 240 °C. Electron impact ionization for MS was used, the source temperature was 20 °C, the electron energy was 70 eV and the scan speed was 0.6 s per decade.

Ethyl 3-substituted prop-2-enoate derivatives **1a** [7]**, 1b,c** [3]**, 1d** [8]**, 1e** [9]**, 1f,g** [10] were prepared according to known procedures.

*General Procedure for synthesis of Ethyl 3-Substituted-4-Nitrobutanoate **2a–c** and Ethyl 2-Substituted 3-Nitropropanoate **3a–c** Derivatives*

Method A. A stirred solution of esters **1a–c** (0.01 *M*) in 20 ml of nitromethane with 1 ml of Triton B (35% sol. in MeOH) was heated at 85 °C for 18 h. After cooling, reaction medium was acidified to pH 2, 2 *M* HCl and 20 ml of water was added. The mixture was extracted with diethylether (3 × 20 ml portions). The combined extracts were washed with water (3×10 ml), dried, and evaporated *in vacuo*, giving crude oils of **2a–c**, which were further purified by distillation under reduced pressure (Table 1).

Method B. After 18 hours reaction time, the crude reaction mixture of pyridine derivatives prepared as above was divided into two equal parts. The first part was evaporated *in vacuo*, the crude oily residue was then dissolved in chloroform and passed through a short column of silica gel to remove Triton B. After vacuum evaporation of the solvent and vacuum distillation, colourless oils containing mixtures of **2d–g**, **3d–f** were isolated (Table 1).

To the second part of the reaction mixture further Triton B (0.5 ml) was added and heating was continued for another 18 hours. The reaction mixture was worked up the same way as the first part. Compounds **4d, g** and **5d, g** altogether with **2d, f** and **3d, f** were detected by GC-MS in the vacuum distilled product (Table 1).

*Ethyl 4-nitro-3-methyl butanoate **2a***

IR (KBr): 2982, 1732, 1553, 1379.

^{1}H-NMR: 1.11 (*d*, *J* = 7.0 Hz, 3H), 1.27 (*t*, *J* = 7.1 Hz, 3H), 2.35 (*dd*, *J* = 16.1, 6.7 Hz, 1H), 2.45 (*dd*, *J* = 16.1, 6.6 Hz, 1H), 2.79 (*d*, *J* = 6.6, 1H), 4.16 (*q*, *J* = 7.1 Hz, 2H), 4.35 (*dd*, *J* = 12.2, 7.1 Hz, 1H), 4.49 (*dd*, *J* = 12.2, 6.2 Hz, 1H).

^{13}C-NMR: 14.2, 17.3, 29.5, 38.0, 60.8, 80.3, 171.2.

MS: 131 (6), 130 (100), 129 (4), 128 (11), 117 (4), 102 (30), 101 (61), 99 (16), 96 (5), 88 (17), 87 (23), 84 (5), 83 (44), 82 (7), 73 (6), 71 (14), 70 (5), 69 (33), 68 (5), 61 (5), 60 (20), 59 (47), 57 (10), 56 (25), 55 (95), 53 (5), 45 (18), 44 (6), 43 (29), 42 (22), 41 (44), 40 (7), 39 (25), 31 (4), 30 (4).

*Ethyl 3-nitro-2-ethylpropanoate **3a***

MS: 131 (5), 130 (85), 115 (9), 114 (19), 102 (14), 101 (7), 99 (13), 87 (6), 84 (4), 83 (34), 82 (10), 74 (20), 73 (90), 72 (5), 71 (17), 69 (32), 68 (6), 60 (8), 59 (100), 56 (10), 55 (74), 54 (4), 45 (6), 43 (15), 42 (14), 41 (28), 39 (14)

*Ethyl 4-nitro-3-furylbutanoate **2b***

IR (KBr): 2986, 2957, 2926, 1736, 1557, 1377.

^{1}H-NMR: 1.24 (*t*, *J* = 7.2 Hz, 3H), 2.74 (*dd*, *J* = 16.0, 6.3 Hz, 1H), 2.84 (*dd*, *J* = 16.0, 6.3 Hz, 1H), 4.09 (*m*, 1H), 4.14 (*q*, *J* = 7.2 Hz, 2H), 4.71 (*d*, *J* = 12.5 Hz, 1H), 4.74 (*d*, *J* = 12.5 Hz, 1H), 6.18 (*d*, *J* = 3.3 Hz, 1H), 6.30 (*dd*, *J* = 3.3, 1.8 Hz, 1H), 7.35 (*d*, *J* = 1.8 Hz, 1H).

