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ON THE MECHANISM OF $LiMe_2Cu$ ADDITION TO CONJUGATED ENONES

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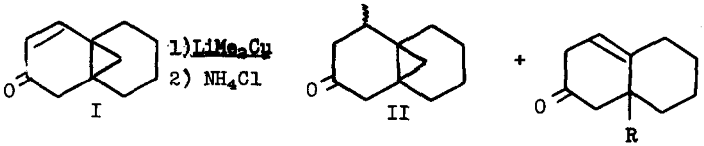
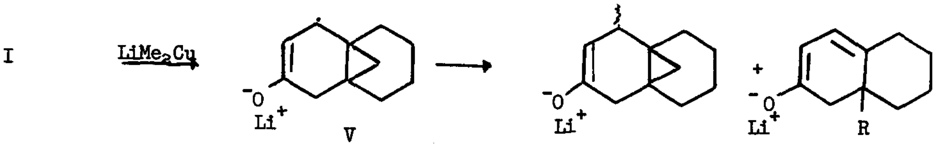
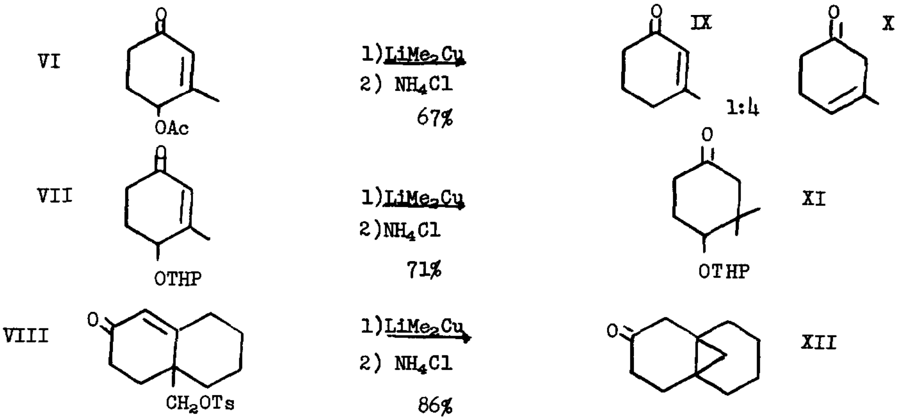
Recently, Marshall and Ruden[1] described the addition of organocuprates to a γ, δ-cyclopropylenone. These workers obtained a mixture of products, which they suggested arose from a common radical anion intermediate[2]. If indeed, an electron transfer process is occurring, then the β carbon of the enone system should become nucleophilic, similar in reactivity to the β carbon of an enone subjected to Li/NH_3 or other dissolving metal processes[3]. In order to study more thoroughly the exact nature of the proposed intermediate, we prepared three substrates with a view towards examining their reaction with organocuprates.



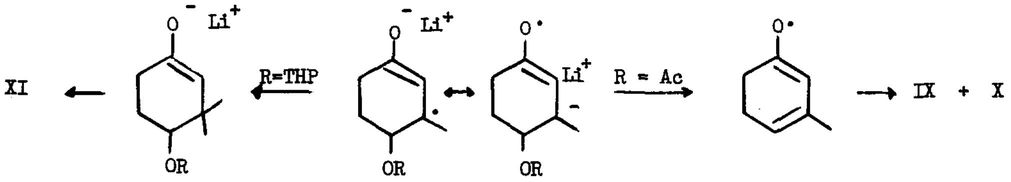
III R = CH_3
IV R = C_2H_5



The products of the reaction of $LiMe_2Cu$ and compounds VI[4], VII[4] and VIII[5] are listed below.



While a two electron transfer from copper to the enone is not ruled out by these experiments[6] we believe that a more comprehensive mechanism can be drawn. One electron transfer to the enone should produce the radical anion, which can undergo a 1,2 elimination (or alkylation) if the leaving group is good, or $CH_3^\cdot$ transfer if the leaving group is poor. These results define more clearly the scope of this reaction and have certain practical implications in synthetic design[7].



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(4) Compounds VI and VII were prepared from the corresponding alcohol by standard procedures. The alcohol was secured by treatment of 3-methyl-3-cyclohexene-1-one with peracetic acid followed by aqueous sodium bicarbonate.

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(6) While this work was under consideration, a similar article appeared, D. Hannah and R. Smith, Tetra. Let., 187 (1975).

(7) The support of the Petroleum Research Fund, administered by the American Chemical Society is gratefully acknowledged.