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FORMATION OF 2-ARYLAMINOTHIAZOLES BY 1,3-DIPOLAR CYCLOADDITION OF "HECTOR'S BASE" WITH ACETYLENES.

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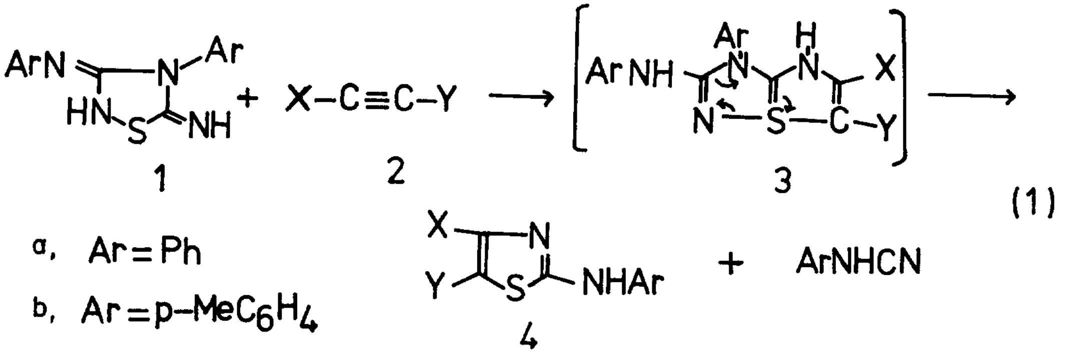
6a-Thia(S^{IV})-1,3,4,6-tetraazapentalene analogues were proposed to be the most probable structure at present for the 1:1 adducts formed by 1,3-dipolar cycloaddition of 4-aryl-3-arylimino-5-imino-1,2,4-thiadiazolidine (Hector's base)[1] with arylcyanamides as was reported in the preceding paper.[2] Then it should be of interest to synthesize another example of 6a-thia(S^{IV})heterapentalene analogue by a similar reaction.

Now we report here 1,3-dipolar cycloaddition of Hector's base with acetylenes (**2**) to give 2-arylaminothiazoles (**4**), which probably proceeds through 6a-thia(S^{IV})-1,3,4-triazapentalene analogue (**3**) as an intermediate. A typical procedure is shown below.

To Hector's base (**1a**, 5.0 mmol) in chloroform (50 ml) was added dibenzoylacetylene (**2a**, 6.5 mmol) in chloroform (50 ml) at room temperature and the solution was stood overnight. After evaporation of the solvent, the red tarry residue was treated with ca. 20 ml of benzene-n-hexane (1:1). The resulting solid was recrystallized from benzene to give 2-anilino-4,5-dibenzoylthiazole (**4a**, 74%). **4b**, **4d**, and **4e** were prepared by the same procedure and the results are shown in Table 1.



(1)

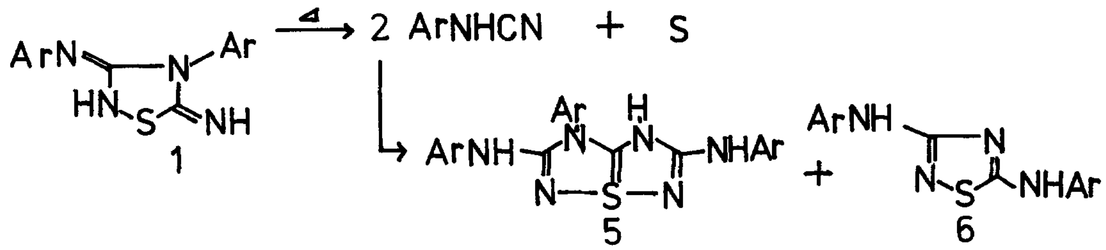
Table 1 The Yield and Melting Point of Thiazole (4)[3]

Acetylene (2)		4 Ar=Ph		4 Ar=p-MeC$_6$H$_4$	
X	Y	Yield (%)	Mp (°C)	Yield (%)	Mp (°C)
a) PhCO	PhCO	a) 74	173.5-175.5	d) 61	203.0-204.0
b) CO$_2$Me	CO$_2$Me	b) 58	115.0-116.0	e) 80	175.5-176.5
c) Ph	CO$_2$Me	c) 4	184.5-185 0	f) 24	180 5-182.0

As the presence of phenylcyanamide in the benzene-n-hexane filtrate was shown by IR, the reaction of 1a (5.0 mmol) with excess dimethyl acetylenedicarboxylate (2b, 20 mmol) was carried out in chloroform (120 ml) at room temperature to trap the resulting phenylcyanamide with 2b. After evaporation of the solvent, the residue was treated with dry column chromatography (DCC) (alumina, dichloromethane) to give 4b (58%) and methyl 2-(N-cyano)anilino-2-methoxycarbonylacrylate (1.2 mmol), which were identified by IR and NMR. Phenylcyanamide or the adduct of phenylcyanamide with 2 was not pursued for other runs

