

[J. Chem. Soc., Chem. Commun., 149 - 150 (1995)]

[Lab. of Pharm. Chemistry]

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 acetal with ethylmagnesium bromide followed by treatment with benzenesulfonyl or benzeneselenenyl chloride. γ -Chalcogen-substituted prop-2-ynyl cations, generated by the reactions of **1** and **2** with $\text{BF}_3 \cdot \text{Et}_2\text{O}$, 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 γ -chalcogen-substituted propynal mono- and diheteroacetals, which would be utilized as a source of prop-2-ynyl cations stabilized by a chalcogen atom.

[J. Chem. Soc., Chem. Commun., 583 - 584 (1995)]

[Lab. of Pharm. Chemistry]

Dehydrosulfonylation of Conjugated Enyne Sulfones: Convenient Synthesis of Diyne CompoundsMITSUHIRO YOSHIMATSU, MASATAKA KAWAHIGASHI, HIROSHI SHIMIZU,
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α -Lithio conjugated enyne sulfones upon reaction with carbonyl compounds followed by treatment with MeLi afforded the 2,4-diyne 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*)-enyne sulfones. Treatment of the (*E*)-enyne sulfones with MeLi causes deprotonation of a β -vinyl hydrogen and the synchronous *syn*-elimination of the sulfonyl group to give the diyne.

[J. Chem. Soc., Perkin Trans. 1, 737 - 739 (1995)]

[Lab. of Pharm. Chemistry]

Generation and Reactions of Butadienylthionium Ions from 2-Vinylcyclopropyl Sulfoxides under Pummerer ConditionsTADASHI KATAOKA,* HARUTOSHI MATSUMOTO, TETSUO IWAMA, TAIZO ITO,
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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 dieneols were obtained by hydrolysis of corresponding dienyl trifluoroacetates during work-up.