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LEWIS ACID MEDIATED CLAISEN-TYPE REARRANGEMENT OF ARYL DIENYL ETHERS

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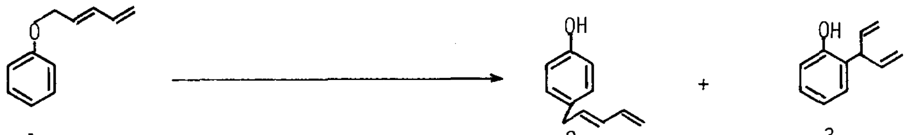
Summary: In the presence of BF_3•OEt_2 aryl dienyl ethers were rearranged under mild conditions to afford dienyl phenols in good yields.

Claisen rearrangement of allyl aryl ethers has long been studied and thermal[1)] or acid catalyzed procedures[2)] have been developed to utilize versatile syntheses.[3)] Only one example, however, has been reported on the rearrangement of aryl 2,4-pentadienyl ether so far regardless of their wide applicability. According to Fráter and Schmid, thermal rearrangement of aryl 2,4-pentadienyl ethers showed low mode selectivity[4)]; *i.e.* the ether gave a mixture of an almost comparable ammont of both [5,5] and [3,3] rearrangement products (Eq. 1a). Although the regioselective dienylation of aromatic ring is highly required in organic synthesis,[5)] the lack of their selectivity prevents its application.

We explored regioselective rearrangement of aryl 2,4-pentadienyl ethers under the presence of Lewis acid, optimized their reaction conditions, and clarified their mode of rearrangement in terms of deuterium labelling technique.



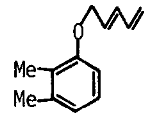
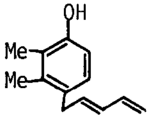
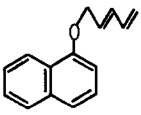
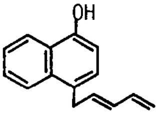
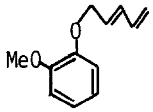
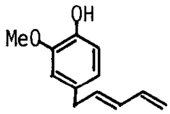
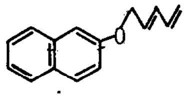
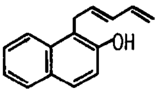
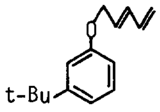
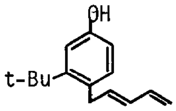
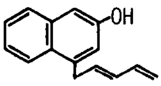
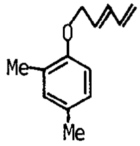
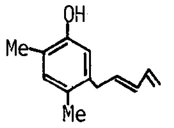
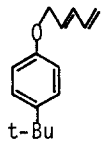
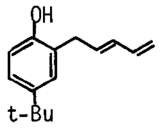
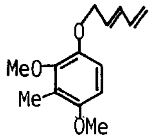
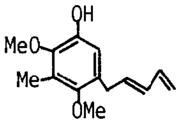
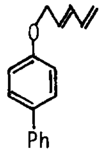
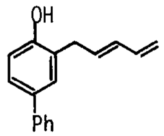
1 2 3

conditions$^{a)}$	2	3	
A	37%	24%	(1a)
B	35%	-	(1b)
C	56%	-	(1c)
D	76%	-	(1d)

$^{a)}$*A*; N,N-diethylaniline, 186 °C, 5 h ; *B*, $TiCl_4$(2 equiv.), $Ti(OPr^i)_4$(1 equiv.), N,O-bis(trimethylsilyl)acetamide(0.5 equiv.), CH_2Cl_2, -78 °C, 0.5 h ; *C*, Et_2AlCl (1.2 equiv.), CH_2Cl_2, -40 °C, 1 h ; *D*, BF_3·OEt_2(1.2 equiv.), CH_2Cl_2, -40 °C, 1 h.

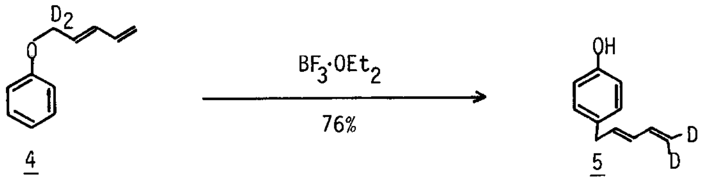
To optimize the reaction conditions, several Lewis acids were examined in the reaction of 2,4-pentadienyl phenyl ether, and $BF_3 \cdot OEt_2$ gave the best result for the present rearrangement (Eq. 1d). The generality of this reaction is observed from Table 1 and good yields were obtained. The results showed the several characteristic modes of rearrangement; (i) in every case, exclusive α (and/or ε) substitution in the pentadienyllic system was observed, no [3,3] re-

Table 1 Lewis acid mediated Claisen-type rearrangement of aryl dienyl ethers[a)]

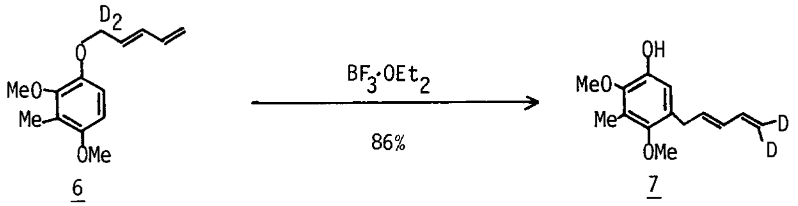
Run	Aryl dienyl[b)] ether	Products[c,d)]	Yield/%	Run	Aryl dienyl ether	Products	Yield/%
1			94	6			80
2			73	7			65 (40 parts)
3			84				(60 parts)
4			70	8			62
5			86	9			43

[a)] All reactions were performed as follow; to a solution of aryl dienyl ether (1.0mmol) in dry CH_2Cl_2 (10 ml), $BF_3 \cdot OEt_2$ (1.2 mmol) was added at -40 °C∿ -20 °C, and this mixture was stirred for 1 h at this temperature. After usual work-up, products were purified by PLC. [b)] The stereochemistry of starting 2,4-pentadienyl ehers (97% trans) was converted in the course of this rearrangement and every product had 100% trans configuration determined by 400 MHz ^{1}H-NMR. [c)] The satisfactory IR, NMR, and mass spectral data were obtained. [d)] The structure was assigned by inspecting the shift value induced by $Eu(fod)_3$ after acetylation.

