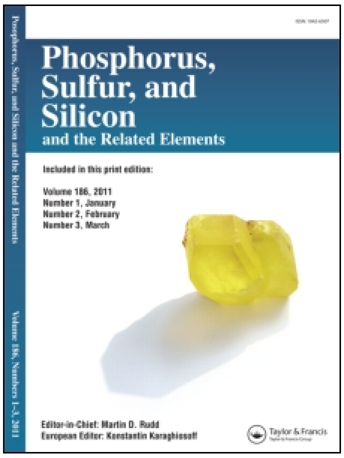

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THE REACTION OF ω-THIOCYANATOACETOPHENONES WITH HYDRAZINES

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ω-Thiocyanatoacetophenones 1a, b react with hydrazine hydrate to yield bis[4-aryl-5-hydro-$\Delta^{3,4}$-thiazol-2-ylidine] azines 2a, b. Compounds 1a, b react with phenyl hydrazine to yield 1-phenyl-6-phenylazo-3,6-diaryl-1,4,5,6-tetrahydropyridazines 5a, b respectively. The phenylhydrazone of 1a was obtained via indirect method.

Key words: phenacylthiocyanate; bis[4-aryl-5-hydro-$\Delta^{3,4}$-thiazol-2-ylidine]azine; 1-phenyl-6-phenylazo-3,6-diaryl-1,4,5,6-tetrahydropyridazine; phenacylthiocyanate phenylhydrazone.

Phenacyl thiocyanate 1a has been extensively utilized in heterocyclic synthesis.[1] Recently we have reported several new syntheses starting from 1a as a cheap available starting compound.[2–5] No reaction of phenacyl thiocyanate 1a with hydrazines has been previously reported.[2–8] In continuation of previous work in this area,[2–5] it was interesting to investigate the reaction of compounds 1a, b with hydrazine hydrate and phenylhydrazine.

It has been found that 1a reacts with hydrazine hydrate in refluxing ethanol to yield a 2:1 product as a pale yellow crystalline product of molecular formula $C_{18}H_{14}N_4S_2$. Three tautomeric structures seemed possible for this product (see structures 2–4, Scheme 1). The IR spectrum of the product did not reveal any NH absorption bands. The ^{1}H-NMR spectrum revealed two doublets at δ 3.32 and 3.64 ppm (J = 13 Hz, gem. coupling) and a multiplet at δ 7.32–7.9 ppm (the ratio between the two integrations is 2:5). Mixing with D_2O shows no exchangeable protons. The tautomeric structures 3a and 4a were thus readily ruled out and structure 2a was established for this product. ^{13}C-NMR spectrum has afforded conclusive evidence of structure 2a. It revealed the ring $\underline{C}H_2$ signal at δ 26.45 ppm split into a triplet in the off-resonance spectrum, and the other expected signals (see exp.).

Similarly, compound 1b reacts with hydrazine hydrate under similar conditions to yield a white/pale yellow solid for which structure 2b was assigned on the basis of spectral and analytical data (Table I).

Compounds 2a, b are assumed to be formed via the reaction of two molecules of the thiocyanate 1a or 1b with one molecule of hydrazine with elimination of two molecules of water. This behaviour is analogous to the reaction of α-thiocyanatoketones with amines and ammonia.[1]

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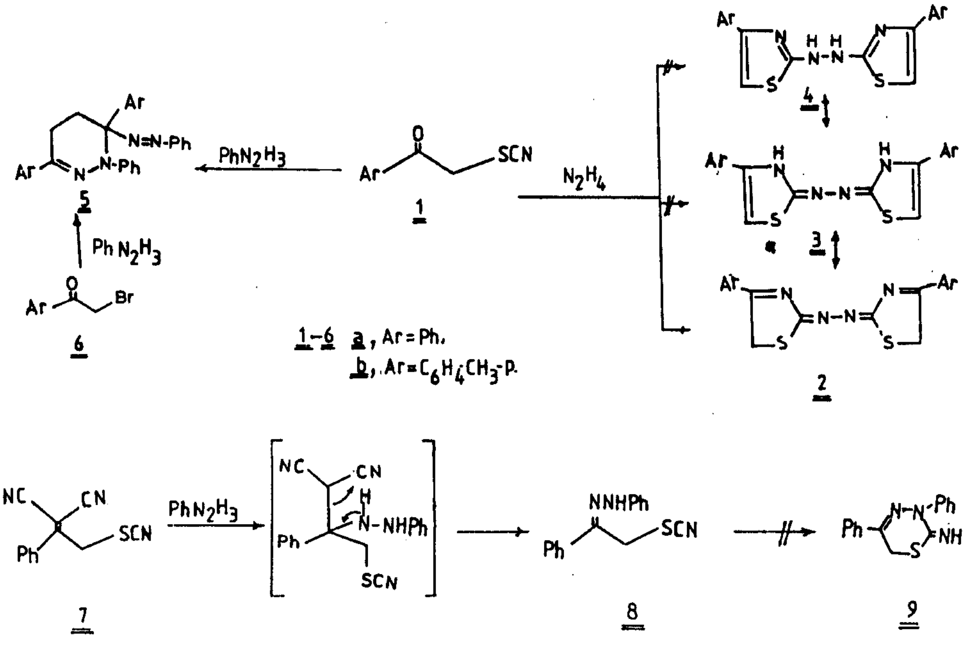

