Stereoselective Preparation of (*E*)-Allyl Alcohols *via* Radical Elimination from *anti*-γ-Phenylthio-β-nitro Alcohols

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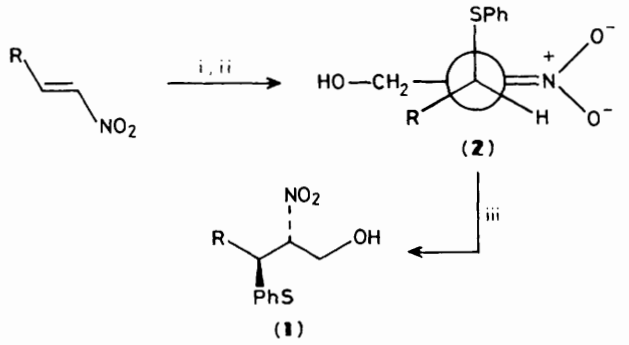
Phenylthio and hydroxymethyl groups may be introduced into nitroalkenes stereoselectively by treatment with benzenethiol and aqueous formaldehyde to give *anti*-γ-phenylthio-β-nitro alcohols, which are converted into (*E*)-allyl alcohols *via* radical elimination induced by Bu_3SnH.

The formation of carbon–carbon double bonds is important and has been widely explored.[1] Radical elimination should provide a new method for preparing carbon–carbon double bonds, because radical reactions often show selectivities which are different from those for ionic reactions.[2] The following compounds have been employed for alkene synthesis *via* radical elimination induced by Bu_3SnH: *vic* dibromides,[3] β-bromosulphides,[4] β-bromosulphoxides,[5] β-bromosulphones,[6] *vic* dixanthates,[7] β-isocyanoxanthates,[8] β-nitrosulphides,[9] β-nitrosulphones,[10,11] and *vic* dinitro compounds.[10] Unfortunately, most of these eliminations proceed non-stereospecifically.[3–8] On the other hand, stereospecific rad-

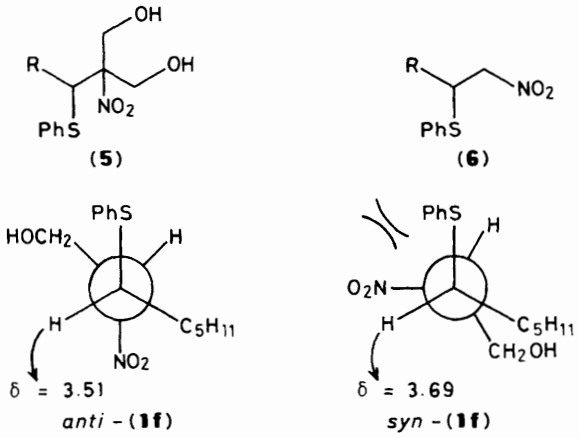
Table 1. Preparation of *anti*-phenylthio-β-nitroalcohols (**1**) and their conversion into allyl alcohols and their derivatives (**4**).

R	% Yield[a] of (**1**)	*Anti*/*syn*[b]	R′	% Yield[a] of (**4**)	*E*/*Z*[c]
Me	(**1a**) 85	87/13	Bz[d]	(**4a**) 75	99/1
Et	(**1b**) 91	93/7	Bz	(**4b**) 76	95/5
Pr^n	(**1c**) 66	86/14	Bz	(**4c**) 85	99/1
Pr^i	(**1d**) 57	87/13	Bz	(**4d**) 78	99/1
Bu^n	(**1e**) 63	87/13	Ac	(**4e**) 58	99/1
n-C_5H_{11}	(**1f**) 89	87/13	Ac	(**4f**) 79	99/1
Ph	(**1g**) 78	87/13	H	(**4g**) 78	95/5
$PhCH_2CH_2$	(**1h**) 79	91/9	H	(**4h**) 80	99/1

[a] Isolated yield. [b] Determined by h.p.l.c. [c] Determined by g.l.c. [d] Bz = PhCO.

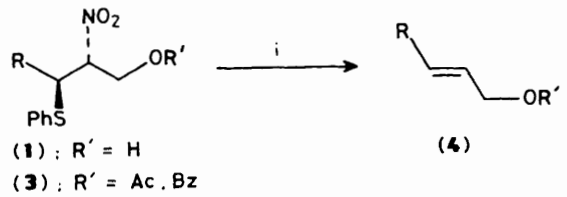


Scheme 1. *Reagents:* i, PhSLi (1.5 equiv.), tetrahydrofuran, room temp., 1 h; ii, 37% HCHO (2.0 equiv.), 3 h; iii, AcOH (2 equiv.), −78 °C, 1 h.

