

CYCLOADDITION-ELIMINATION REACTIONS OF IMINOTHIADIAZOLINES
WITH ACETYLENES: HYPERVALENT SULFUR INTERMEDIATES¹⁾

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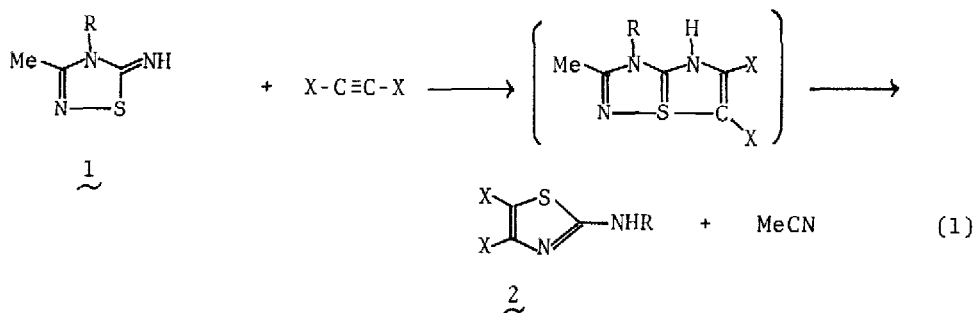
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1,2-Dithiole-3-thiones have been known to react with active acetylenes to afford ring-opened products after 1,3-dipolar cycloaddition.²⁾ Much interest has been paid to these products and similar reactions in relation to the chemistry of thiathiophthenes.³⁾

Recently, we reported an example of cycloaddition-elimination reaction of Hector's base (4-aryl-3-arylimino-5-imino-1,2,4-thiadiazolidine⁴⁾) with active acetylenes to give aminothiazoles in high yields.⁵⁾

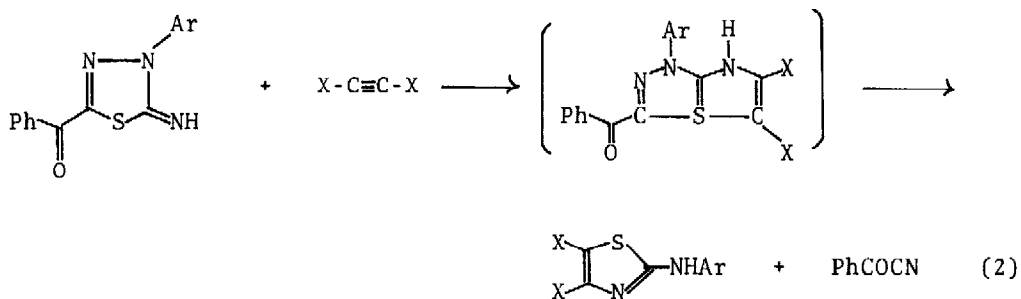
Now we report new examples of the same type of reaction to show that the iminothiazoline moiety generally reacts as a 1,3-dipole with active acetylenes.

4-Alkyl-5-imino-3-methyl- Δ^2 -1,2,4-thiadiazolines (1) reacted exothermally at 0°C with dibenzoyl- and dimethoxycarbonylacetylenes in tetrahydrofuran (THF) to give the corresponding 2-alkylaminothiazoles (2) in high yields.



2: R, X, mp (°C), yield (%): Me, PhCO, 196.5-198.0, 96; Me, CO₂Me, 156.5-158.0, 60; Et, PhCO, 170.8-172.3, 70; Et, CO₂Me, 134.5-135.5, 70.

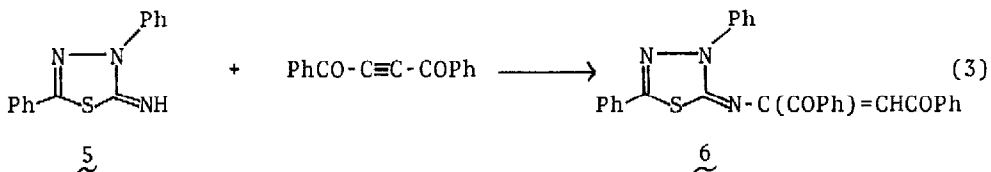
Then, 4-aryl-2-benzoyl-5-imino- Δ^2 -1,3,4-thiadiazolines⁶⁾ (3) were also shown to react with active acetylenes in THF to give the corresponding 2-arylaminothiazoles (4) in high yields.⁷⁾ The reaction proceeds at room temperature for 3a-c and at 100 °C in a sealed tube for 3d.



3: a) Ar=Ph, b) Ar=p-MeC₆H₄
 c) Ar=p-ClC₆H₄, d) Ar=p-NO₂C₆H₄

4: Ar, X, mp (°C), yield (%): Ph, PhCO, 173.5-175.5, 98; p-MeC₆H₄, PhCO, 203.0-204.0, 58; p-ClC₆H₄, PhCO, 186.5-187.0, 77; p-NO₂C₆H₄, PhCO, 249.8-251.5, 83; Ph, CO₂Me, 115.0-116.0, 50; p-MeC₆H₄, CO₂Me, 175.5-176.5, 67; p-ClC₆H₄, CO₂Me, 191.0-192.0, 89; p-NO₂C₆H₄, CO₂Me, 216.0-218.0, 69.

On the other hand, when the benzoyl group at 2-position is substituted by a phenyl, the imine (5) simply added to dibenzoylacetylene to give 6 quantitatively, which is most commonly expected.



Detailed mechanism of these cycloaddition-elimination reactions remains to be explored, however, at present we propose the mechanism that the reactions proceed through 1,3-dipolar cycloaddition of iminothiazoline moiety to activated acetylenes, tetravalent sulfur intermediates being involved.

References and Notes

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- 7) The yields of benzoyl cyanide were not estimated quantitatively.