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[Lab. of Pharm. Chemistry]

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

MITSUHIRO YOSHIMATSU, HIROSHI SHIMIZU, TADASHI KATAOKA\*

$\gamma$ -Chalcogen-substituted propynal diethyl acetals **1** and **2** were prepared by the reaction of propynal diethyl acetal with ethylmagnesium bromide followed by treatment with benzenesulfonyl or benzeneselenenyl chloride.  $\gamma$ -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  $\gamma$ -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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[Lab. of Pharm. Chemistry]

**Dehydrosulfonylation of Conjugated Enyne Sulfones: Convenient Synthesis of Diyne Compounds**MITSUHIRO YOSHIMATSU, MASATAKA KAWAHIGASHI, HIROSHI SHIMIZU,  
TADASHI KATAOKA\*

$\alpha$ -Lithio conjugated enyne sulfones upon reaction with carbonyl compounds followed by treatment with MeLi afforded the 2,4-diyne diols 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  $-78^\circ\text{C}$ , and react with carbonyl compounds without isomerization to give (*E*)-enyne diols. Treatment of the (*E*)-enyne diols with MeLi causes deprotonation of a  $\beta$ -vinyl hydrogen and the synchronous *syn*-elimination of the sulfonyl group to give the diyne diols.

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[Lab. of Pharm. Chemistry]

**Generation and Reactions of Butadienylthionium Ions from 2-Vinylcyclopropyl Sulfoxides under Pummerer Conditions**TADASHI KATAOKA,\* HARUTOSHI MATSUMOTO, TETSUO IWAMA, TAIZO ITO,  
HIROSHI SHIMIZU

Treatment of 2-vinylcyclopropyl sulfoxides lacking an  $\alpha$ -hydrogen with acid anhydrides such as trifluoroacetic anhydride or  $\text{Ac}_2\text{O}$  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.