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

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\( \gamma \)-Chalcogen-substituted propynal diethyl acetals 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\(_3\)-Et\(_2\)O, 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.

Dehydrsulfonylation 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 \( \text{syn} \)-elimination of the sulfonyl group to give the diynols.

Genaration 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 Ac\(_2\)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.