Reaction of Hydrazonyl Halides with Derivatives of Thiourea and Thiosemicarbazide; A New Source of *C*-Amino- and *C*-Hydrazino-1,2,4-triazoles

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Reaction of hydrazonyl halides with (substituted) thioureas and thiosemicarbazides gives mainly 1,3,4-thiadiazolines, the stronger base being preferentially eliminated in the process. Similar reactions in presence of triethylamine give *C*-amino- and *C*-hydrazino-1,2,4-triazoles, respectively, together with the hydrazonyl sulfide.

Potassium cyanide cleavage of a hydrazonyl disulfide gives the corresponding 1,3,4-thiadiazoline and thiohydrazide.

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La réaction des halogénures d'hydrazonyle avec des thiourées et des thiosemicarbazides (substituées) conduit principalement au thiadiazolines-1,3,4; au cours de ce processus, la base la plus forte est éliminée. Des réactions semblables effectuées en présence de triéthylamine donnent respectivement des *C*-amino et des *C*-hydrazinotriazoles-1,2,4 aux côtés de sulfure d'hydrazonyle.

La rupture d'un disulfure d'hydrazonyle par le cyanure de potassium conduit à la thiohydrazide et à la thiadiazoline-1,3,4 correspondante.

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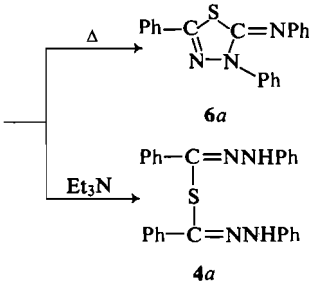
Reaction of hydrazonyl halide **1***a* with phenylthiourea in ethanol in presence of excess triethylamine (molar ratio 2:1:4) was found to give the hydrazonyl sulfide **4***a* in high (88%) yield, contrasting markedly with the formation of 5-phenylimino-2,4-diphenyl-1,3,4-thiadiazoline (**6***a*), when **1***a* and phenylthiourea (molar ratio 1:1) were refluxed together in ethanol (1); see eq. 1. The significant difference in reaction course led us to reexamine and extend the previous work by Fusco on the reaction of hydrazonyl halides (**1**) with various derivatives of thiourea and thiosemicarbazide (1, 2).

[1] $PhCCl{=}NNHPh + PhNHCSNH_2$



The two hydrazonyl halides **1***a* and *b* used in this study together with products isolated are depicted in Scheme 1 and the results of the reactions examined are summarized in Table 1.

The reactions performed in refluxing ethanol reveal two general trends: (*i*) the products isolated are all 1,3,4-thiadiazolines, (*ii*) the least basic part of the sulfur nucleophile (Base–C(S)–Base′) remains in the cyclic product (*cf.* Table 1). These results may be rationalized in terms of a sulfur attack at the α carbon atom in **1** with displacement of the halogen, exemplified in eq. 2 with **1***a* and 4-phenyl-3-thiosemicarbazide, to give a hydrazonylated adduct, which undergoes ring closure; elimination of hydrazine, followed by deprotonation then affords **6***a*. The base elimination step follows principally the sequence $NH_3 > NH_2NH_2 > PhNHNH_2 > PhNH_2$ according to the decreasing order of base strength; in reaction 2, hydrazine is preferred over aniline as the leaving base. Normally the eliminated base

