Synthesis of ω-Nitro Acids and ω-Amino Acids by Ring Cleavage of α-Nitrocycloalkanones

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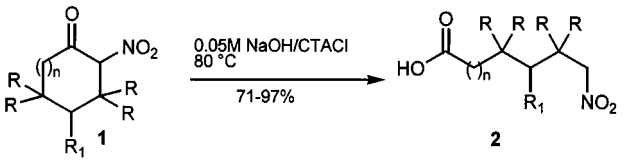
The reaction of various α-nitrocycloalkanones **1** with aqueous 0.05 M NaOH, at 80 °C, in the presence of cetyltrimethylammonium chloride (CTACl) as a cationic surfactant, produces ω-nitro acids **2** in good yields. Reduction of the latter with $HCOONH_4$/Pd-C, in methanol, at 80 °C affords ω-amino acids **3**. The synthesis of methyl 9-oxodecanoate (**8**) is also reported.

Given the well-known chemical differences between of the carbonyl group and the carbon−nitro group moiety, their juxtaposition on two adjacent positions offers an important reactivity pattern, peculiar to α-nitro ketones. In fact the C−C bond between the carbonyl group and the nitro-substituted atom of cyclic α-nitro ketones undergoes cleavage by nucleophilic agents and this retro Claisen reaction is useful for the synthesis of open-chained α,ω-disubstituted compounds, which are difficult to prepare by other methods.[1−10]

Although different routes are known in the literature for the ring cleavage of α-nitrocycloalkanones, only a few methods are known for the production of ω-nitro acids.[1a] Moreover, these methods, which need an aqueous solution of base, seem to have few little applications since just one or two examples have been reported for each procedure; this is perhaps due to problems of solubility of these substrates in water, so that they cannot be considered of general application.

As a continuation of our study on the reactions performed in aqueous media,[11] we have now found that the use of a catalytic amount of cetyltrimethylammonium chloride (CTACl) as a cationic surfactant can dramatically improve (Scheme 1) the cleavage of cyclic 2-nitro ketones **1** to ω-nitro acids **2**, in an aqueous solution of 0.05 M sodium hydroxide, at 80°C.



Scheme 1

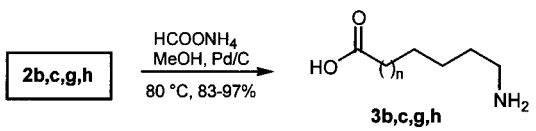
By this C−C bond fission a variety of cyclic nitro ketones are efficiently cleaved in high yields (71−97%, Table 1), regardless of the ring size. Only α-nitrocyclooctanone (**1d**) produces a mixure of unidentified products.

Table 1. ω-Nitro acids **2**

entry	*n*	R	R^1	reaction time [h]	yield [%] of **2**
a	0	H	H	3	90
b	1	H	H	4	97
c	2	H	H	8	84
d	3	H	H	8	mixt. of prod.
e	4	H	H	8	84
f	6	H	H	8	75
g	7	H	H	8	84
h	10	H	H	8	79
i	1	H	CH_3	6	78
j	1	H	*t*Bu	6	71
k	1	H	Ph	6	93
l	1	CH_3	H	8	75

Since these nitro compounds are of special interest in the synthesis of valuable targets,[12][13] our procedure to afford ω-nitro acids becomes important.

Here, we also report a convenient conversion of **2** to ω-amino acids **3** (Scheme 2) which are extensively used as spacer molecules in solid-phase peptide synthesis (SPPS),[14] for the preparation of polyamides,[15] photoconductors,[16] inhibitors of malignant melanoma,[17] antiinflammatory drugs,[18] and anticonvulsants.[19] A number of methods for the preparation of ω-amino alkanoic acids have been reported.[20−23] Generally, the amine group is introduced by the conversion of a ketone to an oxime or a carboxylate to a nitrile followed by reduction, by azide opening of an anhydride followed by Schmidt rearrangement, by Hofmann rearrangement of an amide with aqueous base and bromine, or by lactame formation. However, due to the utility of ω-amino acids, further efficient and simple syntheses are welcomed. Our procedure is performed by a chemoselective reduction using ammonium formate[24] and 10% Pd-C in methanol, at 80°C. Good yields (83−97%) of compound **3** are so obtained (see Table 2).



