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ALIPHATIC CLAISEN REARRANGEMENT PROMOTED BY ORGANOALUMINIUM COMPOUNDS

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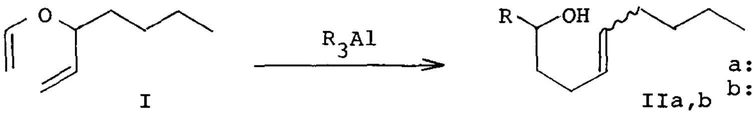
Abstract: Treatment of allyl vinyl ether derivatives with organoaluminium amphoteric reagent, R_3Al or R_2AlSPh, results in the title reaction at room temperature under uptake of R, H, or SPh as a nucleophile on the aldehydic carbon.

Lewis acid catalysis of Diels-Alder reaction[1] or ene reaction[2] has been recently well documented. The attempted aliphatic Claisen rearrangement[3] in the presence of common acidic catalysts such as $TiCl_4$,[4] BF_3,[5] however, failed to success. Here we wish to report that the combined acid-base attack of organoaluminium compounds, R_3Al or R_2AlX as well as Et_2AlSPh or $Et_2AlCl-PPh_3$, on allyl vinyl ether substrates effects the [3,3]sigmatropic rearrangement under mild conditions.



I

IIa,b

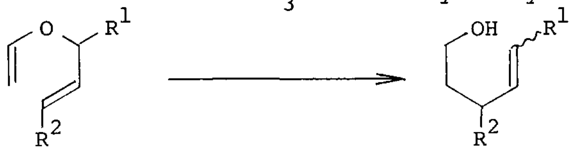
a: R = Me
b: R = Et

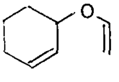
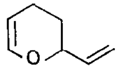
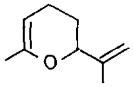
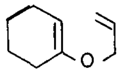
A solution of trimethylaluminium in hexane (1.0 *M*, 4.0 ml, 4.0 mmol) was added to a solution of 1-butyl-2-propenyl vinyl ether I (0.28 g, 2.0 mmol) in 1,2-dichloroethane (15 ml) at 25°C under argon atmosphere and the whole was stirred for 15 min. The mixture was diluted with ether (30 ml) and poured into 1*N* HCl (15 ml). The separated organic layer was washed with brine, dried, and concentrated. Purification by thin layer chromatography on silica gel (ethyl acetate-hexane, 1:2) gave olefinic alcohol IIa[6] (0.28 g, 91% yield, *E*/*Z* = 47/53[7]) as a colourless oil which was produced apparently by the rearrangement and successive methylation.

Methyllithium or diethylzinc was not effective for the transformation and methylmagnesium iodide was marginal.[8] Halogenated hydrocarbon solvents such as 1,2-dichloroethane or dichloromethane gave the best results. In ether or THF, the reaction did not take place.

The use of Et_3Al resulted in formation of a mixture of the corresponding ethylated alcohol IIb (75% yield) as well as hydrogenated one $n\text{-}C_4H_9\text{-}CH{=}CH\text{-}CH_2CH_2CH_2OH$ (19% yield). In contrast, triisobutylaluminium or diisobutylaluminium hydride gave the hydrogenated product exclusively. The reactions between $^{i}Bu_3Al$ and allyl vinyl ether substrates are summarized in Table 1. The *E*/*Z* ratios of newly developed double bond were almost close to unity[9] except in the reaction of run 3 which gave *E* isomer exclusively.

Table 1. Reactions between $^{i}Bu_3Al$ and allyl vinyl ether substrates[a]



Run	Ether[b]		Condition		Yield[c]	*E*/*Z*[d]
	R^1	R^2	Temp(°C)	Time(h)	(%)	
1	^{n}Bu	H	25	0.25	82	38/62
2	^{n}Bu	Me	25	0.25	89	45/55
3	Ph	H	25	0.25	93	*E* only
4	H	Ph	25	0.25	91	——
5			25	0.25	90	——
6			60	2	95	——
7			60	2	97	——
8			25	0.25	78	*trans*/*cis* 23/77

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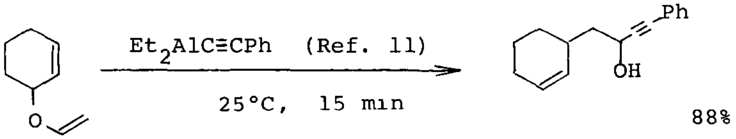
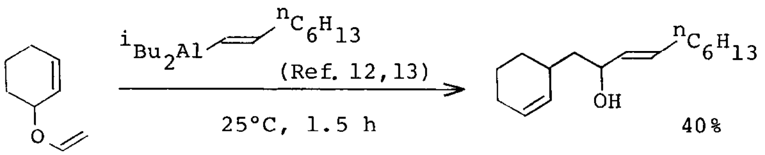
[a] Reactions were performed on 2.0 mmol scale. [b] Prepared by the mercuric acetate catalyzed transetherification using ethyl vinyl ether (run 1-5). See ref. 10. [c] Yields represent isolated purified products. Spectral data were consistent with assigned structures. [d] See ref. 7.

