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Synthesis of [1,3]Thiazino[2,3-*i*]purinium Systems by Halocyclization of 6-(Prenylsulfanyl)- and 6-(But-3-enylsulfanyl)purines

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Abstract—The alkylation of purine-6-thione with prenyl bromide and 3-butenyl bromide in the presence of alkali gave 6-[prenyl(but-3-enyl)sulfanyl]purines which reacted with halogens to afford fused [1,3]thiazino[2,3-*i*]purinium systems.

Keywords: purine-6-thione, 8-halo-7,7-dimethyl-1,7,8,9-tetrahydro[1,3]thiazino[2,3-*i*]purinium halide, 7-halomethyl-1,7,8,9-tetrahydro[1,3]thiazino[2,3-*i*]purinium halide, halocyclization, [1,3]thiazino[2,3-*i*]purine

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Purin-6-thione derivatives (**1**) are known to exhibit diverse biological activities [1–4], in particular, substituted [1,3]thiazino[2,3-*i*]purines are efficient xanthine oxidase inhibitors [4].

The reported syntheses of [1,3]thiazino[2,3-*i*]purine systems include intramolecular cyclization of 6-(3-chloropropyl)sulfanylpurines [5], reaction of purine **1** with 2-(chloromethyl)oxirane [6, 7], and reactions of 8,9-diamino-3,4-dihydro-2*H*,6*H*-pyrimido[6,1-*b*][1,3]-thiazin-6-one with urea, thiourea, and benzamidine [8, 9].

In the present work, aimed at preparing novel fused thiazinopurinium systems, we studied the reactions of 6-prenylsulfanylpurine (**2a**) and 6-(but-3-enylsulfanyl)-purine (**2b**) with halogens.

Compound **2a** was earlier synthesized in DMF in the presence of Na_2CO_3 [10]. We synthesized prenyl sulfide **2a** by alkylating purine **1** with prenyl bromide in an aqueous-alcoholic medium in the presence of KOH (Scheme 1).

The mass spectrum of prenyl sulfide **2a** contain a molecular ion peak $[M]^{+\bullet}$, while the base peak belongs to a peak at *m/z* 187 formed by the elimination of an SH radical to form a pyrrolopurinium cation **A**. The peak at *m/z* 172 is likely associated with the formation of a pyrrolopurinium system **B** via sulfur and methane elimination (Scheme 2).

The S–CH_2 bond cleavage occurs by two routes: the first involves formation of a purine-6-thiol radical cation with *m/z* 152, followed by the elimination of $SH^{\bullet}$ and HCN (*m/z* 119 and 92) and the second, formation of a prenyl cation (*m/z* 69) (Scheme 3).

Butenyl sulfide **2b** was prepared for the first time by the reaction of purine **1** with 3-butenyl bromide in KOH–H_2O–DMF at room temperature (Scheme 1). In the ^{1}H NMR spectrum of compound **2b**, the SCH_2

Scheme 1.