Nitroaldol Reaction in Aqueous Media: An Important Improvement of the Henry Reaction

Roberto Ballini* and Giovanna Bosica

Dipartimento di Scienze Chimiche dell'Università, Via S. Agostino n. 1, 62032 Camerino, Italy

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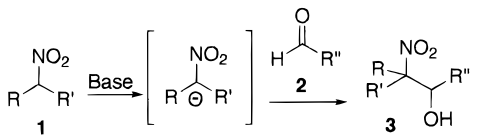
Carbon−carbon bond formation is the essence of organic synthesis; the Henry reaction, an aldol-type reaction, represents one of the classical C−C bond-forming processes, and its variants have been used extensively in many important syntheses.[1−19]

The classical nitroaldol reaction is performed, as routine procedure, in presence of a base (Scheme 1) in an organic solvent. Since basic reagents are also catalysts for the aldol condensation and for the Cannizzaro reaction when aldehydes are used as carbonyl sources, it is necessary to adopt experimental conditions to suppress these competitive reactions.[5−9,17,19] To obtain better yields of 2-nitro alcohols a careful control of the basicity of the reaction medium is necessary, and long reaction times are demanded. Furthermore, the *β*-nitroalkanols formed may undergo base-catalyzed elimination[20] of water to give nitroalkenes that readily polymerize. This elimination is difficult to avoid when aryl aldehydes are employed. In addition, these standard procedures furnish a diastereomeric mixture of nitroalkanols; nevertheless, this seems to be not a problem since the main uses of nitroalkanols are the conversion into α-nitro ketones[1c,8,10−12] or conjugated nitroalkenes,[13−17] in which at least one stereogenic center is lost.

Scheme 1



If a diastereoselective synthesis of nitroalkanols, for specific purposes, is required other procedures are available;[18] however, these methods are highly laborious and/or produce low yields, are of moderate generality, and are not suitable on a large scale.

The need to reduce the amount of toxic waste and byproducts arising from chemical processes requires increasing emphasis on the use of less toxic and environmentally compatible materials in the design of new synthetic methods.[21] The time has now come for ecological factors to be considered in the development of synthetic procedures and for them to play an important role in the assessment of the quality of any new synthesis. Within this context, the reduced use of ecologically suspected solvents is of considerable significance. In recent years, there has been increasing recognition that water is an attractive medium for many organic reactions.[22] The aqueous medium with respect to organic solvent is less expensive, less dangerous, and environment-friendly, while it allows the control of the pH and the use of microaggregates such as surfactants. Generally, the low solubility[23] of most reagents in water is not an obstacle to the reactivity, which, on the contrary, is reduced with the use of cosolvents.

In connection with our interest devoted to the syntheses of natural products *via* α-nitro ketones[24] or nitroalkenes,[25] we decided to investigate the possibility to achieve the nitroaldol reaction in water. After some trials we found that the Henry reaction can be performed under very mild reaction conditions, in aqueous media, using a stoichiometic amount of the nitroalkane **1** and the aldehyde **2** in NaOH 0.025 M, in the presence of cetyltrimethylammonium chloride (CTACl) as cationic surfactant. As showed in Table 1 the yields are from good to excellent when the nitroalkanes react with aliphatic aldehydes, while the yields slightly decrease with the

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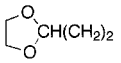
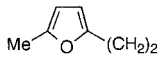
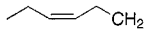
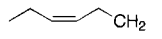
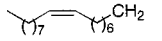
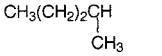
Table 1. Preparation of β-Nitroalkanols

