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Solvent-Free Aziridination of α–Nitroalkenes

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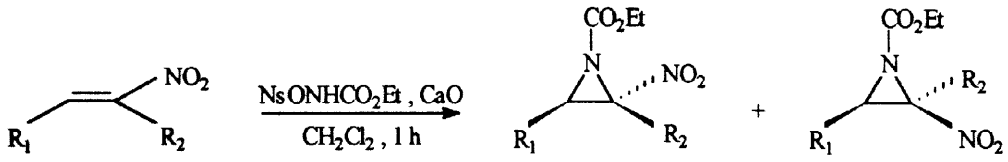
Abstract: NsONHCO$_2$Et in the presence of CaO reacts without solvent with α-nitroalkenes to give 1-(ethoxycarbonyl)-2-nitroaziridines (62-84%). A possible involvement of an aza-Michael route is proposed on the basis of regio- and stereochemical reaction outcome, compared also with the results of thermolysis of ethyl azidoformate on the same α-nitroalkenes.

Previously we have reported that conjugated (*E*)-nitroalkenes[1] can be aziridinated by our procedure, which is based on the use of solid inorganic bases[2] as the deprotonating agents of ethyl [(4-nitrobenzenesulphonyl)oxy]carbamate (NsONHCO$_2$Et).[3] The method provides a useful means for synthesis of 1-(ethoxycarbonyl)-2-nitroaziridines (Scheme 1, 62-84% yields), the main product having the same stereochemistry as the substrate.

We have now expanded the study to improve the methodology and to gain more insight into the reaction pathway. In our procedure, the use of calcium oxide instead of triethylamine allowed us to reduce both the excess of the reactants and the amount of dichloromethane, *i.e.* a threefold excess of the reactants (NsONHCO$_2$Et and CaO) was used with respect to nitroalkene.



1 a-i **2 a-i** (main) **3 c-i**

a: R_1···R_2 = -$(CH_2)_4$- **d**: R_1 = Et ; R_2 = Me **g**: R_1 = $(CH_2)_2$Ph ; R_2 = Me
b: R_1···R_2 = -$(CH_2)_6$- **e**: R_1 = *i*-Pr ; R_2 = Me **h**: R_1 = $(CH_2)_2$Ph ; R_2 = Et
c: R_1 = R_2 = Me **f**: R_1 = Cyclohexyl ; R_2 = Me **i**: R_1 = $(CH_2)_5CH_3$; R_2 = $(CH_2)_2CO_2Me$

Scheme 1

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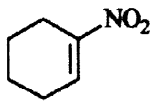
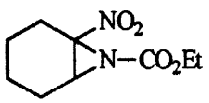
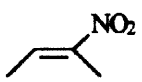
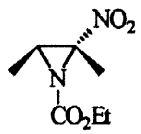
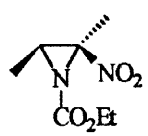
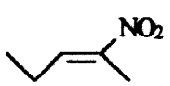
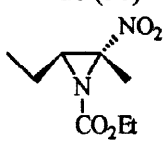
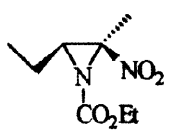
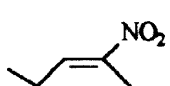
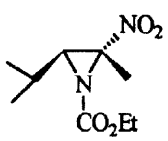
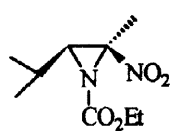
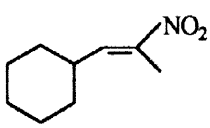
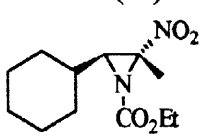
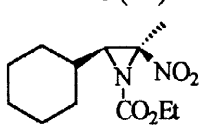
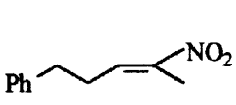
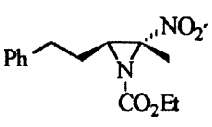
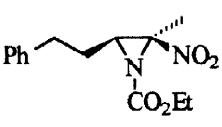
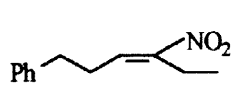
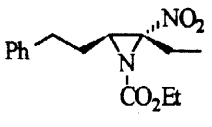
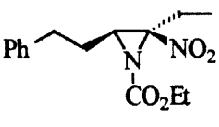
We wish to report here that *the solvent can be completely removed* from the reaction by grinding the reactants together with the substrate in a mortar. In this way, using *equimolar amounts* of reactants and substrate and shorter reaction times became possible and an organic solvent was used just during the work up.

