

STEREOSELECTIVE 1,4-ADDITION OF DIALKYLALUMINUM
BENZENETHIOLATE TO VINYL OXIRANES

A. Yasuda, M. Takahashi,¹ and H. Takaya^{*}

Chemical Materials Center, Institute for Molecular Science
Myodaiji, Okazaki 444, Japan

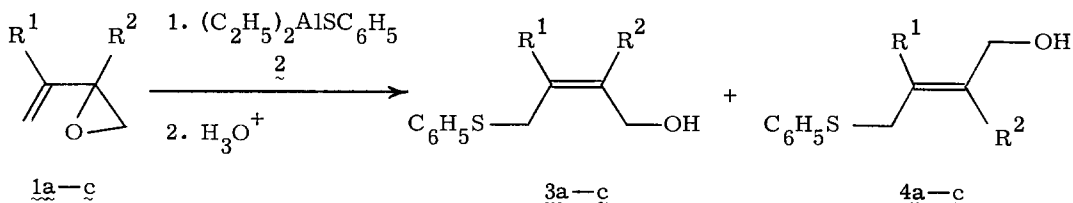
Summary: Reactions of vinyl oxiranes and diethylaluminum benzenethiolate in benzene at room temperature proceed regio- and stereoselectively to afford mainly (Z)-4-phenylthio-2-buten-1-ol derivatives in good yields.

Oxiranes have been widely used as intermediates for the syntheses of a variety of organic compounds because of their easy accessibility and high chemical reactivity.² Reactions of vinyl oxiranes with nucleophiles give rise to 1,2-addition products³ and/or 1,4-addition products^{3a,4} depending on the reagents used. The regio- and stereoselectivities of these types of reactions, however, are not always satisfactory.

Recent communications^{3c,4f} in this field led us to report our results in preliminary forms. We have found that the reactions of alkenyl-substituted oxirane 1 with diethylaluminum benzenethiolate (2) afford selectively 1,4-addition product 3 which has Z configuration concerning the newly formed double bond.

3,4-Epoxy-3-methyl-1-butene (1a) ($R^1 = H$; $R^2 = CH_3$)^{3b} was allowed to react with 2 equiv of 2⁵ in benzene at room temperature for 1 h. Aqueous workup with cold dil. hydrochloric acid followed by purification of the resulting crude product by column chromatography afforded pure samples of the Z allylic alcohol 3a and its E isomer 4a in 92% combined yield in a ratio of 98:2.⁶ No 1,2-addition products were detected. The structures of the products were easily established on the basis of ¹H NMR spectra.⁷ Signals due to the methyl protons of 3a were observed at lower field (δ 1.80) than those of 4a (δ 1.60) as had been reported for structurally related compounds.⁸ The Eu(fod)₃-aided spectra of 3a and 4a also supported the stereochemical assignments.⁷ Similarly, reactions of 1b ($R^1 = H$; $R^2 = C_5H_{11}$)⁹ and 1c ($R^1 = R^2 = CH_3$)¹⁰ afforded the allylic alcohols 3b and 3c accompanied by a small amounts of 4b and 4c, respectively. The results were summarized in Table I.

It is noteworthy that the product distribution is variable dependent on the reaction conditions. Reaction of 1a and 2 in toluene at -78 °C resulted in much reduced regio- and stereoselectivity, affording three products, 3a, 4a, and the regioisomer 5¹¹ in almost equal amounts.

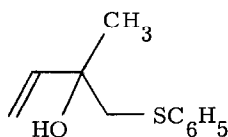
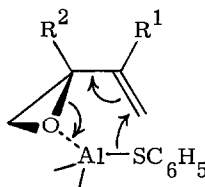
Table I. Reaction of Vinyl Oxiranes with 2.^a

oxirane	R ¹	R ²	% yield ^b	<u>3</u> : <u>4</u> ^c
<u>1a</u>	H	CH ₃	92	98 : 2
<u>1b</u>	H	C ₅ H ₁₁	90	99 : 1 ^d
<u>1c</u>	CH ₃	CH ₃	94	86 : 14

a) The reaction was done with 1 equiv of 1 and 2.0 equiv of 2 at room temperature for 1–4 h. b) Isolation yield after column chromatography on Florisil (benzene–ethyl acetate 50 : 1). c) Product ratio was determined by high pressure liquid chromatography (6 mm x 30 cm JASCOSIL SS-05, hexane–ether 1 : 1, 2 ml/min). d) Dichloromethane was used as solvent.

Use of polar solvents such as ether and THF also promotes the 1,2-addition reactions.

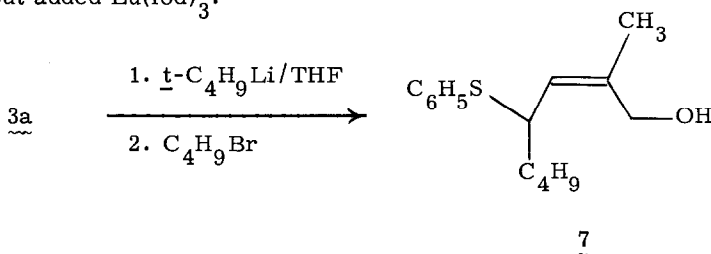
The eminent stereoselectivity producing mainly Z olefinic alcohol 3 suggests that the major product 3 arises via cyclic transition state 6. Such type of transition state has been proposed for the conjugate addition of diisobutylaluminum hydride to vinyl oxiranes.^{4c}