Entry	R	R'	R"	Yield (%)	Reaction time (h)
3a	H	H	C_6H_5	70	2
3b	H	Et	C_6H_5	71	2
3c	H	Me	2-Furanyl	70	3
3d	H	Me	p-$NO_2C_6H_4$	72	4
3e	H	$CH_3(CH_2)_3$	p-$NO_2C_6H_4$	66	6
3f	H	$CH_3(CH_2)_2$	$Ph(CH_2)_2$	85	5
3g	H	Me	$Ph(CH_2)_2$	94	2
3h	H	$THPOCH_2$	$Ph(CH_2)_2$	85	3
3i	H		$Ph(CH_2)_2$	90	3
3j	Me	Me	$Ph(CH_2)_2$	88	6
3k	H	Me	c-C_6H_{11}	86	2
3l	H	$CH_3(CH_2)_4$	c-C_6H_{11}	85	2
3m	H	Me		90	6
3n	H	$CH_3(CH_2)_4$		95	3
3o	H	$HO(CH_2)_6$		75	3
3p	H	$CH_3(CH_2)_2$		85	3
3q	H	$CH_3CO(CH_2)_2$		85	2
3r	H	$MeO_2C(CH_2)_2$	Et	84	3
3s	H	$MeO_2C(CH_2)_6$	Et	80	3
3t		$-(CH_2)_5-$	Et	85	3

aromatic ones. Short times (2−6 h) are required, and both primary and secondary nitroalkanes give good results.

Contrary to other methods, the success of this approach is independent from the ratio catalyst/substrates[4,8] and does not need long reaction times,[1d,9] tedious preparation of the catalyst,[4,9] large excess of the nitroalkane,[4] or severe reaction conditions that are too cumbersome, especially for large-scale preparations.[3] Additionally, the very mild reaction conditions prevent the typical side reactions[1] such as retro-aldol reaction or dehydration of the 2-nitro alcohols into nitroalkenes[20] even if aromatic aldehydes are used. High chemoselectivity is observed since several functionalities such as hydroxy group, ester, acetal, tetrahydropyranyl, (Z)-C,C double bond, and furyl are preserved under these conditions. Moreover, if a nitro ketone is employed as a functionalized nitro derivative (entry **3q**), multiple nitroaldol reactions were not observed.

Compared with the conventional methods,[1−9,17,19] our procedure produces better yields in shorter reaction times even with complex starting materials and, at last, allows us to perform this important reaction on a gram scale under unexpensive and ecological conditions, with evident environmental advantages for widespread industrial use.

Experimental Section

General Procedures. All ^{1}H NMR spectra were recorded in $CDCl_3$ at 300 MHz. Chemical shifts are expressed in ppm downfield from TMS as internal standard. J values are given in hertz. All the reactions were monitored by TLC. The products **3** were purified by flash chromatography[26] on Merck silica gel (0.040−0.063 mm). Cetyltrimethylammonium chloride (CTACl) was purchased from Aldrich.

General Procedure for the Nitroaldol (Henry) Reaction. To a mixture of nitroalkane **1** (50 mmol) and aldehyde **2** (50 mmol), in NaOH 0.025 M (150 mL), was added CTACl (5 mmol) at room temperature. The mixture was stirred at room temperature for the appropriate time (see Table 1) and then saturated with NaCl and extracted with Et_2O (4 × 30 mL). The organic phase was dried ($MgSO_4$) and concentrated, and the crude nitro alcohol **3**, if necessary, was purified by flash chromatography (EtOAc/cyclohexane, 2:8).

1-Phenyl-2-nitroethan-1-ol (entry 3a): IR ν = 3400, 1535 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.6 (m, 1H), 4.47−4.68 (m, 2H), 5.41−5.54 (m, 1H), 7.2−7.58 (m, 5H). Anal. Calcd for $C_8H_9NO_3$ C, 57.48; H, 5.42; N, 8.37. Found: C, 57.65; H, 5.29; N, 8.44.

