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A NEW SYNTHESIS OF ALLYLIC ALCOHOLS OR THEIR DERIVATIVES VIA REDUCTIVE ELIMINATION FROM γ-PHENYLTHIO-β-NITROALCOHOLS WITH TRIBUTYLTINHYDRIDE

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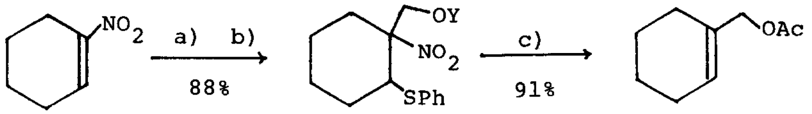
Summary: Allylic alcohols are readily prepared by the Bu_3SnH-promoted elimination reaction from γ-phenylthio-β-nitroalcohls which are obtained by the joint reaction of nitroolefins, thiophenol, and aldehydes.

In this paper we wish to report a new synthetic method of allylic alcohols or their derivatives (4) starting from α-nitro olefins (1). Our new method consists of two key steps, namely, one step-introduction of phenylthio and hydroxyalkyl groups into 1 by the joint reaction of three components (1, PhSH, RCHO) and the regioselective elimination reaction of phenylthio and nitro groups from the product of the first step.[1] As a typical example, conversion of 1-nitrocyclohexene (1a) into 1-acetoxymethylcyclohexene (4a) via 2a and 3a is shown here.



(1)

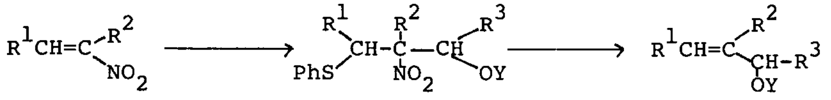
1a 2a (Y = H) 3a (Y = Ac) 4a

(a) PhSH, 37%-HCHO, TMG (cat) (b) Ac_2O (c) Bu_3SnH, AIBN (cat)

Typical procedure: A mixture of 1a (1.27 g, 10 mmol), PhSH (1.36 g, 12.4 mmol), 37%-HCHO(1.12 g, 13.1 mmol) and tetramethylguanidine (TMG, 0.04 g, 0.34 mmol) in acetonitrile (5 ml) was stirred at room temperature for 24 h. The reaction mixture was poured into water, acidified with dilute HCl and extracted with diethyl ether. The crude product obtaied by the usual work-up (washing with water, drying with anhydrous magnesium sulfate, removal of solvents) was subjected to column chromatography (silica gel/hexane-ethyl acetate) to give

2a (2.34 g, 88% yield). Acetylation of 1a with acetic anhydride in pyridine gave 3a in quantitative yield. Then a mixture of 3a (0.62 g, 2.0 mmol), Bu_3SnH (1.2 g, 4.1 mmol) and AIBN (0.08 g, 0.4 mmol) in benzene (4 ml) was heated at 80 °C for 3 h. The crude product was purified by column chromatography (silica gel/benzene-hexane) to give 4a (0.28 g, 91% yield).

The conversion of 1 to 4 can be extended to fairly general substrates. When allylic alcohols are desired, they are directly prepared on treatment of 2 with Bu_3SnH. The results are summarized in Table 1.



(2)

1

2 (Y = H)

3 (Y = Ac or COPh)

4

(a) PhSH, RCHO, TMG (0.03-0.05 eq) at room temp. 4-24 h

(b) $(PhCO)_2O$, DMAP (0.1 eq), pyridine or Ac_2O, H_2SO_4

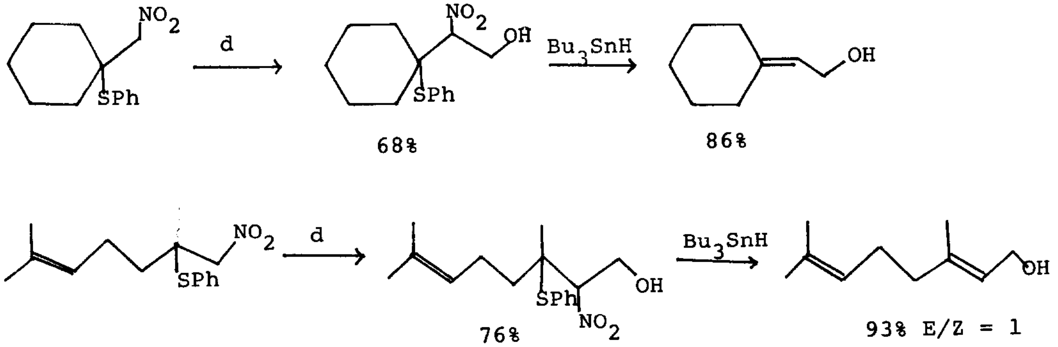
(c) Bu_3SnH (1.5-2 eq), AIBN (0.2-0.3 eq), at 80 °C, 2-3 h.

Table 1 Preparation of allylic alcohols and their derivatives (4)

R^1	R^2	R^3	Y	preparation of 2 time, h	preparation of 2 yield, %	3 yield,%	4 yield,%	E/Z ratio[d)]
H	Me	H	PhCO	5	88	99	87	
H	Et	H	PhCO	6	83	90	71	
H	$n\text{-}C_4H_9$	H	PhCO	5	87	99	92	
H	$n\text{-}C_7H_{13}$	H	PhCO	4	93	98	95	
Ph	Me	H	PhCO	3	97	82	91	59/41
Me	Me	H	PhCO	10	98	87	75	50/50
Et	Me	H	PhCO	10	96	99	93	68/32
$i\text{-}C_3H_7$	Me	H	PhCO	10	95	94	90	70/30
Me	Ph	H	Ac	15	75	79[b)]	85	37/63
Ph	Me	H	H	3	97	—	78	
Ph	H	Et	Ac	24	73[a)]	87	69[c)]	
Me	H	$n\text{-}C_6H_{13}$	Ac	48	66	81	55[c)]	76/24

(a) The reaction was carried out without acetonitrile. (b) Ac_2O in pyridine. (c) Bu_3SnH (3 eq) and AIBN (0.5 eq) were used. (d) The E/Z ratio was determined by GLC and ^1H-NMR.

