Synthesis of α-nitro derivatives of δ-oxocarboxylic and glutaric acids in heterogeneous catalytic system ionic liquid—$KHCO_3$

S. G. Zlotin, G. V. Kryshtal, G. M. Zhdankina, A. V. Bogolyubov, S. G. Postikova, and V. A. Tartakovsky*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5328. E-mail: zlotin@ioc.ac.ru

An expedient method for the synthesis of α-nitro-δ-oxocarboxylic and α-nitroglutaric acid esters, including ones with isoprenoid substituents, by the solvent-free reaction of the corresponding alkyl α-nitrocarboxylates with activated olefins, assisted by heterogeneous catalytic system $KHCO_3$—1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), was elaborated. The product yields remain stable even after eight recycles of the catalytic system. The synthesized dimethyl 2-(poly)prenyl-2-nitropentanedioates upon treatment with Fe in AcOH were reduced to 2-(poly)prenyl-5-oxopyrrolidine-2-carboxylates.

Key words: ionic liquids, the Michael reaction, nitro compounds, olefins, isoprenoids, catalysis, reduction, pyrrolidin-2-ones.

Addition of nitroalkanes to activated olefins (the Michael reaction) is one of the most simple and convenient methods for the formation of a C—C bond.[1] The reaction allows one in a single experimental step from available precursors to obtain complex polyfunctional compounds, intermediate products for the synthesis of natural and biologically active substances.[2] Bases are usually used as the catalysts. The preference is given to the more convenient from the technological point of view heterogeneous catalysts (Al_2O_3,[3] $Al_2O_3 \cdot KF$,[4] Amberlyst-21 [5] *etc.*).

As a rule, the reaction is carried out in organic solvents[2] or in excess of nitroalkane.[6] Ionic liquids (IL) (in particular, [bmim][OH][7] and [bmim][PF_6],[8] bmim is 1-butyl-3-methylimidazolium] are also used as the solvents: due to the low vapor pressure and low solubility in hydrocarbons, they are easy to recover. Reactions in IL were carried out under homogeneous conditions.

Recently, we elaborated a convenient method for the synthesis of γ-nitroketones and γ-nitrocarboxylic acid esters from nitroalkanes (nitroethane, 2-nitropropane, and nitrocyclohexane) and α,β-unsaturated carbonyl compounds with the assistance of simple and efficient heterogeneous catalytic system K_2CO_3—IL depriving of the use of organic solvents (see Ref. 9). The adducts were formed in high yields with the use of minimum amount of IL (90 mol.%). The system preserved its activity in three reaction cycles.

In the present work, α-nitrocarboxylic esters **1** and activated olefins **2** with the use of heterogeneous catalytic system, solid base—IL, were converted to α-nitro derivatives of δ-oxocarboxylic and glutaric acids **3**, including intermediate products for the synthesis of analogs of pharmacologically active substances (Scheme 1). Methyl nitroacetate (**1a**), methyl 5-methyl-2-nitrohex-4-enoate (**1b**), and methyl 5,9-dimethyl-2-nitrodeca-4,8-dienoate (**1c**) were used as the starting α-nitrocarboxylates, acrolein (**2a**), α,β-unsaturated ketones **2b—h**, and esters **2i—k**, as the activated olefins (see Scheme 1).

The earlier unknown α-nitrocarboxylic acid esters **1b,c** were synthesized by alkylation of methyl nitroacetate (**1a**) with prenyl and geranyl bromides, respectively, in DMF in the presence of benzyltriethylammonium chloride ([BTEA]Cl) as the phase-transfer catalyst. The yields of alkylation products **1b,c** were 53—65% (Scheme 2). Homolog of **1b**, ethyl 5-methyl-2-nitrohex-4-enoate, has been synthesized earlier[10] by the base assisted decarboxylation of diethyl 2-prenyl-2-nitromalonate, though the yield of the product did not exceed 25—30%.

Isoprenoid diene **2h** was synthesized by the reaction of citronellal with phenacyltriphenylphosphonium bromide in the presence of potassium carbonate in 62% yield (Scheme 3).

Nitroacetic acid esters, being strong CH-acids, are capable of reacting with activated olefins upon treatment with soft bases.[11] In order to find the optimal composition of the catalytic system, we investigated the reaction of **1a** with 1,3-diphenylprop-2-en-1-one (chalcone **2b**) in the presence of neutral and acidic salts of carbonic acid and various IL. Easily available 1-butyl-3-methylimidazolium ([bmim][BF_4]) and 1-butyl-2,3-dimethylimidazolium ([bdmim][BF_4]) tetrafluoroborates and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) were used as the IL (Table 1). Both the base and IL were

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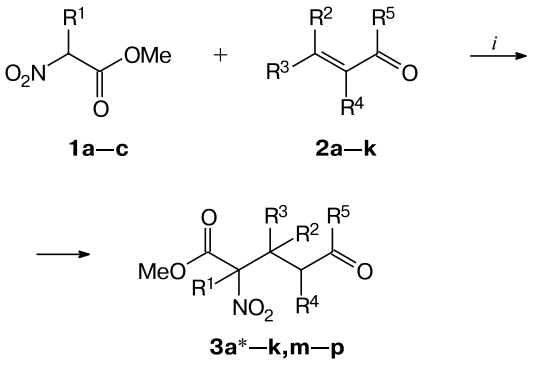
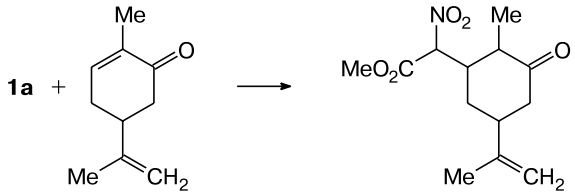
Scheme 1



1a—c **2a—k** **3a*—k,m—p**



1a **2l** **3l**

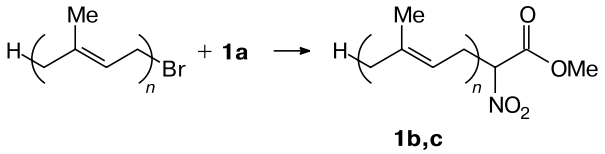
R^1 = H (**1a**, **3a—k**), $Me_2C{=}CHCH_2$ (**1b**, **3m,n**), $H[CH_2C(Me){=}CHCH_2]_2$ (**1c**, **3o,p**)

Compounds	R^2	R^3	R^4	R^5
2a, **3a*,m,o**	H	H	H	H
2b, **3b**	H	Ph	H	Ph
2c, **3c**	H	Me	H	Me
2d, **3d**	H	Ph	H	Me
2e, **3e**	Me	Me	H	Me
2f, **3f**	H	Ph	H	*c*-Pr
2g, **3g**	H	**	H	Me
2h, **3h**	H	**	H	Ph
2i, **3i,n,p**	H	H	H	OMe
2j, **3j**	H	Me	H	OMe
2k, **3k**	H	**	CO_2Et	OEt

* Due to resinification during the reaction **1a** + **2a**, product **3a** could not be obtained. ** $Me_2C{=}CH(CH_2)_2CH(Me)CH_2$.

i. $MHCO_3$ (30 mol.%), [bmim][BF_4] (30 mol.%), 20—40 °C.