1-Phenyl-2-nitrobutan-1-ol (entry 3b):[8] IR ν = 3400, 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.87 (t, 2.4 H, J = 7.4 Hz), 0.94 (t, 0.6 H, J = 7.4 Hz), 1.3−2.0 (m, 2H), 4.5−4.7 (m, 1H), 5.03 (d, 0.8 H, J = 9.2 Hz), 5.2 (d, 0.2 H, J = 4.8 Hz), 7.25 −7.45 (m, 5H). Anal. Calcd for $C_{10}H_{13}NO_3$ C, 61.52; H, 6.71; N, 7.17. Found: C, 61.21; H, 6.99; N, 6.98.

1-(2-Furanyl)-2-nitropropan-1-ol (entry 3c):[8,9] IR ν = 3420, 1540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.4 (d, 2H, J = 6.6 Hz), 1.6 (d, 1H, J = 6.9 Hz), 2.5 (m, 1H), 4.8−5.1 (m, 2H), 6.35−6.42 (m, 2H), 7.4−7.45 (m, 1H). Anal. Calcd for $C_7H_9NO_4$ C, 49.12; H, 5.30; N, 8.18. Found: C, 48.95; H, 5.18; N, 8.30.

1-(*p*-Nitrophenyl)-2-nitropropan-1-ol (entry 3d): IR ν = 3400, 1600, 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.45 (dd, 3H, J = 19.6, 6.9 Hz), 2.8 (m, 1H), 4.65−4.85 (m, 1H), 5.2 (d, 0.6 H, J = 8.1 Hz), 5.55 (d, 0.4 H, J = 4.7 Hz), 7.6 (d, 2H, J = 5 Hz), 8.25 (d, 2 H, J = 5 Hz). Anal. Calcd for $C_9H_{10}N_2O_5$ C, 47.79; H, 4.45; N, 12.38. Found: C, 48.01; H, 4.26; N, 12.52.

1-(*p*-Nitrophenyl)-2-nitrohexan-1-ol (entry 3e): IR ν = 3480, 1600, 1530, 1510 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.8−1.0 (m, 3H), 1.1−2.0 (m, 6H), 4.6−4.75 (m, 1H), 5.15 (d, 0.7 H, J = 8.1 Hz), 5.35 (d, 0.3 H, J = 4.0 Hz), 7.58 (d, 0.7 H, J = 8.9 Hz), 8.05 (d, 0.3 H, J = 9.0 Hz), 8.26 (d, 0.7 H, J = 8.9 Hz), 8.4 (d, 0.3 H, J = 9.0 Hz). Anal. Calcd for $C_{12}H_{16}N_2O_5$ C, 53.72; H, 6.01; N, 10.44. Found: C, 53.88; H, 5.8; N, 10.58.

1-Phenyl-4-nitroheptan-3-ol (entry 3f): IR ν = 3400, 1600, 1540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.8−1.0 (m, 3 H), 1.2−1.45 (m, 2 H), 1.6−2.2 (m, 4 H), 2.6−3.0 (m, 2 H), 3.8−3.92 (m, 0.7 H), 4.0−4.1 (m, 0.3 H), 4.4−4.6 (m, 1 H). Anal. Calcd for $C_{13}H_{19}NO_3$ C, 65.80; H, 8.07; N, 5.90. Found: C, 66.01; H, 8.23; N, 6.08.

2-Nitro-5-phenylpentan-3-ol (entry 3g):[1d,4,15] IR ν = 3400, 1600, 1550 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.85 (t, 3 H, J = 7.2 Hz), 1.05−1.6 (m, 8 H), 1.7−2.2 (m, 4 H), 3.8−4.05 (m, 1 H), 4.3−4.42 (m, 1 H), 7.15−7.38 (m, 5 H). Anal. Calcd for $C_{11}H_{15}NO_3$ C, 63.14; H, 7.22; N, 6.69. Found: C, 63.00; H, 6.98; N, 6.90.

