

C, 79.73; H, 5.10. Found: C, 79.26; H, 4.99.
¹H-NMR of **4** (CDCl₃) δ 6.6-8.5 (m, 16, ArH), 6.2 (s, 4, -C=CH-CO-), 3.4 (s, 8, ArCH₂Ar). ¹³C-NMR of **4** (CDCl₃) δ 188.2 and 186.1 (-CO-), 164.7 (-COO-), 147.5, 134.5, 132.5, 130.5, 129.1 and 125.8 (Ar), 33.2 (ArCH₂Ar). M.P. of **4**: 241-251°C (dec.). IR of **4** (KBr) 1732 (-COO-), 1658 cm⁻¹ (-CO-). UV of **4** (CHCl₃) 320 (log ε=3.39), 440 nm (log ε=1.87). Anal. Calc. for C₁₂H₂₈O₈·3/4 CHCl₃: C, 68.44; H, 3.86. Found: C, 69.71; H, 3.65.
¹H-NMR of **6** (CDCl₃) δ 6.4-8.1 (m, 24, ArH), 6.2 (s, 2, -C=CH-CO-), 3.6 and 3.4 (two s, 8, ArCH₂Ar). ¹³C-NMR of **6** (CDCl₃) δ 187.6 and 185.8 (-CO-), 164.3 and 164.1 (-COO-), 148.3, 147.7, 147.3, 134.1, 133.9, 133.4, 133.3, 132.9, 131.7, 131.0, 130.8, 130.2, 129.7, 128.7, 128.6, 128.1, 128.0, 125.6 and 124.9 (Ar), 37.1 and 333.6 (ArCH₂Ar). m.p. of **6**: 309-316°C (dec.). IR of **6** (KBr) 1736 (-COO-), 1665 cm⁻¹ (-CO-). UV of **6** (CHCl₃) 320 (log ε=1.65). Anal. Calc. for C₁₈H₃₄O₈·1/4 CHCl₃: C, 75.77; H, 4.42. Found: H, 4.49.

A New Procedure To N-Arylcyanothioformamides From 5-Arylimino-4-Chloro-5H-1,2,3-Dithiazoles

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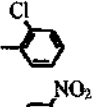

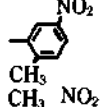
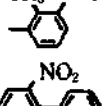

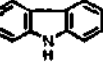
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5-Arylimino-4-chloro-5H-1,2,3-dithiazoles **1** have been known as an interesting class of compounds with their biological activities as fungicides, ovidicides, insecticides, herbicides¹ and pharmaceuticals², and also their potential utility as synthetic intermediates. One reaction reported involves the hydrolysis of **1** under basic condition: N-arylcyanothioformamides **2** were prepared by hydrolysis in a mixture of aq. NH₃ and EtOH (14-86%).² Hydrolysis of **1** with aq. NaOH was also reported to give **2** but the yields were not described.³ Although synthesis of **2** is mainly achieved by the reaction of arylisothiocyanates with cyanides⁴ along with nucleophilic displacement of C-benzenesulfonylthioformamide by cyanide.⁵ No N-(aminoaryl)cyanothioformamide, to our knowledge, has been reported except for N-(N,N-dialkylaminoaryl)cyanothioformamides.^{4a,b} This might be due to uneasy access of aminoarylthioformamide.

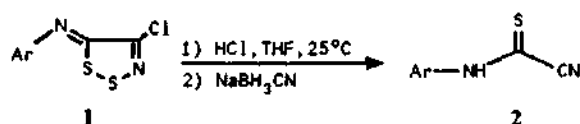
For synthesis of N-(aminoaryl)cyanothioformamide from 5-aminoaryl-imino-4-chloro-5H-1,2,3-dithiazoles, a better method for the synthesis of **2** from **1** was a precondition due to the difficulty in separation of the reaction mixtures obtained using the known method.³ We have found that a heterogeneous reduction of hydrochloride salt of **1** with sodium cyanoborohydride gave good to excellent yield of **2**: HCl gas was bubbled into the solution of **1** (4 mmol) in dry THF (50 ml) at 0°C until hydrochloride salt of **1** precipitated. The

