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A Reaction of γ-Chalcogen-substituted Prop-2-ynyl Cations with Mild Nucleophiles.

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γ-Chalcogen-substituted propynal diethyl acetals **1** and **2** were prepared by the reaction of propynal diethyl acatal with ethylmagnesium bromide followed by treatment with benzenesulfenyl or benzeneselenenyl chloride. γ-Chalcogen-substituted prop-2-ynyl cations, generated by the reactions of **1** and **2** with BF_3-Et_2O, 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 γ-chalcogen-substituted propynal mono- and diheteroacetals, which would be utilized as a source of prop-2-ynyl cations stabilized by a chalcogen atom.

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Dehydrosulfonylation of Conjugated Enyne Sulfones: Convenient Synthesis of Diyne Compounds

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α-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: α-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 β-vinyl hydrogen and the synchronous *syn*-elimination of the sulfonyl group to give the diynols.

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

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Treatment of 2-vinylcyclopropyl sulfoxides lacking an α-hydrogen with acid anhydrides such as trifluoroacetic anhydride or Ac_2O 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.