1-(Tetrahydropyranyloxy)-2-nitro-5-phenylpentan-3-ol (entry 3h): IR ν = 3350, 1540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.1−2.0 (m, 8 H), 2.5−3.05 (m, 2 H), 3.3−4.4 (m, 5 H), 4.5−4.8 (m, 1 H), 7.12−7.35 (m, 5 H). Anal. Calcd for $C_{16}H_{23}NO_5$ C, 62.12; H, 7.49; N, 4.52. Found: C, 61.87; H, 7.29; N, 4.35.

2-(3-Nitro-4-hydroxy-6-phenylhexyl)-1,3-dioxolane (entry 3i): IR ν = 3410, 1535 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.5−2.2 (m, 6 H), 2.6−2.97 (m, 2 H), 3.75−4.0 (m, 5 H), 4.0−4.2 (m, 1 H), 4.45−4.61 (m, 1 H), 4.88 (t, 1 H, t, J = 4.2 Hz), 7.12−7.35 (m, 5 H). Anal. Calcd for $C_{15}H_{21}NO_5$ C, 61.00; H, 7.16; N, 4.74. Found: C, 61.31; H, 7.41; N, 4.54.

2-Methyl-2-nitro-5-phenylpentan-3-ol (entry 3j):[1d] IR ν = 3450, 1550 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.62 (s, 3 H), 1.6−1.85 (m + s, 5 H), 2.6 (m, 1 H), 2.65−3.05 (m, 2 H), 4.02 (dd, 1 H, J

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= 1.9, 10.2 Hz), 7.15−7.4 (m, 5 H). Anal. Calcd for $C_{12}H_{17}NO_3$ C, 64.55; H, 7.67; N, 6.27. Found: C, 64.35; H, 7.95; N, 6.44.

1-Cyclohexyl-2-nitropropan-1-ol (entry 3k):[1d,9] IR ν = 3420, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.9−2.1 (m, 11 H), 1.55 (dd, 3 H, J = 3.7, 6.9 Hz), 3.6−3.7 (m, 0.5 H), 3.92−4.0 (m, 0.5 H), 4.58−4.78 (m, 1 H). Anal. Calcd for $C_9H_{17}NO_3$ C, 57.73; H, 9.15; N, 7.48. Found: C, 57.65; H, 9.34; N, 7.23.

1-Cyclohexyl-2-nitroheptan-1-ol (entry 3l):[15] IR ν = 3500, 1545 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.85 (m, 3 H), 1.0−2.15 (m, 19 H), 3.55−3.65 (m, 0.5 H), 3.7−3.8 (m, 0.5 H), 4.5−4.7 (m, 1 H). Anal. Calcd for $C_{13}H_{25}NO_3$ C, 64.16; H, 10.35; N, 5.75. Found: C, 64.42; H, 10.08; N, 5.38.

2-Nitro-5-(5-methyl-2-furanyl)pentan-3-ol (entry 3m): IR ν = 3320, 1530 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.58 (dd, 3 H, J = 3.9, 10 Hz), 1.62−2.0 (m, 2 H), 2.27 (s, 3 H), 2.65−2.95 (m, 2 H), 3.87−4.00 (m, 0.6 H), 4.2−4.3 (m, 0.4 H), 4.45−4.62 (m, 1 H), 5.82−5.92 (m, 2 H). Anal. Calcd for $C_{10}H_{15}NO_4$ C, 56.32 H, 7.09; N, 6.56. Found: C, 56.11; H, 7.29; N, 6.44.

***(Z)*-8-Nitrotridec-3-en-7-ol (entry 3n)**: IR ν = 3300, 1560 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.8−0.9 (m, 3 H), 0.9−1.0 (m, 3 H), 1.2−1.4 (m, 6 H), 1.5−1.6 (m, 2 H), 1.65-1.85 (m, 2 H), 1.95−2.3 (m, 4 H), 3.85−3.95 (m, 0.6 H), 4.0−4.1 (m, 0.4 H), 4.35−4.5 (m, 1 H), 5.2−5.5 (m, 2 H). Anal. Calcd for $C_{13}H_{25}NO_3$ C, 64.16; H, 10.35; N, 5.75. Found: C, 63.93; H, 10.24; N, 5.57.