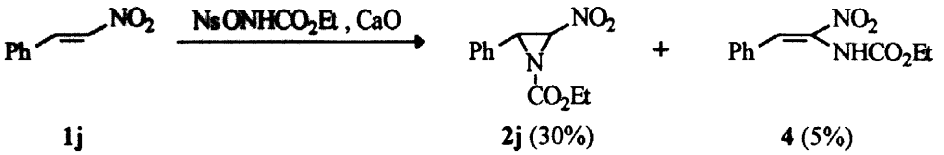
The results in Table 1 show that the main aziridines always retain the same configuration of the substrates and the isomeric aziridines are minor products.

Table 1. Amination of (*E*)-Nitroalkenes with $NsONHCO_2Et$ and CaO without Solvent.

Substrate	Products (yield, %)[a]	
		
1a	**2a** (89)	
		
1c	**2c** (38)	**3c** (5)
		
1d	**2d** (58)	**3d** (6)
		
1e	**2e** (63)	**3e** (12)
		
1f	**2f** (70)	**3f** (8)
		
1g	**2g** (70)	**3g** (16)
		
1h	**2h** (72)	**3h** (13)

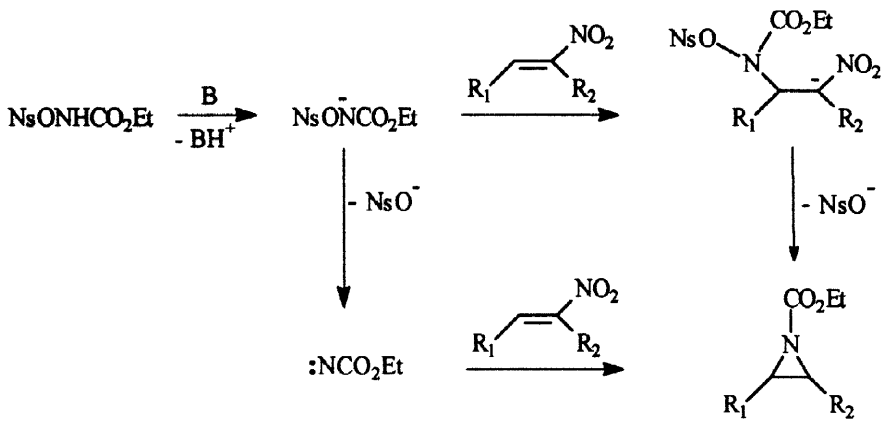
[a] Lower yields observed for the substrates **1c** and **1d** are due to loss of themselves by evaporation during the reaction.

(*E*)-β-Nitrostyrene (**1j**), previously unreactive in reactions performed in dichloromethane, in these conditions gave the corresponding aziridine **2j**, although in modest yield and in mixture with the carbamate **4** (Scheme 2).

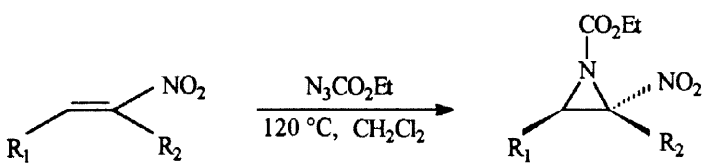


Scheme 2

Aziridination could involve either a direct (ethoxycarbonyl)nitrene (NCO_2Et) addition to the nitroalkenes, or an aza-Michael addition[4] of $NsON^-CO_2Et$ anion[5] to the carbon β to the nitro group followed by ring-closure by elimination of the good leaving group NsO^-.