Scheme 2



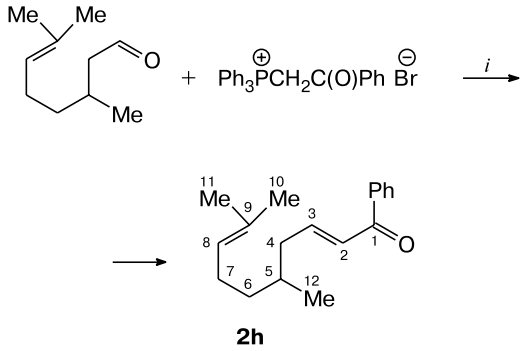
1b,c

n = 1 (**1b**), 2 (**1c**)

Conditions: K_2CO_3, [BTEA]Cl (cat), DMF.

used in amounts of 30—400 mol.%. The reactions were carried out until the disappearance of the CH-form of nitro compound **1a** from the mixture (TLC monitoring).

Scheme 3



2h

i. K_2CO_3, dioxane, 100 °C.

In contrast to nitroalkanes without electron-withdrawing substituent in α-position to the nitro group (for $EtNO_2$ pK_a = 8.6),[12b] nitro ester **1a** (pK_a = 5.8)[12a,b] formed the Michael adduct **3b** in high yield upon treatment with metal bicarbonates (see Table 1, entries *5—7*). However, the yield of **3b** was significantly lower on catalysis with more basic carbonates (see Table 1, entries *1—3*). Apparently in contrast to carbonates (pK_a = 10.25 for conjugate acid HCO_3^-),[12c] bicarbonates (pK_a = 6.37 for conjugate acid H_2CO_3)[12c] are able to selectively deprotonate CH-acid **1a** in the presence of product **3b**, shifting the equilibrium toward the latter. This suggestion was confirmed by the increase in the yield of **3b**, when amount of the base was decreased (see Table 1, entries *2—4*). The reaction proceeded faster in IL containing $[BF_4]^-$ anion

Table 1. Optimization of the reaction conditions between **1a** and **2b**[a]

Entry	Base (mol.%)	IL (mol.%)	*T*/°C	τ/h[b]	Yield of **3b** (%)
1	Na_2CO_3 (30)	[bmim][BF_4] (90)	20	60	37
2	K_2CO_3 (200)	[bmim][BF_4] (400)	20	8	32
3	K_2CO_3 (30)	[bmim][BF_4] (90)	20	8	63
4	K_2CO_3 (15)	[bmim][BF_4] (90)	20	48	94
5	$NaHCO_3$ (30)	[bmim][BF_4] (90)	20	12	92
6	$KHCO_3$ (200)	[bmim][BF_4] (400)	20	2	95
7	$KHCO_3$ (30)	[bmim][BF_4] (90)	20	8	92
8	$KHCO_3$ (30)	[bdmim][BF_4] (90)	20	10	92
9	$KHCO_3$ (30)	[bmim][PF_6] (90)	20	20	87
10	$KHCO_3$ (30)	[bmim][BF_4] (30)	20	14	98
11	$KHCO_3$ (30)	[bmim][BF_4] (30)	40	6	98
12[c]	$KHCO_3$ (30)	[bmim][BF_4] (30)	40	6	99
13	$KHCO_3$ (30)	—	20	70	0

[a] Reagents loading: **1a** (100 mol.%), **2b** (100 mol.%).
[b] The reactions were conducted until **1a** disappeared (TLC monitoring), excluding entry *13*.
[c] The reaction was conducted under sonication

than in IL with $[PF_6]^-$ anion (see Table 1, entries *7—9*). When amount of IL was reduced to 30 mol.%, the yield of **3b** remained high (see Table 1, entries *10* and *11*). Ultrasound may be applied instead of mechanical stirring of the reaction mixture (see Table 1, entry *12*). Further decrease of IL amount (to 10—15 mol.%) led to a decrease in the yield of **3b**. No reaction took place in the absence of IL (see Table 1, entry *13*).

The $KHCO_3$—[bmim][BF_4] catalytic system (30 mol.% each), which in the model reaction provided the highest yield of product **3b** with the minimum amount of catalyst, was applied to the synthesis of esters of α-nitro-δ-oxocarboxylic **3b—h,l,m,o** and α-nitroglutaric **3i—k,n,p** acids, containing substituents of various structure (Table 2).

Acrolein (**2a**) and methyl acrylate (**2i**) devoid of substituents at β-carbon atom were found to be the most reactive. Olefins **2g,h,l** with isoprenoid substituents and mesityl oxide (**2e**) with two methyl groups in β-position were the least reactive. Nevertheless, when the reaction was carried to complete conversion of the olefin, we were able to obtain the earlier unknown nitro compounds of isoprenoid series **3g,h,k—p** (Schemes 4 and 5), as well as products **3b—d**, the yields of which exceeded those found in the literature even with the shorter reaction time (see Table 2, entries *1—3*).