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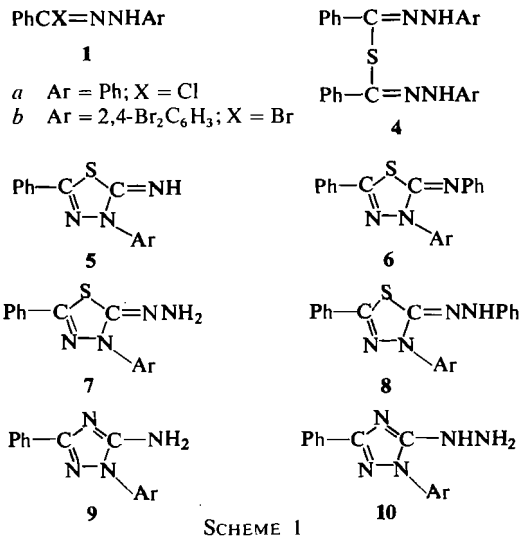
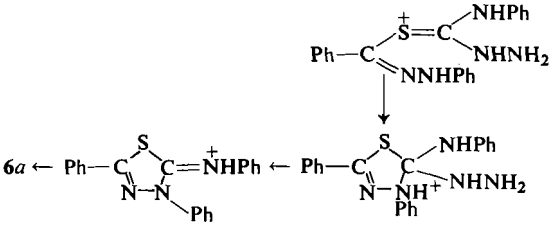


SCHEME 1

[2] $PhCCl{=}NNHPh + PhNHCSNHNH_2 \xrightarrow{-Cl^-}$

1*a*

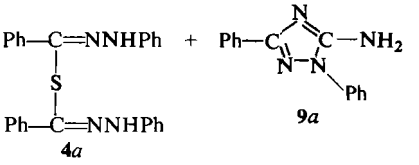


functions as the deprotonating agent but in the reaction of **1***a* with 1,4-diphenylthiosemicarbazide, the eliminated phenylhydrazine is apparently not sufficiently strong for this purpose as **6***a* was isolated as the hydrochloride from this reaction.

Similar experiments (see Table 1) were conducted in the presence of excess triethylamine (4 equiv.) and the general products were found to be the hydrazonyl sulfide (**4**) and a 1,2,4-triazole (**9** and **10**). Thus reacting **1***a* with thiourea in ethanol in presence of triethylamine (molar ratio 2:1:4) gave **4***a* (21%) and 5-amino-1,3-diphenyl-1,2,4-triazole (**9***a*) (59%); see eq. 3. These results

[3] $PhCCl{=}NNHPh + NH_2CSNH_2 \xrightarrow{Et_3N}$

1*a*



may be interpreted in terms of two competitive reactions, one leading to **4** and one to **9** (or **10**, in the case of thiosemicarbazide), via a common intermediate. Hydrogen sulfide abstraction from thiourea by the reactive nitrilimine (**2***a*), formed *in situ* by dehydrochlorination of **1***a* with triethylamine (3), produces a thiohydrazide (**3***a*) and cyanamide (eqs. 4 and 5); **3***a* then becomes the source of **4***a* (eqs. 6–9) by processes already discussed (4).

[4] $PhCCl{=}NNHPh \xrightarrow[-HCl]{Et_3N} PhC{\equiv}\overset{+}{N}\bar{N}Ph$

1*a* **2***a*

[5] $PhC{\equiv}\overset{+}{N}\bar{N}Ph + NH_2CSNH_2 \longrightarrow$

2*a*

$PhCSNHNHPh + NH_2C{\equiv}N$

3*a*

TABLE 1. Reactions examined

Reactant	Hydrazonyl halide	Products (yield %)	
		By refluxing in EtOH	In presence of Et_3N
NH_2CSNH_2	**1***a*		**4***a* (21) + **9***a* (59)
NH_2CSNH_2	**1***b*	**5***b* (70)*	**4***b* (10) + **9***b* (64)
$PhNHCSNH_2$	**1***a*	**6***a* (24)	**4***a* (88) + $PhNHC{\equiv}N$ (18)*
$PhNHCSNH_2$	**1***b*	**6***b* (46)	**4***b* (66) + **5***b* (21)*
$NH_2CSNHNH_2$	**1***a*	†, 7‡	**4***a* (44) + **10***a* (36)§
$NH_2CSNHNH_2$	**1***b*		**4***b* (14) + **10***b* (31)§
$NH_2CSNHNHPh$	**1***a*	**8***a* (31)	
$PhNHCSNHNH_2$	**1***a*	**6***a* (22)	
$PhNHCSNHNHPh$	**1***a*	**6***a*§	
KSCN	**1***a*	**5***a* (48)	**5***a* (66)
KSCN	**1***b*	**5***b* (98)	**5***b* (66)

*Isolated as benzoyl derivative.
†Six spots on t.l.c.
‡Reference 1.
§Isolated as hydrochloride(bromide).

