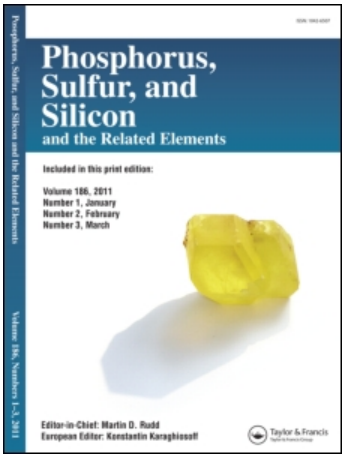

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Sequential Transformations with Thiopyrylium Salts

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SEQUENTIAL TRANSFORMATIONS WITH THIOPYRYLIUM SALTS

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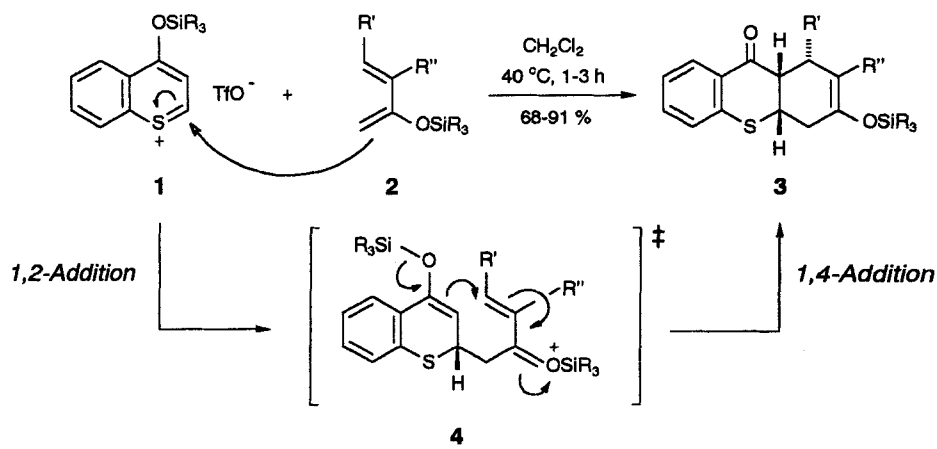
Abstract The sequential transformation of 4-silyloxybenzothiopyrylium salts and 2-silyloxy-1,3-butadienes diastereoselectively gives annulated thiochromanones, which can be used for the selective synthesis of thioxanthene dyes.

INTRODUCTION

Sequential transformations are a powerful strategy in Organic Chemistry very often allowing the synthesis of complex molecules in a single synthetic step.[1] Thiopyrylium salts have not been used in stereoselective sequential transformations so far.

SEQUENTIAL TRANSFORMATIONS WITH BENZOTHIOPYRYLIUM SALTS

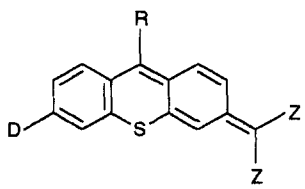
A new method for the efficient and stereoselective construction of annulated thiochromanones based on the sequential 1,2-addition/1,4-addition of 4-silyloxy-1-benzothiopyrylium salts and 2-silyloxy-1,3-butadienes has been reported.



As a typical example, the reaction of the benzothiopyrylium salt **1** (R = *iso*-Propyl) and the 2-silyloxy-1,3-butadiene **2** (R = *iso*-Propyl, R' = Phenyl, R" = H) exclusively gives the all-*cis* thioxanthone **3** in 91 % yield. The structure of **3** (R = *iso*-Propyl, R' = Phenyl, R" = H) was proved unambiguously by X-ray structure analysis.[2] The benzothiopyrylium salts **1** as well as the 2-silyloxy-1,3-butadienes **2** can be prepared *in situ* by reaction of 4-thiochromenone and the corresponding methyl vinyl ketone, respectively, with various trialkylsilyltrifluoromethanesulfonates. The new method crucially relies on the double activation of the 4-silyloxy-1-benzothiopyrylium salt **1**, which first (**1+2→4**) acts as an acceptor and, second (**4→3**) is employed as a donor. Scope and limitation of this new method was reported and the stereochemical outcome of the reactions as well as the mechanistic implications were discussed in detail.

SELECTIVE SYNTHESIS OF THIOXANTHENE DYES

Finally, the use of the thioxanthones **3** for the selective and efficient synthesis of thioxanthene dyes **5** that are assumed to be of benefit in the field of Photodynamic Tumor Therapy has been described. The transformation of **3** (R = *iso*-Propyl, R' = R" = H) to various thioxanthene dyes **5** has been performed in 5 steps starting with the addition of an organolithium reagent to the keto group in **3**, which is followed by hydrolysis of the silylenolether-functionality and Knoevenagel condensation of the resulting keto group with a 1,3-dicarbonyl compound. Subsequent elimination and oxidation give the corresponding thioxanthene dyes of the general structure **5** with high overall yield.



5

D = electrondonor
Z = electronacceptor
R = aryl, alkyl, H

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