

**PALLADIUM CATALYZED POLYHETERO-CLAISEN REARRANGEMENT OF
3-ALLYLTHIO-1,2,4-TRIAZIN-5(2H)-ONES**

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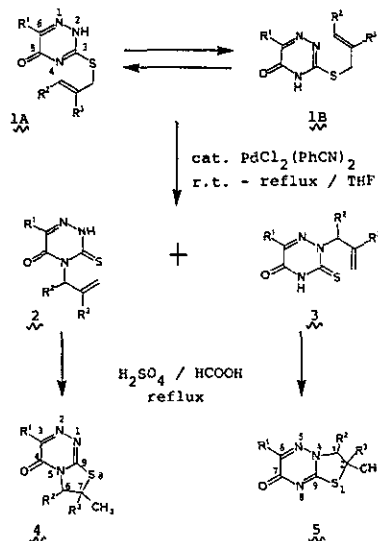
3-Allylthio-1,2,4-triazin-5(2H)-ones(1) are known to exist as a mixture of tautomers 1A and 1B. Spectroscopic analysis shows 1A is the main tautomer². Based on these precedents, the polyhetero-Claisen rearrangement of 1 was undertaken with the expectation of achieving S → N-4 allylic transposition.

The S → N allylic rearrangement was found to be nicely catalyzed by PdCl₂(PhCN)₂³. The reaction proceeded under mild condition to give the rearranged products in high yields. The regioselectivity is highly dependent on the substitution pattern of the allylic moiety, irrespective of R¹. When R²=R³=H, the alkylation takes place selectively at N-4, which seems to reflect more or less the distribution of tautomers 1A and 1B. When R²=CH₃, it provides the N-2 product. The reversed selectivity might be explained in terms of a pseudo A(1,3) strain between C-5 carbonyl oxygen and terminal methyl group in a chair like transition state. These reactions proceed with the kinetic nature.

The thiones 2 and 3 were found to cyclize smoothly in the presence of H₂SO₄ to afford the fused heterocyclic systems 4 and 5 in high yields(78-100%). This present method serves an efficient synthesis of the fused heterocyclic system.

Pd(II) Catalyzed S → N Allylic Rearrangement

1	R ¹	R ²	R ³	yield(<u>2</u> + <u>3</u>)	<u>2</u> / <u>3</u>
a	H	H	H	86 %	88/12
b	CH ₃	H	H	90 %	88/12
c	Ph	H	H	88 %	95/ 5
d	H	CH ₃	H	92 %	30/70
e	Ph	CH ₃	H	100 %	29/71
f	H	H	CH ₃	64 %	74/26



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