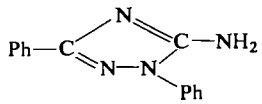
[6] $PhC\equiv\overset{+}{N}NPh + PhCSNHNHPh \longrightarrow$ **4***a*

[7] $PhCSNHNHPh + Et_3N \longrightarrow [PhCSNNHPh]^- + Et_3NH^+$

[8] $PhCCl{=}NNHPh + [PhCSNNHPh]^- \longrightarrow$ **4***a*

[9] $PhC\equiv\overset{+}{N}\overset{-}{N}Ph + [PhCSNNHPh]^- \rightarrow$ Ph—C(S—C=NNPh)=NNHPh

[10] $PhC\equiv\overset{+}{N}\overset{-}{N}Ph + NH_2C\equiv N \longrightarrow$



9*a*

A cycloaddition reaction between **2***a* and the cyanamide formed may give **9***a* (eq. 10) in a similar way to the nitrilimine–nitrile reaction to give 1,2,4-triazoles (5). The initial formation of thiohydrazides and cyanamides is supported in some experiments by examination of reaction mother liquors (t.l.c. and mass spectrum); in the reaction between **1***a*, phenylthiourea, and triethylamine, phenylcyanamide was actually recovered after benzoylation as the benzoyl derivative Ph(PhCO)NC≡N.

The competition between these reactions is very favorable to triazole formation with thiourea, but less so with thiosemicarbazide, and so unfavorable with phenylthiourea that no triazole was obtained in the cases examined. In the last cases, hydrazonyl sulfides are the major products and a new process becomes evident which leads (by loss of aniline) to a 1,3,4-thiadiazoline (**5***b*). The former reactions constitute reasonable sources of the triazole derivatives.

Finally the reactions of **1** with KSCN and the hydrazonyl disulfide **11** with KCN were examined. The reaction with KSCN afforded **5**, independently of reaction conditions and with no detection of a hydrazonyl thiocyanate (**1**; X = SCN) (i.r.).[3] Indirect evidence for an intermediate hydrazonyl thiocyanate was found when **4***b* was isolated as a by-product from treatment of **11** with KCN at room temperature in chloroform, the major products being **5***b* and **3***b*. The isolation of **4***b* may be rationalized in terms of heterolytic cleavage of the hydrazonyl S—S bond by action of the cyanide ion, in a similar way to that known for ordinary disulfides (6), to give the thiohydrazide anion and **1** (X = SCN); see eq. 11. Nucleophilic displacement of thiocyanate ion from **1** (X = SCN), before cyclization to **5***b*, by the thiohydrazide anion would then give the sulfide **4***b*. Compound **11** is very easily cleaved by KCN in refluxing acetonitrile to give approximately equal amounts of **3***b* and **5***b*.

[11] $Ph{-}C(S{-}S{-}C{=}NNH\text{-}2,4\text{-}Br_2C_6H_3){=}NNH\text{-}2,4\text{-}Br_2C_6H_3$ (**11**) $+ CN^- \longrightarrow PhC(S^-){=}NNH\text{-}2,4\text{-}Br_2C_6H_3 + PhC(SCN){=}NNH\text{-}2,4\text{-}Br_3C_6H_3 \longrightarrow$ **5***b*

This work provides a convenient alternative method for the preparation of *C*-amino- and *C*-hydrazino-1,2,4-triazoles (7).