In a number of cases, the reactions lead to the formation of diastereomeric mixtures of **3** in ratios (1 : 1)—(2 : 1) (^{1}H NMR data). For compounds **3k** and **3l** with four chiral centers, the ratio of the detected by ^{1}H NMR

Table 2. Yields and physical and chemical properties of adducts **3**[a]

Entry	Reagents	τ/h	Product	Yield **3** (%) (cycle)	M.p./°C or n_D^{20}	^{1}H NMR spectrum ($CDCl_3$) δ, (*J*/Hz)[b]
1	**1a** + **2b**	6 [48 (20 °C)][13]	**3b**	98 (1), 99 (2), 99 (3), 99 (4), 89 (5), 99 (6)[c], 99 (7), 99 (8) [40][13] dr 2 : 1	114—115 [114—116][10]	3.50—3.70 (m, 2 H, CH_2C=O); 3.60 (s, 1 H, OMe); 3.77 (s, 2 H, OMe); 4.50 (m, 1 H, C<u>H</u>Ph); 5.55 (d, 0.34 H, $CHNO_2$, *J* = 8.5); 5.60 (d, 0.66 H, $CHNO_2$, *J* = 9.5); 7.25 (m, 5 H, Ph); 7.40 (m, 2 H, Ph); 7.50 (m, 1 H, Ph); 7.90 (d, 2 H, Ph, *J* = 7.5)
2	**1a** + **2c**	8[d] [140 (100 °C)][14]	**3c**	76 [44][14] dr 1 : 1	1.4490	1.07 (d, 3 H, Me, *J* = 7.0); 2.13 (s, 3 H, MeCO); 2.45—2.75 (m, 2 H, CH_2); 3.0 (m, 1 H, CH); 3.80 (s, 3 H, OMe); 5.20 (d, 0.5 H, $CHNO_2$, *J* = 5.5); 5.27 (d, 0.5 H, $CHNO_2$, *J* = 6.3)
3	**1a** + **2d**	14, 6[d] [110 (20 °C)[e]][15]	**3d**	90 (1), 87 (2), 85 (3) [84[e]][15] dr 2 : 1	102—103	2.05 (s, 3 H, MeC=O); 2.95—3.15 (m, 2 H, CH_2); 3.60 (s, 1 H, OMe); 3.80 (s, 2 H, OMe); 4.25 (m, 1 H, C<u>H</u>Ph); 5.45 (d, 0.34 H, $CHNO_2$, *J* = 8.2); 5.50 (d, 0.66 H, $CHNO_2$, *J* = 9.0); 7.20—7.40 (m, 5 H, Ph)
4	**1a** + **2e**	22[d] [70 (70 °C)][16]	**3e**	55 [83][16]	1.4500 [1.4507][16]	1.20, 1.23 (both s, 3 H each, Me); 2.10 (s, 3 H, MeC=O); 2.67, 2.82 (both d, 1 H each, CH_2, *J* = 17.7); 3.75 (s, 3 H, OMe); 5.85 (s, 1 H, $CHNO_2$)
5	**1a** + **2f**	16[d]	**3f**	95 dr 2 : 1	70—71	0.75—0.95 (m, 4 H, 2 CH_2 of cyclopropane); 1.85 (m, 1 H, CH, of cyclopropane); 2.95—3.20 (m, 2 H, CH_2C=O); 3.60 (s, 1 H, OMe); 3.80 (s, 2 H, OMe); 4.27 (m, 1 H, C<u>H</u>Ph); 5.45 (d, 0.34 H, $CHNO_2$, *J* = 8.0); 5.52 (d, 0.66 H, $CHNO_2$, *J* = 9.0); 7.20—7.35 (m, 5 H, Ph)
6	**1a** + **2g**	40[d]	**3g**	75	1.4695	0.85—0.95 (m, 3 H, C(12)H_3); 1.10—1.45 (m, 5 H, C(4)H_2, C(5)H, C(6)H_2); 1.57, 1.65 (both s, 3 H each, C(10)H_3, C(11)H_3); 1.90 (m, 2 H, C(7)H_2); 2.15 (s, 3 H, MeC=O); 2.50—3.05 (m, 3 H, CH_2, C(3)H); 3.80 (s, 3 H, OMe); 5.05 (m, 1 H, C(8)H); 5.35 (m, 1 H, C(2)H)
7	**1a** + **2h**	40[d]	**3h**	73 dr 2 : 1	1.5135	0.85—1.00 (m, 3 H, C(12)H_3); 1.20—1.55 (m, 5 H, C(4)H_2, C(5)H, C(6)H_2); 1.57, 1.65 (both s, 3 H each, C(10)H_3, C(11)H_3); 1.95 (m, 2 H, C(7)H_2); 3.05—3.40 (m, 3 H, CH_2, C(3)H); 3.80 (s, 3 H, OMe); 5.05 (m, 1 H, C(8)H); 5.48 (d, 0.66 H, C(2)H, *J* = 6.0); 5.53 (d, 0.34 H, C(2)H, *J* = 7.0); 7.47 (t, 2 H, Ph, *J* = 7.0); 7.58 (t, 1 H, Ph, *J* = 7.0); 7.95 (m, 2 H, Ph)
8	**1a** + **2i**	10[f] [26 (65 °C)][17]	**3i**	90 [75][17] dr 1 : 1	1.4460 [1.4468][18]	2.40, 2.55 (both m, 2 H each, 2 CH_2); 3.65, 3.80 (both s, 3 H each, 2 OMe); 5.30 (t, 1 H, $CHNO_2$, *J* = 7.0)

(*to be continued*)

Table 2 (*continued*)

