NEW MODE OF THERMAL REACTIONS OF CYCLIC SULFUR YLIDES. SOLVENT UPTAKE AND SPIRO-COMPOUND FORMATION

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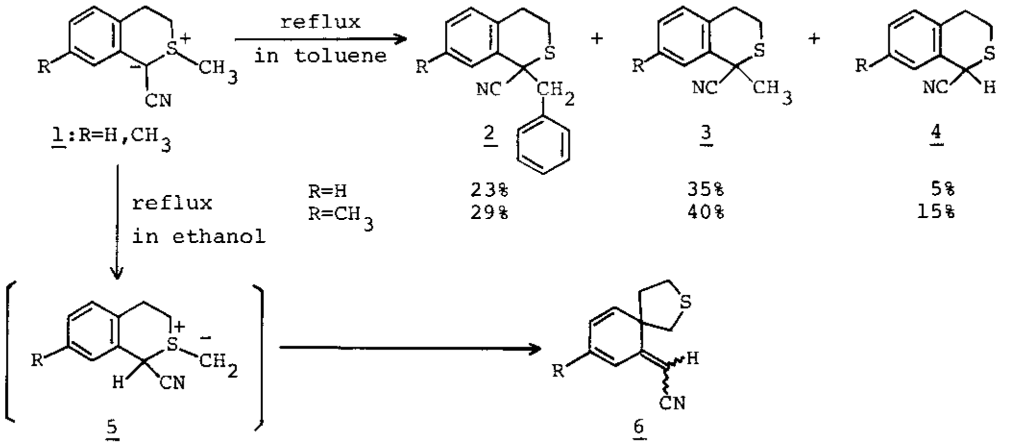
2-Alkyl(or aryl)-1-benzoyl-3,4-dihydro-2-thianaphthalenes underwent very unique thermal reactions, S→O [1,4]-rearrangements, ring-opening reaction with debenzoylation, and ring expansion.1) We carried out the thermal reactions of cyano-stabilized congeners, 2-alkyl-1-cyano-3,4-dihydro-2-thianaphthalenes in expectation of the new reaction.

When the ylide 1 was heated in toluene, 1-cyano-1-benzyl-2-thiochroman derivative 2 was formed together with the [1,2]-rearranged product 3 and 1-cyano-2-thiochroman derivative 4. The similar results were obtained from the thermal reactions of the ylide 1 in p-substituted toluenes. On the other hand, the ylide 1 isomerized to an exo-methylide 5 followed by [2,3]-sigmatropic rearrangement in refluxing ethanol to yield the spiro-compound 6 in 83% yield. This compound was also given from the thermal reaction of the ylide 1 with phenol or succinimide. Diels-Alder reaction of 6 with dimethyl acetylenedicarboxylate formed two isomeric 1:1 adducts. Furthermore, 6 underwent the thermal isomerization to give 1-cyano-1,2,4,5-tetrahydrobenzo[d]thiepin.



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1) M. Hori, et al., Tetrahedron Lett., 22, 3629(1981); 23, 2597(1982).