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TANDEM HETEROCYCLIZATION IN THE SYNTHESIS OF NOVEL IMIDAZO[1,5-*d*][1,3,4]THIADIAZINE

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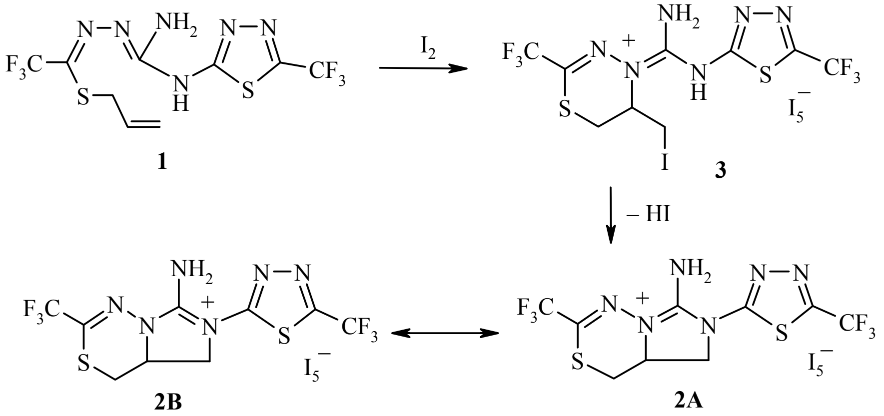
Keywords: 2-(5-allylthio-2-amino-6,6,6-trifuoro-1,3,4-triaza-2,4-hexadien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazole, 7-amino-2-trifluoromethyl-6-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl)-4,4a,5,6-tetrahydroimidazo[1,5-*d*][1,3,4]thiadiazinium pentaiodide.

Imidazo[1,5-d][1,3,4]thiadiazines are little studied systems. Compounds of this series have been synthesized by treating iminophosphoranes with isothiocyanates [1].

We have found that reaction of 2-(5-allylthio-2-amino-6,6,6-trifuoro-1,3,4-triaza-2,4-hexadien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazole (**1**) with iodine is accompanied by a tandem closure of two heterocyclic systems to form the 7-amino-2-trifluoromethyl-6-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl)-4,4a,5,6-tetrahydroimidazo[1,5-*d*][1,3,4]thiadiazinium pentaiodide (**2**). Evidently, the reaction occurs *via* the intermediate thiadiazine **3**.



The structure of compound **2** was confirmed by ^{1}H NMR and X-ray structural analysis data. In the ^{1}H NMR spectrum of compound **2** one of the signals for the NCH_2 group protons occurs at lower field than the signal for the NCH (H-9a) proton and this is evidently caused by a higher contribution of the resonance structure **2B**. The overall view of the cation structure derived from the X-ray structural data is given in Figure 1.

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^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz) in DMSO-d_6 with TMS as internal standard. X-ray structural analysis for compound **2** was carried out on a dark-brown, prismatic fragment of size 0.28×0.18×0.11 mm at 295(2) K. The empirical formula for the compound is $C_9H_7F_6I_5N_6S_2$ and the crystals are triclinic with a = 9.3080(2), b = 10.9851(18), c = 11.9850(2) Å. α = 103.861(16)°, β = 94.305(17)°, γ = 91.590(15)° and space group P-1. X-ray analysis was performed on an Xcalibur 3 automatic four circle diffractometer and the structure was solved and refined using the SHELX [2] program package. Full X-ray structural analysis data has been placed in the Cambridge Structural Database as deposit CCDC 787102 and can be accessed using the address www.ccdc.cam.ac.uk/data_request/cif or supplied on request to the authors.

Compound **1** was prepared by method [3]

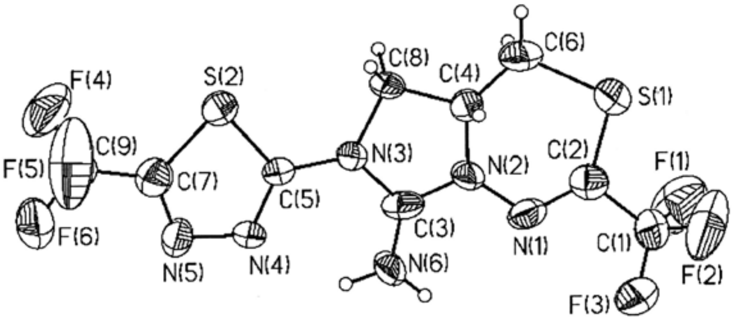

Fig. 1. General view of the compound **2** molecule from X-ray analytical data.

7-Amino-2-trifluoromethyl-6-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl)-4,4a,5,6-tetrahydroimidazo-[1,5-*d*][1,3,4]thiadiazinium Pentaiodide (2). A solution of 2-(5-allylthio-2-amino-6,6,6-trifuoro-1,3,4-triaza-2,4-hexadien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazole (**1**) (0.076 g, 0.2 mmol) in acetic acid (3 ml) was added to a solution of finely powdered iodine (0.203 g, 0.8 mmol) in acetic acid (3 ml). After 10 days the black crystalline pentaiodide **2** was filtered off. Yield 0.046 g (23%); mp 122ºC. ^{1}H NMR spectrum, δ, ppm (J, Hz): 3.41 (1H, dd, J = 9.57, J = 12.10, SCH_2); 3.82 (1H, dd, J = 2.86, J = 12.12, SCH_2); 4.04 (1H, t, J = 8.59, NCH_2); 4.40 (1H, m, NCH); 4.63 (1H, t, J = 8.63, NCH_2); 6.18 (2H, br. s, NH_2). Found, %: C 10.34; H 0.67; N 8.01; S 6.13. $C_9H_7F_6I_5N_6S_2$. Calculated, %: C 10.68; H 0.70; N 8.31; S 6.34.

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