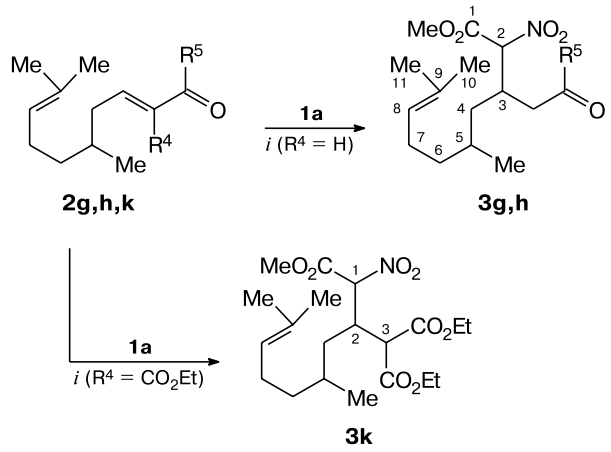
Entry	Reagents	τ/h	Product	Yield **3** (%) (cycle)	M.p./°C or n_D^{20}	^{1}H NMR spectrum ($CDCl_3$) δ, (*J*/Hz)[b]
9	**1a** + **2j**	12[d]	**3j**	69 dr 1 : 1	1.4470	1.12 (d, 3 H, CH_3C, J = 7.0); 2.42 (ddd, 1 H, CH_2, ^1J = 17.2, ^2J = 7.8, ^3J = 2.0); 2.57 (dd, 1 H, CH_2, ^1J = 17.2, ^2J = 5.5); 2.97 (m, 1 H, CH), 3.67 (s, 1.5 H, OMe); 3.80 (s, 1.5 H, OMe); 5.25 (d, 0.5 H, $CHNO_2$, J = 6.5); 5.30 (d, 0.5 H, $CHNO_2$, J = 6.5)
10	**1a** + **2k**	20[d]	**3k**	63 dr 1 : 1 : : 1 : 1	1.4625	0.92 (m, 3 H, Me); 1.10—1.45 (m, 5 H, 2 CH_2, CH); 1.30 (t, 6 H, 2 Me, J = 7.0); 1.60, 1.68 (both s, 3 H each, 2 Me); 1.97 (m, 2 H, CH_2); 3.23, 3.68 (both m, 1 H each, C(2)H, C(3)H); 3.82 (s, 3 H, OMe); 4.20 (q, 4 H, 2 $C\underline{H}_2O$, J = 7.0); 5.08 (t, 1 H, =CH, J = 7.0); 5.55, 5.59, 5.63, 5.68 (all d, 0.25 H each, C(1)H, J = 6.0)
11	**1a** + **2l**	15[d]	**3l**	73 dr 3 : 2 : : 3 : 2	1.4880	1.05—1.25 (m, 3 H, MeC(2)); 1.70 (s, 3 H, MeC=); 1.85—2.80 (m, 7 H, $C(4)H_2$, $C(6)H_2$, C(1)H, C(2)H, C(5)H); 3.85 (m, 3 H, OMe); 4.65—4.85 (m, 2 H, CH_2=); 5.20 (d, 0.2 H, $CHNO_2$, J = 6.0); 5.27 (d, 0.2 H, $CHNO_2$, J = 2.0); 5.36 (d, 0.3 H, $CHNO_2$, J = 6.0); 5.45 (d, 0.3 H, $CHNO_2$, J = 2.0)
12	**1b** + **2a**	4[f]	**3m**	86 (1), 86 (2)	1.4780	1.60, 1.68 (both s, 3 H each, $C(5)Me_2$); 2.42, 2.52 (both m, 2 H each, 2 CH_2); 2.85 (dd, 1 H, $C(3)H_2$, ^1J = 18.5, ^2J = 7.5); 2.95 (dd, 1 H, $C(3)H_2$, ^1J = 18.5, ^2J = 7.5); 3.75 (s, 3 H, OMe); 4.90 (t, 1 H, C(4)H, J = 7.5); 9.70 (s, 1 H, CH=O)
13	**1b** + **2i**	6[f]	**3n**	88 (1), 88 (2)	1.4642	1.60, 1.68 (both s, 3 H each, 2 Me); 2.33, 2.47 (both m, 2 H each, $C(3)H_2$, $C(4)H_2$); 2.83 (dd, 1 H, CH_2, ^1J = 17.5, ^2J = 8.0); 2.93 (dd, 1 H, CH_2, ^1J = 17.5, ^2J = 8.0); 3.63, 3.75 (both s, 3 H each, 2 OMe); 4.89 (t, 1 H, =CH, J = 8.0)
14	**1c** + **2a**	6[f]	**3o**	73	1.4900	1.58, 1.62, 1.68 (all s, 3 H each, 3 Me); 2.00 (br.s, 4 H, $C(6)H_2$, $C(7)H_2$); 2.50, 2.58 (both m, 2 H each, 2 CH_2); 2.90 (dd, 1 H, $C(3)H_2$, ^1J = 16.5, ^2J = 8.0); 2.98 (dd, 1 H, $C(3)H_2$, ^1J = 16.5, ^2J = 8.0); 3.80 (s, 3 H, OMe); 4.92 (t, 1 H, C(4)H, J = 8.0); 5.03 (t, 1 H, C(8)H, J = 7.5); 9.73 (s, 1 H, CH=O)
15	**1c** + **2i**	10[f]	**3p**	82 (1), 82 (2)	1.4765	1.58, 1.62, 1.68 (all s, 3 H each, 3 Me); 2.02 (br.s, 4 H, 2 CH_2); 2.38, 2.50 (both m, 2 H each, $C(3)H_2$, $C(4)H_2$); 2.89 (dd, 1 H, CH_2, ^1J = 16.5, ^2J = 8.0); 2.97 (dd, 1 H, CH_2, ^1J = 16.5, ^2J = 8.0); 3.67, 3.78 (both s, 3 H each, 2 OMe); 4.92 (t, 1 H, =CH, J = 8.0); 5.03 (t, 1 H, =CH, J = 7.5)

[a] Reaction conditions: **1a—c** (100 mol.%), **2a—l** (100 mol.%), $KHCO_3$ (30 mol.%), [bmim][BF_4] (30 mol.%), 40 °C. The literature data are given in brackets.
[b] In the IR spectra of compounds **3b—p**, characteristic signals for nitro and carbonyl groups 1352—1372 (NO_2 symm.), 1556—1564 (NO_2 asymm.), 1716—1760 cm^{-1} (C=O) are presented.
[c] $KHCO_3$ was added (0.30 g, 3 mmol).
[d] The reactions were caried out in an ultrasonic tank without mechanical stirring.
[e] Data for the reaction of **2d** with ethyl nitroacetate.
[f] The reactions were caried out at 20 °C.

spectroscopy diastereomers are 3 : 2 : 3 : 2 and 1 : 1 : 1 : 1, respectively (see Table 2, entries *10* and *11*).

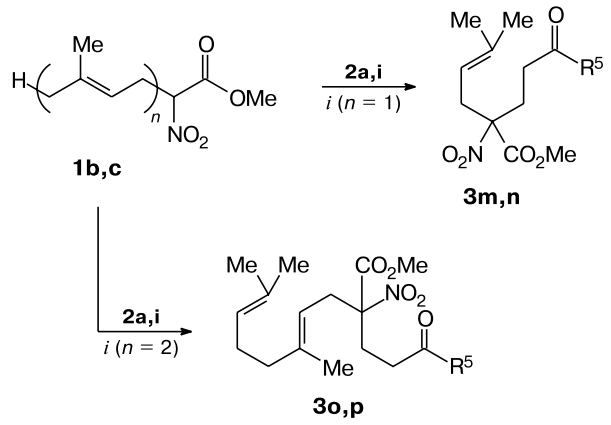
The reaction under consideration proceeds in heterogeneous system, consisting of the solid ($KHCO_3$) and two liquid (IL and eutectic solution of compounds **1—3**) phases (Fig. 1). Apparently, IL in this system simultaneously plays the role of the solvent, decreasing the viscosity of the reaction mixture, and of the phase-transfer catalyst (PTC). Probably, the poorly soluble in the reactants IL forms the so-called omega-phase[19] on the surface of the catalyst, in which the deprotonation of nitro compound **1** and the interaction of nitronate anion with olefin **2** take place. Reaction product **3**, as soon as it forms, is being removed from the zone of contact with the catalyst into organic phase, which increases the selectively of the process. For the reaction to be efficient, it is expedient to use the finely powdered $KHCO_3$. Apparently, ultrasound increases the degree of dispersion of the solid base, resulting in the intensification of the transfer of reagents and product between phases.