Experimental

Melting points were determined using a Reichert microscope. Ethanol (EtOH) used was absolute grade. All experiments performed under basic conditions were stirred at least 2 h before the addition of triethylamine (Et_3N).

Reactions with Thiourea

Et_3N (5 ml) was added to a stirred solution of **1***a* (8, 9) (2.30 g, 10.0 mmol) and thiourea (0.38 g, 5.0 mmol) in EtOH (250 ml). After 7 h the solution was concentrated *in vacuo* to *ca.* 50 ml, filtered, and the solid washed carefully with water to give **4***a* (0.41 g, 21%), m.p. 161–162 °C (lit. (4) 158–160 °C) (0.24 g after crystallization from benzene; identified by i.r. spectrum (4)). The ethanolic filtrate was evaporated and the residue was dissolved in benzene (20 ml). Addition of aqueous HCl (20 ml; 4 *M*) afforded a precipitate which was collected and washed with ether to give a white solid (1.32 g). This was stirred in concentrated ammonia (15 ml) for 30 min, filtered, and dried. Crystallization from benzene–hexane (1:1) gave **9***a* (0.70 g, 59%), m.p. 149–151 °C (after recrystallization, m.p. 149–151 °C); mass spectrum *m/e* 236 (M^+).

Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 70.93; H, 5.05; N, 24.15.

[3]Recently the synthesis of 5-imino-2-benzoyl-4-aryl-1,3,4-thiadiazolines by reacting aroylhydrazonyl halides with KSCN has been reported (13).

The benzene – aqueous HCl filtrate was separated and the benzene layer washed with water, dried, and evaporated; t.l.c. showed one main spot corresponding to **3***a* (4).

Compound **1***b* (10) (4.33 g, 10.0 mmol) and thiourea (1.52 g, 20.0 mmol) were refluxed together in EtOH (25 ml) for 1 h. The solution was filtered and evaporated; dissolution in $CHCl_3$, washing (aqueous NaOH, water), drying and evaporation gave an oil. A mass spectrum showed *m/e* 413, 411, 409 consistent with the formation of **5***b*. The oil was treated with benzoyl chloride (2 ml) in pyridine (20 ml) for 30 min and the mixture was then poured into EtOH (50 ml), stirred, and filtered to give 5-(*N*-benzoylimino)-2-phenyl-4-(2,4-dibromophenyl)-1,3-4-thiadiazoline (3.58 g, 70%), m.p. 201–202 °C (lit. (2) 198 °C).

Compound **1***b* (10.0 mmol), thiourea (0.38 g, 5.0 mmol), and Et_3N (5 ml) were stirred together in EtOH (300 ml) for 3 days. Filtration afforded **4***b* (0.27 g, 7%), m.p. 193–196 °C. Addition of water precipitated a further quantity (0.14 g) of **4***b* contaminated with **9***b* (mass spectrum). The ethanol–water filtrate was extracted with $CHCl_3$ and the chloroform phase was worked-up. Crystallization from benzene afforded **9***b* (1.26 g, 64%), m.p. 221–222 °C; mass spectrum *m/e* 396, 394, 392 (M^+).

Anal. Calcd. for $C_{14}H_{10}Br_2N_4$: C, 42.67; H, 2.56; N, 14.21. Found: C, 42.82; H, 2.73; N, 13.76.

Reactions with Phenylthiourea

Compound **1***a* (1.15 g, 5.0 mmol) and phenylthiourea (0.76 g, 5.0 mmol) were refluxed together in EtOH (25 ml) for 1 h. The solution was chilled overnight (refrigerator) and filtered. Two crystallizations from ether gave **6***a* (0.40 g, 24%), m.p. 113–116 °C (lit. (1) 122 °C); mass spectrum *m/e* 329 (M^+).