SCHEME 1

Compound 1a reacts also with phenylhydrazine in acetic acid at room temperature to yield a yellow product. Analytical data show that this product has a molecular formula $C_{28}H_{24}N_4$ and reveal the absence of sulphur. The IR spectrum of this product shows no characteristic bands in the functional group region. The ^{1}H-NMR

TABLE I

Analytical and spectral data of compounds 2a, b; 5a, b and 8

Compd. No.	Yield %	mp.°C solvent	M.F. (M. Wt.)	Analysis % (Calcd/Found) C	H	N	^{1}H-N.M.R. δ ppm
2a	78	171–2 EtOH	$C_{18}H_{14}N_4S_2$ 350.47	61.69 61.7	4.03 3.9	15.99 15.6	3.32–3.64 (*dd*, 4H, 2CH$_2$; gem. coupl., J = 13 Hz); 7.32–7.9 (*m*, 10H, 2Ph)
2b	80	198–200 EtOH	$C_{20}H_{18}N_4S_2$ 378.52	63.46 63.2	4.79 4.4	14.80 14.3	2.39 (*s*, 6H, 2CH$_3$); 3.29–3.76 (*dd*, 4H, 2CH$_2$); 7.17–7.89 (*m*, 8H, arom.).
5a	76	137–8 EtOH	$C_{28}H_{24}N_4$ 416.52	80.74 80.6	5.81 5.8	13.45 13.2	2.18–2.76 (*m*, 4H, 2CH$_2$); 6.62–7.86 (*m*, 20H, 4Ph).
5b	82	158–9 EtOH	$C_{30}H_{28}N_4$ 444.58	81.05 80.8	6.35 5.9	12.60 12.4	2.1–2.83 (*m*, 10H, 2CH$_3$ + 2CH$_2$); 6.58–8.00 (*m*, 18H, arom.).
8	60	116–8 EtOH	$C_{15}H_{13}N_3S$ 267.35	67.39 67.6	4.90 5.3	15.72 15.8	4.1 (*s*, 2H, CH$_2$); 4.3 (*s*, 1H, NH); 7.2–7.9 (*m*, 10H, arom.).

Compounds 2a, b and 5a, b did not show absorption bands in the functional group region in the IR.

spectrum shows a multiplet at δ 2.18–2.76 ppm and another multiplet at δ 6.62–7.86 ppm. The ratio of integrations is 1:5 respectively. Structure **5a** is suggested for this product based on spectral and analytical data.

^{13}C-NMR spectrum of this compound reveals two signals at δ 18.83 and 33.52 ppm which are split into two triplets in the off-resonance spectrum. These can be easily assigned to the ring $\underline{C}H_2$ groups; as well as the other expected signals (see exp.). Thus structure **5a** was established for this reaction product.

The Mass Spectrum of compound **5a** shows a pattern that can be expected for such compounds containing azo group which readily lose the PhN:N part (M = 105) under the conditions of measurement. It shows an M + 1 peak at 312.

The structure of **5a** was unambiguously established by the comparison with an authentic sample prepared from phenacyl bromide **6a** with phenylhydrazine as previously described.[9] The two products were found to be identical in all respects (mp°C, t.l.c., and ^{1}H-NMR).

ω-Thiocyanato-*p*-methylacetophenone **1b** reacts with phenylhydrazine under the same reaction conditions to yield a yellow crystalline product of mp. 159°C. The structure **5b** was established by spectra and elemental analysis. This product **5b** was found to be identical with an authentic sample prepared from *p*-methylphenacyl bromide **6b** and phenylhydrazine.[9]

Both phenacylthiocyanates **1a**, **b** and phenacyl bromides **6a**, **b** react with phenylhydrazine following the same mechanistic pathway suggested by Curtin *et al.*[9]

