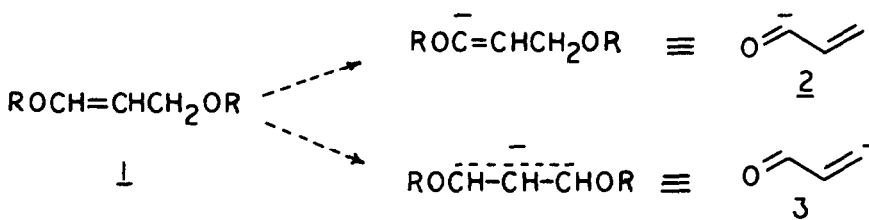


VINYL DEPROTONATION IN PREFERENCE TO ALLYL DEPROTONATION.
 THE REACTION OF 1,3-DIBUTOXYPROPENE WITH *t*-BUTYLLITHIUM.

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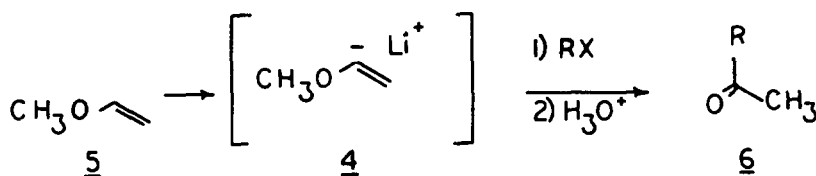
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Lithium reagents of 1,3-dialkoxypropenes 1 could potentially serve as equivalents of acyl anions 2 and vinylogous acyl anions 3. If each could be generated selectively, 1 would then serve as a synthesis "template", capable of accepting two substituents by such "umpolungen"¹,

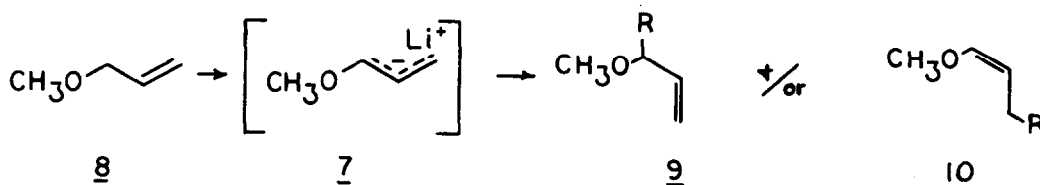


and an additional two substituents by more classical 1,4- and 1,2-nucleophilic additions subsequent to unmasking the enone.²

Baldwin³ has generated methoxyvinyl anion 4 from methylvinyl ether 5 and *t*-butyllithium in the presence of TMEDA, yielding methylketones 6 after alkylation and hydrolysis. Evans⁴ and

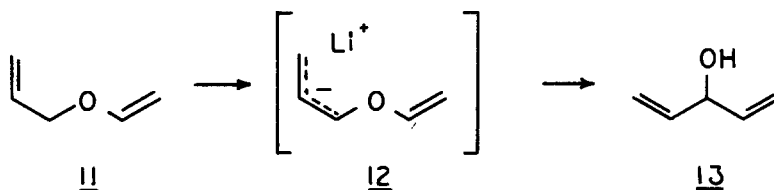


Still⁵ have obtained methoxyallyl anion 7 from methylallyl ether 8 and *sec*-butyllithium. Reaction at the α (9) or γ (10) positions could be controlled by appropriate choice of the metal

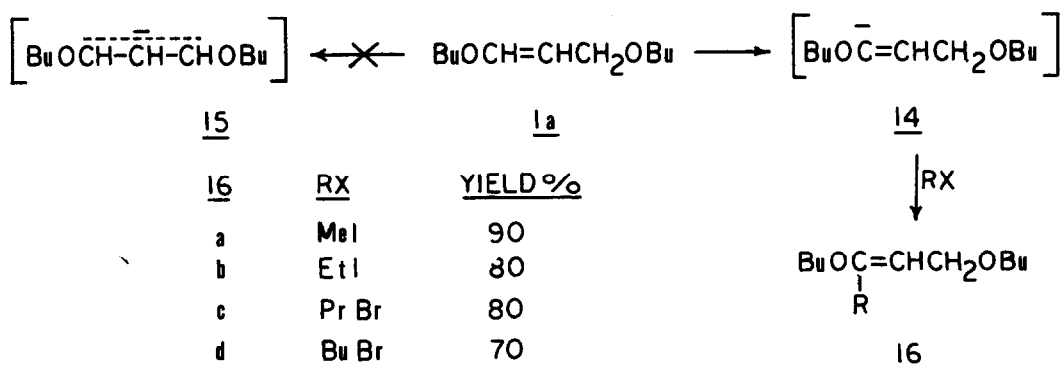


counter ion. Büchi⁶ had shown that allylvinyl ethers 11 preferentially yield allyl anions 12,

which undergo Wittig rearrangement *in situ* to yield divinyl carbinols 13.

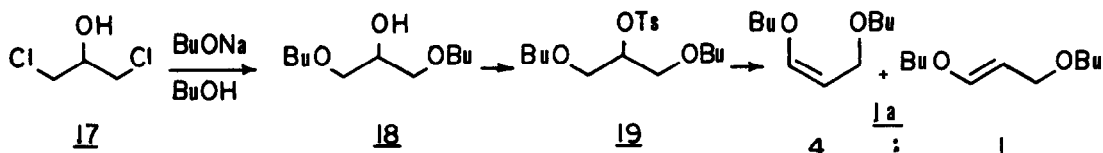


We have prepared 1,3-dibutoxypropene 1a, also containing both a vinyl and allyl ether, and find that treatment with *t*-butyllithium at -65° in the presence of HMPA yields the vinyl anion 14 in complete preference to the allyl anion 15. Anion 14, equivalent to 2, can be alkylated in high yield to give substituted propenes 16.

