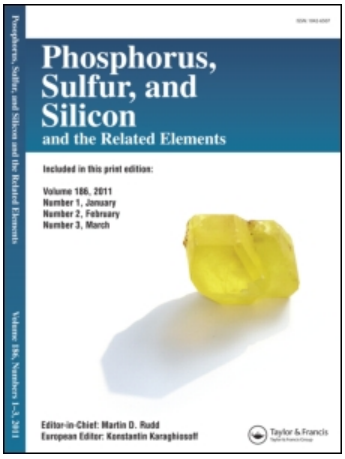


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# SILICA CHLORIDE CATALYZED CYCLIZATION REACTION: UNIQUE SYNTHESIS OF CONDENSED THIAZOLES AND SELENAZOLE

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# SILICA CHLORIDE CATALYZED CYCLIZATION REACTION: UNIQUE SYNTHESIS OF CONDENSED THIAZOLES AND SELENAZOLE

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The facile and regioselective synthesis of thiazoles and selenazoles has been performed by the catalytic action of silica chloride on corresponding propynylthio and propynylseleno derivatives, respectively.

*Keywords:* Condensed thiazoles; selenazole; silica chloride catalysis



Many efforts have been devoted to prepare a variety of heterocyclic system by functionalization of acetylenic moiety[1-3]. Such a functionalization seems to be very attractive because the remaining double bond might be either used for manipulations after cyclization or isomerization, for aromatization may occur. Whilst a wealth of methods exist for the cyclization and functionalization of acetylenic moiety using Pd(II) salt[3-7], bases[8-9], mercury(II) acetate[10] and sulfuric acid[11] the possibility of cyclization of this kind using solid acids have been largely overlooked.

In the course of our investigations directed towards the synthesis of heterocyclic[4-1] and homocyclic[12-14] systems *via* intramolecular functionalization of acetylenic moiety we found that regioselective cyclization of 6-methyl-3-propynylthio-1,2,4-triazin-5(2H)-one **1** can be carried out in

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good yield using silica chloride in refluxing *n*-BuOH. Silica chloride is obtained from reaction of silica gel (art 773 for TLC from merck Darmstadt, FRG) and thionyl chloride according to a literature procedure[15]. In a typical experiment, a mixture of **1**, *n*-BuOH and silica chloride was refluxed under stirring to afford a product. From analytical, spectral and melting point data as well as by comparison with authentic sample, the product was identified as 6,7-dihydro-6-methylene-3-methyl-4H-thiazolo[2,3-c][1,2,3]triazin-4-one **7**. In the $^1$HNMR spectrum of this compound the *exo*-methylene protons appeared as two doublets at δ 5.2 and 6.5 ($J$=1.8 Hz). The relatively large shift (ca. 1.3 ppm) between the olefinic protons can be justified by assigning the downfield signal to the exo-methylene proton which is close to C-4 amide carbonyl in the 1,2,4-triazine ring[3,5].