^{13}C-NMR: 14.1, 34.1, 35.4, 61.1, 77.1, 107.2, 110.5, 142.5, 151.3, 170.5.

MS: 182 (8), 181 (12), 180 (65), 152 (4), 140 (19), 139 (5), 135 (9), 124 (6), 121 (6), 119 (4), 111 (11), 109 (20), 108 (100), 107 (38), 95 (12), 94 (55), 93 (6), 92 (5), 83 (15), 81 (15), 79 (24), 77 (15), 68 (5), 67 (6), 66 (13), 65 (17), 63 (6), 55 (6), 53 (7), 51 (4), 43 (4), 41 (6), 39 (12)

*Ethyl 3-nitro-2-furylmethylenepropanoate **3b***

^{1}H-NMR: 1.24 (*t*, *J* = 7.2 Hz, 3H), 2.78 (*m*, 1H), 3.69 (*s*, 2H), 4.14 (*q*, *J* = 7.2 Hz, 2H), 4.71 (*d*, *J* = 12.5 Hz, 1H), 4.74 (*d*, *J* = 12.5 Hz, 1H), 6.18 (*d*, *J* = 3.3 Hz, 1H), 6.30 (*dd*, *J* = 3.3, 1.8 Hz, 1H), 7.35 (*d*, *J* = 1.8 Hz, 1H).

^{13}C-NMR: 14.1, 35.1, 52.1, 61.1, 77.3, 107.2, 110.5, 142.5, 151.2, 170.9.

MS: 182 (7), 167 (13), 166 (89), 140 (18), 138 (10), 135 (10), 125 (22), 121 (9), 119 (4), 111 (7), 109 (9), 108 (100), 107 (38), 95 (10), 94 (71), 93 (9), 83 (18), 81 (14), 79 (28), 78 (7), 77 (22), 67 (5), 66 (13), 65 (17), 63 (5), 59 (25), 55 (9), 53 (8), 52 (4), 51 (7), 41 (4), 39 (15)

Ethyl 4-nitro-3-thienylbutanoate ***2c***

IR (KBr): 2982, 1732, 1555, 1378.

^{1}H-NMR: 1.20 (*t*, *J* = 7.2 Hz, 3H), 2.72 (*dd*, *J* = 13.0, 4.0 Hz, 1H), 2.79 (*dd*, *J* = 13.0, 4.0 Hz, 1H), 4.10 (*q*, *J* = 7.2 Hz, 2H), 4.62 (*dd*, *J* = 12.5, 7.6 Hz, 1H), 4.72 (*dd*, *J* = 12.5, 5.6 Hz, 1H), 6.97 (*dd*, *J* = 5.3, 1.0 Hz, 1H), 7.12 (*d*, *J* = 3.0 Hz, 1H), 7.31 (*dd*, *J* = 5.3, 2.9 Hz, 1H).

^{13}C-NMR: 14.1, 37.7, 52.0, 60.9, 79.2, 122.2, 126.1, 126.8, 138.9, 170.6.

MS: 198 (28), 197 (21), 196 (75), 179 (4), 162 (5), 156 (5), 155 (5), 153 (5), 152 (4), 151 (32), 138 (5), 137 (13), 136 (6), 135 (11), 127 (8), 126 (5), 125 (24), 124 (84), 123 (100), 122 (8), 112 (5), 111 (20), 110 (55), 109 (23), 108 (7), 97 (23), 85 (10), 84 (17), 79 (12), 77 (6), 69 (5), 66 (6), 65 (10), 58 (4), 45 (20), 39 (8)

Ethyl 3-nitro-2-thienylmethylenepropanoate **3c**

^{1}H-NMR: 1.20 (*t*, *J* = 7.2 Hz, 3H), 3.65 (*s*, 2H), 4.10 (*q*, *J* = 7.2 Hz, 2H), 4.62 (*dd*, *J* = 12.5, 7.6 Hz, 1H), 4.72 (*dd*, *J* = 12.5, 5.6 Hz, 1H), 6.97 (*dd*, *J* = 5.3, 1.0 Hz, 1H), 7.12 (*d*, *J* = 3.0 Hz, 1H), 7.31 (*dd*, *J* = 5.3, 2.9 Hz, 1H).

^{13}C-NMR: 14.1, 35.7, 37.4, 60.9, 79.1, 122.2, 126.1, 126.8, 138.9, 174.3.

