

ANION REARRANGEMENTS: DUALITY OF MECHANISM IN THE DECOMPOSITION OF
ALLYLIC ETHER ANIONS AND SYNTHETIC APPLICATIONS

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During investigations^{3,4} on the rearrangements of sulfonium ylids (I, $X=S^+$, $a=b=c=d=C$) we discovered the existence of two competing mechanistic paths;⁵ a concerted rearrangement with retention of orbital symmetry (A),⁶ and a non-concerted radical dissociation-recombination process (B), the latter providing an explanation of the formation of the Stevens rearrangement products⁷ often noted in these reactions. Since it seemed likely that this specific case is merely one example of a very general dual pathway, where $X=N, O, P$ etc. we have examined a number of related systems. We wish to report here our observations on allylic ether anions (I, $X=O, a=b=c=d=C$) which suggest the same duality and further indicates the utility of the reaction in synthesis.⁸

In this case path (A) provides alcohols containing exclusively inverted allyl groups⁹ whereas (B), involving a radical pair, can provide the Wittig products.¹⁰ Thus treatment of ether (II)¹¹ with n-butyl lithium in tetrahydrofuran, gave after quenching with water, a mixture of two rearrangement products (III) and (IV), separated by distillation.¹² As expected, reduction of temperature (see Table I) gave an increase in the contribution of the more facile path (A). The isomeric ether (V) was rearranged in the same way to yield the same two products but in different proportions and showed a similar temperature dependence (Table I). In these and related cases we have found t-butyl lithium-

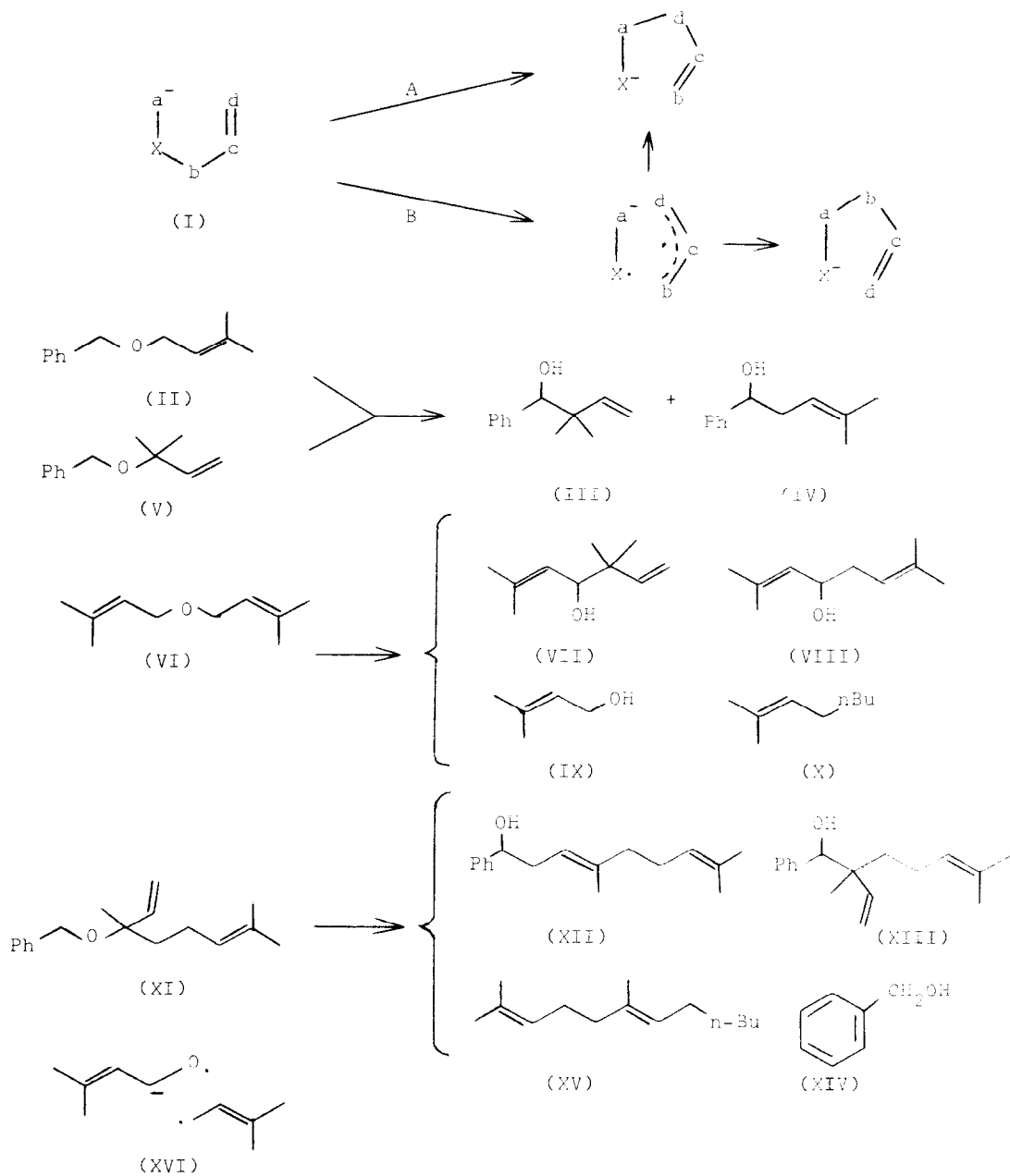


Table I

Reactant	Temp	Product Distribution (GLC %)	
		(III)	(IV)
(II)	25°	95	5
"	-10°	98	2
(V)	25°	23	77
"	-20°	17	83

tetrahydrofuran and methyl sulfinyl carbanion¹³ in dimethyl sulfoxide to be convenient alternatives to n-butyl lithium-tetrahydrofuran.

To demonstrate the synthetic potential of such rearrangements we conducted a simple synthesis of artemisia alcohol as follows. The symmetrical ether (VI)¹⁴ was treated with t-butyl lithium-tetrahydrofuran at -15° and gave after preparative G.L.C. separation the desired alcohol (VII) [31%].¹⁵ It should be noted that the decomposition of ether (VI) also exhibited a marked temperature dependence with n-butyl lithium-tetrahydrofuran at 25° it isomerized to a 1:1 mixture of alcohols (VII) and (VIII) whereas at -15° alcohol (VII) was the exclusive isomerization product. These two compounds were accompanied by decomposition products (IX) and (X).

Finally to demonstrate the facility with which terpenoid chains may be extended we transformed linalyl benzyl ether (XI) with n-butyl lithium-tetrahydrofuran into the mixture of cis and trans alcohols (XII) [45%], with the Wittig product (XIII) [5%]. The two major by-products in this process were benzyl alcohol (XIV) [25%] and the hydrocarbon (XV) [25%], whose structure was proved by composition, spectral data, and ozonolysis to laevulinic aldehyde, identified as the 2,4-dinitrophenyl hydrazone. The origin of these formal displacement products of n-butyl lithium on the ether is not presently clear. A reasonable hypothesis would involve an electron transfer reaction between the radical pair (XVI) and another molecule of n-butyl lithium to give two hydrocarbon radicals and the alkoxy dianion. Coupling of the former would then provide the observed hydrocarbon byproduct and also account for the production of the observed alcohol.

It is evident from these experiments that the sigmatropic rearrangement of ether anions is a convenient synthetic method for chain extension of allyl alcohols, since by operation at sufficiently low temperatures (vide supra) the more useful concerted process can be selected.

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