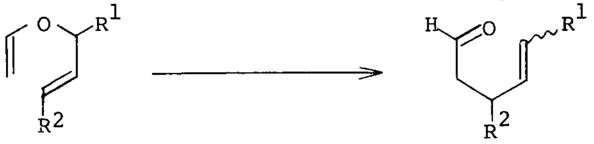
As shown below, not only methyl group or hydrogen but also alkynyl or alkenyl group was introduced selectively in preference to alkyl group.

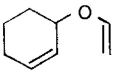
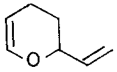
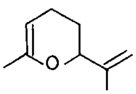
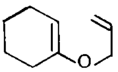




The organoaluminium reagent Et$_2$AlSPh[14] or Et$_2$AlCl-PPh$_3$[15] has been found to be effective for the rearrangement to give aldehydes or ketones (run 9 and 10) without introduction of a nucleophile as exemplified in Table 2. It is worth noting that the rearrangement of 3,4-dihydro-2-vinyl-2H-pyran (run 8) takes place under extremely mild conditions as compared with the pyrolysis (410°C)[16] without catalyst and hence is useful synthetically.[18]

Table 2. Claisen rearrangement promoted by organoaluminium reagents[a]



Run	Ether		Method	Time (h)	Yield (%)	E/Z
	R^1	R^2				
1	^{n}Bu	H	A[b]	0.25	84	39/61[c]
2			B[d]	0.25	81	43/57
3	^{n}Bu	Me	A	0.25	77	52/48[c]
4	Ph	H	A	0.5	67	*E* only
5	H	Ph	A	0.25	86	——
6			B	0.25	87	——
7			A	0.25	78	——
8			B[e]	1	61	——
9			B[e]	0.5	69	——
10			A[e]	0.5	76	——

[a] Reactions were performed on 2.0 mmol scale in 1,2-dichloroethane at 25°C. [b] Treatment with Et$_2$AlSPh (5.0 mmol). [c] See ref. 17. [d] Treatment with a mixture of Et$_2$AlCl and PPh$_3$. See ref. 15. [e] Dichloromethane was used as a solvent.

References and Notes

1. B. M. Trost, J. Ippen, and W. C. Vladuchick, *J. Am. Chem. Soc.*, 99, 8116 (1977).
2. B. B. Snider, *Acc. Chem. Res.*, 13, 426 (1980).
3. In sharp contrast, there have been many reports published on aromatic Claisen rearrangement mediated by Lewis acids. K. Narasaka, E. Bald, and T. Mukaiyama, *Chem. Lett.*, 1975, 1041 and references cited therein. See also following review. G. B. Bennett, *Synthesis*, 1977, 589.
4. It has been reported that $TiCl_4$ did not catalyze the rearrangement of crotyl vinyl ether. R. K. Hill and H. N. Khatri, *Tetrahedron Lett.*, 1978, 4337.
5. Treatment of 1-butyl-2-propenyl vinyl ether with BF_3, $SnCl_4$, or $ZnBr_2$ resulted in formation of complex mixtures containing no detectable amount of the desired rearrangement product.
6. (*E*)-5-Decen-2-ol: bp 75°C (14 Torr, bath temp); IR (neat) 3350, 1125, 1080, 965 cm^{-1}; NMR (CCl_4) δ5.40 (m, 2H), 3.72 (m, 1H), 1.80-2.20 (m, 4H), 0.75-1.70 (m, 12H). (5*Z*)-Isomer: bp 75°C (14 Torr, bath temp); IR (neat) 3400, 1080 cm^{-1}; NMR (CCl_4) δ5.37 (m, 2H), 3.70 (m, 1H), 0.70-2.30 (m, 16H).
7. The crude product was transformed into trimethylsilyl ether whose isomeric ratio was determined by glpc (PEG 20M 10% containing 3% $AgNO_3$ on Celite 545, 70°C).
8. The reaction of I with 3 equivalents of MeMgI took 2 h to be completed, affording IIa (78%, *E*/*Z* = 52/48).
9. Solvent (hexane, PhH, CH_2Cl_2) did not effect the isomer ratios.
10. D. J. Faulkner and M. R. Petersen, *J. Am. Chem. Soc.*, 95, 553 (1973).
11. Prepared from LiC≡C-Ph and Et_2AlCl in hexane.
12. Prepared from 1-octyne and $^{i}Bu_2AlH$ according to the reported procedure. G. Zweifel and C. C. Whitney, *J. Am. Chem. Soc.*, 89, 2753 (1967).
13. Hydrogenated one which is same as that obtained in the reaction of run 5 in Table 1 was also detected (34% yield).
14. A. Itoh, S. Ozawa, K. Oshima, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 54, 274 (1981).
15. A mixture of Et_2AlCl (4.0 mmol) and PPh_3 (4.4 mmol) was dissolved in 1,2-dichloroethane (10 ml total) at room temperature under stirring for 10 min prior to addition of allyl vinyl ether substrates (2.0 mmol). Similar Et_2AlI-Et_3N system was also effective, but the reaction products were not so homogeneous as Et_2AlCl-PPh_3 case.
16. G. Büchi and J. E. Powell, Jr., *J. Am. Chem. Soc.*, 92, 3126 (1970).
17. Sealed tube thermolyses (180°C, 20 min) of these ethers afforded the almost homogeneous rearranged aldehydes (∼95% *E*).
18. Financial support by the Ministry of Education, Science, and Culture, Japanese Government (Grant-in-Aid #56430027), is acknowledged.

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