MS: 198 (18), 195 (4), 187 (93), 184 (6), 183 (20), 182 (93), 162 (5), 156 (4), 154 (9), 152 (5), 151 (27), 141 (25), 139 (5), 137 (10), 136 (7), 135 (10), 127 (11), 126 (5), 125 (18), 124 (71), 123 (100), 122 (10), 121 (5), 112 (5), 111 (16), 110 (64), 109 (27), 108 (5), 99 (7), 98 (5),97 (27), 84 (17), 79 (16), 77 (8), 69 (6), 66 (6), 65 (10), 59 (19), 58 (6), 45 (14), 39 (9)

Ethyl 4-nitro-3-(2-pyridyl)butanoate ***2d***

IR (KBr): 2984, 2934, 1732, 1593, 1556, 1377.

^{1}H-NMR: 1.19 (*t*, *J* = 7.1 Hz, 3H), 2.74 (*dd*, *J* = 16.4, 6.7 Hz, 1H), 2.88 (*dd*, *J* = 16.4, 7.7 Hz, 1H), 4.06 (*m*, 1H), 4.08 (*q*, *J* = 7.1 Hz, 2H), 4.76 (*dd*, *J* = 13.3, 5.9 Hz, 1H), 4.95 (*dd*, *J* = 13.3, 8.6 Hz, 1H), 7.18 (*dd*, *J* = 7.8, 4.0 Hz, 1H), 7.28 (*d*, *J* = 7.7 Hz, 1H), 7.64 (*ddd*, *J* = 7.8, 6.0, 1.7 Hz, 1H), 8.54 (*d*, *J* = 4.0 Hz, 1H).

^{13}C-NMR: 14.1, 36.9, 41.2, 60.9, 77.9, 122.7, 123.7, 136.7, 149.6, 158.1, 170.8.

MS: 193 (44), 192 (70), 191 (8), 178 (12), 174 (4), 173 (7), 162 (7), 159 (8), 158 (4), 157 (17), 151 (8), 148 (4), 147 (13), 146 (54), 145 (9), 134 (5), 133 (4), 132 (30), 131 (33), 130 (12), 129 (4), 122 (5), 120 (11), 119 (22), 118 (100), 117 (32), 106 (22), 105 (12), 104 (22), 103 (4), 93 (10), 92 (5), 91 (6), 79 (32), 78 (28), 76 (4), 75 (4), 65 (4), 52 (8), 51 (12)

Ethyl 3-nitro-2-(2-pyridylmethylene)propanoate ***3d***

^{1}H-NMR: 1.19 (*t*, *J* = 7.1 Hz, 3H), 2.76 (*m*, 1H), 3.63 (*s*, 2H), 4.08 (*q*, *J* = 7.1 Hz, 2H), 4.76 (*dd*, *J* = 13.3, 5.9 Hz, 1H), 4.94 (*dd*, *J* = 13.3, 8.6 Hz, 1H), 7.18 (*dd*, *J* = 7.8, 4.0 Hz, 1H), 7.28 (*d*, *J* = 7.7 Hz, 1H), 7.64 (*ddd*, *J* = 7.8, 6.0, 1.7 Hz, 1H), 8.54 (*d*, *J* = 4.0 Hz, 1H).

^{13}C-NMR: 14.1, 36.6, 51.9, 60.9, 77.9, 122.7, 123.7, 136.7, 149.6, 158.1, 171.5.

MS: 194 (5), 193 (15), 178 (75), 177 (9), 173 (5), 165 (4), 164 (16), 162 (6), 159 (6), 157 (13), 151 (12), 147 (11), 146 (45), 145 (13), 134 (8), 133 (4), 132 (27), 131 (28), 130 (9), 129 (6), 122 (7), 120 (5), 119 (20), 118 (100), 117 (45), 106 (18), 105 (11), 104 (22), 93 (10), 92 (6), 91 (12), 90 (4), 79 (25), 78 (32), 77 (4), 59 (7), 52 (11), 51 (13), 50 (4), 39 (4)

Ethyl 4-nitro-3-(3-pyridyl)butanoate ***2e***

IR (KBr): 2984, 2939, 1732, 1591, 1554, 1379.

