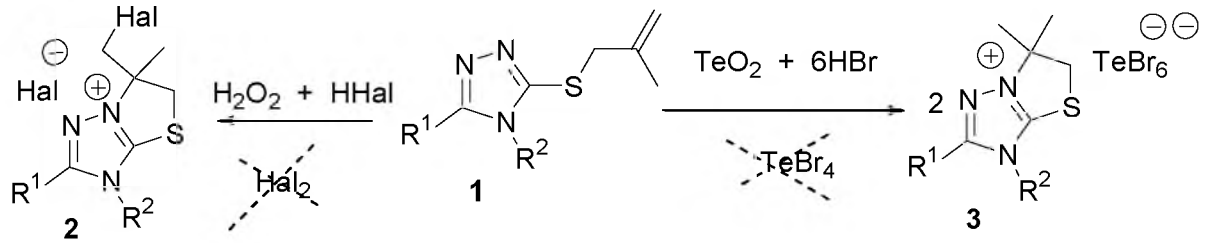
SYNTHESIS OF ADVANCED MATERIALS ON A BASE OF FUNCTIONAL CONDENSED TRIAZOLES

Slivka M.[1], *Aleksyk H.*[1], *Fizer M.*[1], *Krivovjaz A.*[1]
Korol N.[1], *Sharga B.*[1], *Sidey V.*[1], *Mariychuk R.*[2]
[1]Institute of Chemistry and Ecology, Uzhhorod National University, Ukraine,
mikhailo.slivka@uzhnu.edu.ua
[2]FHNS University of Prešov, Slovak Republic

Condensed heterocycles are well known due their excellent biological activity, useful physical properties and have indisputably importance for organic chemistry. Thiazolotriazoles are no exception to this plan! There are a lot of representatives of thiazolotriazoles are known due to their wide application, especially as effective bactericides and fungicides [1]. Earlier we have shown that the introduction of pharmacophoric residues in the triazole moiety via electrophilic reactions (cyclization, addition, and substitution) leads to significant increasing of the bio-activity of the last [2,3]. The object of our research is the developing common approaches to the obtaining of new functional materials on a base of condensed triazoles via sustainable techniques using electrophilic cyclization reactions (ECR). ECR is a powerful synthetic method [4] which uses mild conditions and available reagents, but some electrophile reagents (which contain pharmaphophoric residue) can possess toxicity: halogens, selenium/tellurium halogenides, etc. That is why, the search of alternative non-/or less-toxic electrophilic reagents for ECRs and selection of non-toxic solvents is an actual task of sustainable chemistry for access to new effective antimicrobial agents, as well as to new functional materials with valuable optoelectronic properties.

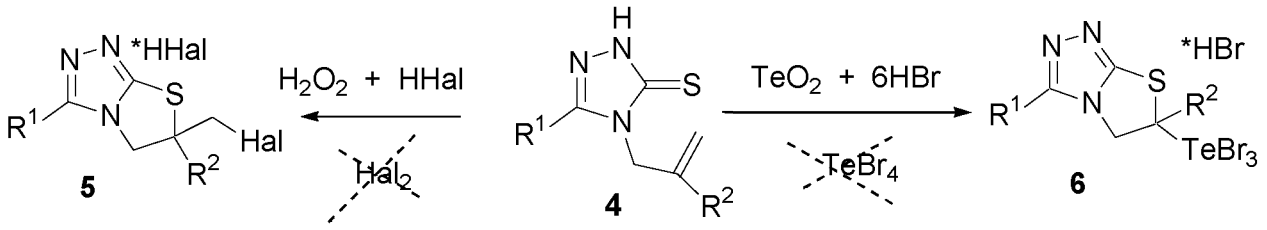
The attempt of replace such toxic classical electrophilic reagents as bromine and tellurium tetrabromide with less toxic reagents using the unsaturated 1,2,4-triazole derivatives is presented. So, 3-Alkenylthioethers of 4,5-disubstituted 1,2,4-triazoles **1** and 4-alkenyl-5-substituted 1,2,4-triazole-3-thiones **4** were used as starting compounds. In the investigation of bromine-induced electrophilic heterocyclization was performed with the use of bromine, which was formed directly in a reaction mixture from less toxic hydrogen bromide and hydrogen peroxide. The yields of the target thiazolotriazoles **2, 5** were 72-84%, and the physicochemical characteristics fully correspond to the corresponding analogues obtained by the traditional bromination technique.



R^1 = Ph, NHPh, 2-HO-C_6H_4, 4-$NO_2C_6H_4$, $C_{15}H_{31}$, $C_{17}H_{35}$
R^2 = Me, Ph

The possibility of obtaining the above mentioned toxic electrophilic reagent from less toxic tellurium dioxide and a 6-fold excess of hydrogen bromide were studied for studying of ECR with the participation of tellurium tetrabromide. When isolating the target thiazolotriazoles **3** and establishing their structure (via using a complex of spectral methods, XRD), the formation of products of proton-induced electrophilic heterocyclization was unexpectedly noted. Presumably, under the conditions of the reaction in the reaction mixture, the formed tellurium tetrabromide is in equilibrium with hexabromotelluridic acid, which entered the ECR to form condensed thiazolotriazolium hexabromotellurides. On the other hand the application of the same conditions on a case of triazoles **4** lead to the formation of salts **6** with the expected presence of the $TeBr_3$-group in the target molecule.

It should be noted that obtained salts **3** – the product of the quarternization of the nitrogen atom in triazole cycle – have perovskite-like structure and can be considered as hybrid organo-inorganic perovskites, which are prospective advanced materials for solar energy.



R^1 = Ph, 4-BrC_6H_4, 4-Py, 2-HO-C_6H_4, 4-$NO_2C_6H_4$, $C_{15}H_{31}$, $C_{17}H_{35}$
R^2 = H, Me

Preliminary testing of microbiological activity for thiazoloriazole **2**, **3, 5, 6** indicates high bactericidal and fungicidal activity of [1,3]thiazolo[1,2,4]triazoles **3, 6** and bactericidal effect of compounds **6**; at the same time, the salts **2, 5** were inactive. These results are perfectly correlated with the well-known fact in the literature that antimicrobial activity increases with the introduction of tellurium-halide residues into an organic molecule [3].

Thus, as a result of the performed research, we showed the possibility of using sustainable electrophilic reagents in ECR for the synthesis of condensed heterocycles, which significantly expands the scope of practical application of the specified method.

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