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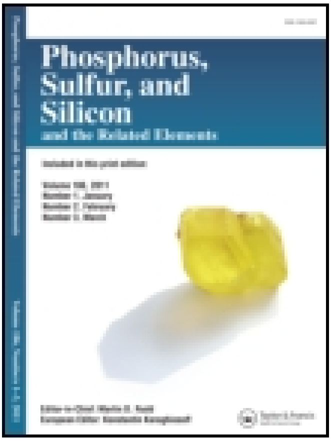

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Thioaroylketene S,N-Acetals: Versatile Intermediates for the Synthesis of 3-Alkylamino-5-Arylthiophenes with a Variety of Functional Group at C-2

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Thioaroylketene *S,N*-Acetals: Versatile Intermediates for the Synthesis of 3-Alkylamino-5-Arylthiophenes with a Variety of Functional Group at C-2

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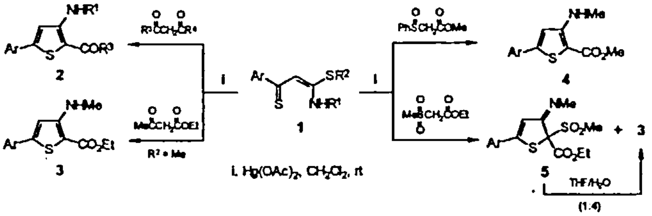
Treatment of 3-alkylthio-5-arylisothiazolium halides with sodium borohydride in EtOH at room temperature gave thioaroylketene *S,N*-acetals **1** in good to excellent yields [1]. Compounds **1** have been utilized as good starting materials for the synthesis of various heterocyclic compounds [2-4].

We have found that treatment of a mixture of compound **1** (0.17-0.31 mmol) and mercury(II) acetate (1.5 molar equiv) in CH_2Cl_2 (10-15 mL) with 1,3-diketones (0.2-1.0 mmol) at room temperature gave 2-acyl- and 2-aroyl-3-alkylamino-5-arylthiophenes **2** (38-91%). Similarly, compounds **1** (R^2 = Me) reacted with ethyl acetoacetate under the same conditions to give 5-aryl-2-ethoxycarbonyl-3-methylaminothiophenes **3** (82-94%). It is interesting to find that treatment of **1** with methyl phenylsulfinylacetate under the same conditions gave 5-aryl-2-methoxycarbonyl-3-methylaminothiophene **4** (89%), whereas with ethyl methanesulfonylacetate under the same conditions, compound **3** and an intermediate **5** were isolated in 16% and 64% yields. The latter was readily converted to **3** (58%) in aqueous THF.

Scheme 1



The isolation of **5** and its transformation to **3** suggests the following mechanism for the formation of compounds **2-4** from the reactions of **1** with active methylene compounds (Scheme 2).

Mercury(II) acetate dissolves in CH_2Cl_2 containing thioaroylketene *S,N*-acetals **1** to form a complex **6** having an iminothiolester functionality. The imino carbon is thought to be far more electron deficient by the interaction of the imino nitrogen with mercury acetate bonding to the thione sulfur. The electron deficient imino carbon would be readily attacked by an enolic carbon of 1,3-dicarbonyl compounds to give an intermediate **7**. Loss of a methanthiol molecule from **6** gives an intermediate **8** which is a 1,3-dicarbonyl compound having an enimino group at C-2. Intramolecular nucleophilic attack of the enolic carbon to sulfur concomitant with the formation of mercury and acetic acid leads to an intermediate **9**. Subsequent hydrolysis of **9** gives compounds **2** and **3**.

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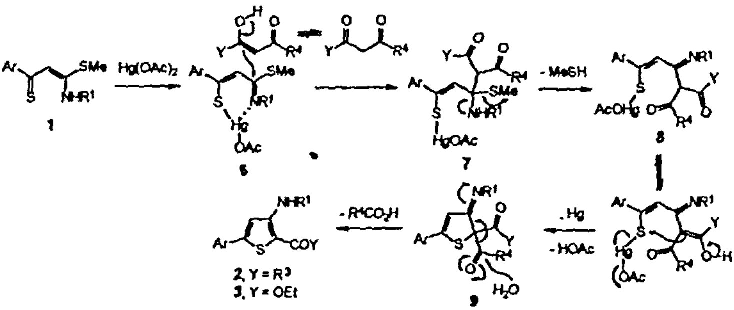
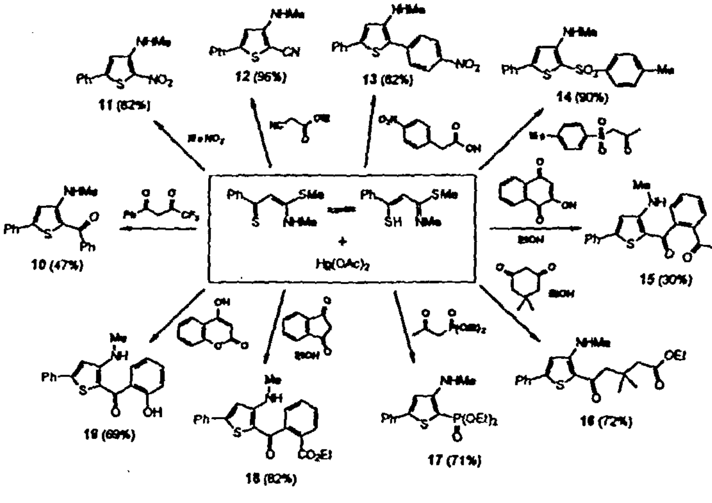
Deacylation of the intermediate 9 is certainly promoted by the driving force derived from aromatization.

Scheme 2



Similarly a variety of other thiophene derivatives have been prepared. Typical examples are shown in Scheme 3.

Scheme 3



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