HETEROCYCLES, Vol 21, No 2, 1984

AUTOCATALYZED ADDITIONS AND CYCLOADDITIONS OF KETENES TO THIAZOLES

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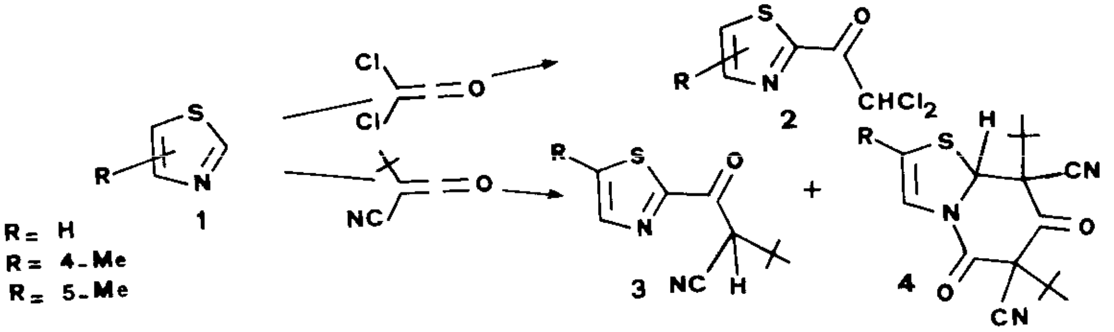
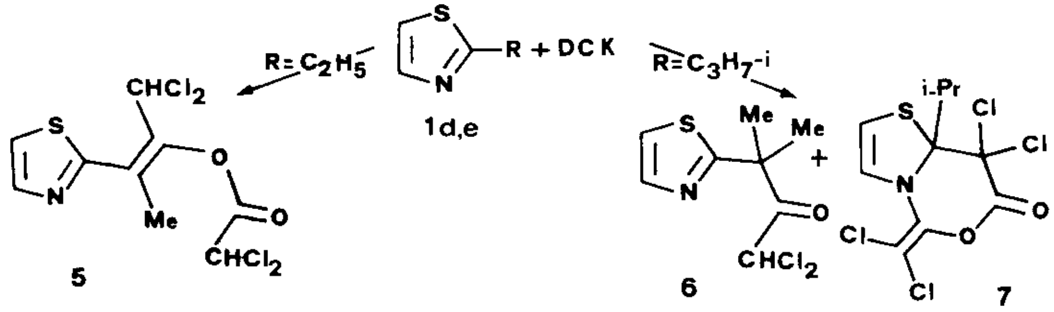
Reactions of 1,3-thiazoles **1** with ketenes have been studied as a new approach toward the direct annulation and the selective carbon-carbon bond formation at the thiazole ring.[1]

1,3-Thiazole **1a** and its 4-methyl **1b** and 5-methyl **1c** derivatives react with dichloroketene (DCK) and *t*-butylcyanoketene (TBCK) affording the corresponding Michael-type adducts, viz. 2-acylthiazoles **2** and **3**. The reactions with TBCK give also a 2:1 cycloadduct which proved by X-ray analysis to be a bicyclic system **4** constituted by a thiazoline and a piperidinedione ring condensed across the C-N bond.



2-Alkylthiazoles **1d** and **1e** treated with DCK undergo acylation at the C_α of the alkyl chain to give the open-chain adducts **5** and **6** and a 2:1 cycloadduct which from X-ray analysis resulted to be the bicyclic system **7** constituted by a thiazoline and an oxazinone ring condensed across the C-N bond.



A mechanism is envisaged where adducts **2**-**7** are formed *via* an *N*-thiazolium ylide or a zwitterion as intermediates resulting from the quaternization of the thiazole nitrogen by a molecule of ketene.

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[1] A. Dondoni et al., J. Org. Chem., **47** 3844 (1983) and previous papers of this series.