THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF S-SUBSTITUTED 2,5-DIPHENYL-1,4-DITHIINS

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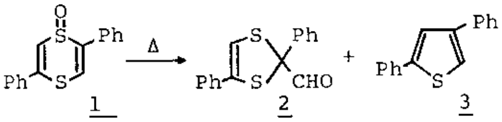
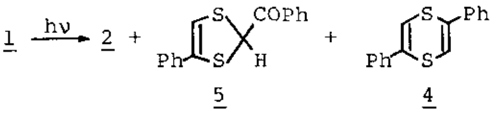
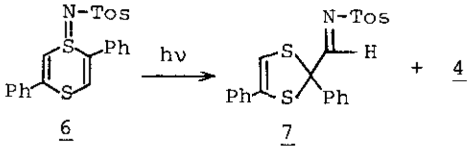
During the course of our investigation to see if the extrusion of a substituted sulfur moiety would occur in sulfoxide, sulfone, and sulfilimine of 2,5-diphenyl-1,4-dithiin we found a variety of novel rearrangements involved in thermolysis as well as photolysis of these dithiin derivatives.

Sulfoxide 1 upon heating in acetonitrile at 70 °C afforded rearranged 1,3-dithiole 2 along with thiophene 3 due to the extrusion of SO. When irradiated in methanol with a high pressure mercury lamp, 1 gave 2, 4, and 5 as well which was not obtained in the thermolysis.





Photolysis of sulfilimine 6 gave rearranged product 7 and dithiin 4, while thermolysis led to the elimination of both S=N-Tos and N-Tos fragments and no rearrangement was observed.



Sulfone 8 showed quite an unusual photochemical behaviour. Upon irradiation in methanol 8 gave rise to 2,5-diphenylthiophene 9 in a low yield other than 2,4-diphenylthiophene 3 solely due to the loss of sulfur dioxide. The formation of 9 most likely proceeds via the valence isomerization to thioketone 10. This mechanism was supported by the photolysis in n-butylamine, which resulted in the formation of isomeric 1-butylpyrroles, 11 and 12.