We cannot rule out that both pathways are operating, although we believe this second hypothesis to be more likely, bearing in mind the electron-poor character of nitroalkenes, that make them useful Michael-acceptors,[6] but not very suitable to undergo an electrophilic addition by a nitrene. On the other hand we tested the same nitroalkenes in thermolysis reactions of ethyl azidoformate (N_3CO_2Et), a reaction that it is known to generate NCO_2Et.[7] The results, depicted in Scheme 3, show that the yields are always lower and only the aziridines with *retention of configuration* are produced, as expected by a singlet nitrene as intermediate.

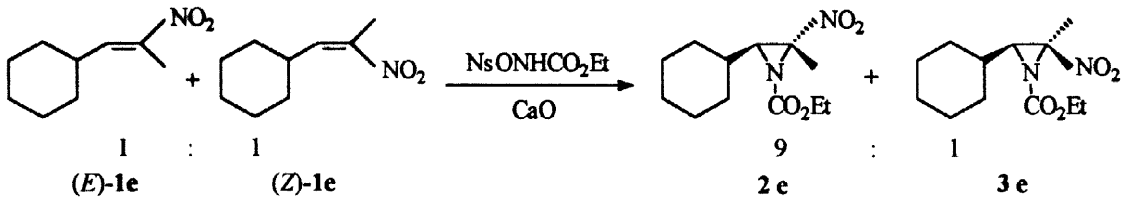


1a, c, e, f

	Yield (%)
2a	24
2c	26
2e	18
2f	24

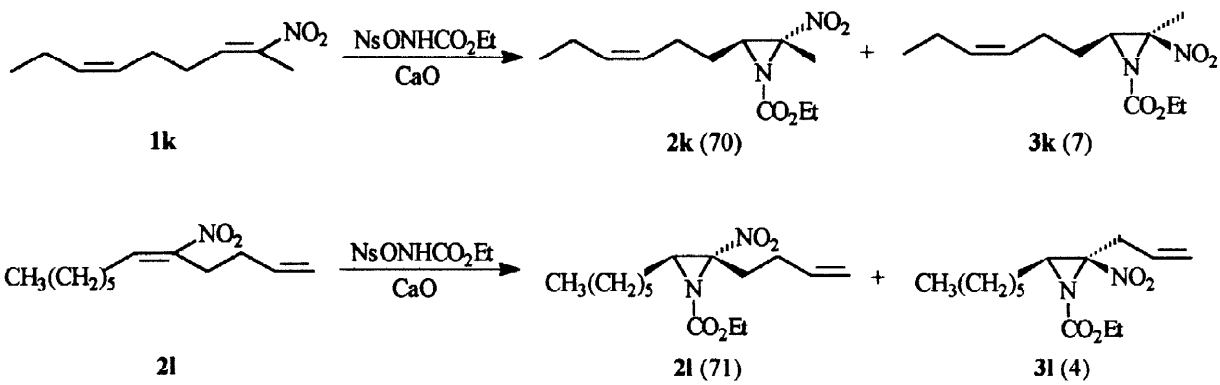
Scheme 3

We believe that an aza-Michael route is also supported by two other experimental findings: an equimolar mixture of the (*E/Z*)-nitroalkene **1e**, obtained by partial photo-isomerization of the (*E*)-isomer and reacted with $NsONHCO_2Et$ and CaO, gave the same ratio of aziridines **2e** and **3e** (Scheme 4) as that coming from the pure (*E*)-isomer **1e**.



Scheme 4

In addition we observed high regioselectivity in the reaction of nitrodienes **1k** and **1l**, under the same conditions where only the aziridines coming from the attack to the conjugated double bond were formed (Scheme 5). This is the first time we have observed this regioselectivity.[8]



Scheme 5

In conclusion we describe two alternative methods to obtain 1-(ethoxycarbonyl)-2-nitroaziridines from α-nitroalkenes with high stereoselectivity in moderate yields by thermolysis of ethyl azidoformate or with lower stereoselectivity but in good yields using $NsONHCO_2Et$ and CaO without any solvent. We believe the latter conditions might be considered an answer to the increasing demand for environmentally friendly methods.[9]

Experimental

GC analyses were performed on a HP 5890 Series II gas chromatograph with a capillary column (methyl silicone, 12.5 m x 0.2 mm). GC-MS were done on a HP G1800A GCD System with a capillary column (phenyl methyl silicone, 30 m x 0.25 mm). ^1H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Varian XL-300 spectrometer, with $CHCl_3$ as an internal standard. IR spectra in CCl_4 were done with a Perkin-Elmer 1600

Series FTIR spectrometer. $NsONHCO_2Et$,[3] N_3CO_2Et[7] (*CAUTION: it might explode and its vapours are toxic*) and the nitroalkenes[10] (excluding **1a** and **1j**, commercially available) were prepared according to literature methods.

