

FORMATION OF 6a-THIOTHIOPHTHEN ANALOGUES
BASED ON (1,2,4)THIADIAZOLO(5,1-e)(1,2,4)THIADIAZOLE SYSTEM.
NOVEL CYCLOADDITION OF "HECTOR'S BASE" WITH NITRILES

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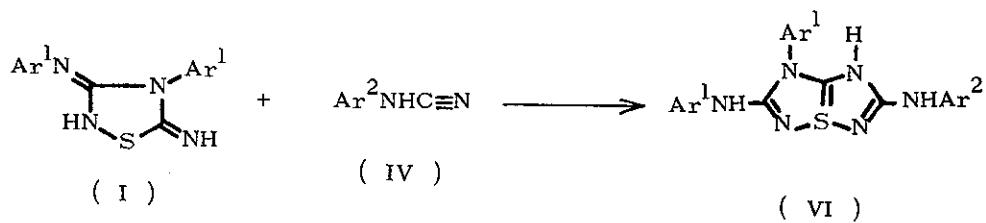
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3-Phenyl-2,5-bis(phenylamino)(1,2,4)thiadiazolo(5,1-e)(1,2,4)thiadiazole (VIa) was obtained in 59 % yield, when Hector's base (Ia) and phenylcyanamide were refluxed in dichloroethane for 2 hr at 80°C. VI (b-d) were obtained similarly.

Spectral evidence (MS, UV and IR) is presented for the new aromatic system (VI) with consideration of two other possible structures V and VII.

When Ia was heated in benzonitrile at 110°C for 2 hr with acetic acid, the following products were obtained.

This result shows that 6a-thia-1,3,4,6-tetraazapentalene (VI) suffered 1,3-dipolarophilic attack by Hector's base. It was further found that VIa reacted with sodium ethoxide in ethanol to give 3,5-bis(phenylamino)-1,2,4-thiadiazole in 70 % yield.



a) $\text{Ar}^1=\text{Ar}^2=\text{Ph}$ (59%)

b) $\text{Ar}^1=\text{Ph}$, $\text{Ar}^2=\text{p-Tolyl}$ (59%)

c) $\text{Ar}^1=\text{p-Tolyl}$, $\text{Ar}^2=\text{Ph}$ (53%)

d) $\text{Ar}^1=\text{Ar}^2=\text{p-Tolyl}$ (50%)

