A Convenient Procedure for the Conversion of (*E*)-Nitroalkenes to (*Z*)-Nitroalkenes *via erythro*-β-Nitroselenides

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erythro-Selective conjugate addition of benzeneselenol to (*E*)-nitroalkenes and subsequent *syn*-elimination of benzeneselenenic acid provide a new method for the conversion of (*E*)-nitroalkenes into (*Z*)-nitroalkenes.

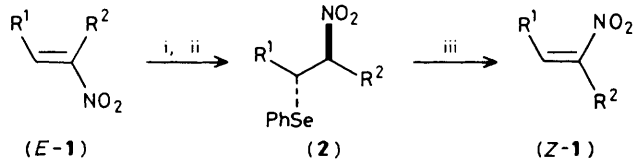
As the nitro group is a strong electron withdrawing group, nitroalkenes are versatile synthetic reagents.[1] For example, conjugate addition,[2] Diels–Alder reaction,[3] or 1,3-dipolar addition,[4] using nitroalkenes are powerful methods for carbon–carbon bond formation. Moreover, since after these reactions the nitro groups can be converted into various functional groups, nitroalkenes have become important intermediates in organic synthesis.[1]

Although many methods for the preparation of nitroalkenes are known, they generally produce (*E*)-nitroalkenes.[1,5] There

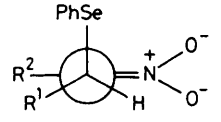
Table 1. Preparation of (*Z*)-nitroalkenes from (*E*)-nitroalkenes.

R^1	R^2	(2) Yield/%[a]	*erythro*-(2) : *threo*-(2)[b]	Step iii yield /%[a]	(*Z*)-(1) : (*E*)-(1)[c]	^{1}H N.m.r. shift of vinyl-H/δ[e]
Me	Me	68	91 : 9	99	90 : 10	5.97 (q)
Et	Me	77	87 : 13	99	88 : 12	5.84 (t)
n-C_7H_{15}	Me	82	87 : 13	99	87 : 13	5.84 (t)
Ph	Me	74	80 : 20	99	99 : 1[d]	7.20 (s)
Bu	Et	68	95 : 5	99	95 : 5	5.78 (t)

[a] Isolated yield. [b] Determined by 400 MHz ^{1}H n.m.r. [c] Determined by g.l.c. [d] Recrystallized pure *erythro*-isomer was used. [e] (*Z*)-(1).



Scheme 1. *Reagents:* i, PhSeNa (1.2 equiv.), EtOH, −78 °C, 1 h; ii, AcOH (2 equiv.), −78 °C, 1 h; iii, H_2O_2 (30%), CH_2Cl_2, 0 °C, 10 min.



(3)

is no general method for the preparation of (*Z*)-nitroalkenes.†[6] Here we report a new convenient procedure for the conversion of readily available (*E*)-nitroalkenes into (*Z*)-nitroalkenes.

Treatment of (*E*)-nitroalkenes (*E*)-(**1**) with sodium benzeneselenolate, generated *in situ* from diphenyl diselenide and $NaBH_4$ in ethanol,[7] followed by protonation with acetic acid at −78 °C afforded *erythro*-β-nitroselenides (**2**) stereoselectively. Treatment of (**2**) with H_2O_2 at 0 °C resulted in the elimination of benzeneselenic acid to give (*Z*)-nitroalkenes (*Z*)-(**1**) in quantitative yields. The results are summarized in Table 1.

The conventional Michael additions of benzenethiol or related compounds to nitroalkenes are carried out using a catalytic amount of base in a polar solvent, giving non-stereoselective addition, with the *erythro–threo* ratio *ca.* 1.0—1.2. However, the reaction conditions described here (Scheme 1) (1 equiv. of base and protonation at −78 °C) produce the *erythro*-isomer predominantly. This selectivity can be explained by assuming that the protonation of the intermediate (**3**) takes place preferentially at the less hindered site.[8]

The elimination of benzeneselenenic acid gave (*Z*)-(**1**) selectively and no allylic nitro compounds were detected. The (*Z*)-geometry of the products was readily assigned on the basis of ^{1}H n.m.r. spectra, the vinylic proton of (*Z*)-isomer appearing at higher field than the corresponding proton of the (*E*)-isomer because of the strong anisotropic effect of the nitro group.[6] As the *syn*-elimination of benzeneselenenic acid is well established,[9] this confirms the *erythro* structure of (**2**).

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† Although some (*Z*)-nitroalkenes can be prepared *via* the nitroselenylation of alkenes and subsequent elimination of selenenic acid, this method cannot be applied to the unsymmetrical alkenes.

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