In general, β,β-disubstituted nitroolefins are difficult to prepare from ketones and nitroalkanes, but some β-nitro sulfides can be prepared by the reaction of ketones with nitromethane in the presence of thiophenol and a catalytic amount of pyperidine in 50-70% yields.[2] Thus obtained β-nitro sulfides were converted into allylic alcohols by the hydroxyalkylation and the subsequent treatment with Bu_3SnH. Two typical examples are presented here.

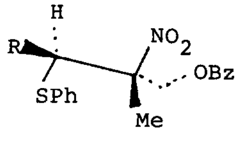


(d) 37%-HCHO, K_2CO_3(0.1 eq), i-PrOH

Thus, α-nitro olefins or ketones are readily converted into allylic alcohols or their derivatives by very simple procedures. Although numerous methods to prepare allylic alcohols are known, the present method may afford a very useful addition, as α-nitro olefins are available from various sources.[3]

The present method affords olefins (4) nonstereoselectively, which is mainly owing to nonstereoselective formation of 2, because the elimination of PhS and NO_2 from 3 proceeds with stereospecificity. Compounds 3 could be separated into two isomers A and B by column chromatography (silica gel/benzene-hexane).[4] Each diastereomer was allowed to react with tributyltin radicals, generated from AIBN and Bu_3SnH in benzene at 80 °C, giving olefins (4) in a stereoselective manner as shown in Table 2.

A :



B:

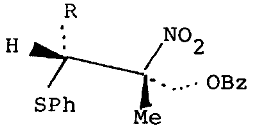


Table 2 Stereochemistry of the elimination of β-nitro sulfides (3) or β-nitro sulfones

Diastereomer	R	E/Z of 4
A	Et	87/13[a] (90/10)[b]
B	Et	27/73 (15/85)
A	i-Pr	74/26 (96/4)
B	i-Pr	46/54 (12/88)

(a) E/Z ratio was determined by GLC and NMR. (b) E/Z ratio of the elimination from the corresponding sulfones.

Interestingly, higher stereoselectivity was observed in the elimination from β-nitro sulfones than that from β-nitro sulfides.[5] This is in sharp contrast with nonstereospecific elimination of thiophenoxy radicals or penylsulfonyl radicals from β-phenylthio radicals or β-phenylsulfonyl radicals which are generated by the reaction of the corresponding bromides with tributyltin radicals.[6] These data suggest that the elimination reactions of β-nitro sulfides or β-nitro sulfones with tin radicals do not involve free alkyl radicals, but proceed by the concerted mechanism.[7] Further studies are currently in progress on the mechanism of the reaction of aliphatic nitro compounds with tin radicals.

References and Notes

1) β-Nitro sulfones and vicinal dinitro compounds undergo similar radical elimination on treatment with tin radicals. N. Ono, H. Miyake, R. Tamura, and A. Kaji, Chem. Lett., 1139 (1981).

2) W. E. Parham and F. L. Ramp, J. Am. Chem. Soc., 73, 1293 (1951).

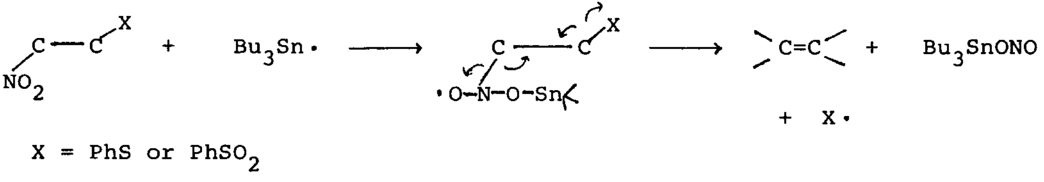
3) Review: A. Yoshikoshi, Yuki Gosei Kagaku Kyokai Shi, 40, 427 (1982), and references following recent papers: M. Miyashita, T. Yanami, T. Kumazawa, and A. Yoshikoshi, J. Am. Chem. Soc., 106, 2149 (1984). A. Kunai, Y. Yanagi, and K. Sasaki, Tetrahedron Lett., 4443 (1983). D. Seebach and P. Knochel, Helv. Chim. Acta., 67, 261 (1984).

4) The structure of β-nitro sulfones was determined by X-ray analysis, and the structure of olefins was determined by NMR. [D. J. Faulker, Synthesis, 175 (1971)]. It turns out that trans-elimination is favored over cis-elimination. So E-rich olefins may be produced from diasteromer A. Details of the stereochemisty of the present reaction will be published elsewhere.

5) In a previous paper we reported that elimination of β-nitro sulfones with tin radicals proceed with very high stereospecificity.[1] As thiophenoxy radicals are better leaving groups than phenylsulfonyl radicals, higher specificity will be expected in the elimination of β-nitro sulfides if the reaction proceeds via β-phenylthio radicals.

6) T. E. Boothe, J. L. Greene, and P. B. Shevlin, J. Am. Chem. Soc., 98, 951 (1976). T. E. Boothe, J. L. Greene, P. B. Shevlin, J.Org. Chem. 45, 794 (1980).

7) One of possible routes is presented here.



X = PhS or $PhSO_2$

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