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Enantioselective Reduction of Nitroalkene Mixtures by in Situ Equilibration

Constantin Czekelius and Erick M. Carreira*

Laboratorium für Organische Chemie, ETH Zürich, ETH Hönggerberg, CH-8093 Zürich, Switzerland

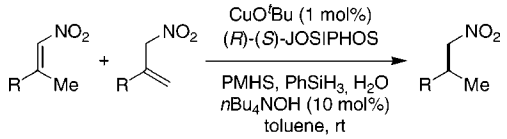
Abstract:

We document an easy protocol for the enantioselective conjugate reduction of isomeric mixtures of nitroalkenes. Employing a catalyst from CuO^{t}Bu and JOSIPHOS, conjugated and nonconjugated isomers are interconverted by the action of quaternary ammonium bases, and both reduced enantioselectively to the corresponding nitroalkanes.

Introduction

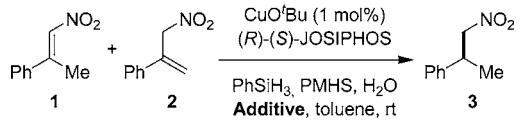
Optically active nitro compounds are highly interesting intermediates in organic synthesis because they can be transformed to other chiral building blocks like amines, acids, oximes, etc. by a number of methods.[1] Significant progress in asymmetric catalytic processes yielding such compounds was achieved recently by the enantioselective addition of *C*-nucleophiles to nitroalkenes.[2] In this context, we reported a novel enantioselective conjugate reduction of α,β-disubstituted nitroalkenes by using a catalyst prepared from copper(I) butoxide and a bis-phosphine ligand.[3] An inherent property of most trisubstituted nitroalkenes is the tendency to isomerize under basic conditions or upon prolonged storage. These mixtures of conjugated and nonconjugated isomers are most often difficult to separate, especially on a large scale, resulting in a significant loss of material. In this communication we would like to report a simple protocol for this enantioselective conjugate reduction employing an isomeric mixture of nitroalkenes without prior separation by base-catalyzed *in situ* equilibration (Scheme 1).

Scheme 1. **Conjugate reduction of an isomeric mixture of nitroalkenes[a]**



[a] JOSIPHOS = 1-[2-Diphenylphosphino)ferrocenyl]ethyldicyclohexylphosphine; PMHS = poly(methylhydrosiloxane).

Scheme 2. **Additive screening for *in situ* equilibration**



Results and Discussion

When a mixture of 2-phenyl-1-nitropropene (**1**) and 2-phenyl-3-nitropropene (**2**) was submitted to reaction conditions previously reported,[3] clean reduction of **1** was observed keeping the isomer **2** untouched indicating that the presence of nonconjugated nitroalkenes does not lead to catalyst inhibition (Scheme 2, no additive). This finding encouraged us to investigate conditions under which nitroalkene isomers can be equilibrated *in situ* without catalyst inactivation, or any decomposition of the silane or the nitroalkane products. Possible side reactions could include Nef reaction, overreduction to oximes, Michael addition to the nitroalkene acceptor, or elimination reactions under strongly basic conditions. Addressing this complex task, it was reasoned that the choice of a base with a carefully balanced pK_a would be a key to success. Since it is known that amine bases like triethylamine or DBU effect immediate isomerization (equilibrium reached within 1 min for most substrates as followed by ^{1}H NMR), different amine bases (Et_3N, piperidine, DBU, DMAP, 2,6-lutidine) were tested in the conjugate reduction of a mixture of 1-nitro-2-phenyl-1-propene (**1**) and 3-nitro-2-phenyl-1-propene (**2**) (Scheme 2).

In the case of Et_3N, piperidine, and DBU, effective catalyst inhibition was observed. In contrast, the pyridine derivatives did not effect isomerization of the nitroalkenes. Therefore, hydroxides and alkoxides were tested as bases. To ensure sufficient solubility in toluene, different quaternary ammonium bases, in particular nBu$_4$NOH and nBu$_4$NOMe, which are commercially available as the hydrate and as a solution in methanol, respectively, were investigated. The

* To whom correspondence should be addressed. E-mail: carreira@org.chem.ethz.ch.

