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Radical C-Se Bond Cleavage of Selenonium Salts with Grignard Reagents or Magnesium Metal.

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The reaction of 2-methylisoselelenochromanium salt with Grignard reagents afforded the reductive ring-opened product by the single electron transfer mechanism, not by the self-decomposition of σ -selenurane. The same reduction was observed in the reaction of the selenonium salt with magnesium metal. Some other selenonium salts bearing a double bond or a carbonyl group were easily reduced by magnesium metal to give ring-opened products. A sulfonium salt was similarly ring-opened.

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Reactions of 1*H*-2-Benzothiopyran 2-Oxides with Active Methylene Compounds: A Novel Ring Contraction of 1-Aryl Derivatives to Benzo- $\{c\}$ thiophenes. X-Ray Molecular Structure of 1-(2,2-Diacetylvinyl)-3-phenylbenzo $\{c\}$ thiophene.

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1-Aryl-1*H*-2-benzothiopyran 2-oxides reacted with active methylene compounds in acetic anhydride to undergo a novel ring contraction, affording benzo $\{c\}$ thiophene derivatives, whose structures have been established by X-ray crystallography. In contrast, 1-unsubstituted 1*H*-2-benzothiopyran 2-oxide, under the similar conditions, afforded no benzothiophene derivatives, but instead gave 1-substituted 1*H*-benzothiopyrans in good yields.

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Synthesis and Analgetic Activity of Sulfur-Containing Morphinans and Related Compounds.

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3-Acylthiomorphinans, 3-carbamoylthio-3-deoxydihydromorphine and 3-benzoylthio-9-aza-17-carbamorphinan were synthesized by Newman-Kwart rearrangement of the corresponding *O*-thiocarbamates. The analgetic activities were lower than that of pentazocine, and the opioid receptor binding affinities were very weak. These acylthiomorphinans showed low antinociceptive activity compared with corresponding sulfur-containing benzomorphans. 3-Carbamoylthiodeoxydihydromorphine had no significant analgetic activity.