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A REGIO- AND STEREOSELECTIVE SYNTHESIS OF γ,δ-UNSATURATED ALCOHOLS

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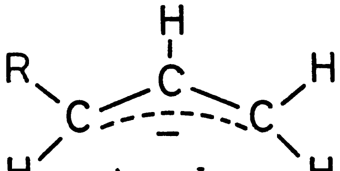
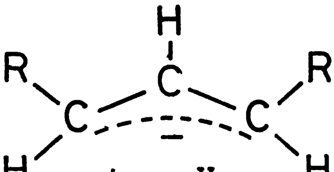
(E)-Erythro-γ,δ-unsaturated alcohols are obtained in good yields by the regio- and stereoselective addition reaction of allylboranes, generated from lithiated 2-butenyloxybenzimidazole and trialkylboranes, with aldehydes and ketones.

γ,δ-Unsaturated alcohols are important intermediates in organic synthesis, and one of the preparative methods is the addition of allylic organometallics to aldehydes and ketones.1),2),3) There appeared several reports concerning the regio- and stereoselective addition of unsymmetrical allylic organometallics of crotyl and related systems (type I) to aldehydes.3) However, few investigation2) has been done on the addition reaction of di-substituted allylic organometallic compound such as type II, which is generally a rapidly interconvertible mixture of isomers,4) and adds to aldehydes and ketones to afford a mixture of regioisomers.

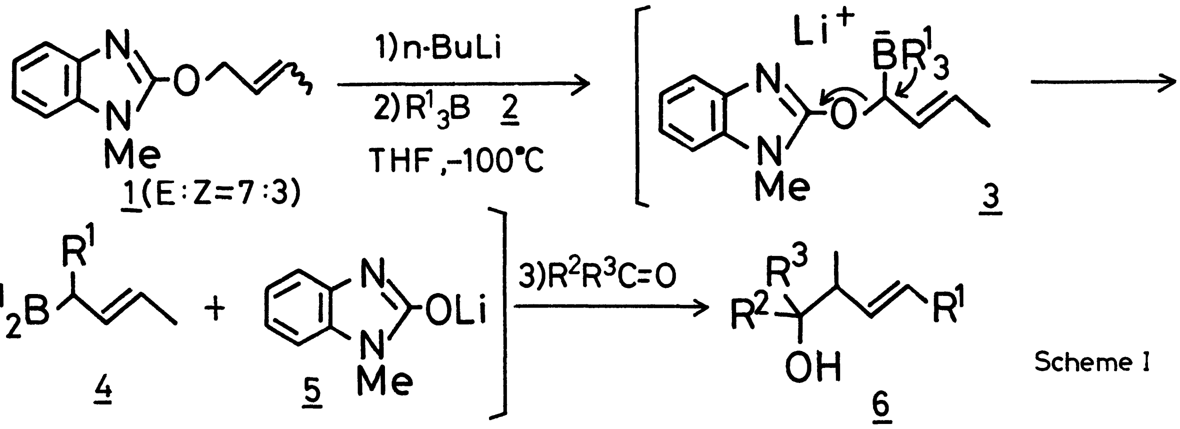

type I


type II

In this communication, we wish to report the first example of regio- and stereoselective formation of γ,δ-unsaturated alcohols by the controlled addition of allylic organometallics of the type II to aldehydes and ketones.

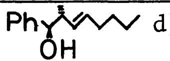
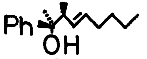
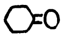
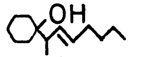
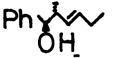
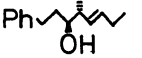
The present synthesis is based on the following observations. 1) Allyldialkylboranes (4) are generated regioselectively by the reaction of trialkylboranes (2) and lithiated 2-(2-butenyloxy)benzimidazole (1).5) In the course of the reaction, alkyl moiety of trialkylboranes migrates exclusively to the α-carbon of 2-butenyloxybenzimidazole to afford boranes (4) by the loss of 2-benzimidazolone (5) (Scheme I). 2) Allyl transposition of allylboranes (4) does not take place at -100°C. This temperature is critical, and stirring the solution at -78°C for 1 h causes the isomerization leading to a mixture of isomeric adducts when treated with an aldehyde.

Based on these facts, allylboranes (4), generated from trialkylboranes (2) and 2-butenyloxybenzimidazole (1) were treated with aldehydes and ketones, and γ,δ-unsaturated alcohols (6) were formed regioselectively as shown in the Scheme I. The results are summarized in Table.



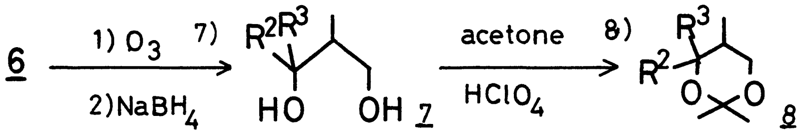
Scheme I

Table The Synthesis of γ,δ-Unsarurated Alcohols

R^1	$R^2R^3C=O$	product$^{a)}$	yield(%)	erythro:threo$^{b)}$	E:Z$^{c)}$
n-Bu	PhCHO	 d)	84	>95:5	≥90:10
	$PhCOCH_3$		75	>95:5	≥90:10$^{e)}$
			91	———	≥90:10
Et	PhCHO	 d)	67	>95:5	≥90:10
	$PhCH_2CH_2CHO$		52	97:3	≥90:10

a) These products gave satisfactory spectral data (NMR, IR).

b)



Adducts (6) were converted to 7 or 8, and configuration was determined following the reported results; K. Koga and S. Yamada, Chem. Pharm. Bull., 20, 526 (1972); J. Canceill, J. Gabard, and J. Jacques, Bull. Soc. Chim. Fr., 1966, 2653; T. Nakata and T. Oishi, Tetrahedron Lett., 1980, 1641.

