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

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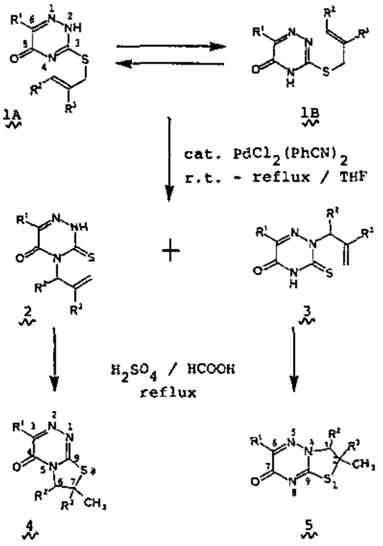
3-Allylthio-1,2,4-triazin-5(2H)-ones(1) are known to exist as a mixture of tautomers 1A and 1B. Spectoroscopic analysis shows 1A is the main tautomer[2]. Based on these precedents, the polyhetero-Claisen rearrangement of 1 was undertaken with the expectation of achieving S → N-4 allylic transposition.

The S → N allylic rearrangement was found to be nicely catalyzed by $PdCl_2(PhCN)_2$[3]. 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 R^1. When $R^2=R^3=H$, the alkylation takes place selectively at N-4, which seems to reflect more or less the distribution of tautomers 1A and 1B. When $R^2=CH_3$, 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 H_2SO_4 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(2+3)	2 / 3
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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