Tetrahedron Letters No. 42, pp 4115 - 4118, 1973. Pergamon Press. Printed in Great Britain.

A SIMPLE PROCEDURE FOR PREPARING ALLYLLITHIUM AND METHALLYLLITHIUM, AND ITS APPLICATION TO COUPLING WITH ORGANIC HALIDES

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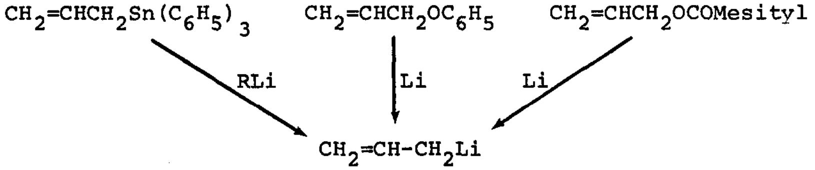
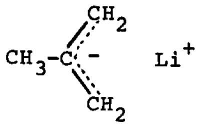
(Received in USA 14 August 1973; received in UK for publication 10 September 1973)

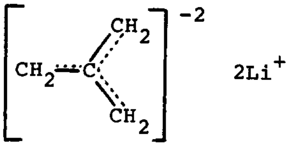
The undesired coupling associated with the metal-allylic halide reaction, which is but slightly troublesome for preparing allylic Grignard reagents,[1] becomes especially severe when attempting similar syntheses of corresponding lithio derivatives. As a result, allyllithium is usually generated by (alkyl) aryllithium-induced transmetalation or lithium metal promoted cleavage of suitable allylic precursors (e.g., allyltriphenyltin,[2] allyl phenyl ether,[3] allyl mesitoate[4]). When applied to coupling processes with simple primary organic halides, the yields of allylation product usually range from 0-52%.

$$\begin{array}{lll} CH_2{=}CH{-}CH_2X \xrightarrow{M} & CH_2{=}CH{-}CH_2M(X) \; + & CH_2{=}CH{-}CH_2CH_2{-}CH{=}CH_2 \\ X = Cl,\ Br & M = Mg,\ \text{major} & \text{minor} \\ & M = Li,\ \text{minor} & \text{major} \end{array}$$



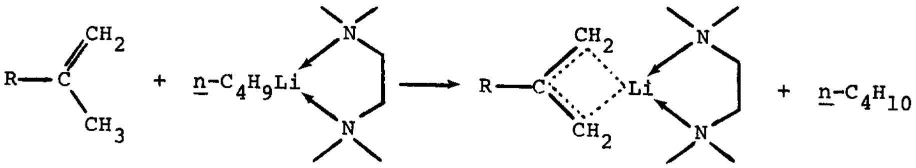
Recently and in another context, mixtures of the lithio methallyl anion and dilithio trimethylenemethane dianion have been produced by metalation ($\underline{n}$-$C_4H_9Li{\cdot}TMEDA$) of isobutylene.[5]





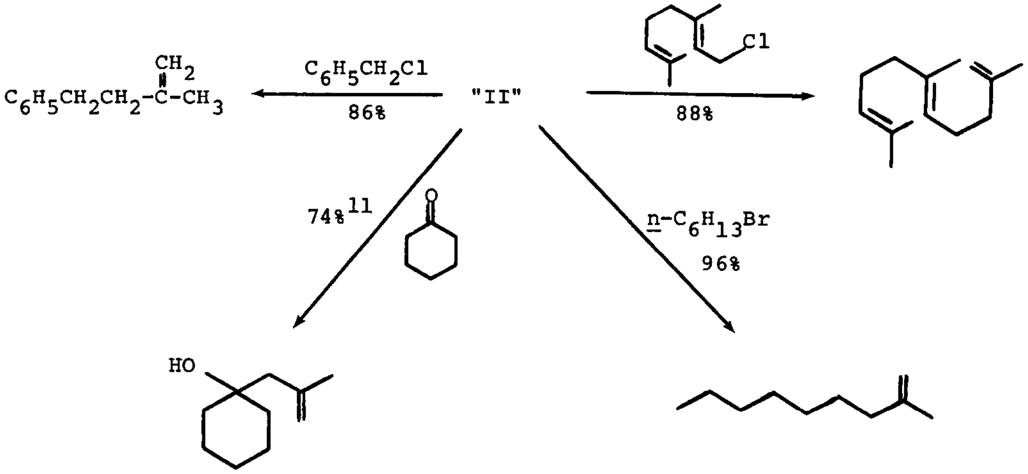
Reported in the present communication is a description of an improved and simplified procedure we have often employed for generating both allyllithium and methallyllithium by metalation of propene and isobutylene, respectively, with the *n*-C_4H_9Li·TMEDA complex,[6] and the application of this method to coupling processes.