^{1}H-NMR: 1.18 (*t*, *J* = 7.1 Hz, 3H), 2.77 (*dd*, *J* = 16.0, 6.0 Hz, 1H), 2.82 (*dd*, *J* = 16.0, 6.0 Hz, 1H), 4.02 (*m*, 1H), 4.09 (*q*, *J* = 7.1 Hz, 2H), 4.67 (*dd*, *J* = 12.9, 8.0 Hz, 1H), 4.79 (*dd*, *J* = 12.9, 6.6 Hz, 1H), 7.29 (*dd*, *J* = 7.9, 4.8 Hz, 1H), 7.58 (*dd*, *J* = 6.1, 2.0 Hz, 1H), 8.54 (*dd*, *J* = 4.7, 1.7 Hz, 1H), 8.56 (*d*, *J* = 1.6 Hz, 1H).

^{13}C-NMR: 14.0, 37.8, 37.9, 61.2, 78.8, 134.1, 134.9, 149.2, 149.5, 170.1.

MS: 194 (16), 193 (41), 192 (59), 191 (44), 176 (8), 175 (5), 174 (44), 173 (16), 165 (6), 164 (33), 163 (10), 162 (57), 160 (8), 159 (10), 158 (11), 157 (30), 156 (6), 151 (5), 150 (18), 149 (5), 148 (23), 147 (53), 146 (36), 145 (19), 135 (8), 134 (9), 133 (11), 132 (24), 131 (30), 129 (9), 128 (4), 123 (4), 122 (41), 121 (6), 120 (67), 119 (63), 118 (100), 117 (47), 116 (6), 108 (5), 107 (6), 106 (27), 105 (76), 104 (60), 103 (58), 93 (8), 92 (23), 91 (26), 90 (9), 89 (5), 80 (9), 79 (16), 78 (31), 77 (23), 76 (17), 75 (9), 74 (6), 66 (4), 65 (15), 64 (4), 63 (10), 53 (5), 52 (14), 51 (23), 50 (16), 46 (7), 45 (12), 44 (10), 43 (8), 42 (5), 41 (5), 39 (9).

Ethyl 3-nitro-2-(3-pyridylmethylene)propanoate ***3e***

^{1}H-NMR (300 MHz,): 1.18 (*t*, *J* = 7.1 Hz, 3H), 2.79 (*m*, 1H), 3.65 (*s*, 2H), 4.09 (*q*, *J* = 7.1 Hz, 2H), 4.67 (*dd*, *J* = 8.0, 12.9 Hz, 1H), 4.79 (*dd*, *J* = 6.7, 12.9 Hz, 1H), 7.29 (*dd*, *J* = 4.8, 7.9 Hz, 1H), 7.58 (*dd*, *J* = 2.0, 6.1 Hz, 1H), 8.54 (*dd*, *J* = 1.7, 4.7 Hz, 1H), 8.56 (*d*, *J* = 1.6 Hz, 1H).

^{13}C-NMR: 14.0, 37.4, 52.1, 61.2, 78.8, 134.1, 134.9, 149.2, 149.5, 170.7.

MS: 194 (8), 193 (21), 190 (7), 188 (4), 179 (7), 178 (55), 177 (87), 174 (7), 173 (10), 163 (8), 162 (53), 160 (6), 159 (6), 158 (10), 157 (31), 156 (8), 149 (4), 148 (8), 147 (26), 146 (21), 145 (28), 137 (4), 136 (37), 135 (5), 134 (20), 133 (8), 132 (26), 131 (23), 130 (27), 129 (10), 128 (5), 122 (7), 121 (4), 120 (11), 119 (57), 118 (100), 117 (45), 107 (6), 106 (12), 105 (50), 104 (56), 103 (20), 94 (5), 93 (7), 92 (17), 91 (20), 90 (7), 89 (4), 79 (14), 78 (25), 77 (17), 76 (11), 75 (9), 65 (15), 63 (10), 59 (28), 52 (11), 51 (28), 50 (13), 44 (4), 39 (9).

Ethyl 4-nitro-3-(4-pyridyl)butanoate ***2f***

IR (KBr): 3026, 2982, 2939, 2907, 1732, 1716, 1597, 1556, 1379.

^{13}C-NMR: 14.3, 17.3, 40.5, 60.3, 65.9, 119.6, 119.7, 120.7, 150.2, 166.2.