Scheme 2

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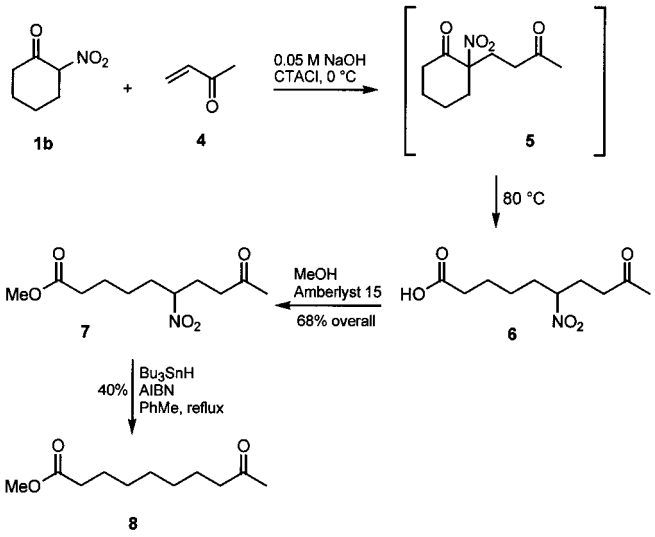
Table 2. ω-Nitro acids **3**

entry	*n*	yield [%] of **3**
b	1	97
c	2	87
g	7	85
h	10	83



Scheme 3

It is important to point out that our method for the production of ω-nitro acids is performed in aqueous medium and, in the recent years, there has been increasing recognition that water is an attractive medium for many organic reactions.[25] The aqueous medium is less expensive, less dangerous, and more environmentally friendly than organic solvents. Furthermore, reaction in an aqueous medium allows the control of the pH, and often enables to perform several steps in the same flask. To demonstrate the latter concept we report here a three-step synthesis (Scheme 3) of 9-oxodecanoate (**8**), a key prostaglandin intermediate,[26] and a good starting material for (2*E*)-9-oxo-2-decenoic acid (queen substance),[27] from α-nitrocyclohexanone (**1b**). Thus, **1b** is treated with methyl vinyl ketone (**4**) (MVK), at 0°C, in an aqueous solution of 0.05 M NaOH and in the presence of CTACl, then after 8 h at 0°C the mixture is heated at 80°C for 6 h, affording, in one pot, the nitro acid **6**. This crude acid can be directly converted into their methyl ester **7** with methanol in the presence of Amberlyst 15 ion-exchange resin (68% overall yield).[28] Treatment of **7** with Bu_3SnH in toluene at reflux temperature, and in the presence of AIBN[29] affords 9-oxodecanoate **8** in 40% yield.

Experimental Section

General: All ^{1}H-NMR spectra were recorded with a Varian Gemini 200 instrument in $CDCl_3$ or CD_3OD, at 300 MHz. Chemical shifts are expressed in ppm downfield from TMS as internal standard. *J* values are given in Hertz. − Mass spectra were determined with a Hewlett-Packard GC/MS 5970 by means of the EI technique (70 eV). − The reactions were monitored by TLC or GC performed with a Carlo Erba Fractovap 4160 using a capillary column of Duran Glass. − The α-nitrocycoalkanones are commercially available or were prepared by standard procedures.[1] − All the products were purified by flash chromatography[30] on Merck silica gel (0.040−0.063 mm) or by reversed-phase chromatography.

Ring Cleavage of α-Nitrocycloalkanones 1 to ω-Nitro Acids 2: To a mixture of α-nitrocycloalkanone **1** (10 mmol) in 0.05 M NaOH (12 mmol), was added cetyltrimethylammonium chloride (CTACl, 0.8 mmol). The mixture was heated at 80°C for the appropriate time (TLC, GC, see Table 1), then cooled, saturated with NaCl and extracted with EtOAc (4 × 20 mL). The organic phase was dried ($MgSO_4$), concentrated, and the crude product **2** was purified by flash chromatography (EtOAc/cyclohexane, 5:5).