Reaction with $NsONHCO_2Et$ and CaO. General Procedure. Equimolar amounts of nitroalkene, CaO and $NsONHCO_2Et$ were ground in a mortar. After 20 min petroleum ether was added to precipitate the salt. After filtration, the crude mixture was concentrated *in vacuo* and the 1-(ethoxycarbonyl)-2-nitroaziridines were purified by flash chromatography on silica gel (hexane/ethyl acetate, 8:2). The yields were reported in Table 1.

2a: IR (CCl_4) 1731, 1555 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (*t*, 3 H, CH_3), 1.31-1.52 (*m*, 4 H, CH_2), 1.87-1.98 (*m*, 2 H, CH_2), 2.30-2.44, 2.61-2.79 (*m*, 2 H, CH_2CH), 3.36 (*dd*, 1 H, CH), 4.15 (*q*, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 13.90 (CH_3), 18.93, 19.34, 22.94, 23.5 (CH_2), 44.01 (CH), 63.69 (OCH_2), 75.38 (C), 157.90 (CO); GC-MS *m/z* 168 (M^+ -46, 7), 96 (42), 95 (32), 94 (14), 79 (11), 69 (21), 68 (11), 67 (32), 55 (100), 54 (23), 42 (21), 41 (60).

2b: IR (CCl_4) 1736, 1543 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (*t*, 3 H, CH_3), 1.39-1.69 (*m*, 10 H, CH_2), 2.28-2.39, 2.95-3.08 (*m*, 2 H, CH_2CH), 3.35 (*dd*, 1 H, CH), 4.18 (*q*, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 13.97 (CH_3), 25.07, 25.19, 26.08, 26.84, 27.35 (CH_2), 47.47 (CH), 63.04 (OCH_2), 78.71 (C), 157.51 (CO) ; GC-MS *m/z* 196 (M^+ -46, 10), 168 (11), 124 (30), 122 (37), 120 (22), 110 (15), 108 (13), 107 (40), 96 (12), 95 (30), 94 (25), 83 (17), 82 (35), 81 (53), 80 (32), 79 (50), 69 (22), 68 (21), 67 (42), 56 (17), 55 (100), 54 (35), 53 (16), 44 (10), 43 (17), 42 (19), 41(59).

3c:[11] ^1H NMR ($CDCl_3$) δ 1.25 (*t*, 3 H, CH_2CH_3), 1.35 (*d*, 3 H, CH_3CH), 1.94 (*s*, 3 H, CH_3), 2.74 (*q*, 1 H, CH), 4.19 (*m*, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 12.74 (CH_3CH), 14.32 (CH_2CH_3), 17.02 (CH_3), 44.05 (CH), 63.44 (CH_2), 76.39 (C), 157.71 (CO).

2d: IR (CCl_4) 1742, 1561 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (*t*, 3 H, CH_2CH_3), 1.24 (*t*, 3 H, CH_3CH_2O), 1.48-1.69 (*m*, 2 H, CH_3CH_2), 1.87 (*s*, 3 H, CH_3), 3.17 (*dd*, 1 H, CH), 4.18 (*q*, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 10.78 (CH_2CH_3), 14.01 (CH_3), 14.21 (CH_3CH_2O), 21.91 (CH_2), 50.04 (CH), 63.12 (OCH_2), 76.59 (C), 157.29 (CO); GC-MS *m/z* 156 (M^+ -46, 4), 110 (10), 96 (11), 84 (18), 74 (10), 70 (12), 68 (34), 59 (10), 57 (26), 43 (11), 42 (100), 41 (29).

