

THE REDUCTIVE REARRANGEMENT OF CYCLOPROPYLCARBINYL MESITOATES

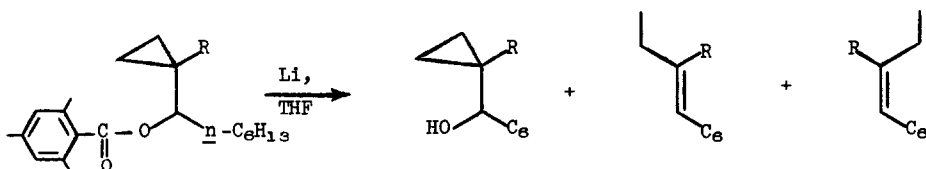
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We have recently reported a novel means of generating allylic lithium reagents by the reduction of allyl mesitoates with lithium metal in tetrahydrofuran (THF).¹ In the course of establishing the scope of this route to stabilized lithium reagents, we investigated the lithium-THF reduction of cyclopropylcarbinyl mesitoates. As both the cyclopropylcarbinyl anion² and radical³ are known to be in equilibrium with the corresponding homoallyl species, we were intrigued by the possible use of this reaction as a preparative route to olefins.

When the mesitoates 1 and 4 are treated with lithium in THF at 25°, a mixture of unrearranged alcohol and two olefin isomers are produced. The product ratios and yields are summarized in the table below.



R = H 1
R = CH₃ 4

2
5

3-E
6-E

3-Z
6-Z

Mesitoate	Conditions	Ratio ^a Alcohol/Olefin	Ratio ^a E/Z	Yield ^b Olefin
<u>1</u>	25° 4 hr	18 : 82	62 : 38	53%
<u>4</u>	25° 6 hr	22 : 78	37 : 63	48%

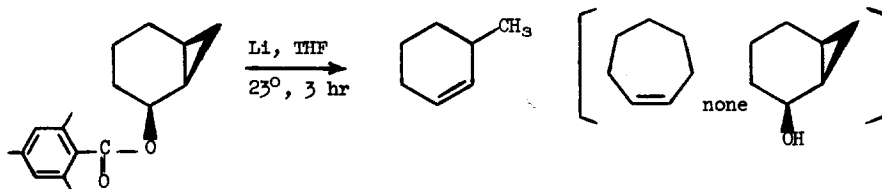
^a Determined by glpc

^b Isolated Yield

The facility of the reaction and the alcohol to olefin ratio show marked sensitivity to solvent: In liquid ammonia (-30°, 3 hr) only acyl-oxygen cleavage occurs; in ethyl ether, glyme, or dioxane no detectable reaction takes place (23°, 5 hr). The alcohol is the only product resulting from reduction of the benzoate corresponding to 4; no reaction is observed

with the acetate.

Reduction of endo-2-mesityloxy-[4.1.0]-bicycloheptane (γ) gave 3-methylcyclohexene as the exclusive product in good yield; no cycloheptene or alcohol was detected.



Although the cyclopropylcarbinyl to homoallyl cation rearrangement displays a very high stereoselectivity for the E-type olefin,⁴ we find no such selectivity in the rearrangement we are observing. At present it is not known whether the intermediate undergoing rearrangement is an anion or a radical. Attempts to trap an anionic species with methyl iodide in situ or by deuterium oxide quench failed to give any methylated or deuterated material. These findings, coupled with the sterically indiscriminate nature of the decyclization, suggest that a radical species undergoes the rearrangement and then abstracts a hydrogen atom from the solvent. However, as these reductions are conducted at room temperature in THF, the possibility of proton abstraction from solvent by a carbanion cannot be discounted.

Experiments are currently in progress to establish definitively the nature of the intermediate and to investigate the stereochemistry of the rearrangement in systems in which radical and anionic species can be generated unambiguously.

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References:

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