5-Nitropentanoic Acid (2a): IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 1705, 1545. − ^{1}H NMR ($CDCl_3$): δ = 1.6−1.8 (m, 2 H), 2.0−2.15 (m, 2 H), 2.45 (t, 2 H, *J* = 7.1 Hz), 4.4 (t, 2 H, *J* = 6.9 Hz), 9.2 (s, 1 H). − $C_5H_9NO_4$ (147): calcd. C 40.81, H 6.16, N, 9.52; found C 40.89, H, 6.13, N, 9.61.

6-Nitrohexanoic Acid (2b): IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 1710, 1550. − ^{1}H NMR ($CDCl_3$): δ = 1.4−1.5 (m, 2 H), 1.6−1.75 (m, 2 H), 1.95−2.1 (m, 2 H), 3.35 (t, 2 H, *J* = 6.7 Hz), 4.35 (t, 2 H, *J* = 7.7 Hz), 10.3 (s, 1 H). − $C_6H_{11}NO_4$ (161.1): calcd. C 44.72, H 6.88, N 8.69; found C 44.66, H 6.95, N 8.62.

7-Nitroheptanoic Acid (2c): IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 1710, 1550. − ^{1}H NMR ($CDCl_3$) δ = 1.3−1.45 (m, 4 H), 1.5−1.7 (m, 2 H), 1.9−2.1 (m, 2 H), 2.35 (t, 2 H, *J* = 7.2 Hz), 4.35 (t, 2 H, *J* = 7.0 Hz). − $C_7H_{13}NO_4$ (175.1): calcd. C 47.99, H 7.48, N 7.99; found C 48.06, H 7.55, N 8.04.

9-Nitrononanoic Acid (2e): IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 1710, 1550. − ^{1}H NMR ($CDCl_3$): δ = 1.2−1.4 (m, 4 H), 1.7−1.8 (m, 2 H), 1.95−2.1 (m, 2 H), 2.35 (t, 2 H, *J* = 7.3 Hz), 4.15 (t, 2 H, *J* = 7.3 Hz), 9.8 (s, 1 H). − $C_9H_{17}NO_4$ (203.1): calcd. C 53.19, H 8.43, N 6.89; found C 53.11, H 8.49, N 6.94.

11-Nitroundecanoic Acid (2f): IR (film): $\tilde{\nu}$ = 2990 cm^{-1}, 1700, 1550. − ^{1}H NMR ($CDCl_3$): δ = 1.2−1.4 (m, 12 H), 1.55−1.7 (m, 2 H), 1.9−2.1 (m, 2 H), 2.35 (t, 2 H, *J* = 7.4 Hz), 4.4 (t, 2 H, *J* = 7.1 Hz), 4.9 (s, 1 H). − $C_{11}H_{21}NO_4$ (231.1): calcd. C 57.12, H 9.15, N 6.06; found C 57.07, H 9.13, N 5.99.

12−Nitrododecanoic Acid (2g): IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 1710, 1550. − ^{1}H NMR ($CDCl_3$): δ = 1.2−1.4 (m, 14 H), 1.5−1.7 (m, 2 H), 1.95−2.05 (m, 2 H), 2.35 (t, 2 H, *J* = 7.4 Hz), 4.35 (t, 2 H, *J* = 7.1 Hz), 6.0 (s, 1 H). − $C_{12}H_{23}NO_4$ (245.2): calcd. C 58.75, H 9.45, N, 5.71; found C 58.68, H 9.53, N 5.78.

15-Nitropentadecanoic Acid (2h): IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 1710, 1550. − ^{1}H NMR ($CDCl_3$): δ = 1.1−1.4 (m, 20 H), 1.55−1.75 (m, 2 H), 1.9−2.1 (m, 2 H), 2.38 (t, 2 H, *J* = 6.5 Hz), 4.38 (t, 2 H, *J* = 7.1 Hz), 5.8 (s, 1 H). − $C_{15}H_{29}NO_4$ (287.2): calcd. C 62.69, H 10.17, N 4.87; found C 62.75, H 10.13, N 4.81.