Scheme 4



i. $KHCO_3$ (30 mol.%), [bmim][BF_4] (30 mol.%), 40 °C, ultrasound.

Scheme 5



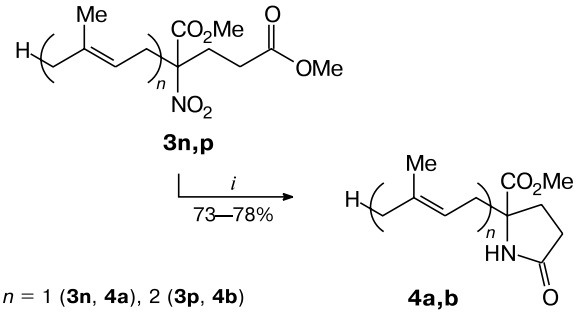
i. $KHCO_3$ (30 mol.%), [bmim][BF_4] (30 mol.%), 20 °C.

The $KHCO_3$—[bmim][BF_4] system is more chemically stable than the earlier proposed base—IL heterogeneous systems, containing the highly basic hydroxides[19c,20] or metal carbonates.[9,21] In contrast to the latter, no side deprotonation of 1-butyl-3-methylimidazolium cation to the corresponding carbene and its further transformations[22] under the reaction conditions take place.

The $KHCO_3$—[bmim][BF_4] catalytic system (see Fig. 1, the region bounded by a double line) is easily regenerated. After the removal of organic phase, fresh portions of reagents **1** and **2** were added to the residue and the process was carried out anew (see Table 2, entries *1*, *3*, *12*, *13*, and *15*). The system retained its activity at least in eight reaction cycles. Though after the fifth cycle, a small amount of the base (30 mol.%) was required to be added to make up for the loss by its gradual conversion to H_2CO_3.

The obtained α-nitro derivatives of δ-oxocarboxylic and glutaric acids **3g,h,k—p** containing isoprenoid substituents are of interest as intermediate products in the synthesis of isoprenoid amino acid analogs of the wound-healing medicine "metaprogerol".[23] On the model compounds **3n,p**, it was shown that the nitro group in the compounds obtained can be selectively reduced to amino groups upon treatment with Fe powder in AcOH with the C=C bond remaining intact (see also Ref. 24). Under the reaction conditions, the formed amino derivatives undergo cyclization to the corresponding 2-(poly)prenyl-5-oxopyrrolidine-2-carboxylates **4a,b** (Scheme 6).

Scheme 6



i. Fe, AcOH, reflux, 4 h.

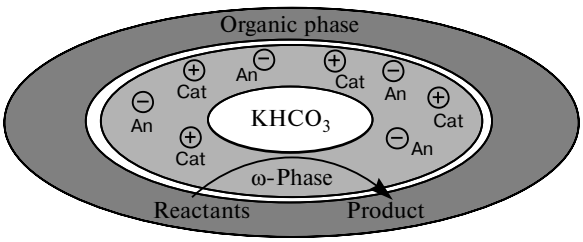


Fig. 1. Schematic representation of the catalytic system action. Cat = bmim, An = BF_4

In conclusion, we elaborated an efficient and meeting with the "green chemistry" requirements[25] method for the synthesis of α-nitro derivatives of glutaric and δ-oxocarboxylic acids by the reaction of nitroacetic ester derivatives with the electron-deficient olefins in heterogeneous catalytic system $KHCO_3$—[bmim][BF_4]. By this method, we were able to obtain the earlier unknown nitro derivatives of isoprenoids **3g,h,k—p**, including intermediate products for the synthesis of pharmacologically active isoprenoid amino acids.[26] Apparently, the regeneratable heterogeneous catalytic system $KHCO_3$—IL can be successfully used for the other base-promoted reactions of strong CH-acids with electrophiles.

Experimental

NMR spectra were recorded on a Bruker AM-300 (300.13 MHz (^{1}H)) and Bruker WM-250 (250.13 MHz (^{1}H) and 69.9 MHz (^{13}C)) spectrometers in $CDCl_3$. Chemical shifts for ^{1}H were determined from the internal standard, $SiMe_4$, for ^{13}C, from $CDCl_3$. IR spectra were recorded on a Specord M-82 instrument in KBr pellets or for the neat samples. Elemental analysis was performed on a Perkin—Elmer 2400 microanalyser. In ultrasound experiments, a 1.6-L RELTEK 1/100 TH ultrasonic tank with operating frequency 47 kHz was used. The conversion of reagents and the products purity were monitored by TLC on Silufol plates with 5% EtOAc in benzene as the eluent, the visualization was done by the UV-light and I_2 vapors. Purification of the synthesized compounds, if not stated otherwise, was performed by column chromatography on Acros silica gel (1.060—0.200 μm).

Starting compounds **1a** and **2a,b,d,e,i,j,l**, citronellal, phenacyltriphenylphosphonium bromide, 1-methylimidazole, 1,2-dimethylimidazole, K_2CO_3, Na_2CO_3, $KHCO_3$, and $NaHCO_3$ were purchased from Acros, prenyl bromide and geranyl bromide, from Aldrich and were used in the reactions without additional purification. Activated olefins **2c**,[27] **2f**,[16c] **2g**,[28] and **2k** [29] and ionic liquids [bmim][BF_4],[30] [bmim][PF_6],[31] and [bdmim][BF_4][32] were synthesized by the known procedures.

