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[Lab. of Pharm. Chemistry]

Synthesis and Reactions of Lactam Sulfonium Salts with a Sulfonio Bridgehead. I.**1,4,4a-Trihydro-5-oxo-2H-thiopyrano[1,6-a]-1,4-benzothiazinium****Perchlorates.**Tadashi KATAOKA,* Yoshihide NAKAMURA, Harutoshi MATSUMOTO, Tetsuo IWAMA,
Hirohito KONDO, Hiroshi SHIMIZU, Osamu MURAOKA and Genzoh TANABE

Tricyclic benzothiazinium salts **1** were prepared by [2⁺+4] polar cycloaddition of thionium intermediates, generated from corresponding α -chloro sulfides and dienes in the presence of AgClO₄. Ring transformation of **1** with a reducing agent such as Mg, NaBH₄ and Zn-AcOH or with a base furnished spiro-vinylcyclopropane derivatives **2**. Electrolysis of **1** at -1.4 V vs SCE in acetonitrile also afforded **2** in 60% yield. 10-Membered lactam sulfides were given as a major product by SmI₂ reduction of **1**.

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Acid-promoted Isomerisation of 1-Acceptor-1-sulfenyl-substituted 2-Vinylcyclopropanes**with C₁-C₂ Bond Fission and Novel 1,5-Sulfenyl Rearrangement.**

Tetsuo IWAMA, Harutoshi MATSUMOTO and Tadashi KATAOKA*

1-Acceptor-1-sulfenyl-substituted vinylcyclopropanes **1** underwent the C₁-C₂ bond fission and 1,5-sulfenyl rearrangement to give 6-sulfenyl- $\alpha,\beta,\gamma,\delta$ -unsaturated carboxylic esters and nitriles **2** by treatment with an acid. The reactions proceeded smoothly by use of a sulfonic acid such as *p*-TsOH·H₂O, CF₃SO₃H and so on in a nonpolar solvent. The results, obtained from reactions of the vinylcyclopropanes **1**, imply that the C₁-C₂ bond cleavage and deprotonation from the C₂-methyl group of **1** occur *via* the concerted process. The cross-over experiment showed that 1,5-sulfenyl shift proceeded intermolecularly. Addition of a catalytic amount of *m*-MeC₆H₄SH improved the yield of the rearranged product **2**.

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[Lab. of Pharm. Chemistry]

Synthesis and Reactions of Lactam Sulfonium Salts with a Sulfonio Bridgehead. II.**1,1a,4,5,6-Pentahydro-6-oxo-2H-thiopyrano[1,6-d]-4,1-benzothiazepinium****Perchlorates.**Tadashi KATAOKA,* Yoshihide NAKAMURA, Harutoshi MATSUMOTO,
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Tricyclic benzothiazepinium salts **1** were prepared by [2⁺+4] polar cycloaddition of thionium intermediates, generated from corresponding α -chloro sulfides and dienes in the presence of AgClO₄. Reactions of **1** with NaBH₄ or NaH afforded 3,6-epithiobenzazocinones **2** in high yields by [2,3]-sigmatropic rearrangement of an ylide intermediate. The stereochemistry of **2** was determined by X-ray analysis of a sulfoxide derived from **2**. Alkylation of **2** afforded 3-alkyl-3,6-epithiobenzazocinones with retention of the configuration at C-3. Dihydrothiopyran derivatives were given by SmI₂ reduction of **1**.

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[Lab. of Pharm. Chemistry]

A Convenient Synthesis of Alkynylpyrazoles.Mitsuhiro YOSHIMATSU, Masataka KAWAHIGASHI, Eiji HONDA
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Daizomethane added to the enyne sulfones regio- and stereo-selectively to give the 4-alkynyl-5-phenylsulfonyl-4,5-dihydro-3H-pyrazoles, which underwent dehydrosulfonylation by methyllithium to afford the 4-alkynyl-1H-pyrazoles in good yields. The dehydrosulfonylation was performed with other bases such as LDA, NaH, *t*-BuOK; however, the yields of the pyrazoles were rather low. The reactions of 5,5-bis(sulfonyl)pyrazoles with methyllithium produced a trace of the alkynylcyclopropanes together with mono-sulfonylpyrazoles. The cyclopropane derivatives were given by the denitrogenation under room light. 4,5-Bis(alkynyl)-4,5-3H-pyrazoles were also obtained by the reactions of (*Z*)-enediynesulfones with diazomethane.