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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### SYNTHESIS AND REACTIONS OF 2H-1,3-THIAZETES

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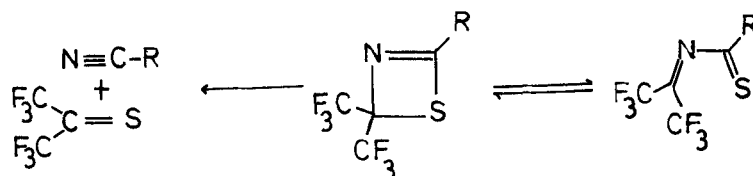
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## SYNTHESIS AND REACTIONS OF 2H-1,3-THIAZETES

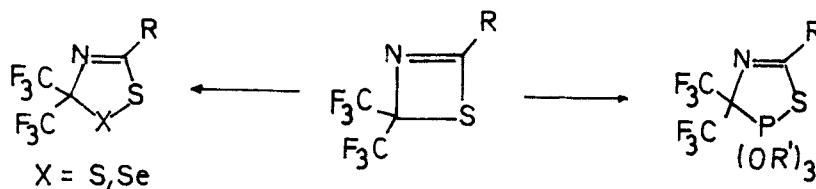
Klaus Burger and Ralph Ottlinger

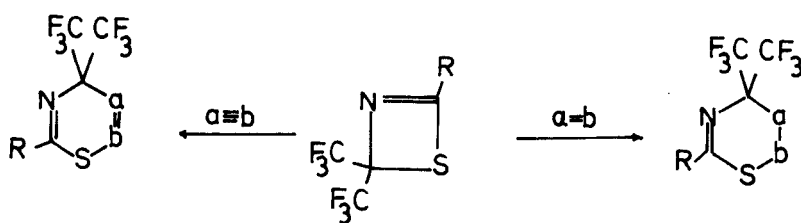
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2H-1,3-Thiazetes have been supposed to be the intermediates of the photoaddition of thiocarbonyl compounds to nitriles, yielding N-(alkylidene)thiocarboxamides<sup>1</sup>. Using the stabilizing effect of trifluoromethyl groups on small ring systems<sup>2</sup> we succeeded in synthesizing 2H-1,3-thiazetes as stable compounds<sup>3</sup>. At elevated temperatures a thermal mobile valence tautomeric equilibrium with N-(perfluoroisopropylidene)thiocarboxamides was observed, which competes with a [2+2] cycloreversion process.

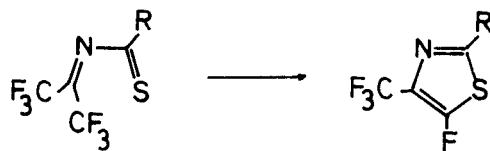


The sulfur containing hetero-1,3-dienes easily accessible by this reaction turned out to be very versatile reagents. By [4+1] and [4+2] cycloaddition reactions numerous 5- and 6-membered sulfur heterocycles became readily available.





Partially fluorinated thiazoles are the result of a new type of reaction, which includes an addition-elimination process followed by an electrocyclic reaction with a successive elimination step. The fluorine atom present at C-(5) is readily exchangeable by various nucleophiles.



- <sup>1</sup> D.S.L. Blackwell, P. deMayo, and R. Suau, *Tetrahedron Lett.* 1974, 91.
- <sup>2</sup> D.M. Lemal, and L.H. Dunlap jr., *J. Amer. Chem. Soc.* 94, 6562 (1972); W. Adam, J.-C. Liu, and O. Rodriguez, *J. Org. Chem.* 38, 2269 (1973).
- <sup>3</sup> K. Burger, J. Albanbauer, and M. Eggersdorfer, *Angew. Chem.* 87, 816 (1975); K. Burger, R. Ottlinger, and J. Albanbauer, *Chem. Ber.* 110, 2114 (1977).