4-Methyl-6-nitrohexanoic Acid (2i): IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 1710, 1560. − ^{1}H NMR ($CDCl_3$): δ = 0.86 (d, 3 H, *J* = 6.1 Hz), 1.45−1.6 (m, 1 H), 1.75−1.85 (m, 2 H), 1.95−2.1 (m, 2 H), 2.35 (t, 2 H, *J* = 6.6 Hz), 4.38 (t, 2 H, *J* = 6.9 Hz), 10.45 (s, 1 H). − $C_7H_{13}NO_4$ (175.1): calcd. C 47.99, H 7.47, N 7.99; found C 48.06, H 7.54, N 7.90.

4-*tert*-Butyl-6-nitrohexanoic Acid (2j): IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 1710, 1545. − ^{1}H NMR ($CDCl_3$): δ = 0.86 (s, 9 H), 1.2−1.5 (m, 2 H), 1.8−2.0 (m, 2 H), 2.2−2.5 (m, 2 H), 2.4 (t, 2 H, *J* = 6.9 Hz), 2.4 (t, 2 H, *J* = 7.0 Hz), 10.7 (s, 1 H). − $C_{10}H_{19}NO_4$ (217.1): calcd. C 55.28, H 8.81, N 6.45; found C 55.37, H 8.74, N 6.53.

6-Nitro-4-phenylhexanoic Acid (2k): IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 1720, 1560. − ^1H NMR ($CDCl_3$): δ = 1.2−1.35 (m, 2 H), 1.8−2.3 (m, 2 H), 2.5 (t, 2 H, *J* = 6.1 Hz), 4.2 (t, 2 H, *J* = 7.1 Hz), 5.5 (m, 1 H), 7.1−7.3 (m, 5 H). − $C_{12}H_{15}NO_4$ (237.1): calcd. C 60.75, H 6.37, N 5.90; found C 60.83, H 6.29, N 5.97.

3,3,5,5-Tetramethyl-6-nitrohexanoic Acid (2l): IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 1720, 1560. − ^1H NMR ($CDCl_3$): δ = 1.1 (s, 3 H), 1.17 (s, 3 H), 1.23 (s, 3 H), 1.3 (s, 3 H), 1.5−1.7 (m, 2 H), 2.3−2.4 (m, 2 H), 4.27−4.38 (m, 2 H), 10.45 (s, 1 H). − $C_{10}H_{19}NO_4$ (217.1): calcd. C 55.28, H 8.81, N 6.45; found C 55.33, H 8.90, N 6.37.

Synthesis of ω-Amino Acids 3: To a stirred solution of nitro acid **2** (5 mmol) and 10% Pd-C (0.25 g), in methanol (10 mL), anhydrous ammonium formate (23 mmol) was added under N_2, and the obtained mixture was heated, at 80°C, for 30 min. The catalyst was then filtered off, and the filtrate was concentrated to give the almost pure amino acid **3**. However, if necessary compond **3** can be purified by reversed-phase chromatography.

6-Aminohexanoic Acid (3b): M.p. 210−212°C. − IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 1630, 1460. − ^1H NMR (CD_3OD): δ = 1.35−1.45 (m, 2 H), 1.55−1.75 (m, 4 H), 2.25 (t, 2 H, *J* = 7.2 Hz), 2.93 (t, 2 H, *J* = 7.4 Hz). − $C_6H_{13}NO_2$ (131.1): calcd. C 54.94, H 9.99, N 10.68; found C 55.01, H 10.06, N 10.57.