***(Z)*-8-Nitrotetradec-3-ene-7,14-diol (entry 3o)**: IR ν = 3350, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.95 (t, 3 H, J = 7.4 Hz), 1.2−2.3 (m, 16 H), 3.65 (t, 2 H, J = 6.4 Hz), 3.8−3.95 (m, 0.5 H), 3.96−4.1 (m, 0.5 H), 4.32−4.52 (m, 1 H), 5.2−5.5 (m, 2 H). Anal. Calcd for $C_{14}H_{27}NO_4$ C, 61.51; H, 9.95; N, 5.12. Found: C, 61.24; H, 10.19; N, 5.34.

***(Z)*-19-Nitrotrodocos-9-en-18-ol (entry 3p)**: IR ν = 3450, 1535 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (t, 3 H, J = 7.1 Hz), 0.95 (t, 3 H, J = 7.2 Hz), 1.1−1.6 (m, 28 H), 1.9−2.15 (m, 4 H), 3.78−3.95 (m, 0.6 H), 3.96−4.08 (m, 0.4), 4.4−4.55 (m, 1 H), 5.3−5.42 (m, 2 H). Anal. Calcd for $C_{22}H_{43}NO_3$ C, 71.49; H, 11.72; N, 3.79. Found: C, 71.65; H, 11.99; N, 3.62.

5-Nitro-6-hydroxy-7-methyldecan-2-one (entry q): IR ν = 3460, 1700, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.86−1.03 (m, 3 H), 0.95 (d, 3 H, J = 7.2 Hz), 1.17−1.58 (m, 5 H), 1.78−2.25 (m, 2 H), 2.16 (s, 3 H), 2.48−2.58 (m, 3 H), 3.65 (t, 0.2 H, J = 6.2 Hz), 3.89 (dd, 0.8 H, J = 3.5, 8.3 Hz), 4.57−4.78 (m, 1 H). Anal. Calcd for $C_{11}H_{21}NO_4$ C, 57.12; H, 9.15; N, 6.05. Found: C, 57.35; H, 9.29; N, 6.23.

Methyl 4-nitro-5-hydroxyheptanoate (entry 3r):[1d] IR ν = 3425, 1715, 1510 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.0−1.1 (t, 3 H, J = 7.3 Hz), 1.45−1.7 (m, 2 H), 2.1−2.6 (m, 4 H), 3.68 (s, 3 H), 3.8−3.9 (m, 0.6 H), 3.95−4.05 (m, 0.4 H), 4.48−4.65 (m, 1 H). Anal. Calcd for $C_8H_{15}NO_5$ C, 46.82; H, 7.36; N, 6.82. Found: C, 47.04; H, 7.29; N, 6.59.

Methyl 8-nitro-9-hydroxyundecanoate (entry 3s): IR ν = 3450, 1715, 1535 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.12 (dt, 3 H, J = 1.9, 7.3 Hz), 1.2−2.1 (m, 12 H), 2.3 (t, 2 H, J = 7.3 Hz), 3.62 (s, 3 H), 3.7−3.87 (m, 0.6 H), 3.87−4.0 (m, 0.4 H), 4.38−4.52 (m, 1 H). Anal. Calcd for $C_{12}H_{23}NO_5$ C, 55.15; H, 8.87; N, 5.35. Found: C, 55.33; H, 9.03; N, 5.50.

1-(1-Nitrocyclohexyl)propan-1-ol (entry 3t): IR ν = 3450, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.85−1.78 (m, 10 H), 1.25 (t, 3 H, J = 8.5 Hz), 2.4−2.6 (m, 2 H), 3.5 (dd, 1 H, J = 1.8, 10.1 Hz). Anal. Calcd for $C_9H_{17}NO_3$ C, 60.28; H, 8.59; N, 7.03. Found: C, 60.06; H, 8.40; N, 6.88.

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