Methyl 5-methyl-2-nitrohex-4-enoate (1b). A solution of 1-bromo-3-methylbut-2-ene (1.49 g, 10 mmol) in DMF (2 mL) was added dropwise with stirring to a cooled to −10 °C suspension of K_2CO_3 (1.66 g, 12 mmol), [BTEA]Cl (0.10 g, 0.5 mmol), and methyl nitroacetate (1.19 g, 10 mmol) in the same solvent (3 mL). The reaction mixture was vigorously stirred for 0.5 h at −10 °C, then for 2 h at 20 °C (TLC monitoring), cooled with ice-cold water to +5 °C, carefully acidified with 1 *N* HCl to pH ~2. The obtained solution was extracted with Et_2O (3×10 mL), the combined organic extract was sequentially washed with brine (2×20 mL) and water (20 mL) and dried with $MgSO_4$. The filtrate was concentrated at reduced pressure (40 °C, 40 Torr), the residue was distilled *in vacuo* to obtain **1b** (1.22 g, 65%), b.p. 120—125 °C (10 Torr), n_D^{20} 1.4530. Found (%): C, 51.58; H, 6.84; N, 7.30. $C_8H_{13}NO_4$. Calculated (%): C, 51.33; H, 7.00; N, 7.48. ^{1}H NMR, δ: 1.62, 1.70 (both s, 3 H each, 2 Me); 2.80, 2.95 (both m, 1 H each, CH_2); 3.80 (s, 3 H, OMe); 4.95—5.50 (m, 2 H, =CH, $CHNO_2$). ^{13}C NMR, δ: 17.8 (Me); 23.7 (Me); 24.2 (C(3)); 53.4 (OMe); 87.7 (C(2)); 115.8 (C(4)); 138.1 (C(5)); 164.8 (C(1)).

Methyl 5,9-dimethyl-2-nitrodeca-4,8-dienoate (1c). The product was synthesized similarly to **1b** from methyl nitroacetate (1.19 g, 10 mmol), geranyl bromide (2.17 g, 10 mmol), K_2CO_3 (1.66 g, 12 mmol), and [BTEA]Cl (0.10 g, 0.5 mmol). The initial reaction temperature, 0 °C, the stirring time at 20 °C, 7 h. Product **1c** (1.35 g, 53%) was obtained, b.p. 135—142 °C (0.5 Torr), n_D^{20} 1.4757. Found (%): C, 61.41; H, 8.49; N, 5.34. $C_{13}H_{21}NO_4$. Calculated (%): C, 61.16; H, 8.29; N, 5.49. ^{1}H NMR, δ: 1.55—1.75 (m, 9 H, 3 MeC=); 1.97—2.12 (m, 4 H, CH_2CH_2); 2.85, 3.02 (both m, 1 H each, C$\underline{H}_2$CHNO$_2$); 3.81 (s, 3 H, OMe); 5.00—5.12 (m, 3 H, 2 =CH; $CHNO_2$). ^{13}C NMR, δ: 16.1 (C(5)$\underline{Me}$); 17.6, 25.6 (both C(9)$\underline{Me}$); 26.4 (C(7)); 29.1 (C(3)); 39.6 (C(6)); 53.4 (OMe); 87.7 (C(2)); 115.7 (C(4)); 123.6 (C(8)); 131.8 (C(9)); 141.7 (C(5)); 164.8 (C(1)).

(2*E*)-5,9-Dimethyl-1-phenyldeca-2,8-dien-1-one (2h). Citronellal (1.54 g, 10 mmol) was added to a stirred suspension of K_2CO_3 (2.10 g, 15 mmol) and phenacyltriphenylphosphonium bromide (4.60 g, 10 mmol) in dioxane (15 mL). The reaction mixture was vigorously stirred for 6 h at 100 °C and cooled to ~20 °C, the precipitate was filtered off, the filtrate was concentrated under reduced pressure (40 °C, 40 Torr), the residue was distilled *in vacuo* to afford **2h** (1.60 g, 62%), b.p. 130—135 °C (0.7 Torr), n_D^{20} 1.5305. Found (%): C, 84.59; H, 9.26. $C_{18}H_{24}O$. Calculated (%): C, 84.32; H, 9.44. ^{1}H NMR, δ: 0.97 (m, 3 H, C(12)H_3); 1.20—1.45 (m, 2 H, C(6)H_2); 1.60, 1.67 (both s, 3 H each, C(10)H_3, C(11)H_3); 1.90—2.35 (m, 5 H, C(4)H_2, C(5)H, C(7)H_2); 5.10 (t, 1 H, C(8)H, J = 7.5 Hz); 6.85 (d, 1 H, C(2)H, J = 16.0 Hz); 7.05 (m, 1 H, C(3)H); 7.40—7.50 (m, 3 H, Ph); 7.90 (d, 2 H, Ph, J = 7.0 Hz). ^{13}C NMR, δ: 17.7 (C(10)); 19.6 (C(12)); 25.6, 25.8 (C(7), C(11)); 32.7 (C(5)); 36.8 (C(6)); 40.3 (C(4)); 124.5 (C(8)); 127.2 (C(2)); 128.0, 128.4, 132.6 (all CH of phenyl); 131.5 (C(9)); 138.1 (C of phenyl); 148.8 (C(3)); 190.7 (C(1)).

Reaction of nitro compounds 1 with activated olefins 2 (general procedure). A mixture of the powdered in a porcelain mortar $KHCO_3$ (0.30 g, 3 mmol), [bmim][BF_4] (0.70 g, 3 mmol), nitro compound **1** (10 mmol), and olefin **2** (10 mmol) was vigorously stirred with a magnetic stirrer or kept in ultrasonic tank for 4—40 h at 20—40 °C (Table 2) until the starting compounds disappeared (TLC monitoring). The reaction mixture was sequentially extracted with Et_2O (2×5 mL) and benzene (2×5 mL). The combined organic extract was washed with water (3×25 mL), dried with $MgSO_4$, and the solvent was evaporated at reduced pressure (40 °C, 40 Torr). The crude product was purified on a column with SiO_2, sequentially eluenting with *n*-hexane, *n*-hexane—benzene mixture (1 : 1), and benzene. The yields, physical and chemical properties, and ^{1}H NMR spectroscopic data of compounds **3** are given in Table 2. Elemental analysis data and ^{13}C NMR spectroscopic data of the newly synthesized products **3f—h,j—p** are given below.

Methyl 5-cyclopropyl-2-nitro-5-oxo-3-phenylpentanoate (3f). Colorless crystals, m.p. 70—71 °C (*n*-hexane). Found (%): C, 62.07; H, 6.04; N, 4.65. $C_{15}H_{17}NO_5$. Calculated (%): C, 61.85; H, 5.88; N, 4.81. ^{13}C NMR, δ: 10.4, 10.5, 10.7, 10.8, 16.8, 17.5 (all C of cyclopropyl); 44.6, 47.7 (both C(3)); 45.9, 46.0 (both OMe); 86.3, 87.0 (both C(2)); 127.4, 127.6, 128.0, 128.2, 128.5, 128.8, 128.9 (all C of phenyl); 138.2 (C(1)); 206.9, 207.6 (both C(5)).