Compound **1***a* (4.60 g, 20.0 mmol), phenylthiourea (1.52 g, 10.0 mmol), and Et_3N (10 ml) were stirred together in EtOH (200 ml) for 6 h. Filtration and careful washing with water gave **4***a* (3.70 g, 88%), m.p. 162–164 °C (after crystallization from benzene 3.13 g (75%), m.p. 162–164 °C (corr.); identified by i.r. spectrum). The ethanolic filtrate was evaporated, the residue was dissolved in benzene, and the solution washed with water, dried (Na_2SO_4), and evaporated. The residual oil was treated with benzoyl chloride (1 ml) in pyridine (10 ml) for 30 min and the mixture was poured into water whereupon an oil deposited. The aqueous phase discarded. Addition of EtOH afforded a white solid which crystallized from EtOH to give *N*-benzoyl-*N*-phenylcyanamide (0.40 g, 18%), m.p. 122–125 °C; ν_{max} 2240 (C≡N) and 1730 cm^{-1} (C=O); mass spectrum *m/e* 222 (M^+).

Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 75.65; H, 4.54; N, 12.61. Found: C, 75.68; H, 4.06; N, 12.44.

Compound **1***b* (2.16 g, 5.0 mmol) and phenylthiourea (0.76 g, 5.0 mmol) were refluxed together in EtOH (25 ml) for 1 h. An oil separated on cooling; the ethanol phase was discarded and the oil dissolved in ether, filtered, and left at room temperature for evaporation. Crystallization from ethanol–chloroform (2:1) afforded **6***b* (1.12 g, 46%), m.p. 111–117 °C (lit. (1) 116 °C); mass spectrum *m/e* 487, 485, 483 (M^+).

Compound **1***b* (4.32 g, 10.0 mmol), phenylthiourea (0.76 g, 5.0 mmol) and Et_3N (5 ml) were stirred together in EtOH (300 ml) for 20 h. Filtration give **4***b* (2.41 g, 66%), m.p. 193–195° C (after crystallization from benzene, 2.15 g (58%); m.p. 202–204° C; identified by i.r. spectrum (4)). The ethanolic filtrate was evaporated, the residue was dissolved in benzene, and the solution washed with aqueous acetic acid and water, dried, and evaporated. The residual oil was treated with benzoyl chloride (1 ml) in pyridine (10 ml) for 30 min. Addition of EtOH (25 ml), stirring (30 min), and filtration gave 5-(*N*-benzoylimino)-2-phenyl-4-(2,4-dibromophenyl)-1,3,4-thiadiazoline (0.54 g, 21%), m.p. 198–201 °C; mass spectrum *m/e* 517, 515, 513 (M^+).

Reactions with Thiosemicarbazide

Compound **1***a* (2.30 g, 10.0 mmol), thiosemicarbazide (0.46 g, 5.0 mmol), and Et_3N (5 ml) were stirred together in EtOH (100 ml) for 4 h. Filtration followed by careful washing with water gave **4***a* (0.93 g, 44%), m.p. 166–167 °C (after crystallization from benzene, 0.67 g (32%), m.p. 162–164 °C; identified by i.r. spectrum). The ethanolic filtrate was evaporated. The residue, which appeared to consist of **10***a* contaminated with **7***a* and possibly **3***a* and **5***a* (mass spectrum), was suspended in $CHCl_3$ (20 ml) and filtered. Crystallization from acetonitrile gave the hydrochloride of **10***a* (0.51 g, 36%), m.p. 251–253 °C (dec.) (second crystallization).

Anal. Calcd. for $C_{14}H_{13}N_5 \cdot HCl$: C, 58.43; H, 4.90; N, 24.34. Found: C, 58.45; H, 4.91; N, 24.28.