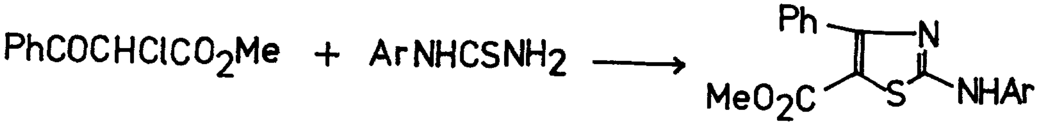
On the other hand, the reaction of 1 with 2c did not occur under mild conditions. 1b (5 05 mmol) and 2c (14.8 mmol) in 1,2-dichloroethane (50 ml) were refluxed for 48 hr when 1b was almost consumed. The products were treated with DCC (alumina, dichloromethane) to give unchanged 2c (8.9 mmol), 4f (24%), 5b (31%), and 3,5-bis(p-tolylamino)-1,2,4-thiadiazole (6b, 20%).

Formation of 5b and 6b is ascribable to thermal decomposition of 1b as supported by the fact that the reflux of 1a and 1b separately in 1,2-dichloroethane for 50 hr afforded 5a (59%), 6a (10%), and 5b (50%), 6b (10%), respectively.[2]



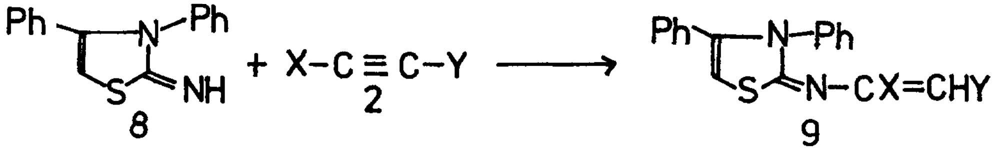
4a-4f were acetylated to give monoacetyl derivatives (7) by reflux in acetic anhydride with pyridine for 30 min, 7a, mp 136.5-137.5°C; 7b, 162.5-163.5 °C, 7c, 203.0-204.0 °C, 7d, 182.5-183.5 °C, 7e, 166.0-167.0 °C; and 7f, 183.5-184.5 °C

To make sure the structure of 4c and 4f and also the orientation of 1,3-dipolar cycloaddition of Hector's base, 4c and 4f were prepared by the following reaction[4] and monoacetyl derivatives (7c and 7f) were also prepared to show the identity of the reaction products with authentic samples.

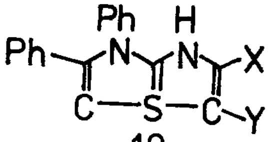


4c,f

Reactions of 2-imino-3,4-diphenylthiazoline (8) with acetylenes (2) were carried out with the hope to prepare 6a-thia-3,4-diazapentalene analogues (10), which turned out to give simple addition compounds (9)[5] in high yields 9a, mp 186.5-188.0 °C, yield 88%, 9b, 162.0-163.0 °C, 83%; and 9c, 162.0-163.5 °C, 46%.



(2)



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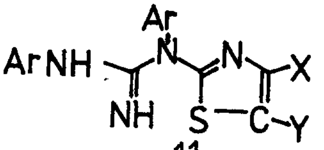

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Although the presence of **3** as an intermediate is assumed here based on the analogy of the finding in the preceding paper,[2] it is worthwhile to mention that a new C-S bond formation occurred by 1,3-dipolar cycloaddition of **1** with **2** followed by expulsion of phenylcyanamide under mild conditions, because the isomer (**11**) of **3** would be stable under the reaction condition, if it were once formed. On the other hand, a new C-S bond formation was not observed in the reaction (2)

References and Notes

1) D S. Hector, Ber , 22, 1179 (1889). F. Kurzer, J Chem. Soc., 1956, 2345.

2) K. Akiba, T. Tsuchiya, M. Ochiumi, and N. Inamoto, the preceding paper.

3) All new compounds described as **4**, **5**, **6** and **9** gave correct elemental analyses. IR, NMR and MS spectra are consistent with the proposed structures

4) E. L. Hirst, A. K. Macbeth, and D. Trail, Proc. Royal Irish Acad., 37B, 47 (1925).

5) Detailed stereochemistry of **9** has not been determined, but the presence of two vinyl proton signals (each singlet) in NMR spectra are decisive evidence for **9**.