

1938

## Ethynylmetallic and Substituted Ethynylmetallic Reactions in Various Solvents

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### Recommended Citation

McCorkle, Miles R. and Gilman, Henry (1938) "Ethynylmetallic and Substituted Ethynylmetallic Reactions in Various Solvents," *Proceedings of the Iowa Academy of Science*, 45(1), 133-133.

Available at: <https://scholarworks.uni.edu/pias/vol45/iss1/26>

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HIGH MOLECULAR WEIGHT, NORMAL AND  
BRANCHED ALIPHATIC COMPOUNDS

FRED HOYT AND HENRY GILMAN

A series of high molecular weight compounds (hydrocarbons, alcohols, amines, etc.) is being examined for correlations between molecular weight and viscosity. In some of the syntheses (particularly those of hydrocarbons, alcohols and ketones) long-chained aliphatic organometallic compounds have been used. Some of these have been prepared in adequate yields for the first time. Actually, compounds like *n*-octadecylmagnesium bromide ( $n\text{-C}_{18}\text{H}_{37}\text{MgBr}$ ) are obtainable in 95 per cent yields. In addition to a variety of organometallic compounds (particularly those having magnesium and lithium) with radicals like dodecyl ( $\text{C}_{12}\text{H}_{23}$ ) tetradecyl ( $\text{C}_{14}\text{H}_{29}$ ) and hexadecyl ( $\text{C}_{16}\text{H}_{33}$ ), new substituted ethynylmetallic types like those derived from eicosine ( $\text{C}_{18}\text{H}_{37}\text{C}\equiv\text{CM}$ ) have been used.

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ETHYNYLMETALLIC AND SUBSTITUTED ETHYNYL-  
METALLIC REACTIONS IN VARIOUS SOLVENTS

MILES R. McCORKLE AND HENRY GILMAN

Incidental to a study of the relative reactivities of ethynylmetallic and substituted ethynylmetallic compounds, in various media including liquid ammonia, it has been shown that these organometallic compounds react in a customary manner, not only with RX compounds but also with a large variety of compounds having a functional group. The ethynyl tertiary alcohols formed from ketones lose acetylene on heating and give the original ketone. For example, myristone and ethynylsodium give di-tridecyl-ethynylcarbinol, which when heated gives an almost quantitative yield of myristone and acetylene.

In the presence of small amounts of organolead compounds, the ethynylsodium behaves like sodium carbide to give, for example, with benzophenone, -tetraphenylbutyndiol.

Ethynylsodium with nitriles gives dimeric basic compounds.

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