# THE STRUCTURE AND REACTION OF 1:1 ADDUCT OF IMINOTHIAZOLINES AND NITRILES BOND SWITCH ON HYPERVALENT SULFUR

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The structure of 1:1 adduct (2) of 4-aryl-3-arylimino-5-imino-1,2,4-thiadiazolidines (2: Hector's base) with arylcyanamides was determined to be 5-(1', 3'-diarylguanidino)-3-arylamino-1,2,4-thiadiazole by X-ray structure analysis of the single crystal of tris-p-bromophenyl derivative of 1.

The analysis of $^{13}$C-NMR chemical shifts of 1 and analogs revealed the presence of considerable charge transfer from the guanidino group to the thiadiazole ring.

This effect and the bond switch in the course of the reaction can be attributed to the contribution of hypervalency of the sulfur.

Similar 1:1 adducts (3) of 3,4-disubstituted 5-imino-1,2,4-thiadiazolines with ethyl imidates (with extrusion of ethanol) were prepared and the structure was shown to be 3-substituted 5-(1'-substituted amidino)-1,2,4-thiadiazole. Again, bond-switch on the hypervalent sulfur is exemplified.

Alkylation of 1 and 3 with Meerwein reagents occurred on the thiadiazole ring to give the corresponding 5-iminothiadiazoline type derivatives, where re-bond switch was observed on the hypervalent sulfur.

3 is decomposed with butyllithium at low temperature to give 3-substituted 5-alkylamino-1,2,4-thiadiazoles in high yields.