

Supporting Information for

**C(sp²)-H bond sulfenylation of aminouracils and enamines from aryl
halides**

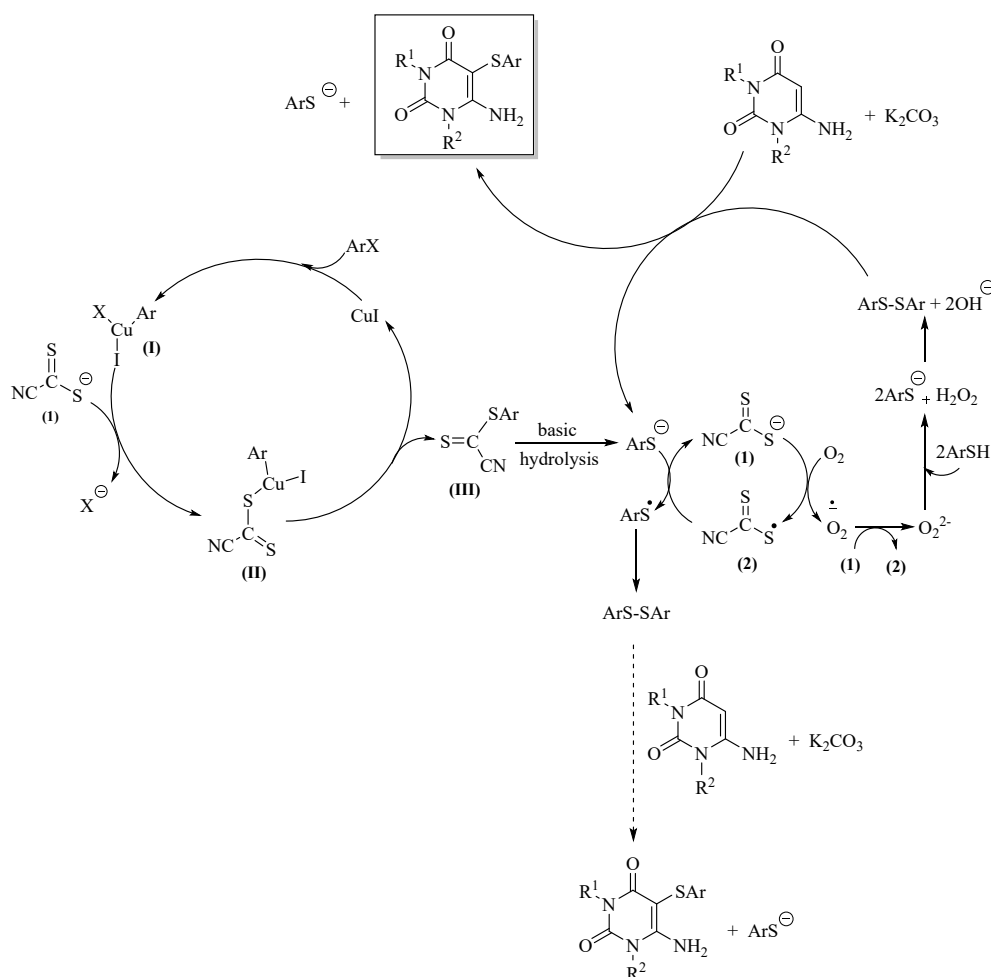
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Proposed Mechanism:

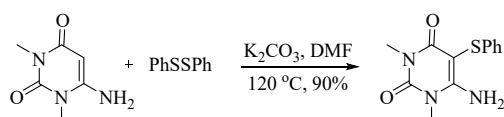
According to previous reports on copper-catalyzed C-S bond formation¹⁻⁵ and current results, a proposed mechanism for thioarylation reaction using aryl halide is shown in Scheme 1.



Scheme 1. A possible mechanism for thioarylation reaction.

At first, CuI undergoes oxidative addition by insertion into the aryl C–X bond to produce ArCuXI intermediate **(I)**. Replacement of the halide ion in the complex **(I)** by cyanodithioformate **1**, affords intermediate **(II)**. This step is followed by reductive elimination to give S-arylcyanodithioformate **(III)** and the CuI catalyst. Hydrolysis of intermediates **III** in basic medium, generates the corresponding thiolate which undergo aerobic oxidation to produce symmetric disulfides. The nucleophilic attack of activate carbon of amino uracil on the diaryl disulfide, in the presence of CuI and K₂CO₃, yields the desired sulfenylated product .

As shown in the mechanism, the desired product is formed from the reaction of in situ generated disulfide with aminouracil in the presence of base. Although TLC analysis during the reaction confirms the presence of disulfide, however, another control reaction was performed. In this reaction, diphenyl disulfide was used directly in reaction with aminouracil and potassium carbonate in DMF at 120 °C (Scheme 2). In this case, the product was formed in 90% yield which indicates that the reaction can proceed well through disulfide intermediates. This result also shows that CuI does not play a role in the final step of the reaction (reaction of disulfide with aminouracil).



Scheme 2. Direct application of disulfide in thioarylation reaction.

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