# PREPARATION OF BRIDGED THIONIN, BRIDGED THIECINONE, AND RELATED COMPOUNDS

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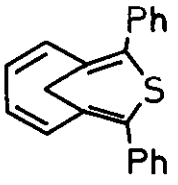
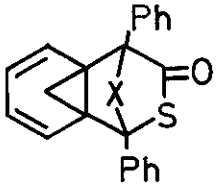
Diphenyl-3,8-methanothionin (1), the first example of bridged ten-$\pi$-electron [9]annulene, could be isolated by thermal fragmentation of the cycloadduct (2a), which was formed by the reaction between benzocyclopropene and a mesoionic dithiolone (3). Photolysis of the adduct (2), on the other hand, gave a cyclohepta[c]thiophene (4), an isomer of the methanothionin.

Peracid oxidation of the adduct (2a) gave the corresponding S-oxide (2b). Although pyrolysis of the S-oxide resulted in a complex mixture, photolysis of the S-oxide gave two isomers of cyclohepta[d]thiopyranones (5a and 5b) as the main products, and a fraction which may be considered as consisting of a 4,7-methanothiecinone (6) and an isomer of the S-oxide.

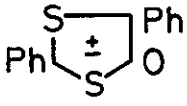



(1)

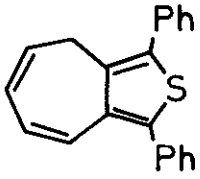



(2a): X = S

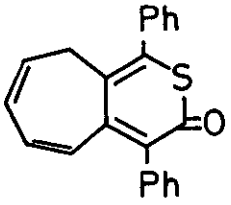
(2b): X = SO



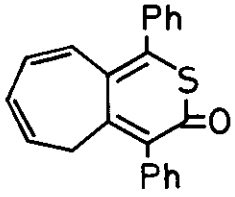

(3)



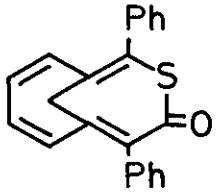

(4)




(5a)




(5b)




(6)