Stereoselective Synthesis of β-Hydroxy Substituted *trans*-Alkenes by the Reaction of *trans*-Alkenyltrialkylaluminates with Epoxides

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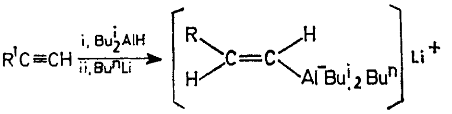
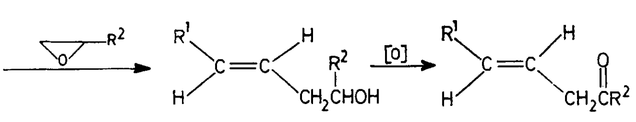
Summary Lithium *trans*-alkenyltrialkylaluminates, prepared by the hydroalumination of alkynes followed by treatment with n-butyl-lithium, react with epoxides to produce β-hydroxy-substituted *trans*-alkenes, which are readily convertible into βγ-unsaturated carbonyl derivatives.

Despite the ready availability of stereo-defined alkenylaluminium compounds *via* hydroalumination, their reactions with certain typical organic electrophiles, such as alkyl halides and sulphonates and epoxides, have remained unexplored. We have found that lithium *trans*-alkenyltrialkylaluminates (**1**), prepared by the reaction of terminal alkynes with Bu^i_2AlH[1] followed by treatment with Bu^nLi, react with epoxides to produce β-hydroxy-substituted *trans*-alkenes, which are readily convertible into the corresponding βγ-unsaturated *trans*-alkenones [equation (1)].



(1) (1)



(2)

The experimental results are summarized in the Table. The reaction of propylene oxide is regioselective producing only secondary alcohols. On the other hand, styrene oxide gives a roughly 1:1 mixture of two possible regioisomers. The reaction of (**1**) with cyclohexene oxide does not proceed at appreciable rates at 25 °C, the desired alcohol being produced in <5% yield in 24 h. Heating the reaction mixture to 50 °C does not improve the yield.

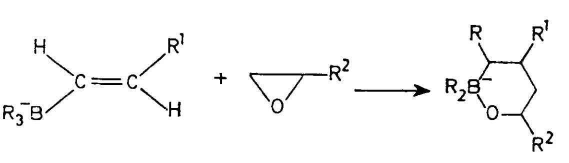
That the stereoisomeric purity of *trans*-non-4-en-2-ol is >95% has been established by g.l.c. analysis (Carbowax 20M) using an authentic sample of the *cis*-isomer which has a longer retention time than the *trans*-isomer. Each of the other products also showed a sharp single g.l.c. peak and a strong i.r. band at *ca.* 970 cm^{-1}. *trans*-Non-4-en-2-ol was readily converted into *trans*-non-4-en-2-one in 87% yield by Jones oxidation.

Table

R^1 of $HC\equiv CR^1$	R^2 of epoxide $\overline{OCH_2}CHR^2$	Yield[a] (%) of (**2**) *via* (**1**)	*via* alane
Bu^n	H	75(63)	47
Bu^n	Me	74	33
Cyclohexyl	Me	77	—
Bu^t	Me	82(68)	—
Bu^n	Ph	57[b]	—

[a] By g.l.c. Numbers in parentheses are isolated yields. [b] *Ca.* 1:1 mixture of regioisomers.

The reaction of the corresponding alkenylalanes produces the alkenols in considerably lower yields. Moreover, products containing two epoxide units as well as the regioisomers, when possible, are detected. It is instructive to note that the reaction of alkenyltrialkylborates with epoxides[2] takes an entirely different course [equation (2)] and that the alkenylboranes do not react readily with epoxides. Thus, the aluminate reaction reported here represents a unique, stereoselective conversion of alkynes into β-hydroxy substituted *trans*-alkenes.



(2)

The experimental procedure is simple. Hydroalumination is carried out in hexane at 50 °C (2 h).[1] Addition of Bu^nLi in hexane at 25 °C gives (**1**) as a white precipitate which dissolves on addition of an epoxide. After treating the mixture with 3N HCl and drying the organic layer over $MgSO_4$, the product is isolated by distillation.

The present reaction, in conjunction with related recent developments,[3,4] demonstrates the highly efficient and selective nature of the organoaluminium routes to certain stereo-defined molecules.

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