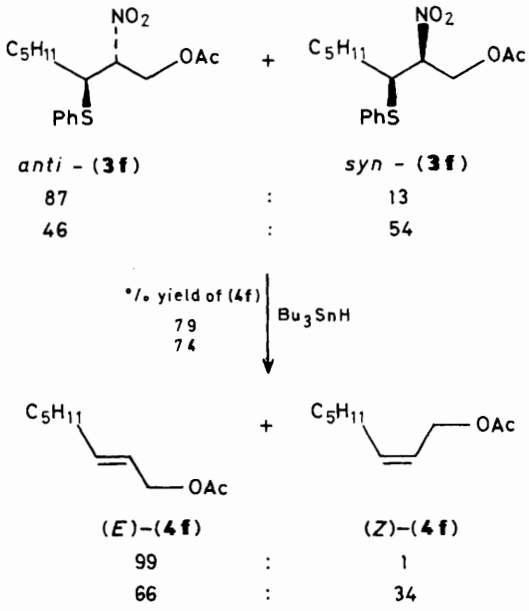


ical elimination occurs in the reaction of β-nitrosulphides or β-nitrosulphones with Bu_3SnH,[9,10] where the nitro group and the sulphur group are eliminated in the *anti* conformation.[11] Previously, we reported a convenient method for preparing *anti*-β-nitrosulphides and β-nitroselenides by kinetically controlled protonation.[12] We now report a new method for preparing (*E*)-allyl alcohols, which consists of a one-step preparation of *anti*-γ-phenylthio-β-nitro alcohols from nitroalkenes, and radical elimination induced by Bu_3SnH.

A mixture of lithium benzenethiolate and the nitroalkene in tetrahydrofuran (THF) was stirred at room temperature for 1 h and then 37% aqueous HCHO was added. The resulting solution was stirred at room temperature for 3 h, and then cooled to −78 °C. Acetic acid (2 equiv.) was added to this solution at −78 °C; the usual work up afforded the γ-phenylthio-β-nitro alcohols (**1**) in good yield with the *anti*-isomer predominating. The results are summarized in Table 1.



Scheme 2. *Reagents*: i, Bu_3SnH (3.5 equiv.), azoisobutyronitrile (AIBN) (1.0 equiv.), toluene, 110 °C, 30 min.



Scheme 3

Thus, phenylthio and hydroxymethyl groups are introduced into the nitroalkene in one step with *anti*-selectivity, the *anti*/*syn* ratio being ~9 : 1. If the reaction was carried out in the conventional way[9] using the nitroalkene, benzenethiol, 37% aqueous HCHO, and catalytic amounts of base, complex mixtures of products, namely, a 1 : 1 mixture of *anti*-(**1**) and *syn*-(**1**), bis-hydroxymethylated compounds (**5**), and β-nitrosulphides (**6**), were obtained. The present diastereoselectivity is presumed to arise in the protonation of (**2**) at low temperature as shown in Scheme 1. The stereochemistry of (**1**) was based on ^1H n.m.r. data. For example, the –C*H*R–SPh signal of *syn*-(**1f**) (δ 3.69) appeared at lower field than that of *anti*-(**1f**) (δ 3.51), because of the strong anisotropic effects of the nitro group. This tendency is generally observed for *syn*- and *anti*-β-nitrosulphides and β-nitroselenides.[12]†

Compounds (**1**) and their acylated derivatives (**3**) were converted into allyl alcohols and their derivatives (**4**) on treatment with Bu_3SnH (3.5 equiv.) in the presence of azoisobutyronitrile (AIBN) (1 equiv.) in toluene at 110 °C (Scheme 2). The results are summarized in Table 1.

It is noteworthy that pure (*E*)-allyl alcohols are selectively obtained from *anti*-rich (**1**) or (**3**). For example, the elimina-

† The 3-H signal of *anti*- and *syn*-2-nitro-3-phenylselenopentane appeared at δ 3.37 and 3.52, respectively. The *anti*-isomer gave pure (*Z*)-2-nitro-pent-2-ene on thermal elimination of selenenic acid.[12]

tion reaction of *anti*-rich (**3f**) gave almost pure (*E*)-(**4f**). However, the elimination reaction from a 1:1 mixture of *anti*-(**3f**) and *syn*-(**3f**) results in the formation of an *E*/*Z* mixture of (**4f**), the *E*/*Z* ratio being about 7:3 (Scheme 3).

These results suggest that the stereoselective formation of (*E*)-(**4**) is mainly derived from *anti*-stereospecific radical elimination of *anti*-(**1**) or *anti*-(**3**). The isomerization of (*Z*)-(**4**) to (*E*)-(**4**) occurs to some extent, but this contribution to the stereoselective formation of (*E*)-(**4**) is very small.

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