Methyl 5,9-dimethyl-2-nitro-3-(2-oxopropyl)dec-8-enoate (3g). Colorless viscous oil. Found (%): C, 61.17; H, 8.71; N, 4.61. $C_{16}H_{27}NO_5$. Calculated (%): C, 61.32; H, 8.68; N, 4.47. ^{13}C NMR, δ: 17.6, 18.8, 19.2, 19.3, 19.9 (all Me); 25.0, 25.1, 25.2, 25.6 (all C(7)); 29.5, 29.6, 29.7, 29.8, 30.1 (all C(5)); 32.6, 32.7, 32.8 (all $\underline{Me}$C=O); 35.9, 36.6, 36.8, 37.1, 37.4, 37.8, 38.1 (all C(3), C(4), C(6)); 43.0, 43.3, 43.6, 43.9 (all $\underline{C}H_2$C=O); 53.2, 53.3 (both OMe); 89.0, 89.4, 89.5, 90.0 (all C(2)); 124.2, 124.3 (both C(8)); 131.4, 131.5 (both C(9)); 164.3, 164.4, 164.6, 164.7 (all C(1)); 205.8, 206.0, 206.1, 206.3 (all C=O).

Methyl 5,9-dimethyl-2-nitro-3-(2-oxo-2-phenylethyl)dec-8-enoate (3h). Colorless viscous oil. Found (%): C, 66.89; H, 7.60; N, 3.88. $C_{21}H_{29}NO_5$. Calculated (%): C, 67.18; H, 7.79; N, 3.73. ^{13}C NMR, δ: 17.7 (C(10)); 19.1, 19.5, 20.0 (all C(12)); 25.2, 25.3, 25.4, 25.7 (all C(7), C(11)); 29.8, 30.0, 30.1, 30.4 (all C(5)); 33.0, 33.1, 33.2, 33.3 (all C(3)); 36.1, 37.0, 37.5, 38.0, 38.1, 38.3, 38.4, 38.7, 38.9, 39.3 (all C(4), C(6), $\underline{C}H_2$C=O); 53.3, 53.4, 53.5 (all OMe); 89.3, 89.8, 90.3 (all C(2)); 124.3, 124.4 (both C(8)); 128.0, 128.8, 133.5, 136.7

(all C of phenyl); 131.6 (C(9)); 163.1, 164.8 (both C(1)); 197.3 (C=O).

Dimethyl 3-methyl-2-nitropentanedioate (3j). Colorless oil. Found (%): C, 44.03; H, 6.11; N, 6.26. $C_8H_{13}NO_6$. Calculated (%): C, 43.84; H, 5.98; N, 6.39. ^{13}C NMR, δ: 15.8, 15.9 (both C(3)Me); 31.4 (C(3)); 36.5, 36.6 (both C(4)); 51.8, 53.3 (both OMe); 90.6 (C(2)); 164.0, 171.5 (both C=O).

Methyl 3-bis(ethoxycarbonyl)methyl-5,9-dimethyl-2-nitrodec-8-enoate (3k). Colorless oil. Found (%): C, 58.05; H, 7.93; N, 3.21. $C_{20}H_{33}NO_8$. Calculated (%): C, 57.82; H, 8.01; N, 3.37. ^{13}C NMR, δ: 13.9 (MeCH$_2$); 17.6 (MeCH); 18.8; 19.0, 19.2, 19.5 (all MeC=); 25.2, 25.3, 25.5, 25.6 (all CH$_2$CH=); 30.0, 30.2, 30.4, 30.6 (all MeCH); 35.7, 36.0, 36.1, 36.4, 36.7, 36.8, 37.0, 37.3 (all CH$_2$CH); 52.1, 52.5 (C(2), C(3)); 53.2, 53.4 (OMe); 62.0 (MeCH$_2$O); 88.3, 88.5, 88.7, 89.1 (all C(1)); 124.3 (=CH); 131.5 (Me$_2$C=); 163.0, 164.4; 167.7, 167.8, 167.9, 168.0 (all CO$_2$).

Methyl 2-[2-methyl-3-oxo-5-(prop-1-en-2-yl)cyclohexyl]-2-nitroacetate (3l). Colorless oil. Found (%): C, 58.23; H, 7.28; N, 5.06. $C_{13}H_{19}NO_5$. Calculated (%): C, 57.98; H, 7.11; N, 5.20. ^{13}C NMR, δ: 11.3, 11.4, 12.4, 12.9 (all C(2)Me); 21.1, 21.2, 21.4, 21.5 (all MeC=); 27.8, 28.1, 31.3, 31.9 (all C(6)); 39.6, 39.8, 40.0, 40.4 (all C(5)); 43.3, 43.5, 43.7, 44.0, 44.8, 45.0, 45.3, 45.6, 45.7, 45.9, 46.2, 46.3 (all C(1), C(2), C(4)); 53.3, 53.5, 53.6, 53.7 (all OMe); 88.2, 88.3, 88.4, 88.7 (all C(2)); 110.5, 110.6, 112.6, 112.8 (all CH$_2$=C); 145.6, 146.2 (both C=CH$_2$); 163.6, 163.9, 164.0, 164.1 (all CO$_2$); 208.4, 209.3 (both C(3)).

Methyl 5-methyl-2-nitro-(3-oxopropyl)hex-4-enoate (3m). Colorless oil. Found (%): C, 54.50; H, 6.92; N, 5.59. $C_{11}H_{17}NO_5$. Calculated (%): C, 54.31; H, 7.04; N, 5.76. ^{13}C NMR, δ: 18.0 (C(6)); 26.0 (C(5)Me); 26.2 (C(3)); 34.0, 38.5 (both CH$_2$); 53.4 (OMe); 94.8 (C(2)); 114.4 (C(4)); 138.9 (C(5)); 166.9 (C(1)); 199.1 (C=O).