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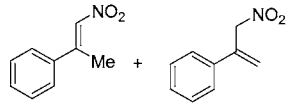
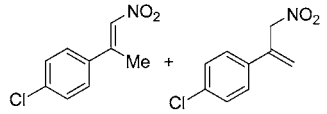
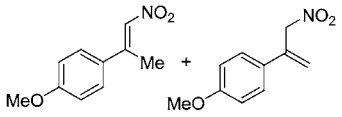
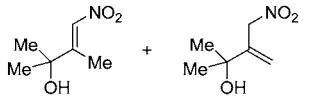
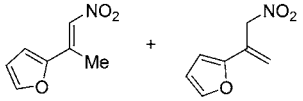
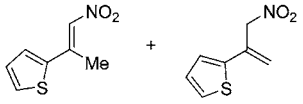
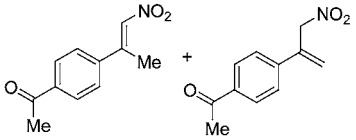
Table 1. **Reduction of mixtures of α,*β*- and *β*,*γ*-unsaturated nitroalkenes[a]**

Entry	Substrates	Ratio [NO_2 : NO_2]	Catalyst	Yield	ee
1		3.2 : 1	1 mol%	73%	88%
2		2.3 : 1	1 mol%	76%	87%
3		5.3 : 1	1 mol%	82%	90%
4		4.0 : 1	1 mol%	62%	90%
5		8.6 : 1	1 mol%	82%	88%
6		5.0 : 1	1 mol%	77%	84%
7		1.1 : 1	3 mol%	51%	80%

[a] Reaction conditions: $PhSiH_3$ (1.5 equiv), PMHS (0.1 equiv), CuO^tBu (1 or 3 mol %), JOSIPHOS (1.1 or 3.3 mol %), H_2O (1.5 equiv), $^nBu_4NOH \cdot 30\ H_2O$ (10 mol %), toluene, 6 h at rt.

addition of 10 mol % of one of these bases to the reaction mixture led to a complete conversion of both **1** and **2** to nitroalkane **3**. The use of nBu$_4$NOMe was found to be inferior since formation of siloxanes was observed which were difficult to separate from the product by chromatographic methods. It was found that the workup of the reaction was best performed as soon as the reaction is finished to avoid substantial loss of product by base-mediated decomposition. In the optimized reaction procedure, the isomeric mixture of nitroalkenes was added to a solution of 1 mol % of the preformed catalyst, the silane, and water. After stirring for 2 h at 23 °C, the base was added and the reaction was completed within four additional hours. Following this protocol, the catalyst loading as well as the contact time of base and nitroalkane can be kept at a minimal level.

In order to evaluate the applicability of this new procedure the substrate scope was investigated. As starting material a mixture of nitroalkenes representing the thermodynamic ratio was used. For its preparation, nitroalkenes were equilibrated in chloroform by adding an excess of triethylamine until no further change in the isomeric ratio was observed as followed by ^{1}H NMR (Table 1). Aromatic, aliphatic, and heteroaromatic substrates as well as substrates bearing unprotected hydroxy groups are entirely reduced. The products can be easily purified by flash column chromatography without tedious separation from any nitroalkene isomers.

The limits of this method were reached when acetophenyl-substituted nitroalkenes (Table 1, entry 7) were submitted to reduction. Base-mediated elimination of nitrous acid reduced the isolated yield of the corresponding nitroalkane with the concomitant formation of *p*-acetyl-α-methylstyrene. A slight decrease in the enantioselectivity was observed (80% ee compared to 90% ee under base free conditions).

Conclusion

We document an easy protocol for the reduction of isomeric mixtures of nitroalkenes. Conjugated and non-conjugated isomers are interconverted by the action of quaternary ammonium bases, and both reduced enantioselectively to the corresponding nitroalkanes. This new method allows a large scale synthesis of optically active nitroalkanes. In addition to the practical value, these results provide more insight into copper-catalyzed reactions and could potentially lead to new applications of inexpensive copper catalysts in large-scale and fine-chemical synthesis.

