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SYNTHESES AND THERMAL STABILITIES OF VARIOUS NAPHTHOTHIEPINS

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Because of the ease of sulfur extrusion, extremely mild conditions have to be employed for synthesis of the thiepin system. In this paper, we report the syntheses and thermal properties of various unknown naphthothiepins which was prepared by the application of ring expansion reaction through carbene intermediates.

The diazo compounds obtained from the reaction of the naphthothiapyrylium tetrafluoroborates with ethyl lithiodiazoacetate were treated with Pd(II) catalyst under the low temperature to afford the desired naphthothiepin derivatives.

Although these thiepins are fairly unstable at room temperature, the existence of some mono-ethoxycarbonyl derivatives of naphtho[1,2-d]thiepin, naphtho[1,2-b]thiepin, and naphtho[2,1-b]thiepin could be confirmed by the PMR signals consistent with these thiepins at appropriate temperatures. On the other hand, 2- and 3-ethoxycarbonylnaphtho[2,3-b]thiepins could be isolated in pure forms even at room temperature. A substantial stabilizing and destabilizing effects of the ethoxycarbonyl group are found when this group substituted at 2- and 3-positions of the theipin ring, respectively. The analysis of PMR suggests the absence of paramagnetic properties and the presence of bond althernation in these thiepins.

The synthetic procedures and the properties of these thiepins will be discussed in detail.