Compound **1***b* (2.16 g, 5.0 mmol) and thiosemicarbazide (0.46 g, 5.0 mmol) were refluxed together in EtOH (50 ml) for 1 h. Thin-layer chromatography of the reaction mixture showed six spots, one corresponding to thiohydrazide **3***b* (4). The solution was left for one week at room temperature and filtered. Crystallization of the crude product (0.65 g) from benzene–ethanol (4:1) gave a solid (0.10 g), m.p. 286–289 °C (lit. (1) 285–286 °C). Attempts to isolate **7***b* were not pursued, but it was confirmed that **1***b* and acetone thiosemicarbazone gave the acetone derivative of **7***b* (1).

Compound **1***b* (10.0 mmol), thiosemicarbazide (0.46 g, 5.0 mmol), and Et_3N (5 ml) were stirred together in EtOH (300 ml) for 4 h. Filtration gave **4***b* (0.51 g, 14%), m.p. 195–197 °C (after crystallization, m.p. 202–204 °C; identified by i.r. spectrum). From the ethanolic filtrate was isolated the hydrobromide of **10***b* (0.77 g, 31%) (after crystallization from acetonitrile), m.p. 252–254 °C (dec.).

Anal. Calcd. for $C_{14}H_{11}Br_2N_5 \cdot HBr$: C, 34.31; H, 2.47; N, 14.29. Found: C, 34.20; H, 2.54; N, 14.46.

Reactions with Substituted Thiosemicarbazides

Compound **1***a* (1.15 g, 5.0 mmol) and 1-phenyl-3-thiosemicarbazide (0.84 g, 5.0 mmol) were refluxed together in EtOH (25 ml) for 2 h. Thin-layer chromatography of the dark green reaction mixture showed one main spot together with four minor ones, one of these corresponding to the thiohydrazide **3***a* (4). The solution was cooled for 5 h and filtered. Crystallization of the crude product (1.12 g) from ethanol–water (5:1) gave **8***a* (0.53 g, 31%) as brown prisms, m.p. 121–125 °C; ν_{max} 3280 cm^{-1} (N—H); mass spectrum *m/e* 344 (M^+).

Anal. Calcd. for $C_{20}H_{16}N_4S$: C, 69.74; H, 4.68; N, 16.27; S, 9.31. Found: C, 69.60; H, 4.88; N, 16.29; S, 9.32.

Compound **1***a* (1.15 g, 5.0 mmol) and 4-phenyl-3-thiosemicarbazide (0.84 g, 5.0 mmol) were refluxed together in EtOH (25 ml) for 45 min. The solution was chilled overnight (refrigerator) and filtered. The crude product

was **6***a* apparently contaminated with **7***a* (mass spectrum). Crystallization from EtOH gave **6***a* (0.37 g, 22%), m.p. 111–113 °C; identified by i.r. and mass spectrum.

Compound **1***a* (2.30 g, 10.0 mmol) and 1,4-diphenylthiosemicarbazide (2.44 g, 10.0 mmol) were refluxed together in EtOH (25 ml) for 90 min. The solution was evaporated to dryness and the residue suspended in benzene. Water was added and the solid was filtered off and washed with water. Crystallization of the crude product (2.08 g) from acetonitrile gave the hydrochloride of **6***a*, m.p. *ca.* 260 °C (dec.); ν_{max} 2730 (broad) (N^+—H) and 1575 cm^{-1} (strong) (C=N) (lit. (11) 1575 cm^{-1}).

Anal. Calcd. for $C_{20}H_{15}N_3S \cdot HCl$: C, 65.65; H, 4.41; N, 11.49; Cl, 9.69. Found: C, 65.50; H, 4.00; N, 11.70; Cl, 9.58.

Reactions with KSCN

Compound **1***a* (1.15 g, 5.0 mmol) and KSCN (0.50 g, 5.0 mmol) were refluxed together in EtOH (25 ml) for 30 min and filtered. Evaporation and treatment of the residue with benzene followed by filtration and evaporation afforded an oil with properties consistent with **5***a* (1.25 g, 99%); mass spectrum *m/e* 253 (M^+). Benzoyl chloride (1 ml) in pyridine (5 ml) for 1 h in the normal way afforded 5-(*N*-benzoylimino)-2,4-diphenyl-1,3,4-thiadiazoline (0.85 g, 48%), m.p. 164–165 °C (lit (2) 166 °C).