3d: ^1H NMR ($CDCl_3$) δ 1.06 (*t*, 3 H, CH_2CH_3), 1.30 (*t*, 3 H, CH_3CH_2O), 1.48-1.69 (*m*, 2 H, CH_3CH_2), 1.92 (*s*, 3 H, CH_3), 2.62 (*dd*, 1 H, CH), 4.18 (*m*, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 10.59 (CH_2CH_3), 14.30 (CH_3), 17.23 (CH_3CH_2O), 21.06 (CH_2), 49.87 (CH), 63.49 (OCH_2), 76.59 (C), 157.29 (CO).

2e: IR (CCl_4) 1749, 1565 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (*d*, 3 H, CH_3CH), 1.14 (*d*, 3 H CH_3CH), 1.21 (*t*, 3 H, CH_3CH_2), 1.23-1.34 (*m*, 1 H, CH), 1.86 (*s*, 3 H, CH_3), 2.93 (*d*, 1 H, CHN) 4.14 (*q*, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 13.94, 14.02 (CH_3CH_2), 18.76, 19.87 (CH_3CH), 28.76 (CH), 54.74 (CHN), 63.02 (CH_2), 76.79 (C), 157.52 (CO); GC-MS *m/z* 170 (M^+ -46, 5); 98 (12), 82 (29), 55 (14), 43 (20), 42 (100), 41 (19).

3e: ^{1}H NMR ($CDCl_3$) δ 0.90 (*d*, 3 H, C*H*$_3$CH), 1.14 (*d*, 3 H C*H*$_3$CH), 1.21 (*t*, 3 H, C*H*$_3$CH$_2$), 1.23-1.34 (*m*, 1 H, CH), 1.92 (*s*, 3 H, CH_3), 2.35 (*d*, 1 H, CHN) 4.14 (*m*, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 13.67, 13.85 (*C*H$_3$CH$_2$), 18.44, 20.03 (*C*H$_3$CH), 27.67 (CH), 54.48 (CHN), 63.38 (CH_2), 76.79 (C), 157.52 (CO).

2f: IR (CCl_4) 1749, 1542 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (*t*, 3 H, C*H*$_3$CH$_2$), 1.10-1.72 (*m*, 11 H, CH_2, CH), 1.82 (*s*, 3 H, CH_3), 2.93 (*d*, 1 H, CHN), 4.23 (*q*, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 13.89 (CH_3), 14.09 (*C*H$_3$CH$_2$O), 24.92, 24.97, 25.52, 29.16, 30.12 (CH_2), 37.65 (CH), 53.32 (CHN), 62.94 (OCH_2), 76.54 (C), 157.54 (CO); GC-MS *m/z* 210 (M^+ -46, 3), 95 (22), 83 (11), 81 (16), 67 (15), 55 (20), 54 (10), 42 (100), 41 (21).

3f: ^{1}H NMR ($CDCl_3$) δ 1.05 (*t*, 3 H, C*H*$_3$CH$_2$), 1.10-1.72 (*m*, 11 H, CH_2, CH), 1.90 (*s*, 3 H, CH_3), 2.38 (*d*, 1 H, CHN), 4.13 (*m*, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 13.61 (CH_3), 13.98 (*C*H$_3$CH$_2$O), 24.77, 24.83, 25.14, 28.88, 30.21 (CH_2), 36.38 (CH), 52.02 (CHN), 65.34 (OCH_2), 76.54 (C), 157.54 (CO).

2g: IR (CCl_4) 1757, 1568 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (*t*, 3 H, C*H*$_3$CH$_2$), 1.66 (*s*, 3 H, CH_3), 1.81-1.90 (*m*, 2 H, C*H*$_2$CH), 2.82-2.93 (*m*, 2 H, PhC*H*$_2$), 3.27 (*dd*, 1 H, CH), 4.21 (*q*, 2 H, OCH_2), 7.20-7.31 (*m*, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 13.99, 14.26 (CH_3), 30.40, 32.84 (CH_2), 48.46 (CH), 63.25 (OCH_2), 76.72 (CNO_2), 126.58, 128.44, 128.73 (CH), 140.04 (C), 157.33 (CO); GC-MS *m/z* 278 (M^+, <1), 232 (16), 143 (22), 128 (10), 117 (10), 92 (13), 91 (100), 68 (28), 65 (12), 42 (39).