Dimethyl 2-(3-methylbut-2-enyl)-2-nitropentanedioate (3n). Colorless oil. Found (%): C, 52.92; H, 6.88; N, 4.95. $C_{12}H_{19}NO_6$. Calculated (%): C, 52.74; H, 7.01; N, 5.13. ^{13}C NMR, δ: 18.0, 28.7 (both Me); 26.1 (CH$_2$); 28.9 (C(3)); 33.7 (C(4)); 51.9, 53.3 (both OMe); 94.8 (C(2)); 114.4 (=CH); 138.7 (=CMe$_2$); 166.9 (C(1)); 172.1 (C(5)).

Methyl (*E*)-5,9-dimethyl-2-nitro-2-(3-oxopropyl)deca-4,8-dienoate (3o). Colorless oil. Found (%): C, 61.49; H, 7.93; N, 4.68. $C_{16}H_{25}NO_5$. Calculated (%): C, 61.72; H, 8.09; N, 4.50. ^{13}C NMR, δ: 19.2, 20.7, 25.1 (all MeC=); 28.0, 28.4, 28.6, 31.9, 39.9 (all CH$_2$); 54.5 (OMe); 93.9 (C(2)); 112.6 (C(4)), 121.4 (C(8)); 129.4 (C(9)); 142.4 (C(5)); 162.7 (C(1)); 193.4 (C=O).

Dimethyl 2-((*E*)-3,7-dimethylocta-2,6-dienyl)-2-nitropentanedioate (3p). Colorless oil. Found (%): C, 60.15; H, 8.11; N, 3.97. $C_{17}H_{27}NO_6$. Calculated (%): C, 59.81; H, 7.97; N, 4.10. ^{13}C NMR, δ: 16.3, 17.7, 25.7 (all MeC=); 26.3, 28.7 (CH$_2$CH=); 28.8 (C(3)); 33.4, 33.5 (both C(4)); 39.8 (CH$_2$); 51.9, 53.3 (both OMe); 94.8 (C(2)); 114.4, 123.6 (both =CH); 131.8 (=CMe$_2$); 142.3 (=C(Me)CH$_2$); 166.9 (C(1)); 172.1 (C(5)).

Recovery and recycle of KHCO$_3$—[bmim][BF$_4$] catalytic system in the Michael reaction between compounds 1 and 2. New portions of reagents **1** and **2** (10 mmol each) were added to a mixture of KHCO$_3$ and [bmim][BF$_4$] left after the extraction of adduct **3**, and further reaction was carried out as described above (see Table 2, entries *1*, *3*, *12*, *13*, and *15*). After the reaction was repeated five times, KHCO$_3$ (0.30 g, 3 mmol) was added to the residue and the activated catalyst was used again. After the reaction was repeated eight times, CHCl$_3$ (10 mL) was added to the recovered catalytic system, precipitate of KHCO$_3$ was filtered off, the filtrate was concentrated on a rotary evaporator, the oily residue was kept 3 h at 50 °C (10 Torr) to recover 0.51 g (78%) of IL, which according to the ^{1}H NMR data was identical to the freshly prepared sample of [bmim][BF$_4$] (see Ref. 30).

Methyl 2-(3-methylbut-2-enyl)-5-oxopyrrolidine-2-carboxylate (4a). A mixture of nitro compound **3n** (0.20 g, 0.73 mmol), Fe powder (0.41 g, 7.3 mmol), and glacial AcOH (2 mL) was refluxed for 4 h (until **3n** disappeared, TLC monitoring). The reaction mixture was cooled to 20 °C, the excess of AcOH was removed on a rotary evaporator (40 °C, 15 Torr). Ethyl acetate (15 mL) was added to the residue, the inorganic precipitate was filtered off and washed on the filter with EtOAc (2×5 mL). The combined filtrate was concentrated on a rotary evaporator, the residue was chromatographed on a column with silica gel, sequentially eluting with Et$_2$O—light petroleum (1 : 5) and EtOAc—light petroleum (from 1 : 5 to 1 : 1) to obtain 0.11 g (73%) of **4a**. Yellow oil, n_D^{20} 1.4838. Found (%): C, 62.73; H, 8.26; N, 6.49. $C_{11}H_{17}NO_3$. Calculated (%): C, 62.54; H, 8.11; N, 6.63. IR, ν/cm^{-1}: 1700 (C=O), 1740 (C=O), 3432 (NH). ^{1}H NMR, δ: 1.61, 1.71 (both s, 3 H each, Me$_2$C=); 2.02—2.20 (m, 1 H, =CHCHH); 2.30—2.65 (m, 5 H, 2 CH$_2$, =CHCHH); 3.75 (s, 3 H, OMe); 5.02 (t, 1 H, =CH, J = 7.3 Hz); 6.08 (br.s, 1 H, NH). ^{13}C NMR, δ: 17.9, 25.9 (Me$_2$C=, CH$_2$CH=); 29.9 (CH$_2$C=O); 37.4 (CH$_2$); 52.5 (OMe); 66.0 (CCO$_2$Me); 116.6 (=CH); 137.1 (=CMe$_2$); 174.0, 177.2 (both C=O).

Methyl 2-((*E*)-3,7-dimethylocta-2,6-dienyl)-5-oxopyrrolidine-2-carboxylate (4b). The product was obtained similarly to **4a** from nitro compound **3p** (0.20 g, 0.58 mmol), Fe powder (0.33 g, 5.8 mmol), and glacial AcOH (2 mL) to isolate 0.13 g (78%) of **4b**. Yellow oil, n_D^{20} 1.4872. Found (%): C, 69.01; H, 9.14; N, 4.88. $C_{16}H_{25}NO_3$. Calculated (%): C, 68.79; H, 9.02; N, 5.01. IR, ν/cm^{-1}: 1704 (C=O), 1740 (C=O), 3428 (NH). ^{1}H NMR, δ: 1.60 (s, 6 H, 2 MeC=); 1.68 (s, 3 H, MeC=); 1.80—2.15 (m, 5 H, 2 CH$_2$, =CHCHH); 2.30—2.60 (m, 5 H, 2 CH$_2$, =CHCHH); 3.72 (s, 3 H, OMe); 5.01 (t, 2 H, 2 =CH, J = 7.3 Hz); 6.29 (br.s, 1 H, NH). ^{13}C NMR, δ: 16.2, 17.7, 25.6 (all MeC=); 26.3, 29.9, 30.0 (all CH$_2$CH=, CH$_2$C=O); 37.4 (CH$_2$); 39.8 (CH$_2$C=); 52.5 (OMe); 66.0 (CCO$_2$Me); 116.6, 123.9 (both =CH); 131.7, 140.8 (both =CMe$_2$); 173.9, 177.2 (both C=O).

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