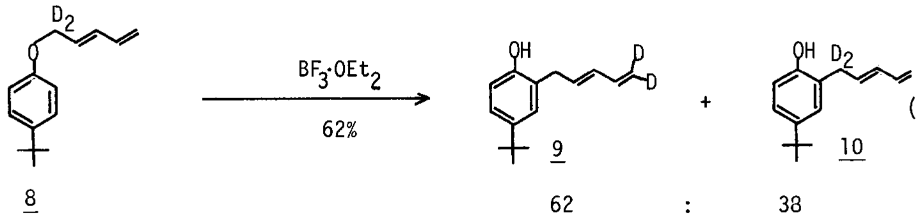
Claisen-type rearrangement of aryl α-deuteriodienyl ethers



(2)



(3)

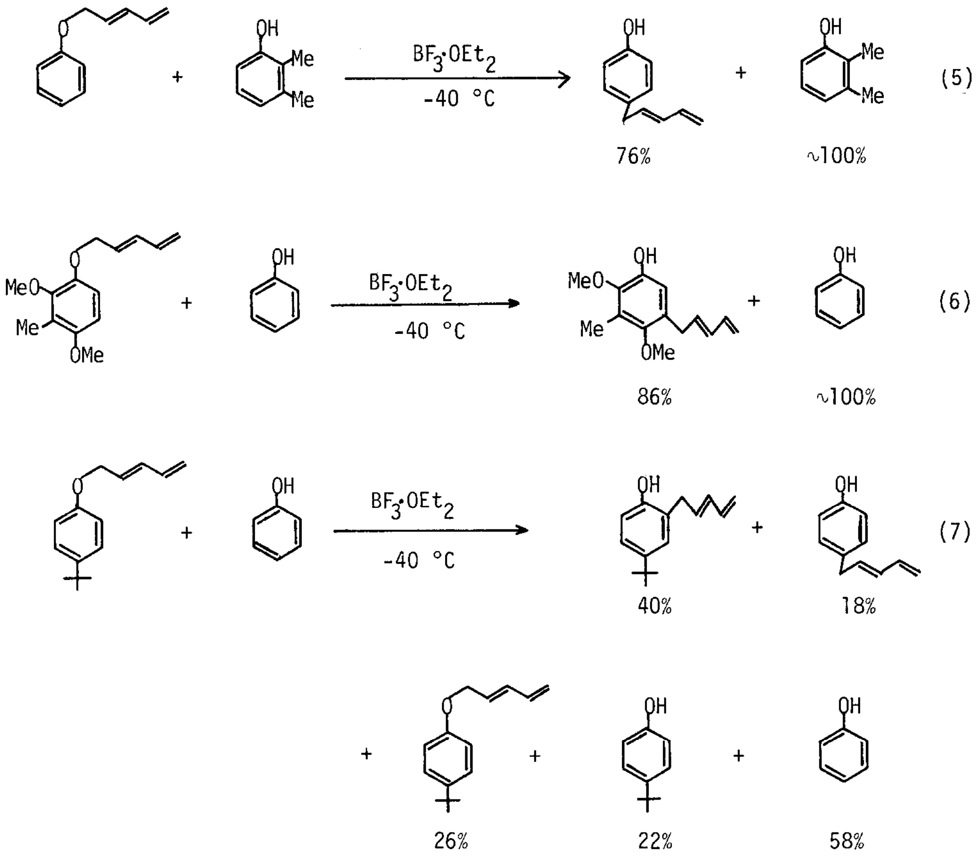


(4)

arrangement occurred, (ii) when para position of the corresponding aryl group is free from substituent, the rearrangement selectively occurred at this position (type A), (iii) when para position has a simple alkyl or an electron donating group, the rearrangement preferencially occurred at meta position (type B), (iv) if bulky group blocks para position, ortho rearrangement was observed (type C). Other Lewis acids also gave no products through [3,3] rearrangement.

To clarify the mode of rearrangement in the pentadienyllic systems, the corresponding ethers, 4, 6, and 8, with regioselectively α-deuterated pentadienyl group were synthesized and submitted to the rearrangement. Type A and B ethers (4 and 6 respectively) exclusively gave ε-deuterated products, while type C ether (8) gave two regioisomers (9 and 10). Since the latter example was seemed to include intermolecular dienyl transfer process, these reactions were examined under the presence of free phenol. Type A and B ethers did gave no cross coupling products (Eq. 5 and 6) and the added free phenol was recovered quantitatively. Type C ether, however, gave the corresponding cross coupling product and phenols (Eq. 7). Conclusively, rearrangement of type A and B ethers proceeds *via* concerted [5,5] and [4,5] modes, respectively, while that of type C include inter- and intramolecular processes. At the present stage, the degree of contribution between inter- and intramolecular rearrangements is hardly estimated and the definitive mode of the rearrangement remains uncertain.

Cross coupling reaction



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