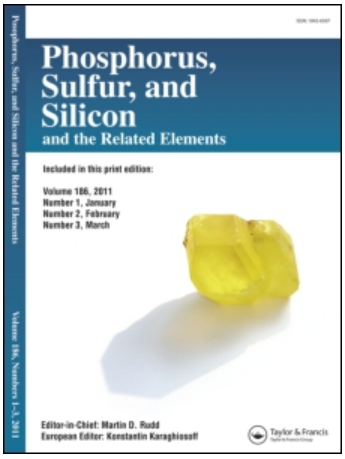

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THERMIC REACTION OF THIOPYRIDONES

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THERMIC REACTION OF THIOPYRIDONES

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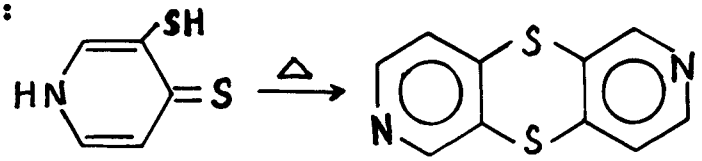
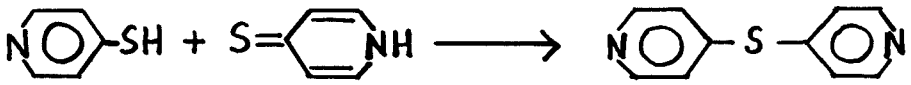
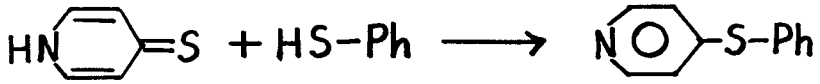
In course of our investigations on dimercaptopyridines it was discovered that 3-mercaptothiopyrid-4-one easily undergoes a thermic reaction with generation of hydrogene sulfide and diazathianthrene:



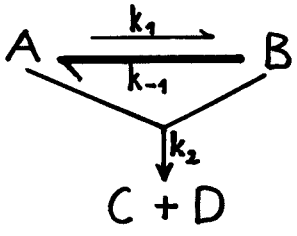
The reaction was found to be general for thiopyridones. Both tautomers thione and thiol take part in the process:



If the reaction proceeds in presence of a mercapto aromatic or mercapto heteroaromatic compound, the product is mixed sulfide, because of a very low concentration of competitive thiol species in thiopyridones tautomeric equilibria:



Kinetic studies were undertaken for to explain better the reaction. If 4- or 2-thiopyridone reacted with 3-mercaptopyridine or 4-phenoxythiophenol, the reactions were found to be of second order. 4- or 2-thiopyridones alone reacted accordingly to first order. It is a special case: reversal reaction of first order (tautomerization) is followed by an irreversal reaction of second order:



The thione form A being always very predominant as compared to the thiol form B, it is possible to applicate the Bodenstein's method of stationary state:

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[A][B] = 0$$

$$[B] = \frac{k_1[A]}{k_{-1} + k_2[A]}$$

for the rate of C formation:

$$\frac{d[C]}{dt} = k_2[A][B] \qquad \frac{d[C]}{dt} = \frac{k_2 k_1 [A]^2}{k_{-1} + k_2[A]}$$

in another form:

$$\frac{d[C]}{dt} = \frac{k_2 k_1 [A]^2}{k_{-1}\ 1 + \frac{k_2}{k_{-1}}[A]}$$

If $k_{-1} \ll k_2$ the value $\frac{k_2}{k_{-1}}$ is high and

$$1 + \frac{k_2}{k_{-1}}[A] \approx \frac{k_2}{k_{-1}}[A]$$

thus

$$\frac{d[C]}{dt} = k_1[A]$$

It is just the case observed. For $k_2 \ll k_{-1}$ and $k_2 \approxeq k_{-1}$ the reaction could not be of first order.