3g: ^{1}H NMR ($CDCl_3$) δ 1.30 (*t*, 3 H, C*H*$_3$CH$_2$), 1.78-1.88 (*m*, 2 H, C*H*$_2$CH), 1.91 (*s*, 3 H, CH_3), 2.69 (*dd*, 1 H, CH), 2.83 (*m*, 2 H, PhC*H*$_2$), 4.26 (*m*, 2 H, CH_2O), 7.20-7.30 (*m*, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.89, 17.50 (CH_3), 29.82, 30.01 (CH_2), 48.49 (CH), 64.10 (OCH_2), 77.50 (CNO_2), 126.87, 129.03, 129.10 (CH), 140.51 (C), 157.56 (CO).

2h: IR (CCl_4) 1747, 1559 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (*t*, 3 H, C*H*$_3$CH$_2$), 1.24 (*t*, 3 H, C*H*$_3$CH$_2$O), 1.62-1.75 (*m*, 1 H, C*H*$_2$CH), 1.87 (*q*, 2 H, CH$_3$C*H*$_2$), 2.18-2.29 (*m*, 1 H, C*H*$_2$CH), 2.63-2.95 (*m*, 2 H, PhC*H*$_2$), 3.23 (*dd*, 1 H, CH), 4.20 (*q*, 2 H, OCH_2), 7.15-7.30 (*m*, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 8.79 (*C*H$_3$CH$_2$), 14.00 (*C*H$_3$CH$_2$O), 20.99 (CH$_3$*C*H$_2$), 30.43, 32.72 (CH_2), 49.30 (CH), 63.15 (OCH_2), 81.05 (CNO_2), 126.58, 128.56, 128.81 (CH), 140.25 (C), 157.81 (CO); GC-MS *m/z* 292 (M^+, <1), 246 (18), 157 (12), 129 (10), 117 (10), 92 (14), 91 (100), 82 (30), 65 (15), 41 (11).

3h: ^{1}H NMR ($CDCl_3$) δ 1.12 (*t*, 3 H, C*H*$_3$CH$_2$), 1.32 (*t*, 3 H, C*H*$_3$CH$_2$O), 1.66-1.83 (*m*, 2 H, CH$_3$C*H*$_2$), 1.87-2.02, 2.32-2.50 (*m*, 2 H, C*H*$_2$CH), 2.68 (*dd*, 1 H, CH), 2.72 (*dt*, 2 H, PhCH), 4.22 (*m*, 2 H, OCH_2), 7.15-7.30 (*m*, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 8.78 (*C*H$_3$CH$_2$), 14.04 (*C*H$_3$CH$_2$O), 24.88 (CH$_3$*C*H$_2$), 29.72, 32.36 (CH_2), 45.50 (CH), 63.48 (OCH_2), 82.55 (CNO_2), 126.46, 128.66, 128.68 (CH), 140.27 (C), 158.56 (CO).

2i (yield 60%, in dichloromethane[2]) : IR (CCl_4) 1736, 1750, 1564 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (*t*, 3 H, C*H*$_3$CH$_2$), 1.21 (*t*, 3 H, C*H*$_3$CH$_2$O), 1.20-1.65 (*m*, 10 H, CH_2), 1.97-2.07 (*m*, 1 H, CH_2C), 2.60-2.67 (*m*, 2 H, CH_2CO), 2.78-2.87 (*m*, 1 H, CH_2C), 3.20 (*dd*, 1 H, CH), 3.66 (*s*, 3 H, CH_3O), 4.15 (*q*, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 13.90 (*C*H$_3$CH$_2$), 14.10 (*C*H$_3$CH$_2$O), 22.39, 23.13, 26.47, 28.44, 28.54 (CH_2), 29.39 (*C*H$_2$C), 31.47

(CH_2CO), 50.40 (CH), 51.82 (OCH_3), 63.21 (OCH_2), 79.24 (C), 157.11 ($CO_2CH_2CH_3$), 172.35 (CO_2CH_3); GC-MS *m/z* 240 (M^+ -90, 5), 209 (28), 197 (18), 183 (22), 181 (60), 170 (37), 151 (39), 138 (100), 123 (10), 113 (18), 110 (15), 85 (18), 82 (20), 70 (12), 69 (37), 59 (23), 55 (64), 54 (17), 43 (53), 42 (15), 41 (46).

