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REACTIONS OF CYCLIC SULFOXIDES AND SULFONIUM SALTS WITH ORGANOMETALLIC REAGENTS

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By the reactions of 9-phenylthioxanthene 10-oxide (I) and 1-phenyl-2-thiochromene 2-oxide (II) with aryllithium and/or arylmagnesium halide, two novel methods for the synthesis of thiabenzene analogs, such as 9,10-diphenyl-10-thiaanthracene or 1,2-diphenyl-2-thianaphthalene have been found. The mechanism of the reactions is considered to proceed through a thiopyryl radical.

In the course of the studies, I and 10-(p-methoxyphenyl)-9-phenylthioxanthenium perchlorate (III) have been separated into two geometrical isomers. The latter case is the first success in these investigations. The conformation of I and III was considered in some detail.

The reactions of cyclic sulfonium salts (III and related compounds) with Grignard reagents and with organolithiums were investigated using III and 10-methyl-9-phenylthioxanthenium perchlorate (IV) as two typical substrates. The main products thus obtained were 9-(p-methoxyphenyl)-9-phenylthioxanthene and 9-methyl-9-phenylthioxanthene. The reaction pathway via a intramolecular Stevens-type rearrangement is postulated.