Table 1. Yields and Physical Properties of N-arylcyanothioformamides **2**

2	Ar	Yield ^a (%)	mp ^b (°C)	Color
a		71	130-131 (CHCl ₃ /n-hexane) (lit ⁷ 126.5-128.5)	orange
b		84	128-130 (CHCl ₃ /n-hexane) (lit ⁶ 128-130)	grey yellow
c		75	106-108 (CHCl ₃ /n-hexane) (lit ⁷ 108-110.5)	reddish yellow
d		88	103-104 (petroleum ether/CH ₂ Cl ₂) (lit ⁷ 99-102)	grey yellow
e		93	118-119 (petroleum ether/CH ₂ Cl ₂)	red
f		78	97-98 (petroleum ether/CH ₂ Cl ₂)	yellow
g		90	146-147 (petroleum ether/Et ₂ O)	orange
h		100	158-159 (dec) (CH ₂ Cl ₂ /n-hexane)	yellow

^aYield of isolated product. ^bmp was determined on a Fisher-Johns melting point apparatus as uncorrected.

mixture was stirred (10 min), followed by the addition of NaBH₃CN (6 mmol) in dry THF (20 ml). After the solid had disappeared, the mixture was stirred (10 min) at room temperature, followed by the addition of water (20 ml), which was neutralized with saturated sodium bicarbonate. After removal of THF in vacuo, the residual aqueous solution was extracted with CH₂Cl₂ (3×20 ml). The combined organic layers were dried (MgSO₄), concentrated in vacuo, and the residue was chromatographed on silica gel (10×3 cm, Merck 70-230 mesh). After sulfur and an unknown mixture were removed by sequential elution with petroleum ether/CH₂Cl₂ (2:1, 60 ml) and CH₂Cl₂ (30 ml), **2** was eluted with CH₂Cl₂/EtOAc (1:1, 60 ml). Yields and physical properties of **2** are summarized in Table 1 and all unknown compounds (**2e-2h**) have been characterized by their ¹H-NMR, IR and MS data.⁷



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7. ¹H-NMR spectra (internal standard TMS) were recorded on a Varian EM 360-A (60 MHz) spectrometer. IR spectra were measured on a Perkin-Elmer 782 spectrometer and MS data were obtained using VG 12-250 mass spectrometer. **2e**: ¹H-NMR (CDCl₃/DMSO-d₆) δ 2.40 (s, 3H, Me), 7.75 (d, 1H, *J*=9 Hz), 8.30 (dd, 1H, *J*=9, 3 Hz), 8.46 (d, 1H, *J*=3 Hz); IR (KBr) 3248, 2235 cm⁻¹; MS (*m/z*) 221 (P⁺), 194 (P⁺-HCH). **2f**: ¹H-NMR (CDCl₃/DMSO-d₆) δ 2.36 (s, 3H, Me), 7.52-8.15 (m, 3H); IR (KBr) 3240, 2246 cm⁻¹; MS (*m/z*) 221 (P⁺), 206 (P⁺-Me), 194 (P⁺-HCN). **2g**: ¹H-NMR (CDCl₃/DMSO-d₆) δ 7.24-7.60 (m, 6H), 8.40 (dd, 1H, *J*=9, 2 Hz), 8.91 (d, 1H, *J*=2 Hz); IR (KBr) 3270, 2220 cm⁻¹; MS (*m/z*) 283 (P⁺) 256 (P⁺-HCN). **2h**: ¹H-NMR (CDCl₃/DMSO-d₆) δ 7.05-7.82 (m, 4H), 7.95-8.30 (m, 2H), 8.73 (d, 1H, *J*=2 Hz), 10.32 (s, 1H); IR (KBr) 3395, 3250, 2220 cm⁻¹; MS (*m/z*) 251 (P⁺), 224 (P⁺-HCN).

A Convenient Preparation of Enamines with N,N'-Sulfinyldiamines

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Following the first publication on alkylation and acylation of enamine in 1954 by Stork¹, utilization of enamines in a variety of reactions such as electrophilic substitution and addition, oxidation and reduction, cycloaddition expanded rapidly.² These useful enamines are usually prepared from the corresponding carbonyl compounds and secondary amines; effective methods are based on the concept of convenient removal of water produced by carbonyl-amine condensation. The usual auxiliary reagents for dehydration are K₂CO₃,³ CaO³, TsOH⁴, Dowex-50 resin⁵, BF₃·OEt₂⁶, AcOH⁷, MgSO₄,⁸ CaH₂,⁹ TiCl₄¹⁰ and molecular sieves¹¹.