3i (yield 8%, in dichloromethane[2]): ^{1}H NMR ($CDCl_3$) δ 0.85 (*t*, 3 H, CH_3CH_2), 1.26 (*t*, 3 H, CH_3CH_2O), 1.20-1.65 (*m*, 10 H, CH_2), 2.29-2.27 (*m*, 1 H, CH_2C), 2.60-2.67 (*m*, 2 H, CH_2CO), 2.72 (*dd*, 1 H, CH), 2.83-2.92 (*m*, 1 H, CH_2C), 3.67 (*s*, 3 H, CH_3O), 4.22 (*m*, 2 H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 13.94 (CH_3CH_2), 14.17 (CH_3CH_2O), 22.45, 26.30, 27.13, 27.63, 28.59 (CH_2), 29.42 (CH_2C), 31.49 (CH_2CO), 47.58 (CH), 52.01 (OCH_3), 64.98 (OCH_2), 80.36 (C), 157.85 ($CO_2CH_2CH_3$), 171.89 (CO_2CH_3).

2j: IR (CCl_4) 1748, 1565 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (*t*, 3 H, CH_3), 4.25 (*q*, 2 H, CH_2), 4.20 (*d*, *J*=1.2 Hz 1 H, CH), 5.20 (*d*, *J*=1.2 Hz 1 H, $CHNO_2$), 7.30-7.41 (*m*, 5 H, CH); ^{13}C NMR ($CDCl_3$) δ 14.12 (CH_3), 46.74 (CH), 63.87 (CH_2), 70.99 ($CHNO_2$), 126.68, 128.94, 129.59 (CH), 131.70 (C), 156.30 (CO); GC-MS *m/z* 148 (M^+ -90, 5), 146 (81), 104 (10), 103 (100), 89 (10), 77 (20), 76 (20), 63 (10), 51 (18), 50 (10).

4: IR (CCl_4) 3298, 1765, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (*t*, 3 H, CH_3), 4.14 (*q*, 2 H, CH_2), 6.67 (*s*, 1 H, CH), 7.26-7.50 (*m*, 5 H, Ph), 10.45 (*br*, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 14.37 (CH_3), 63.75 (CH_2), 120.02 (CH), 126.84, 127.51, 129.48, 130.07 (Ph), 131.61, 132.02 (C), 150.39 (CO); GC-MS *m/z* 236 (M^+, 0.4), 190 (53), 163 (10), 162 (100), 117 (14), 116 (21), 105 (10), 104 (56), 103 (13), 91 (24), 90 (12), 89 (20), 77 (26), 51 (13).

2k: IR (CCl_4) 1744, 1554 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (*t*, 3 H, CH_3CH_2), 1.25 (*t*, 3 H, CH_3CH_2O), 1.52-1.69 (*m*, 2 H, CH_2CHN), 1.88 (*s*, 3 H, CH_3), 1.95-2.10 (*m*, 2 H, CH_3CH_2), 2.23 (*q*, 2 H, CH_2CH), 3.22 (*dd*, 1 H, CHN), 4.19 (*q*, 2 H, CH_2O), 5.25-5.52 (*m*, 2 H, CH); ^{13}C NMR ($CDCl_3$) δ 14.14, 14.20 (CH_3), 20.44, 24.10, 26.55 (CH_2), 48.57 (CHN), 63.14 (OCH_2), 76.52 (C), 126.25, 133.63 (CH), 157.23 (CO); GC-MS *m/z* 210 (M^+ -46, 2), 154 (11), 142 (31), 136 (10), 122 (10), 121 (24), 96 (25), 95 (10), 94 (10), 93 (12), 82 (18), 81 (29), 79 (12), 70 (45), 69 (40), 68 (73), 67 (27), 55 (24), 54 (11), 53 (15), 44 (13), 43 (16), 42 (100), 41 (70).

