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1,3-DIPOLAR CYCLOADDITION OF "HECTOR'S BASE" WITH ARYLCYANAMIDES

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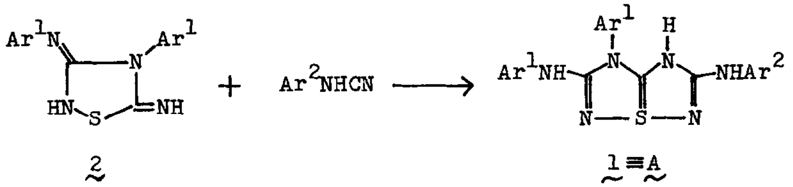
Chemistry of hypervalent heterocyclic system related to 6a-thiathiophthene has been in considerable current interest and several systems were synthesized, in which X and Y are nitrogen and/or oxygen (**4**) [1]

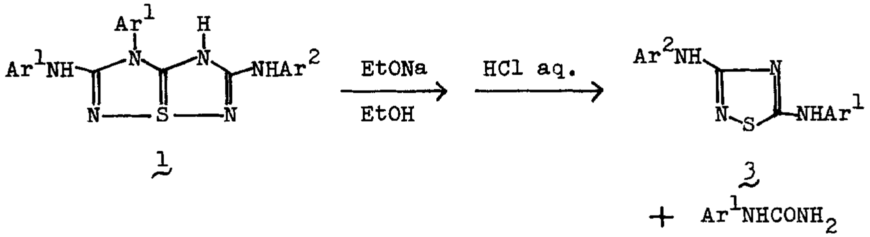
We report here the reaction of 4-aryl-3-arylimino-5-imino-1,2,4-thiadiazolidines (**2**, Hector's base)[2] with arylcyanamides in tetrahydrofuran at 70°C for 1-2 hr, which afforded 1 1 adducts (**1**) The reaction mixture was treated with column chromatography (alumina) and the products were recrystallized from ethanol[3] **1a**, $Ar^1=Ar^2=Ph$, mp 196 0-198 0°C, yield 68%, **1b**, $Ar^1=Ph$, $Ar^2=p\text{-}MeC_6H_4$, 206.0-206.5°C, 40%, **1c**, $Ar^1=p\text{-}MeC_6H_4$, $Ar^2=Ph$, 216 5-217.5°C, 58%, **1d**, $Ar^1=Ar^2=p\text{-}MeC_6H_4$, 218.0-219.0°C, 32%.

Refluxing **1a**-**d** in anhydrous ethanol for 1 hr in the presence of sodium ethoxide (2 molar) gave 3,5-bis(arylamino)-1,2,4-thiadiazoles (**3**)[4] **3a**, $Ar^1=Ar^2=$ Ph, mp 218.0-219 0°C, yield 40%, **3b**, $Ar^1=Ph$, $Ar^2=p\text{-}MeC_6H_4$, 186.5-187 0°C, 35%, **3c**, $Ar^1=p\text{-}MeC_6H_4$, $Ar^2=Ph$, 195.0-196.0°C, 53%, **3d**, $Ar^1=Ar^2=p\text{-}MeC_6H_4$, 212 0-212 5°C, 66%.

These facts can best be rationalized by 1,3-dipolar cycloaddition of **2** with arylcyanamides (equation 1) and by nucleophilic attack of ethoxide ion followed by elimination of O-ethyl isoureas which were hydrolyzed with aqueous hydrochloric acid (equation 2).



(1)



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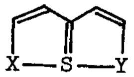

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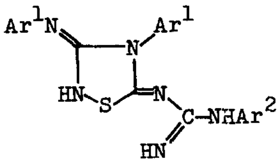

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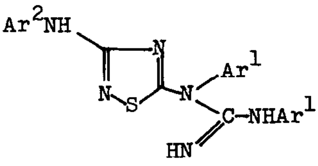

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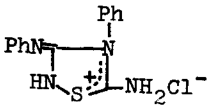
Table 1 UV Spectra of the Adduct (**1a**) and Some Reference Compounds

Compounds	λ_{max}^{EtOH}, nm ($\varepsilon \times 10^{-4}$)
1a	257 (3.50), 292 (1.0)
2a	239 (1.75)
2e	256 (2.35), 272 (1.8) 336 (1.15)
2f	262 (3.40), 307 (2.46)
3a	268 (4.24)

UV spectra of the adduct (**1a**), **2a**, 5-N-benzoyl (**2e**) and -phenylcarbamoyl (**2f**) derivatives of **2a**, and **3a** are shown in Table 1 The UV spectra of **1a**-**d** are superimposable and have distinct shoulder at around 292 nm ($\varepsilon = 1 \times 10^4$). UV of **6** is expected to be the sum of those of **3** and 1,1,3-triphenylguanidine and cannot have any distinct shoulder above 270 nm.[5]

There would be no serious contradiction if the UV spectra of the adduct (**1**) were assigned as those of **5** However, UV spectrum of the hydrochloride (**2g**) of **2a** (λmax 239 nm) in acetonitrile shifted to longer wavelength by 11 nm as expected for the structure **2g** which has a carbonium ion stabilized in a heterocycle, while that of the hydrochloride of

