A Reaction of $\gamma$-Chalcogen-substituted Prop-2-ynyl Cations with Mild Nucleophiles.

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$\gamma$-Chalcogen-substituted propynal diethyl acetalts 1 and 2 were prepared by the reaction of propynal diethyl acetal with ethylmagnesium bromide followed by treatment with benzenesulfenyl or benzeneselenenyl chloride. $\gamma$-Chalcogen-substituted prop-2-ynyl cations, generated by the reactions of 1 and 2 with BF$_3$-EtO, reacted with various mild nucleophiles without isomerization to allenyl cations to afford the prop-2-ynylated products in good yields. Reactions of 1 and 2 with sulfur or selenium nucleophiles provided $\gamma$-chalcogen-substituted propynal mono- and diheteroacetals, which would be utilized as a source of prop-2-ynyl cations stabilized by a chalcogen atom.

Dehydrsulfonification of Conjugated Enyne Sulfones: Convenient Synthesis of Diyne Compounds

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$\alpha$-Lithio conjugated enyne sulfones upon reaction with carbonyl compounds followed by treatment with MeLi afforded the 2,4-diynols in high yields. The reaction mechanism is as follows: $\alpha$-Lithio enyne sulfones are easily generated by treatment of the (E)-enyne sulfones with MeLi at -78 °C, and react with carbonyl compounds without isomerization to give (E)-enynols. Treatment of the (E)-enynols with MeLi causes deprotonation of a $\beta$-vinyl hydrogen and the synchronous syn-elimination of the sulfonyl group to give the diynols.

Generation and Reactions of Butadienylthionium Ions from 2-Vinylcyclopropyl Sulfoxides under Pummerer Conditions

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Treatment of 2-vinylcyclopropyl sulfoxides lacking an $\alpha$-hydrogen with acid anhydrides such as trifluoroacetic anhydride or Aco$_2$O produced butadienylthionium ion intermediates to give cyclic or acyclic conjugated dienes. Reactions of disubstituted vinylcyclopropanes furnished the cyclic dienes in moderate yields. On the other hand, treatment of un- or mono-substituted vinylcyclopropanes afforded acyclic conjugated dienyl acetates or trifluoroacetates. The dienols were obtained by hydrolysis of corresponding dienyl trifluoroacetates during work-up.