Experimental Section

General Aspects. All reactions were carried out in dried glassware under an atmosphere of argon. Toluene was dried by passage over A-2 alumina (8 × 14 mesh, Macherey & Nagel; activated at 300 °C under nitrogen atmosphere for 12 h). Chemicals were purchased from Strem, Aldrich, Fluka, or Acros and used as is unless mentioned otherwise. Evaporation of organic solutions was achieved by rotary evaporation with a water bath temperature below 40 °C. Product purification by flash column chromatography was accomplished using silica gel 60 (32−63 μm particle size from Fluka or Brunschwig) at 0.1−0.3 bar pressure. Technical grade solvents were used for chromatography and distilled prior to use. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} glass plates. Visualization was achieved either by fluorescence quenching or by staining with aqueous potassium permanganate solution. Melting points were measured using a Büchi 510 melting point apparatus in open glass capillaries and are uncorrected. NMR spectra were recorded at room temperature on a Varian Mercury operating at 300 MHz (^{1}H) and 75 MHz (^{13}C), respectively. Residual solvent signals are internally referenced. Chemical shift δ is referred to in terms of ppm, and coupling constants are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, q = quartett, m = multiplet or unresolved, br = broad signal. Infrared spectra were recorded on a Perkin-Elmer Spektrum RX I FT-IR System and reported in cm^{-1}. Samples were prepared by a thin film technique. Combustion analysis was performed by the Mikroelementaranalytisches Laboratorium at ETH Zurich. Mass spectra were obtained from the MS Service of the ETH Zurich or the MS service of the University of Fribourg/Switzerland. MALDI-mass spectra were recorded using an Ion Spec Ultima HR FT-ICR MS MALDI-FT-ICR MS using the DHB-tl (2,5-dihydroxybenzoic acid two layers) method at 4.7 T. High-resolution EI mass spectra were performed on a Micromass AutoSpec Ultima and were calibrated with perfluorotributylamine (PFTBA) prior to data acquisition. Enantiomeric ratios were determined with a Merck Hitachi LaChrom D-7000 HPLC using a Chiracel OD-H column, a Knauer differential refractometer, and hexane/isopropanol as eluents.

General Procedure for the Formation of Isomeric Mixtures of Nitroalkenes. Triethylamine (3.0 equiv) was added to a solution of the 1-nitroalkene (0.2 M in $CHCl_3$), and the mixture was left at rt for 12 h. The solution was washed with dilute hydrochloric acid (1 M) and dried over sodium sulfate, and the solvent was evaporated.[4]

General Procedure for the Reduction of an Isomeric Mixture of Nitroolefins. In a 10 mL Schlenk flask copper(I) *tert*-butoxide (6.8 mg, 50 μmol) and (*R*)-(*S*)-Josiphos (33 mg, 55 μmol) were dissolved in toluene (5 mL). After the solution was stirred for 30 min at rt, 1.0 mL (10 μmol of complex) was taken and mixed with toluene (4.0 mL) in a second 10 mL Schlenk flask. PMHS (6.0 μL, 0.10 mmol) was added followed by phenylsilane (185 μL, 1.50 mmol) and water (27.0 μL, 1.50 mmol). After stirring for 5 min the isomeric mixture of nitroolefins (1.00 mmol) was added with vigorous stirring. The dark mixture turned yellow, and gas evolution was observed. After stirring for 2 h at rt nBu$_4$NOH·30H$_2$O (80.0 mg, 0.10 mmol) was added. Gas evolution was observed. After the mixture was stirred for 4 h, TBAF solution (4 mL, 1.0 M in THF, 4.0 mmol) was added and stirring was continued for 10 min. Water (20 mL) was added, and the mixture extracted with ether (2 × 30 mL). After drying over sodium sulfate, the solvent was evaporated. Flash chromatography (hexane/EtOAc) provided the product as a colorless oil (for yields and enantiomeric ratios, see Table 1).

(*E*)-2-Phenyl-1-nitro-1-propene:[3] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.45 (m, 5H, arom. *H*), 7.31 (m, 1H, C1-*H*), 2.65 (m, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 149.8, 138.1, 136.1, 130.2, 128.9, 126.7, 18.6. IR (film): ν = 1623, 1576, 1514, 1445, 1375, 1340, 1257, 921, 835, 765, 738, 696, 609 cm^{-1}.