MS (EI, 70 eV): 194 (10), 193 (32), 192 (44), 191 (28), 176 (10), 174 (16), 173 (13), 164 (31), 163 (8), 162 (43), 159 (15), 158 (11), 157 (35), 150 (18), 148 (23), 147 (44), 146 (35), 145 (17), 133 (9), 132 (21), 131 (27), 130 (31), 129 (11), 122 (34), 120 (51), 119 (52), 118 (100), 117 (41), 106 (23), 105 (46), 104 (41), 103 (25), 93 (8), 92 (15), 91 (16), 90 (9), 79 (10), 78 (17), 77 (17), 76 (11), 65 (10), 63 (9), 51 (16), 50 (10), 46 (9), 45 (8), 39 (9)

Ethyl 3-nitro-2-(4-pyridylmethylene)propanoate ***3f***

^{13}C-NMR: 14.3, 17.3, 40.5, 61.1, 65.9, 119.6, 119.7, 120.7, 150.2, 170.7.

MS : 194 (10), 193 (26), 190 (11), 188 (6), 179 (8), 178 (61), 177 (78), 173 (12), 163 (10), 162 (51), 161 (5), 160 (5), 159 (10), 158 (16), 157 (43), 156 (12), 150 (4), 149 (5), 148 (12), 147 (49), 146 (37), 145 (32), 137 (8), 136 (65), 135 (6), 134 (24), 133 (9), 132 (33), 131 (35), 130 (42), 129 (15), 128 (9), 122 (12), 121 (5), 120 (18), 119 (68), 118 (100), 117 (52), 116 (6), 107 (6), 106 (17), 105 (59), 104 (55), 103 (21), 102 (16), 94 (6), 93 (8), 92 (20), 91 (30), 90 (7), 89 (7), 79 (16), 78 (30), 77 (25), 76 (12), 75 (12), 74 (5), 66 (4), 65 (17), 64 (5), 63 (10), 59 (26), 51 (25), 50 (15), 44 (9), 39 (11)

Methyl 4-nitro-3-(4-pyridyl)butanoate ***2g***

MS: 178 (10), 177 (82), 176 (22), 162 (7), 147 (12), 146 (100), 145 (36), 119 (5), 118 (25), 117 (61), 116 (8), 92 (5), 91 (27), 90 (13), 89 (11), 78 (5), 76 (4), 65 (16), 63 (9), 59 (6), 52 (5), 51 (18), 50 (9), 39 (10)

Methyl 3-nitro-2-(4-pyridylmethylene)propanoate ***3g***

MS: 178 (11), 177 (100), 176 (6), 149 (11), 148 (5), 146 (17), 145 (5), 134 (15), 132 (21), 119 (22), 118 (42), 117 (50), 116 (5), 104 (4), 93 (12), 92 (6), 91 (22), 90 (9), 89 (9), 78 (4), 65 (9), 63 (8), 59 (23), 51 (13), 50 (6), 39 (7)

1,5-Dinitro-4-(2-pyridyl)-2-pentanone ***4d***

MS: 192 (8), 191 (40), 162 (22), 147 (12), 146 (64), 145 (54), 119 (30), 118 (78), 117 (100), 104 (8), 92 (8), 91 (18), 90 (12), 89 (10), 79 (11), 78 (19), 65 (8), 63 (4), 58 (7), 52 (8), 51 (12), 39 (4)

1,5-Dinitro-4-(4-pyridyl)-2-pentanone ***4f***

MS: 192 (8), 191 (60), 190 (5), 163 (12), 162 (24), 147 (9), 146 (100), 145 (36), 119 (4), 118 (17), 117 (39), 116 (4), 91 (16), 90 (71), 89 (6), 65 (9), 63 (5), 51 (8), 39 (3)

1,4-Dinitro-3-(2-pyridylmethylene)-2-butanone ***5d***

MS: 192 (6), 191 (40), 162 (20), 147 (9), 146 (60), 145 (57), 132 (4), 119 (28), 118 (90), 117 (100), 104 (12), 91 (13), 90 (11), 89 (7), 79 (11), 78 (17), 65 (7), 58 (5), 51 (12), 38 (5)

1,4-Dinitro-3-(4-pyridylmethylene)-2-butanone ***5f***

MS: 192 (14), 191 (93), 163 (46), 162 (4), 147 (8), 146 (54), 135 (6), 132 (7), 120 (6), 119 (49), 118 (100), 117 (46), 116 (5), 107 (8), 106 (7), 104 (8), 93 (11), 92 (7), 91 (25), 90 (9), 89 (9), 79 (11), 78 (5), 77 (4), 65 (13), 63 (7), 59 (4), 52 (4), 51 (14), 50 (6), 39 (70)

Acknowledgement: This work was supported by the Slovak grant agency, grant No. 95/5195/202.

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