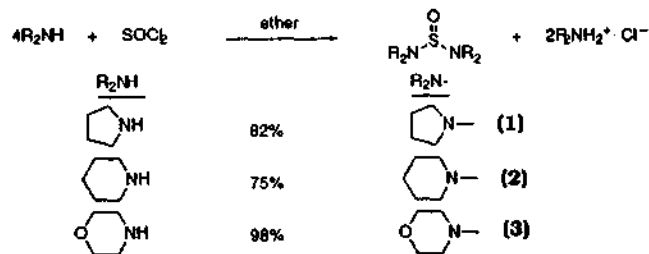
Other methods which chemically convert water to something else during the reaction have been introduced: it was shown that a mixture of tris(pyrrolidiny)borane, a ketone, pyrrolidine and a catalytic amount of TsOH in refluxing benzene for about 30 min gives the corresponding pyrrolidine enamines in good yield.¹² The same reasonings have been applied to tris(dimethylamino)arsine, and tin, silicon, germanium and titanium amides of M(NR₂)₄.^{13,14} However, a competing reaction is the formation of metal enolates.¹⁴

Table 1. Reactions of N,N'-Sulfinyldimorpholine **3** with Aldehydes and Ketones

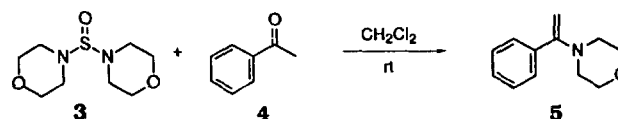
Entry	Carbonyl compounds	Reagent 3 (equiv)	Morpholine (extra equiv)	Enamine products yield(%) ^a
1	acetophenone	1.0	0	68
2	propiophenone	1.0	0	47
3	cyclohexanone	1.0	0	73
4	3-phenylpropanal	1.0	0.1	72
5	4-phenylbutanal	1.0	0.1	79
6	4-phenylbutanal	1.0	0.1	(83.0) ^b
7	4-phenylbutanal	1.0	1.0	(83.4) ^c
8	4-phenylbutanal	2.0	0.1	(86.1) ^c
9	4-phenylbutanal	3.0	0.1	(88.3) ^c

^a Isolated but unoptimized yields of the products, whose identity was confirmed by spectral analysis and/or independent synthesis. The yields in parenthesis refer to yield by HPLC. ^b HPLC condition (254 nm, flow rate 2 ml/Min, C 18 column, MeCN : H₂O = 7 : 3). ^c HPLC condition (254 nm, flow rate 2 ml/min, C18 column, MeOH : AcOH : H₂O = 50 : 1 : 49).

Our research was aimed at finding out a new and versatile process for enamine formation under mild condition by indirect dehydrative reactions of N,N,N',N'-tetraalkylsulfinyldiamines derived from secondary amines such as pyrrolidine, piperidine and morpholine¹⁵.



Thus, to a solution of 4 equiv of a secondary amine such as pyrrolidine, piperidine and morpholine in ether, SOCl₂ was added dropwise at 0°C, which was stirred at rt for 3 h. After filtration and evaporation of ether, unreacted SOCl₂ and amine, liquid product was obtained in almost quantitative yields after distillation. But in the case of the reaction product with morpholine, the liquid soon changed to crystalline solid, which had a long shelf life. Because of this crystallinity of N,N'-sulfinyldimorpholine **3** and ease of its isolation and handling, N,N'-sulfinyldimorpholine was selected as a model enamination reagent. Thus, N,N'-sulfinyldimorpholine **3** (1.0 equiv) was treated with acetophenone in methylene chloride at room temperature. After washing the ethereal solution with aqueous NaHCO₃ and drying with Na₂SO₄, morpholine enamine of acetophenone was obtained in 68% yield after vacuum distillation.



Consequently, reactions with some selected carbonyl compounds using N,N'-sulfinyldimorpholine were carried out, the