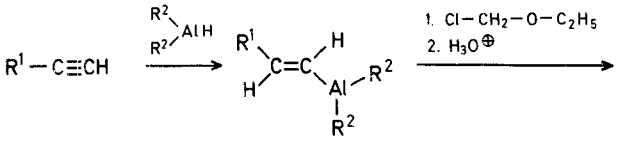
A Stereoselective Synthesis of *trans*-Allyl Ethyl Ethers from 1-Alkynes

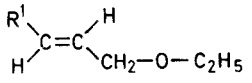
George ZWEIFEL*, Richard A. LYND

Department of Chemistry, University of California, Davis, California 95616, U.S.A.

In exploring the chemistry of vinylalanes (**1**) derived *via* the *cis*-monohydroalumination of 1-alkynes with diisobutylaluminum hydride, we have uncovered an operationally simple method for their direct conversion into isomerically pure *trans*-allyl ethyl ethers in high yields[1].



1



2

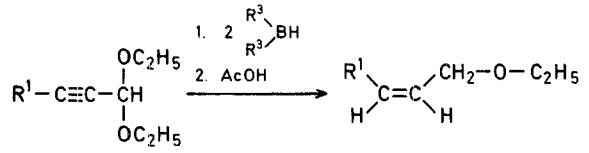
R^1 = alkyl

R^2 = *i*-C_4H_9

It has been demonstrated that the reactivities of vinylalanes toward certain electrophilic reagents are markedly enhanced by conversion into the corresponding *ate*-complexes with alkyllithium reagents[2]. Thus, it was reported recently that lithium alkenyltrialkylaluminate derived from *trans*-1-hexen-1-yldiisobutylalane (**1**, $R^1 = n$-C_4H_9—) and butyllithium reacted with chloromethyl methyl ether in tetrahydrofuran solvent to afford a 51% yield (G.L.C.) of 1-methoxy-*trans*-2-heptene[3]. Our investigations, however, have revealed that for the synthesis of allyl ethyl ethers, conversion of the vinylalanes into their *ate*-complexes is unnecessary, since the reaction of vinylalanes **1** with chloromethyl ethyl ether directly provides the desired products in high yields. Thus, treatment of **1** ($R^1 = n$-C_4H_9—) in hexane with chloromethyl ethyl ether afforded an 80% yield of the isolated *trans*-allylic ether **2** ($R^1 = n$-C_4H_9—)[4, 5].

A summary of the yields of *trans*-allylic ethers **2** obtained in selected examples of these reactions is presented in the Table.

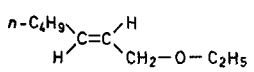
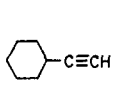
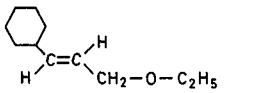
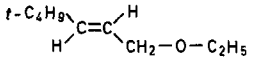
It should be noted that the corresponding *cis*-allyl ethyl ethers are readily available *via* sequential treatment of acetylenic acetals with bis[3-methyl-2-butyl]borane and acetic acid[6].



R^3 = H_3C—CH(CH$_3$)—CH(H_3C)—

Preparation of 1-Ethoxy-*trans*-2-heptene (2, $R^1 = n$-C_4H_9):
Into a dry, nitrogen-flushed flask kept under a static pressure of nitrogen was added 1-hexyne (8.2 g, 0.10 mol), *n*-hexane (40 ml) and diisobutylaluminum hydride (18.6 ml, 0.10 mol) while main-

Table. Yields of 1-Ethoxy-*trans*-2-alkenes from Reaction of Vinylalanes and Chloromethyl Ethyl Ether

Alkyne	*trans*-Allylic ether[a]	Hydro-alumination conditions	Yield [%]	b.p./torr	n_D^{24}	Brutto formula[b]
n-C_4H_9—C≡CH		50°/4 h	80	80–82°/30	1.4223	$C_9H_{18}O$ (142.2)
		25°/24 h	72	68°/3	1.4585	$C_{11}H_{20}O$ (168.3)
t-C_4H_9—C≡CH		25°/4 h	75	69°/50	1.4174	$C_9H_{18}O$ (142.2)

[a] The spectral data of the reported compounds are consistent with the assigned structures.
[b] All allylic ether gave satisfactory elemental analyses (C ±0.15%, H ±0.10%).

taining the temperature during the addition at 25–30° by means of a water bath. The solution was stirred at room temperature for 30 min, that heated at 50° for 4 h. After cooling to room temperature, chloromethyl ethyl ether (9.2 ml, 0.10 mol) in *n*-hexane was added at such a rate as to maintain the temperature during the addition between 25–40°. The resultant solution was stirred for an additional 30 min at room temperature before being poured slowly into a mixture of 6*N* sodium hydroxide (200 ml) and ice (200 g). The organic phase formed was separated and the aqueous phase was extracted with ether. The combined extract was dried with magnesium sulfate. After removal of the solvent, the residue obtained was distilled through a short Vigreux column; yield: 11.35 g (80%); b.p. 80–82°/30 torr; $n_D^{24} = 1.4223$.

$C_9H_{18}O$ (142.2) calc. C 76.02 H 12.75
found 75.98 12.77

I.R. (neat): $\nu_{max} = 1665$ (>C=C<), 1105 (—CH_2OCH_2—), 970 cm^{-1} (*trans*-CH=CH—).

^{1}H-N.M.R. (CCl_4): $\delta = 5.5$ (m, 2H, —C<u>H</u>=C<u>H</u>—), 3.84 (m, 2H, —CH=CHC<u>H</u>$_2$O—), 3.35 (q, 2H, —OC<u>H</u>$_2$CH$_3$, $J = 7$ Hz), 2.0–0.6 ppm (m, 14H).

This research was supported by the National Science Foundation through Grants No. GP-26393-A1 and CHE 76-03738.

Received: August 5, 1976

* To whom correspondance should be addressed.

[1] For recent syntheses of *trans*-allylic ethers see: P. Binger, R. Köster, *Synthesis* **1974**, 350.
W. W. Zajac, Jr., K. J. Byrne, *J. Org. Chem.* **40**, 530 (1975).
[2] G. Zweifel, R. B. Steele, *J. Am. Chem. Soc.* **89**, 2754 (1967).
G. Zweifel, J. T. Snow, C. C. Whitney, *J. Am. Chem. Soc.* **90**, 7139 (1968).
J. J. Eisch, G. A. Damasevitz, *J. Org. Chem.* **41**, 2214 (1976).
K. Uchida, K. Utimoto, H. Nozaki, *J. Org. Chem.* **41**, 2215 (1976).
[3] S. Baba, D. E. Van Horn, E. Negishi, *Tetrahedron Lett.* **1976**, 1927.
[4] The allylic ether contained a small amount (2%) of a compound having the same G.L.C. retention time as 1-ethoxy-2-heptyne.
[5] Addition of chloromethyl ethyl ether to lithium *trans*-1-hexen-1-yldiisobutylmethylaluminate followed by hydrolysis of the reaction mixture gave a 74% G.L.C. yield of **2** ($R^1 = n$-C_4H_9—).
[6] G. Zweifel, A. Horng, J. E. Plamondon, *J. Am. Chem. Soc.* **96**, 316 (1974).