NONCONCERTED CYCLOADDITION REACTIONS OF FUSED 2-VINYLTHIOPHENES WITH DIMETHYL ACETYLENEDICARBOXYLATE

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As shown recently [1,2], fused polycyclic system of benzothieno[3,2-b]benzothiophene can serves successfully as a new type of core for design of antiferroelectric liquid crystals. Thus, our effort was focused on development of smart synthetic methods for preparation of this core, e.g. by involving Diels-Alder reactions. However, in a preliminary study [3] we found that cycloaddition reaction of 2-vinylthieno[3,2-b]benzothiophene with dimethyl acetylenedicarboxylate afforded a broad range of products. Among them compounds with a novel heterocyclic cyclopenta[5,6]thiopyran[3,2-b][1]benzothiophene system were identified. Herein we report results of an exhaustive study of this cycloaddition reaction of various related vinylthiophene (and 2-vinylselenophene) 1 derivatives with dimethyl acetylenedicarboxylate. Based on the structures of isolated products and their distribution (only principal products are shown in Scheme 1), a nonconcerted mechanisms of the cycloaddition were postulated [3]. Formation of all products will be discussed.

Scheme 1

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