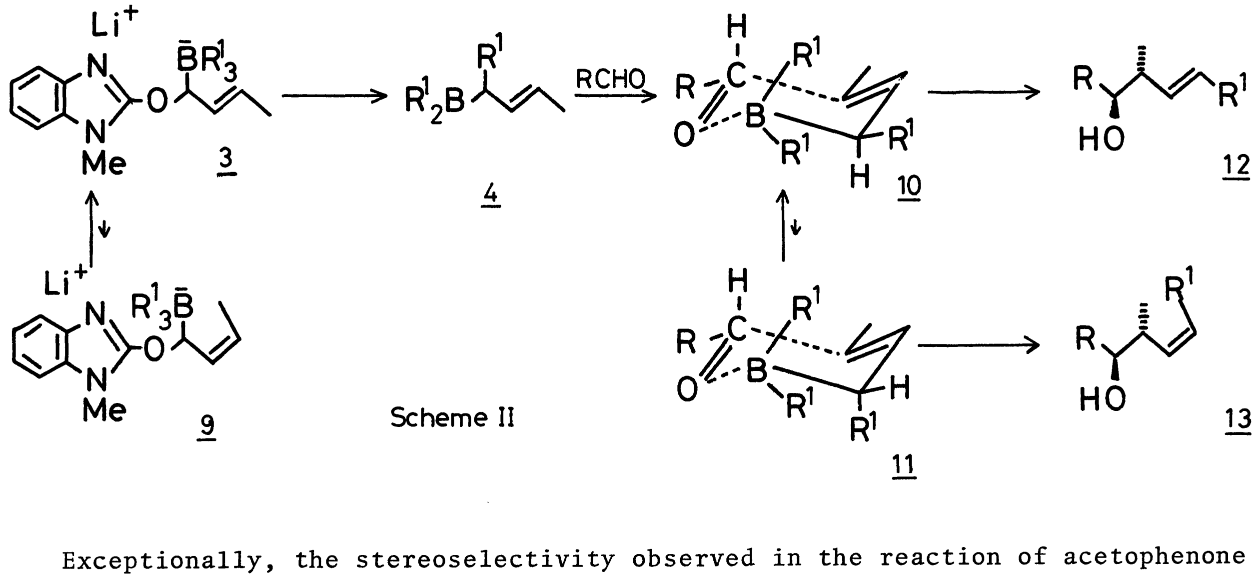
c) The ratio was determined by the comparison of NMR or GLC with that of authentic cis compounds. In each case, a small amount (less than 10%) of cis compounds were detected.

d) Satisfactory elemental analyses were obtained for these compounds.

e) The configuration was determined on the basis of the coupling constant of the vinyl protons.

A typical procedure is described for the synthesis of (E)-erythro-2-methyl-1-phenyl-3-octene: To a tetrahydrofuran (THF, 4ml) solution of 2-(2-butenyloxy)-1-methylbenzimidazole (120mg, 0.6mmol) was added a hexane solution (0.45ml) of n-butyllithium (0.7mmol) at -100°C (a methanol-liquid nitrogen bath) under an argon atmosphere, and the mixture was stirred for 30 min to give a pale yellow solution. Then, tributylborane (0.25 ml, 1.5 mmol) was added and the mixture rapidly lost its color. After 30 min at -100°C, a THF (2 ml) solution of benzaldehyde (53 mg, 0.5 mmol) was added and the resulted solution was stirred overnight at -78°C. The reaction was quenched with a small amount of ethanol and aqueous ammonium chloride. Then, an aqueous solution of hydrogen peroxide was added, and stirring was continued for 30 min. The organic materials were extracted with ether, and the extracts were dried over $MgSO_4$. (E)-Erythro-2-methyl-1-phenyl-3-octene (108 mg, 84%) was isolated by thin layer chromatography (silica gel). Bp 150°C/1 mmHg (by bulb to bulb distillation); Found: C, 82.70; H, 10.46%. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16%. NMR ($CDCl_3$) δ 0.67 (3H, d, J=7Hz), 0.74 (3H, t, J=6Hz), 1.0-1.3 (4H, m), 1.8-2.0 (2H, m), 2.1-2.4 (2H, m), 4.07 (1H, d, J=7Hz) 5.19 (1H, dd, J=16, 7Hz) 5.42 (1H, dt, J=16,6 Hz), 7.14 (5H, s); IR (neat) 3400, 980 cm^{-1}.

The examination of the stereochemistry of the adducts (6) revealed a high selectivity in the addition reaction which forms (E)-erythro-γ,δ-unsaturated alcohols (Table). The results may be explained by assuming 1) a preference of (E)-form in the ate complexes (3, 9); 2) a six membered transition state with chair form (10, 11) in the addition reaction of allyldialkylboranes (4) to aldehydes (Scheme II).[6] Presumably, 1,3-diaxial interaction between proton and alkyl group in the transition state (11) causes 10 to be more favorable and, consequently, results in the formation of (E)-adducts (12).



Scheme II

Exceptionally, the stereoselectivity observed in the reaction of acetophenone is reverse to the above mentioned expectation, and it cannot fully be explained at the present time.

It is reported that γ,δ-unsaturated alcohols are prepared regio- and stereoselectively by the addition reaction of allylboranes, generated from 2-butenyloxybenzimidazole and trialkylboranes, with aldehydes and ketones. The present reaction would provide a useful and general method for the preparation of (E)-erythro-γ,δ-unsaturated alcohols.

References

1) For example:
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