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[Lab. of Manufacturing Pharmacy]

**First Successful [4<sup>+</sup>+2]-type Polar Cycloadditions of 2-Benzothiopyrylium Salt with Dienes.**

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2-Benzothiopyrylium salt **1** reacted with 1,3-dienes **2** in the presence of methanol to afford benzo-fused bicyclo[2.2.2] compounds **3**, while in the absence of methanol cycloaddition of **1** with 2,3-dimethylbuta-1,3-diene **2a** afforded a novel benzo-fused tricyclic compound **4a**, whose structure has been confirmed by X-ray crystallography. A plausible mechanism for the formation of the cycloadducts **3** and **4a** is discussed in terms of a [4<sup>+</sup>+2]-type polar cycloaddition.

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[Lab. of Manufacturing Pharmacy]

**Polar Cycloaddition of 1-Benzothiopyrylium Salts with Conjugated Dienes and Some Transformations of the Cycloadducts.**

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Polar cycloaddition of 1-benzothiopyrylium salts **1** with conjugated dienes proceeds regio- and stereo-specifically to afford the corresponding benzo-fused bicyclic sulfonium salts **2** in good yields. Reaction of the cycloadduct **2** with nucleophiles such as methanol or water causes ring opening to give 2-(bu-2-enyl)- and 2-(but-3-enyl)-substituted 2*H*-1-benzothiopyrans **3** and **4**. Treatment of the cycloadduct **2** bearing a cyano group at 9-position with a variety of bases affords the spirocyclopentene derivative **5** and the spiro-1,2-dioxolane derivative **6**. A mechanism involving a biradical intermediate is discussed for the formation of the above products **5** and **6** on the basis of chemical evidence. Reduction of the cycloadduct **2** with sodium borohydride or sodium cyanoborohydride is also described.

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[Lab. of Health and Physical Education]

**Effect of Crude Fractions *Psoralea corylifolia* Seed Extract on Bone Calcification**

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Non-polar crude fractions (Ho-O and Ho-1) of an acetone extract of *Psoralea corylifolia* seeds were administrated orally to untreated and experimental rachitic rats. In the biological screening of the fractions, Ho-1, an elution with n-hexane-ethyl acetate by column chromatography over silica gel of the acetone extract, untreated rats showed a significant elevation of the serum inorganic phosphorus and revealed histomorphometrically a significant increase in bone calcification. These results suggested that Ho-O and Ho-1 are useful as a remedy for bone fracture, osteomalacia, osteoporosis, and related conditions.