56

Thus, in the present reaction the product composition lies heavily in favor of Z olefinic alcohol 3, which allows us easy preparation of hitherto not readily accessible compounds in good yields. This is in contrast with the reaction of 1a with thiophenol in methanol in the presence of 3 equiv of triethylamine (room temperature, overnight) which gave E isomer 4a as the sole product in 85% yield.¹² Use of lithium perchlorate in place of triethylamine did not produce any isolable products, while lithium benzenethiolate did not cause the cleavage of the

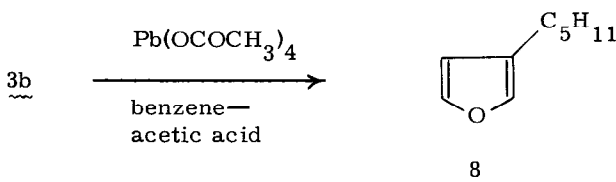
oxirane ring at room temperature.

The present reaction has potential synthetic utility. For example, 3 was easily alkylated with retention of the olefin configuration. Dilithio derivative of 3a was formed in THF from 3a and 2 equiv of *t*-butyllithium in hexane at $-95\text{ }^{\circ}\text{C}$. To this was added 1.2 equiv of butylbromide and the mixture was stirred at room temperature for 4 h. Usual aqueous workup followed by purification of the product by column chromatography (Florisil, benzene—ethyl acetate 50:1) afforded the alkylated product 7 in 71% yield. No trace of the E isomer of 7 was detected by the analysis on high pressure liquid chromatography. The structure was ascertained from NMR data with or without added $\text{Eu}(\text{fod})_3$.



The compound 3 can be converted to furan derivatives. Thus, 3b was treated with 1 equiv of lead tetraacetate in a mixture of benzene and acetic acid (4:1) at $0\text{ }^{\circ}\text{C}$ for 1 h and then at room temperature overnight. Neutralization with aqueous sodium hydrogencarbonate at $0\text{ }^{\circ}\text{C}$ followed by usual workup and purification of the crude product by column chromatography (Florisil, pentane) gave pure 3-pentylfuran (8)¹³ in 24% yield.

We are currently exploring these reactions for use in syntheses of some interesting terpenoids.



References and Notes

- 1) Research student, Faculty of Science, Nagoya University, April 1979—March 1981.
- 2) a) A. Rosowsky, "The Chemistry of Heterocyclic Compounds," A. Weissberger Ed., Wiley, New York, 1964, Vol. 19, Part 1, Chapter 1; b) G. Berti, Topics Stereochem., 7, 93 (1973); c) J. G. Buchanan and H. Z. Sable, "Selective Organic Transformation," B. S. Thyagarajan, Ed., Wiley, New York, 1972, Vol. 2, p 1; d) K. B. Sharpless and T. R. Verhoeven, Aldrichimica Acta, 12, 63 (1979).
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- 5) Diethylaluminum benzenethiolate (2) was prepared according to the reported procedure from triethylaluminum and 1.15 equiv of thiophenol in benzene and used in the next step without isolation: T. Mole and E. A. Jeffery, "Organoaluminum Compounds," Elsevier, Amsterdam, 1972, Chapter 10.
- 6) All new compounds gave correct elemental analyses or high-resolution mass spectra consistent with the assigned structures.
- 7) 3a: $^1\text{H NMR}$ (CDCl_3) δ 1.80 (s, =CCH₃), 3.57 (d, \underline{J} = 8 Hz, CH₂S), 3.8—4.2 (m, CH₂O), 5.45 (broad t, =CH), and 7.1—7.6 (m, aromatic protons). When the Eu(fod)₃-induced shifts were plotted against the mole ratio, Eu(fod)₃/substrate, linear relationship was observed for each group of protons. The gradients, ppm/mole of Eu(fod)₃ per mole of substrate, of these lines were 16.2 (CH₂O), 7.5 (=CCH₃), 5.0 (=CH), and 5.0 (CH₂S).
- 4a: $^1\text{H NMR}$ (CDCl_3) δ 1.60 (s, =CCH₃), 3.53 (d, \underline{J} = 7 Hz, CH₂S), 3.8—4.2 (m, CH₂O), 5.54 (broad t, =CH), and 7.0—7.5 (m, aromatic protons). The gradients of the lines derived from the Eu(fod)₃-aided spectra were 16.8 (CH₂O), 9.4 (=CH), 6.5 (=CCH₃), and 3.3 (CH₂S).
- 8) NMR signals assigned to the methyl protons of (Z)-6-acetoxy-3-methyl-1-phenylthiohex-2-ene appear at δ 1.75, while those due to the E-isomer are observed at δ 1.59; B. M. Trost, M. J. Bogdanowicz, W. J. Frazee, and T. N. Salzmann, J. Am. Chem. Soc., 100, 5512 (1978).
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- 10) This compound was prepared from 3-methylene-1-octene and m-chloroperbenzoic acid in dichloromethane (0 °C, 2 h) in 58% yield.
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- 13) 8: $^1\text{H NMR}$ (CCl_4) δ 0.90 (t, \underline{J} = 6 Hz, CH₃), 1.0—1.8 (m, 3CH₂), 2.38 (t, \underline{J} = 7 Hz, =CCH₂), 6.15 (s, =CH), 7.11, and 7.23 (s, 2=CHO).

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