By adding isobutylene (100 mmole) to a stirred solution of the *n*-C_4H_9·TMEDA reagent (from 33 mmole of *n*-C_4H_9Li in hexane and 33 mmole of TMEDA in 20 ml of ether) at -78°, then stirring overnight (N_2) at room temperature,[7] there results a white crystalline[8] precipitate, represented merely for convenience as II[9], and a pale yellow supernatant. Subsequent addition of a halide (16.5 mmole) dissolved in ether (*ca.* 0.8 M) at -78°, warming the resultant mixture to room temperature for 3 hr. prior to adding saturated ammonium chloride solution, leads (after washing the pentane extract with dil. HCl solution and drying (Na_2SO_4)) to acceptable yields of methallylated coupling product.[10]

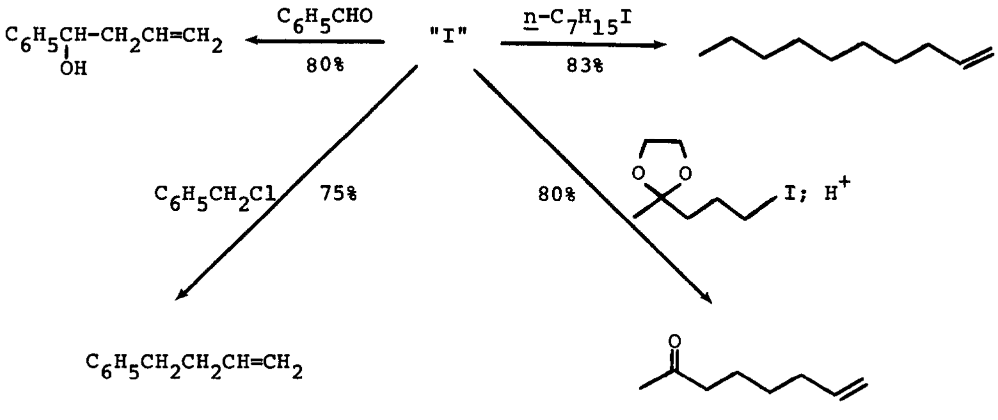


I, R = H

II, R = CH_3



Using a similar procedure, metalation-allylation of propene (165 mmole) also proceeds with facility but in slightly diminished yields to provide the corresponding allylated derivatives.[10]



Although conditions have not been optimized and can doubtless be improved, the present procedure recommends itself as an attractively simple route to allyl- and methallyllithium reagents.

Acknowledgment: We thank the National Research Council of Canada for financial support.

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(5) J. Klein and A. Medlik, *J.C.S. Chem. Comm*., 275 (1973), report that a 1:1 mixture of mono- and dialkylated products results when the olefin:*n*-C_4H_9Li:TMEDA stoichiometry is 1:1:1, followed by alkylation with *n*-C_4H_9Br. This respective product ratio changes to 1:11 using a 1:2:2 ratio of olefin: *n*-C_4H_9Li:TMEDA.

(6) G.G. Eberhardt and W.A. Butte, *J. Org. Chem*., **29**, 2928 (1964); C. Agami, *Bull. Soc. Chim. Fr*., 1619 (1970); R.J. Crawford, *J. Org. Chem*., **37**, 3543 (1972), and references therein.

(7) The cooling bath is removed, and the coolant (acetone-Dry Ice) in the Dewar type condenser is allowed to gradually evaporate.

(8) Crystalline complexes between alkyllithium reagents and tertiary amines are described by C.G. Screttas and J.F. Eastham, *J. Amer. Chem. Soc*., **87**, 3276 (1965).

(9) No commitment to structural detail is intended; rather this formulation is employed for simplicity and by consideration of stoichiometry and analogy.

(10) Structures of all products were verified by compatible spectral data (i.r., n.m.r., mass spectrum) and satisfactory (±0.3%) combustion analyses.

(11) Approximately 10% enolization occurs.