

SYNTHESIS OF SIMPLE THIEPINS WITH ALKYL GROUPS AND THEIR STABILITY

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Although studies on azepines and oxepins of seven-membered unsaturated heterocycles have been accumulated, studies on thiepins have not been developed, mainly because of easy extrusion of sulfur atom from them even at low temperature giving rise to the corresponding aromatic hydrocarbons. Since above feature is particularly serious in the case of monocyclic thiepins, acceptable synthetic approaches associated with the synthesis of monocyclic thiepins require mild methods.

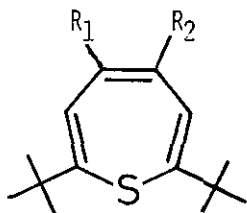
We have recently reported the synthesis of the remarkably stable monocyclic thiepins (1) - (5) stabilized by bulky groups at C₂ and C₇, with their physical properties.

For the purpose of gaining further insight into monocyclic thiepins, synthetic approaches to the isolable less substituted thiepins have been continued by us, keeping with this trend.

We now wish to report synthesis of the simple thiepins having only alkyl groups and their properties. Although attempted direct conversions from (3) or (5) to (10) were unsuccessful, reductive cleavage of (6) with DIBALH gave (7), but suffering from low yield (11%), whereas the thiepin (8) gave a mixture of complicated products. The alcohol (3) was treated with (n-Hex)₃P-CCl₄ under very mild condition (-20°C) followed by reduction with LAH at room temperature to give the desired 2,7-di-tert-butyl-4-methyl-thiepin (9) in 66% yield.

Their physical properties including thermal stability will be discussed.

The attempted synthesis of the 2,7-di-tert-butyl-thiepin (10) which would be expected to be the simplest isolable one will be reported.



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| 1) R ₁ =CH ₃ , R ₂ =COOC ₂ H ₅ | 6) R ₁ =CH ₃ , R ₂ =CH ₂ OCH ₃ |
| 2) R ₁ =H, R ₂ =COOC ₂ H ₅ | 7) R ₁ =CH ₃ , R ₂ =CH ₃ |
| 3) R ₁ =H, R ₂ =CH ₂ OH | 8) R ₁ =H, R ₂ =CH ₂ OCH ₃ |
| 4) R ₁ =H, R ₂ =CH ₂ OTMS | 9) R ₁ =H, R ₂ =CH ₃ |
| 5) R ₁ =H, R ₂ =CHO | 10) R ₁ =R ₂ =H |