1-(1-Nitroprop-2-en-2-yl)benzene:[5] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.31−7.47 (m, 5H, arom. *H*), 5.83 (s, 1H, C(3)*H*^{1}), 5.54 (s, 1H, C(3)*H*^{2}), 5.37 (s, 2H, C(1)H_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 137.8, 136.7, 128.7, 128.6, 125.6, 121.7, 79.6. IR (film): ν = 3060, 2916, 1633, 1555, 1520, 1498, 1446, 1432, 1373, 1339, 1205, 1029, 928, 783, 738, 702, 569 cm^{-1}. Anal. Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.15; H, 5.64; N, 8.45.

(*E*)-2-(4-Chlorophenyl)-1-nitro-1-propene:[3] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.40 (m, 4H, arom. *H*), 7.28 (q, J = 1.6 Hz, 1H, C1-*H*), 2.62 (d, J = 1.6 Hz, 3H, Me). ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C): δ = 147.0, 136.7, 136.0, 135.0, 128.9, 128.7, 17.7. IR (film): ν = 3106, 1622, 1591, 1515, 1490, 1435, 1402, 1374, 1342, 1255, 1097, 1012, 921, 823, 756 cm^{-1}.

1-Chloro-4-(1-nitroprop-2-en-2-yl)benzene: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.36 (m, 5H, arom. *H*),

(4) In case both isomers could be separated by flash column chromatography (silica gel, hexane/ethyl acetate) and isolated in pure form, new compounds were completely characterized; otherwise spectroscopic data of the mixtures are reported.

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5.81 (s, 1H, C(3)H^1), 5.56 (t, J = 0.9 Hz, 1H, C(3)H^2), 5.33 (d, J = 0.9 Hz, 2H, C(1)H_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 136.8, 135.1, 134.6, 128.9, 127.1, 122.3, 79.4. IR (film): ν = 1555, 1494, 1431, 1372, 1320, 1111, 1090, 1012, 929, 835, 638, 553 cm^{-1}. Anal. Calcd for $C_9H_8NO_2Cl$: C, 54.70; H, 4.08; N, 7.09. Found: C, 54.46; H, 4.17; N, 7.13.

(*E*)-2-(4-Methoxyphenyl)-1-nitro-1-propene and 1-Methoxy-4-(1-nitroprop-2-en-2-yl)benzene:[3] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): (conjugated isomer) δ = 7.43 (d, J = 8.1 Hz, 2H, arom. *H*), 7.33 (s, 1H, C1-*H*), 6.94 (d, J = 8.1 Hz, 2H, arom. *H*), 3.85 (s, 3H, OMe), 2.64 (s, 3H, Me); (nonconjugated isomer) δ = 7.35 (m, 2H, arom. *H*), 6.86 (m, 2H, arom. *H*), 5.70 (s, 1H, C(3)H^1), 5.40 (s, 1H, C(3)H^2), 5.32 (m, 2H, C(1)H_2), 3.74 (s, 3H, O*Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): (conjugated isomer) δ = 161.4, 149.6, 135.0, 130.1, 128.3, 114.3, 55.5, 18.4; (nonconjugated isomer) δ = 159.8, 129.8, 126.8, 119.7, 113.9, 113.7, 79.5, 23.6.

(*E*)-3-Hydroxy-2,3-dimethyl-1-nitro-1-butene and 2-Methyl-3-(nitromethyl)but-3-en-2-ol:[3] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): (conjugated isomer) δ = 7.35 (m, 1H, C1-*H*), 2.17 (d, J = 1.6 Hz, 3H, *C*2-*Me*), 2.10 (br s, 1H, O*H*), 1.42 (s, 6H, C3-*Me*$_2$); (nonconjugated isomer) δ = 5.43 (s, 1H, C(3)H^1), 5.24 (m, 1H, C(3)H^2), 5.01 (d, J = 0.6 Hz, 2H, CH_2NO$_2$), 2.36 (s, 1H, O*H*), 1.35 (s, 6H, *Me*$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): (conjugated isomer) δ = 156.9, 134.9, 73.4, 28.4, 15.3; (nonconjugated isomer) δ = 145.5, 118.8, 77.0, 72.4, 29.2.