3k: ^{1}H NMR ($CDCl_3$) δ 0.95 (*t*, 3 H, CH_3CH_2), 1.30 (*t*, 3 H, CH_3CH_2O), 1.48-1.60 (*m*, 2 H, CH_2CHN), 1.92 (*s*, 3 H, CH_3), 1.97-2.13 (*m*, 2 H, CH_3CH_2), 2.23 (*q*, 2 H, CH_2CH), 2.68 (*dd*, 1 H, CHN), 4.24 (*m*, 2 H, CH_2O), 5.25-5.52 (*m*, 2 H, CH); ^{13}C NMR ($CDCl_3$) δ 14.21, 14.31, 17.20 (CH_3), 20.46, 23.92, 27.62 (CH_2), 48.31 (CHN), 63.53 (OCH_2), 77.76 (C), 126.40, 139.52 (CH), 158.06 (CO).

2l: IR (CCl_4) 1740, 1643, 1559 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (*t*, 3 H, CH_3CH_2), 1.30 (*t*, 3 H, CH_3CH_2O), 1.44-1.60 (*m*, 10 H, CH_2), 1.70-1.83 (*m*, 1 H, CH_2C), 2.30-2.42 (*m*, 2 H, $CH_2CH{=}CH_2$), 2.54-2.67 (*m*, 1 H, CH_2C), 3.18 (*dd*, 1 H, CHN), 4.21 (*q*, 2 H, CH_2O), 5.00-5.15 (*m*, 2 H, $CH_2{=}CH$), 5.79-5.98 (*m*, 1 H, $CH_2{=}CH$); ^{13}C NMR ($CDCl_3$) δ 13.99, 14.19 (CH_3), 22.47, 26.57, 27.21, 28.57, 28.64, 28.87, 31.54 (CH_2), 50.02 (CHN), 63.16 (CH_2O), 79.82 (C), 115.79 ($CH_2{=}CH$), 136.46 ($CH_2{=}CH$), 157.47 (CO); GC-MS *m/z* 252 (M^+ -46, 0.2), 82 (86), 69 (11), 67 (11), 56 (13), 55 (97), 54 (35), 53 (13), 43 (52), 42 (19), 41 (100).

3l: ^{1}H NMR ($CDCl_3$) δ 0.89 (*t*, 3 H, CH_3CH_2), 1.30 (*t*, 3 H, CH_3CH_2O), 1.44-1.60 (*m*, 10 H, CH_2), 1.70-1.83 (*m*, 1 H, CH_2C), 2.30-2.42 (*m*, 2 H, $CH_2CH{=}CH_2$), 2.54-2.67 (*m*, 1 H, CH_2C), 2.69 (*dd*, 1 H, CHN), 4.26 (*m*, 2 H, CH_2O), 5.00-5.15 (*m*, 2 H, $CH_2{=}CH$), 5.79-5.98 (*m*, 1 H, $CH_2{=}CH$); ^{13}C NMR ($CDCl_3$) δ 13.95, 14.14 (CH_3), 23.90, 26.31, 27.80, 28.38, 29.00, 29.63, 31.76 (CH_2), 46.90 (CHN), 63.44 (CH_2O), 81.04 (C), 116.38 ($CH_2{=}CH$), 135.44 ($CH_2{=}CH$), 158.12 (CO).

Thermolysis of Ethyl Azidoformate with (E)-Nitroalkenes. N_3CO_2Et (1.5 mol) and the nitroalkene **1a**, **c**, **e** or **f** (1 mol) in CH_2Cl_2 (1 ml) were heated at 120 °C. When the azide band disappeared in the IR spectrum (3 h), the solvent was evaporated *in vacuo* and the 1-(ethoxycarbonyl)-2-nitroaziridine was purified by flash chromatography on silica gel (hexane/ethyl acetate, 8:2). The yields were reported in Scheme 3.

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11. Compound **2c** was previously described.[2] IR and MS spectra of compounds **3** are not reported because similar to those of the corresponding isomers **2**.