We have succeeded in preparing the phenyl hydrazone **8** of phenacylthiocyanate **1a** via indirect method. On refluxing the Knoevenagel condensation product **7** previously described[2,4,5] with phenylhydrazine in ethanol, a bright yellow solid of mp. 116°C was separated. The IR spectrum of this product reveals an SCN absorption band at ν 2150 cm^{-1} and an NH band at ν 3400–3200 cm^{-1}. The ^{1}H-NMR spectrum of this product shows a singlet of (2H) at δ 4.1 ppm, another singlet (1H) at δ 4.3 ppm in addition to an aromatic multiplet (10H) at δ 7.2–7.9 ppm. Based on these data and analytical data structure **8** was assigned to this product. Under our reaction conditions compound **8** was not cyclized to the thiadiazine derivative **9** as deduced from the presence of the SCN absorption band in the IR spectrum. This may be attributed to the instability of thiadiazines as previously reported.[3]

The formation of **8** from **7** and phenylhydrazine is assumed to take place via initial addition of $PhNHNH_2$ to the activated C=C followed by elimination of malononitrile (Scheme 1). A similar mechanism has been previously reported.[10]

EXPERIMENTAL

All melting points are uncorrected. I.R. spectra were recorded as KBr pellets on a Perkin Elmer 580 spectrophotometer. ^{1}H-N.M.R. and ^{13}C-N.M.R. spectra were recorded on a Bruker WH 90 and WP 200 spectrometers in $CDCl_3$ using TMS as internal reference. Assignments were made by correlation of the off-resonance decoupled ^{13}C-N.M.R. spectra and determination of ^{1}H chemical shifts. Mass spectra were taken on a Finnigen MAT 312 with ionization potential 70 e.v. at 130°C. Spectral measurements and elemental analyses were made in the Institut of Organic Chemistry, University of Hannover (Germany) and the microanalytical center at Cairo University.

Bis[4-aryl-5-hydro-$\Delta^{3,4}$-thiazol-2-ylidine]azines (**2a**, **b**). Hydrazine hydrate (0.5 ml, 0.01 mol) was added to a solution of each of the thiocyanates **1a** or **1b** (0.02 mol) in ~30 ml of ethanol followed by 5 drops of triethylamine as catalyst. The reaction mixture was then refluxed for 5h in each case (t.l.c.). On

leaving overnight, pale yellow solids were precipitated which were filtered off and recrystallized from ethanol to afford 2.7 g of **2a** and 3 g of **2b** respectively.
(**2a**): ^{13}C-n; m; r; 26.45 (*t*); 127.16 (*d*); 128.78 (*d*); 130.13 (*d*); 135.16 (*s*) 151.64 (*s*).
MS (m/e): 268, 267, 266, 164, 163, 135, 117, 103, 91, 77.

1-Phenyl-6-phenylazo-3,6-diaryl-1,4,5,6-tetrahydropyridazine derivatives (**5a**, **b**): Compounds **1a** or **1b** (0.01 mole) was dissolved in ca. 30 ml of ethanol. The resulting solution was filtered from any undissolved material and then cooled in an ice-water bath. To this was added portionwise with stirring a solution of phenylhydrazine (0.01 mole; 1.08 g) in 20 ml of glacial acetic acid. After complete addition the reaction mixture was allowed to stand at room temperature for about 30 min. On dilution with ice cold water, a yellow precipitate separated in each case, which was filtered off and recrystallized from ethanol to afford 1.6 g of **5a** and 1.8 g of **5b** respectively.

Authentic samples were prepared from the bromo derivative **6a** and **6b** with phenylhydrazine as previously described.[9]
(**5a**): ^{13}C-n.m.r. 18.83 (*t*), 33.52 (*t*); 85.74 (*s*); 119.75 (*d*): 120.54 (*d*); 122.88 (*d*); 124.70 (*d*); 126.76 (*d*); 127.47 (*d*); 127.55 (*d*), 127.93 (*d*); 128.21 (*d*); 128.57 (*d*); 128.95 (*d*); 131.03 (*d*), 139.40 (*s*); 139.91 (*s*); 142.67 (*s*); 145.45 (*s*); 151.59 (*s*).
MS (m/e): 312, 311, 310, 309, 233, 219, 206, 180, 105, 77.

Preparation of the phenylhydrazone derivative (**8**): To a solution of 2.25 g (0.01 mole) of **7** in 30 ml of ethanol was added 1.08 g (0.01 mole) of phenylhydrazine followed by few drops of triethylamine as catalyst. The reaction mixture was refluxed for 4 h, during which the colour turned dark red, then left to cool overnight. On acidification with dil. ice-cold HCl a yellow solid precipitated which was filtered off, washed with ice-cold water, dried and recrystallized from ethanol to afford 1.6 g of **8**.
I.r. ν cm^{-1}: 3400–3200 (br. NH); 2150 (SCN).

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