(*E*)-2-(Furan-2-yl)-1-nitro-1-propene and 2-(3-Nitroprop-1-en-2-yl)furan:[3] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): (conjugated isomer) δ = 7.67 (m, 1H, C1-*H*), 7.54 (m, 1H, arom. *H*), 6.90 (d, J = 3.7 Hz, 1H, arom. *H*), 6.55 (m, 1H, arom. *H*), 2.55 (m, 3H, *Me*); (nonconjugated isomer) δ = 7.40 (m, 1H, arom. *H*), 6.45 (m, 1H, arom. *H*), 6.41 (m, 1H, arom. *H*), 5.95 (s, 1H, C(3)H^1), 5.41 (s, 1H, C(3)H^2), 5.20 (s, 2H, C(1)H_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): (conjugated isomer) δ = 150.5, 145.5, 136.6, 132.9, 115.8, 112.8, 14.9; (nonconjugated isomer) δ = 144.9, 142.7, 118.2, 118.0, 111.3, 107.4, 77.5.

(*E*)-2-(Thiophen-2-yl)-1-nitro-1-propene and 3-(3-Nitroprop-1-en-2-yl)thiophene:[3] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): (conjugated isomer) δ = 7.57 (q, J = 1.3 Hz, 1H, C1-*H*), 7.46−7.50 (m, 2H, arom. *H*), 7.13 (dd, J = 5.0, 3.7 Hz, 1H, arom. *H*), 2.70 (d, J = 1.3 Hz, 3H, *Me*); (nonconjugated isomer) δ = 7.25 (dd, J = 5.5, 1.1 Hz, 1H, arom. *H*), 7.08 (dd, J = 3.6, 1.1 Hz, 1H, arom. *H*), 7.00 (dd, J = 5.5, 3.6 Hz, arom. *H*), 5.83 (s, 1H, C(3)H^1), 5.41 (m, 1H, C(3)H^2), 5.30 (d, J = 0.8 Hz, 2H, CH_2NO$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): (conjugated isomer) δ = 142.8, 140.4, 133.6, 129.5, 129.1, 128.5, 18.0; (nonconjugated isomer) δ = 140.5, 131.5, 127.6, 125.6, 124.5, 119.8, 79.1.

1-(4-((*E*)-1-Nitroprop-1-en-2-yl)phenyl)ethanone: Mp: 53 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.01 (m, 2H, arom. *H*), 7.54 (m, 2H, arom. *H*), 7.31 (q, J = 1.6 Hz, 1H, C*H*NO$_2$), 2.65 (d, J = 1.2 Hz, 3H, C(3)H_3), 2.64 (s, 3H, CO*Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 196.9, 148.3, 142.5, 138.1, 137.0, 128.8, 127.0, 26.8, 18.6. IR (film): ν = 3107, 1683, 1621, 1605, 1563, 1514, 1428, 1406, 1340, 1267, 1191, 1014, 957, 920, 828, 683 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.41; H, 5.44; N, 6.86.

1-(4-(1-Nitroprop-2-en-2-yl)phenyl)ethanone: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.97 (m, 2H, arom. *H*), 7.53 (m, 2H, arom. *H*), 5.93 (s, 1H, C(3)H^1), 5.66 (t, J = 0.8 Hz, 1H, C(3)H^2), 5.39 (d, J = 0.8 Hz, 2H, C(1)H_2), 2.61 (s, 3H, *Me*). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 197.1, 141.1, 137.0, 136.9, 128.7, 125.9, 123.8, 79.2, 26.7. IR (film): ν = 3008, 2915, 1682, 1606, 1554, 1405, 1371, 1269, 1195, 958, 935, 845, 753, 595 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.26; H, 5.53; N, 6.96.

1-(4-(1-Nitropropan-2-yl)phenyl)ethanone: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.91 (m, 2H, arom. *H*), 7.32 (m, 2H, arom. *H*), 4.57 (dd, J = 12.1, 7.8, 1H, C(1)H^1), 4.51 (dd, J = 12.5, 7.5, 1H, C(1)H^2), 3.69 (m, 1H, C(2)*H*), 2.57 (s, 3H, CO*Me*), 1.38 (d, J = 7.2 Hz, 3H, C(3)H_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 197.2, 146.1, 136.2, 128.8, 127.0, 81.1, 38.5, 26.6, 18.7. IR (film): ν = 2974, 2932, 1682, 1609, 1552, 1431, 1417, 1382, 1360, 1269, 1132, 1015, 959, 835, 664 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.74; H, 6.48; N, 6.69. $[\alpha]_D^{28}$ ($CHCl_3$, c = 1.750): + 40.8.

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