7-Aminoheptanoic Acid (3c): M.p. 193−195°C. − IR (film): $\tilde{\nu}$ = 2970 cm^{-1}, 1640, 1460. − ^1H NMR (CD_3OD): δ = 1.3−1.45 (m, 4 H), 1.55−1.75 (m, 4 H), 2.1−2.4 (m, 2 H), 2.95 (t, 2 H, *J* = 7.5 Hz). − $C_7H_{15}NO_2$ (145.2): calcd. C 57.90, H 10.41, N 9.65; found C 57.82, H 10.33, N 9.57.

12-Aminododecanoic Acid (3g): M.p. 184−186°C. − IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 1640, 1440. − ^1H NMR (CD_3OD): δ = 1.25−1.35 (m, 14 H), 1.45−1.7 (m, 4 H), 2.10−2.2 (m, 2 H), 2.85−2.95 (m, 2 H). − $C_{12}H_{25}NO_2$ (215.2): calcd. C 66.93, H 11.70, N 6.50; found C 66.96, H 11.78, N 6.42.

15-Aminopentadecanoic Acid (3h): M.p. 180−182°C. − IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 1640, 1460. − ^1H NMR (CD_3OD): δ = 1.3−1.45 (m, 20 H), 1.5−1.75 (m, 4 H), 2.15−2.20 (m, 2 H), 2.85−2.95 (m, 2 H). − $C_{15}H_{31}NO_2$ (257.2): calcd. C 69.99, H 12.14, N 5.44; found C 70.06, H 12.13, N 5.38.

6-Nitro-9-oxodecanoate (7): To a mixture of α-nitrocyclohexanone (**1b**) (10 mmol) and 0.05 M NaOH (12 mmol), methyl vinyl ketone (**4**) (11 mmol) and CTACl (1 mmol) were added at 0°C. The mixture was stirred at 0°C for 8 h, and at 80°C for another 8 h. After cooling, the solution was saturated with NaCl and extracted with EtOAc (4 × 20 mL), and dried ($MgSO_4$). Removal of the solvent afforded the crude product **6** which was dissolved in methanol (30 mL) and stirred for 18 h in the presence of Amberlyst 15 ion exchange resin (1 g). The resin was removed by filtration, and then, after evaporation of the solvent, the crude ester was purified by flash chromatography (EtOAc/cyclohexane, 3:7), affording 1.67 g (68%) of pure **7**. − Oil. − IR (film): $\tilde{\nu}$ = 1740 cm^{-1}, 1715, 1540. − ^1H NMR ($CDCl_3$): δ = 1.1−1.3 (m, 2 H), 1.35−1.45 (m, 2 H), 2.15 (s, 3 H), 2.28 (t, 2 H, *J* = 7.3 Hz), 2.48 (t, 2 H, *J* = 6.9 Hz), 3.65 (s, 3 H), 4.4−4.6 (m, 1 H). − $C_{11}H_{19}NO_5$ (245.3): calcd. C 53.87, H 7.81, N 5.71; found C 53.96, H 7.75, N 5.80.

Methyl 9-Oxodecanoate (8): A dried, N_2-flushed flask was charged with compound **7** (1.2 g, 4.9 mmol) and AIBN (312 mg, 1.92 mmol) in dry toluene (12 mL). Tri-*n*-butyltin hydride (24 mmol) was added and the resulting solution refluxed for 3 h. After that, the solvent was evaporated and the crude product was purified by flash chromatography (EtOAc/cyclohexane, 2:8) yielding 0.39 g (40%) of the pure compound **8**. − B.p. 70°C/0.4 Torr. − IR (film): $\tilde{\nu}$ = 1735 cm^{-1}, 1710. − ^1H NMR ($CDCl_3$): δ = 1.2−1.4 (m, 6 H), 1.5−1.7 (m, 4 H), 2.15 (s, 3 H), 2.28 (t, 2 H, *J* = 6.7 Hz), 2.4 (t, 2 H, *J* = 7.3 Hz), 3.65 (s, 3 H). − MS; *m/z* (%) = 200 [M^+], 185, 169, 143, 111, 83, 55, 43 (100). − $C_{11}H_{20}O_3$ (200.1): calcd. C 65.97, H 10.07; found C 66.03, H 10.13.

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