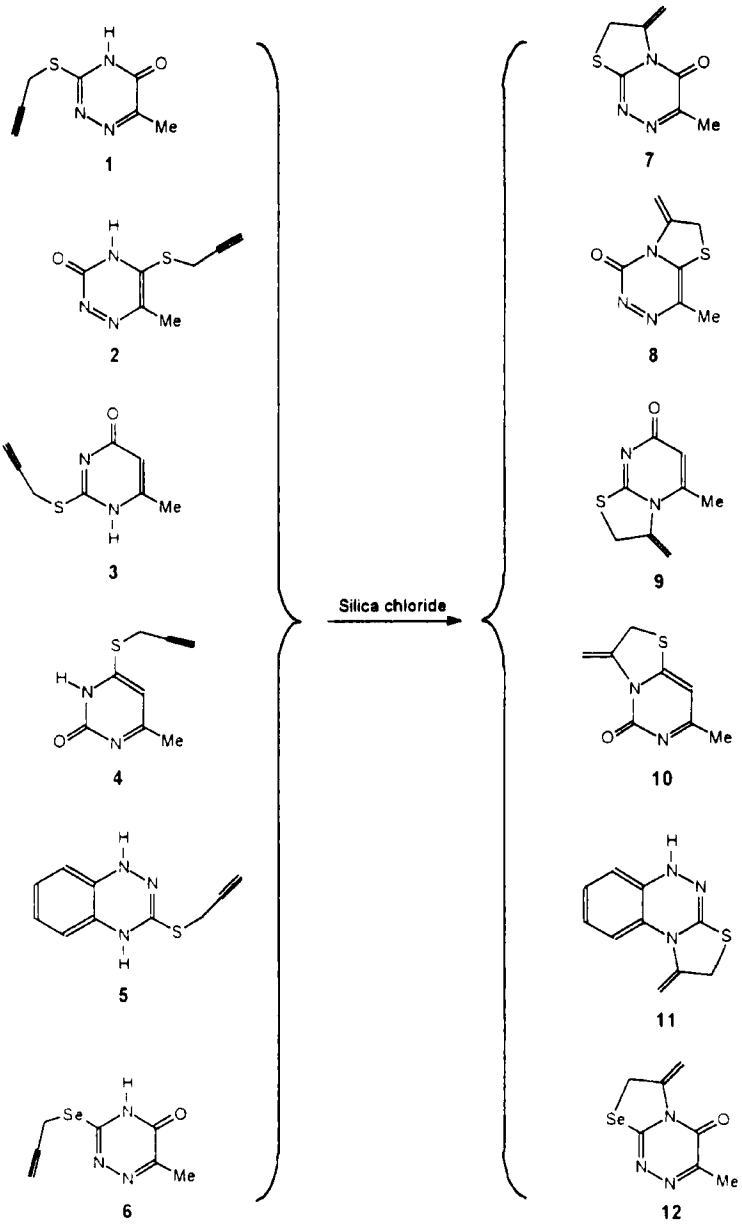
The methylene protons in this compound appear as a triplet showing geminal and allylic types of coupling. It means silica chloride has smootly catalyzed cyclization of the acetylenic moiety of the propynylthio group regioselectively. Various propynylthio-1,2,4-triazines **1** and **2**, propynylthiopyrimidines **3** and **4**, 3-propynylthio – 1,2,4-benzotriazine **5** and 3-propynylseleno-1,2,4-triazine **6** (Scheme) were employed in order to prepare condensed thiazoles **7–11** and selenazole **12**and to establish the generality of the method. We found that cyclization of **1–6**to **7–12** can be carried out in high regioselectivity and good yield (Table). Melting points, yield, propynyl compounds used and obtained are reported in the Table.



TABLE Preparation of condensed thiazoles and selenazole

| *Substrate* | *Reaction time (h)* | *Product* | *Yield (%)* | *mp (Lit) (°C)* |
|---|---|---|---|---|
| **1** | 8 | **7** | 75 | 147–48 (146–47)[3] |
| **2** | 6 | **8** | 88 | 190–92 (190–92)[2] |
| **3** | 6 | **9** | 65 | 190–92 (191–92)[4] |
| **4** | 5 | **10** | 85 | 196–97 (197–98)[4] |
| **5** | 6 | **11** | 72 | 97–98 (97–98)[5] |
| **6** | 6 | **12** | 61 | 198–99 (197–98)[16] |

All compounds were known and their spectral and analytical data were in accord with authentic compounds.




SCHEME 1

In conclusion in comparison with the presently available synthetic methods of condensed thiazoles and selenazoles which show draw back from the stand point of yields, price and limited availability of catalyst $[PdCl_2(PhCN)_2]$ or low regioselectivity, the efficiency of the present method is apparent from the availability of inexpensive silica gel and thionyl chloride and the unique regioselectivity as well as high yield and with the lack of side products. The superiority of silica chloride over sulphuric acid catalyzed regioselective cyclization of propynylthio heterocycles[10], can be clearly visualized in the clean and exceedingly simple work-up procedure, involving only filtration of catalyst and removal of solvent to obtain the product in a high state of purity and also in the replacement of the corrosive and polluting sulphuric acid by more environmentally attractive silica chloride. In this connection the present methodology for the synthesis of various thiazoles and selenazoles is noteworthy.



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