REACTION MECHANISM OF S,N-DOUBLE REARRANGEMENT

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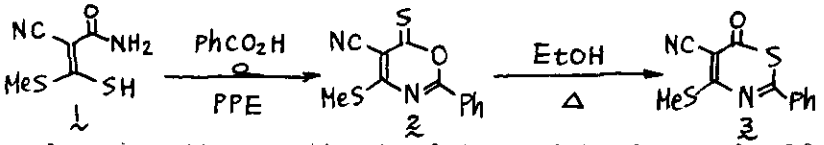
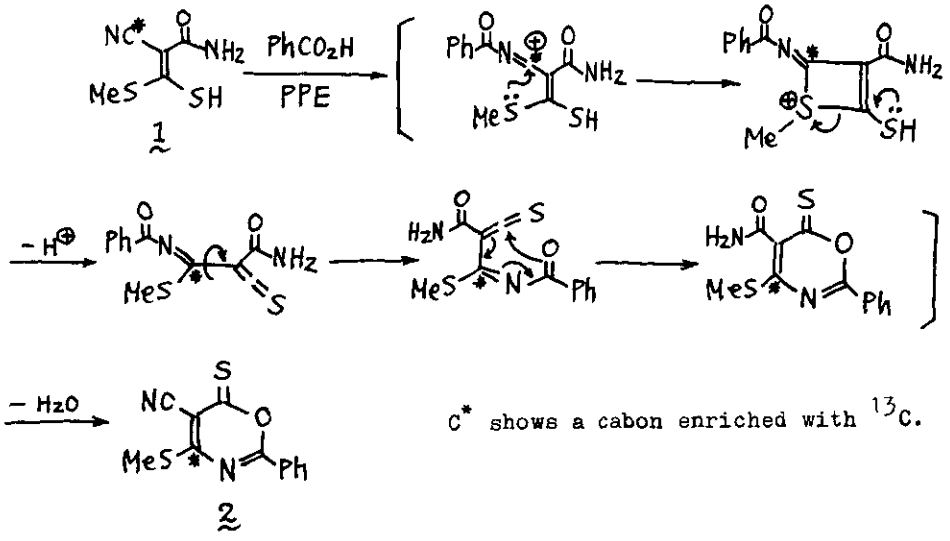
In our continuing study on the chemistry of thiazines and related compounds, we found that 2-cyano-3-mercapto-3-methylthioacrylamide 1 reacted with benzoic acid in the presence of polyphosphate ester (PPE) to give 5-cyano-4-methylthio-2-phenyl-1,3-oxazine-6-thione 2, which, on treatment with refluxing ethanol, underwent a ring-transformation to form the corresponding thiazine derivative 3.



This novel condensation reaction involving an interchange of sulfur and nitrogen atoms was termed "S,N-double rearrangement".[1,2] Herein, we present a reaction pathway which is explained on the basis of chemical reactions, ^{13}C labeling, and crossover experiments.



C* shows a cabon enriched with ^{13}C.

References: (1) M.Yokoyama et al., J. Chem. Soc. Chem. Commun., 1981, 560.
(2) M.Yokoyama et al., J. Org. Chem., 1982, 47, 1090.