Compound **1***a* (1.15 g, 5.0 mmol) KSCN (0.50 g, 5.0 mmol), and Et_3N (2.5 ml) in EtOH (150 ml) gave **5***a* (1.23 g, 98%); mass spectrum *m/e* 253 (M^+). Treatment with benzoyl chloride gave 5-(*N*-benzoylimino)-2,4-diphenyl-1,3,4-thiadiazoline (1.17 g, 66%), m.p. 163–164 °C; mass spectrum *m/e* 357 (M^+).

Compound **1***b* (2.16 g, 5.0 mmol) and KSCN (1.00 g, 10.0 mmol) gave a semicrystalline mass (2.15 g). The mass spectrum was consistent with formation of **5***b* (*m/e* 413, 411, 409 (M^+)); i.r. spectrum showed no SC≡N. Benzoylation afforded 5-(*N*-benzoylimino)-2-phenyl-4-(2,4-dibromophenyl)-1,3,4-thiadiazoline (98%), m.p. 202–203 °C.

Compound **1***b* (2.16 g, 5.0 mmol), KSCN (0.50 g, 5.0 mmol), and Et_3N (2.5 ml) gave after benzoylation 5-(*N*-benzoylimino)-2-phenyl-4-(2,4-dibromophenyl)-1,3,4-thiadiazoline (1.70 g, 66%), m.p. 200–201 °C (after crystallization from ethyl acetate); mass spectrum *m/e* 517, 515, 513 (M^+); i.r. spectrum showed no SC≡N.

Cleavage of Hydrazonyl Disulfide ***11***

(*i*) Compound **11** (12) (3.08 g, 4.0 mmol) and KCN (0.52 g, 8.0 mmol) were stirred together in $CHCl_3$ (50 ml) for 2 days. The solution was filtered and the solvent removed *in vacuo*; the residue was suspended in EtOH (25 ml) and filtered. Crystallization from benzene gave **4***b* (0.15 g, 5%), m.p. 198–201 °C; identified by i.r. spectrum. The ethanolic filtrate was evaporated and the residue was dissolved in benzene and extracted twice with aqueous NaOH. The benzene layer was washed with water, dried, evaporated, and benzoylated (in pyridine) to give 5-(*N*-benzoylimino)-2-phenyl-4-(2,4-dibromophenyl)-1,3,4-thiadiazoline (1.62 g, 79%), m.p. 201–203 °C; identified by i.r. spectrum. The aqueous NaOH phase was neutralized and extracted with benzene; the benzene phase was washed with water, dried, and evaporated. Crystallization of the crude product (1.60 g) from benzene–hexane (1:1) gave **3***b* as small pale yellow needles (0.70 g, 46%), m.p. 107–109° C (lower melting polymorph); identified by i.r. spectrum ($CHCl_3$) (4); mass spectrum *m/e* 388, 386, 384 (M^+).

Anal. Calcd. for $C_{13}H_{10}Br_2N_2S$: C, 40.44; H, 2.61; N, 7.26. Found: C, 40.55; H, 2.76; N, 7.34.

(*ii*) Compound **11** (1.54 g, 2.0 mmol) and KCN (0.52 g, 8.0 mmol) were refluxed together in CH_3CN for 30 min. The i.r. spectrum of the filtered and evaporated reaction mixture showed no presence of SC≡N. Work-up (as above) gave 5-(*N*-benzoylimino)-2-phenyl-4-(2,4-dibromophenyl)-1,3,4-thiadiazoline (0.75 g, 73%), m.p. 202–204° C and **3***b* (0.71 g, 92%); crystallization from benzene–hexane (1:1) gave **3***b* (45%), m.p. 106–108 °C.

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