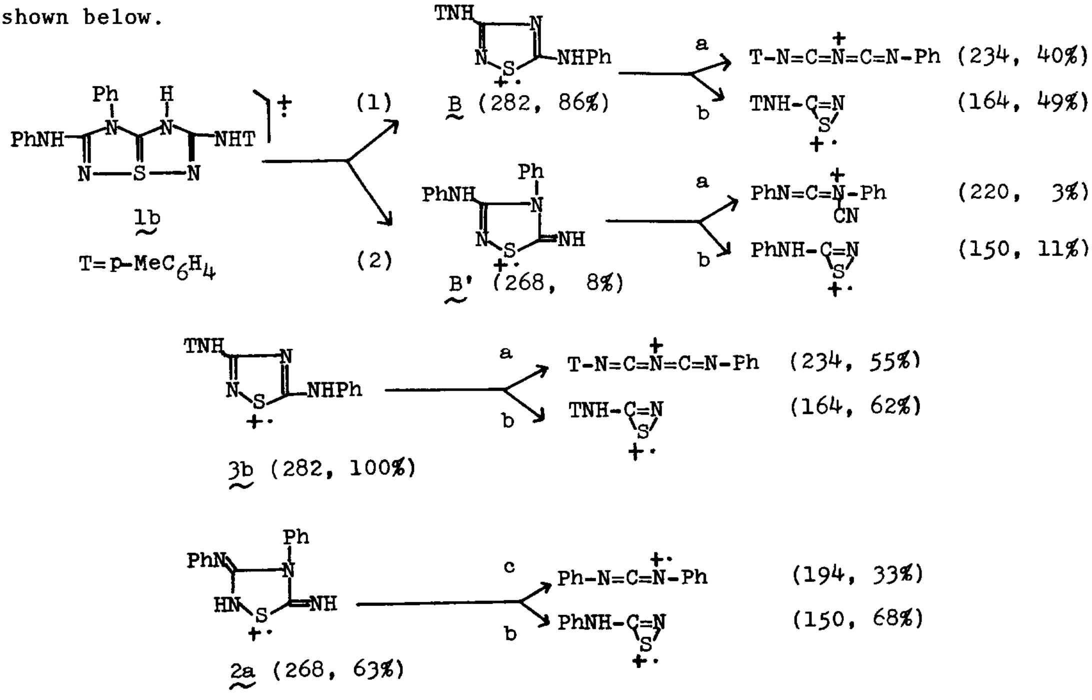


2g

the adduct (1) showed no change probably because of dissociation in dilute acetonitrile solution. This fact implies that adduct (1) does not contain a guanidino group as in 5 and 6.

IR spectra of the adducts (1) show a common strong band at 1660-1670 cm^{-1} and there is no other absorption between 1600 and 2800 cm^{-1} In view of IR spectra of 2,3 and guanidines[5], this strong band can be ascribed neither to 5 nor to 6 and can only be realized as that of C=N bond contained in a five-membered ring (A) as influenced by electron-withdrawing effect of the hypervalent sulfur atom[6] or non-conjugating arylimino bond in a five-membered ring (tautomeric forms of A[7]).

MS spectra of 1 are rather simple. Each spectrum of 1 shows weak but distinct parent peak ($M^{+\cdot}$ 0.3-0.5%) and $(M-S)^{+\cdot}$ peak (0.2-0.4%). Major fragmentation pattern of 1b is realized such as that the parent radical cation affords B and B' as intermediates, with loss of phenylcyanamide and p-tolylcyanamide, respectively. The intensity of B is always greater than that of B' for all 1 Fragmentation patterns of B and B' can be simulated by those of 3b and 2a as shown below.



5-N-Acetyl, -carbamoyl, -benzoyl (2e), -phenylcarbamoyl derivatives (2f) of 2a, show the same type of fragmentation pattern below m/e 268 as that of 2a, including the pattern c as a common path, which is not observed in 1 and 3. From these facts, it can be concluded that the structure of the parent radical cation is as shown for 1b with N-S-N bond, although this fact cannot be strong support for the presence of N-S-N bond in 1, because of possible cyclisation of parent radical cations from 5 and 6

Considering all the data described in the text, we now assign the most probable structure of the adduct (1) to be 3-aryl-2,5-bis(arylamino)[1,2,4]thiadiazolo[5,1-e][1,2,4]thiadiazole-7-S^{IV} (A) or its tautomeric form, however, at present we cannot definitely exclude the structure 5 with strong S-N interaction without the result of X-ray crystallographic analysis of the adduct (1).

References and Notes

1) D. H. Reid, J. Chem Soc. (C), 1971, 3187, D. H. Reid and J. D. Symon, Chem. Commun., 1969, 1314, D H. Reid and R. G Webster, ibid , 1972, 1283, A. S Ingram, D H. Reid, and J D. Symon, J. Chem Soc. Perkin I, 1974, 242, E. Klingsberg, J. Org Chem., 33, 2915 (1968), J.-L. Derocque, M. Perrier, and J. Vialle, Bull Soc. Chim. France, 1968, 2062

2) D. S. Hector, Ber., 22, 1179 (1889), F. Kurzer, J. Chem. Soc., 1956, 2345. For the structure determination of Hector's base, see "Advances in Heterocyclic Chemistry", Vol.5, Academic Press, New York, 1965, p 119.

3) All new compounds described in the text gave correct elemental analyses.

4) F. Kurzer and P. M. Sanderson, J Chem Soc., 1963, 3333.

5) UV spectra of guanidines $(PhMeN)_2C=NH$ (EtOH), 231 (ε=1.5×10^4) and 250 (1.2×10^4), $(PhNH)_2C=NH$ (MeOH), 242 (1 4×10^4), $Ph_2NC(=NH)NHPh$ (MeOH), 240 (1.50×10^4) and 260 (1 43×10^4), $(Ph_2N)_2C=NH$ (EtOH), 265 nm (2.3×10^4 broad) IR absorption band (νC=N) of these and some other guanidines lies between 1595 and 1620 cm^{-1}. IR absorption band (νC=O) of 2e and 2f lies at 1610 and 1640 cm^{-1}, respectively

6) L. J Bellamy, "Advances in Infrared Group Frequencies", Methuen, London, 1968, p 49

7) Tautomeric forms of A with arylimino bond(s)