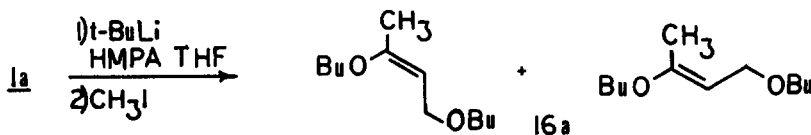


Compound 1a⁷ was prepared from the *sym*-dichlorohydrin 17 via 1,3-dibutyl glycerol 18⁸ and elimination of the tosylate from 19 with potassium *t*-butoxide in DMSO,⁹ yielding a 4:1 mixture of *cis* and *trans* products,¹⁰ as shown in Scheme 1. When 1a in THF containing HMPA (10%) was treated with *t*-butyllithium, a deep yellow color immediately appeared but dissipated after stirring for one hour.¹¹ Addition of methyl iodide afforded, after work up, a nearly quantitative yield of 16a. The 60 MHz NMR spectrum of 16a was lacking the signal from the α -vinyl hydrogen

Scheme 1



and now contained a methyl singlet at δ 1.85. However, the 270 MHz spectrum clearly revealed



both *Z* and *E* products in the ratio of 4:1, as shown in Figure 1. Methyl signals appear at δ 1.86 (d, $J=1.1$ Hz) and 1.84 (broad s) for the *Z* and *E* isomers, respectively. Thus, the product is

exclusively methylated at the α -vinyl position. We have also separated the *cis* and *trans* isomers of 1a by HPLC, and found that, as expected, they afford the *Z* and *E* products, respectively.

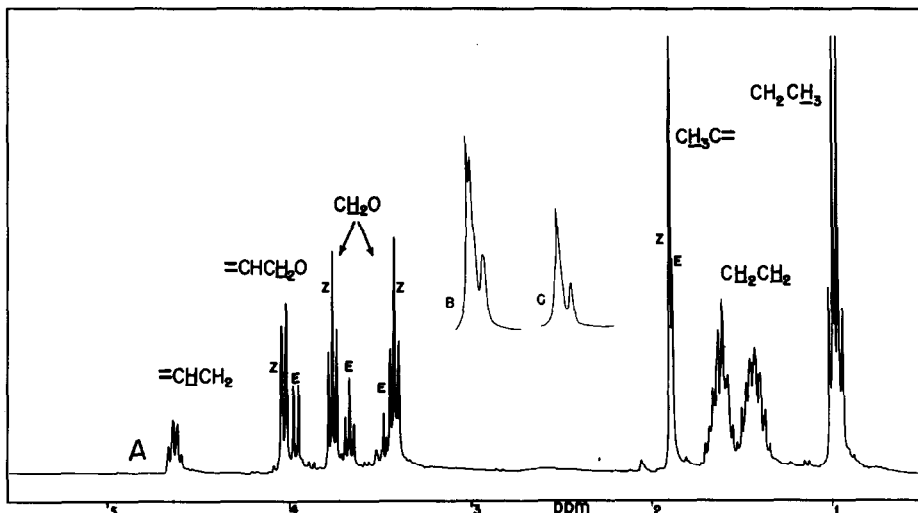
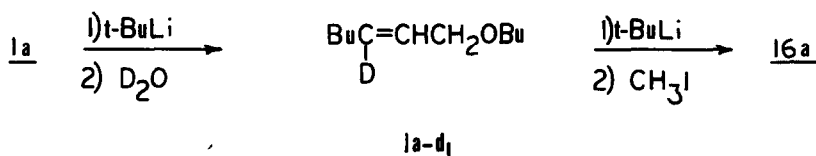
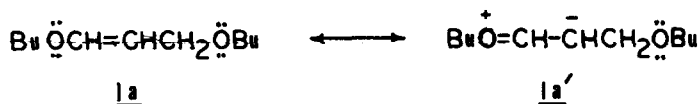


Figure 1. a. 270 MHz FT-PMR spectrum of 16a in CDCl_3 ; b. Expansion of the 1.80 δ to 1.92 δ region; c. Expansion of the 1.80 δ to 1.92 δ region with irradiation at 4.62 δ .

In order to confirm that 16 was arising from initial vinyl lithiation, rather than from double bond isomerization of an allyl anion¹² or of an allyl-alkylated product, the anion of 1a was quenched with D_2O . This afforded monodeutero 1a-d₁ (> 95 atom % D by mass spectrometry), the NMR spectrum of which lacked the signal at δ 6.50 from the α -vinyl hydrogen. The anion from 1a-d₁ was then generated and treated with methyl iodide to afford 16a (35% yield), devoid of deuterium (< 5 atom % D as shown by NMR and mass spectrometry). These results can only be explained by vinyl lithiation of 1a.



The exclusive vinyl lithiation of 1a appears to be due to the polarization of the vinyl double bond. In the NMR spectrum of 1a, the signal from the β -vinyl hydrogen appears at δ 4.50, 2.0 ppm upfield from the α -vinyl hydrogen signal, as would be expected from the polarization.¹³ Therefore, as shown in 1a, the allylic methylene is flanked by two electron-rich centers. This should perturb the relative acidities of the methylene and α -vinyl hydrogens, as well as destabilize the



allylic anion 15. In fact, ab initio molecular orbital calculations reported in the accompanying paper¹⁴ support this explanation.

Further work on the chemistry of this system is in progress.

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