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### THERMIC REACTION OF THIOPYRIDONES

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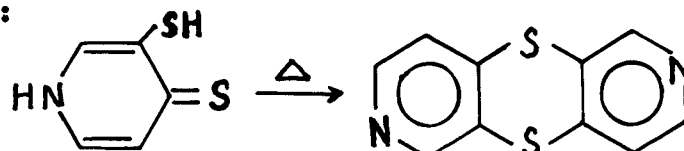
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## THERMIC REACTION OF THIOPYRIDONES

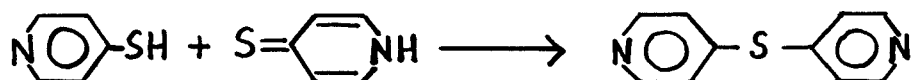
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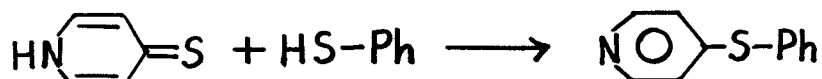
In course of our investigations on dimercaptopyridines it was discovered that 3-mercaptothiopyrid-4-one easily undergoes a thermic reaction with generation of hydrogen sulfide and diazathianthrene:



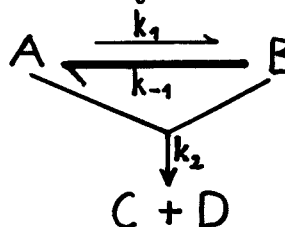
The reaction was found to be general for thiopyridones. Both tautomers thione and thiol take part in the process:



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 irreversible 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:

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

in another form:

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

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  $k_2 \approx k_{-1}$  the reaction could not be of first order.