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Vicarious Nucleophilic Substitution of Hydrogen Proceeding *via* Heterocyclic Ring Opening

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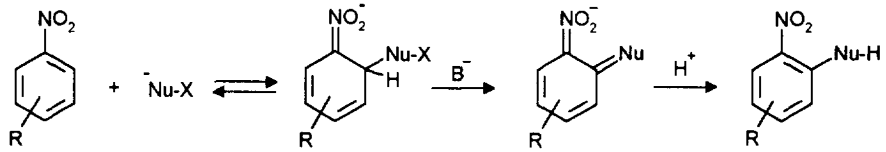
Abstract Carbanions of five-membered *S*-heterocycles react with nitroarenes *via* the ring-opening VNS reaction or oxidative nucleophilic substitution of hydrogen. The reaction course is affected by rigidity of the ring.

Vicarious nucleophilic substitution of hydrogen is presently a well established method for introduction of carbon,[1] oxygen,[2] and nitrogen[3] substituents into aromatic rings *via* direct replacement of hydrogen. The reaction proceeds as addition of nucleophiles containing leaving group X to electrophilic aromatic rings followed by base induced *β*-elimination of HX from the intermediate σ-adducts.

Scheme 1



There are a variety of substituents able to act as leaving groups in the VNS reaction: Cl, Br, PhO, RO, PhS, $PhSO_2$,[4] CF_3SO_2,[5] R_2NCSS, NC,[6] R_3N^+ [7] etc. In spite of numerous examples of VNS in which nucleophiles containing such groups reacted, there is not sufficient knowledge of the effect of the leaving group on the reaction course.

In this connection, of particular interest are reactions of those carbanions in which leaving groups and carbanionic centers form a heterocyclic ring system so that the elimination proceeds *via* the heterocyclic ring opening process. An example of such a reaction in which cyanooxirane carbanions react with 1-nitronaphtalene and the elimination proceeds *via* the oxirane ring-opening was reported.[8] In our previous paper[9] we found that the reaction course of carbanions of 1,3-dithiane derivatives with nitroarenes depends on the kind of leaving group involved. The ylide generated from methylsulfonium salt of 1,3-dithiane entered the ring opening VNS reaction whereas the carbanion of 1,3-dithiane-1,1-dioxide gave products of the oxidative nucleophilic substitution of hydrogen. Apparently in the latter case the ring opening *β*-elimination of thiolate or sulfinate anions in the σ-adducts was a rather slow process, which caused the oxidation to proceed faster, whereas the sulfonium group, known as an excellent leaving group, assured fast ring opening elimination.

In this paper we wish to report results of our studies of the VNS reaction proceeding *via* the heterocyclic five-membered ring opening. Since RS- substituents are generally better leaving groups than analogous RO- thiaheterocycles, 2-cyanotetrahydrothiophene **1**, 2,3-dimethylthiazolidine-4-one **2** and 3-methylthiazolidine-2,4-dione **3** have been chosen as model compounds. All these starting heterocycles are readily available: **1** was prepared by cyclization of 3-chloropropylthioacetonitrile in PTC conditions,[10] **2** was prepared from chloroacetic acid and thiourea followed by methylation of the resulting thiazolidine-2,4-dione,[11] **3** was prepared in a one-pot reaction from methylamine, methylthioglycolate and acetaldehyde.[12]

The reaction of **1** with nitroarenes was carried out under typical VNS conditions: DMF and ca. 5 fold excess of *t*-BuOK; it proceeded smoothly giving the expected VNS products. (Scheme 2, Table 1)

Scheme 2

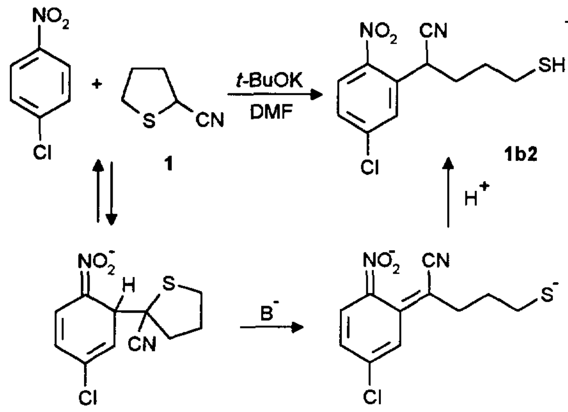


Table 1

nitroarene	product*	yield %
nitrobenzene	**1a2**	43
	1a4	19
p-chloronitrobenzene	**1b2**	74
2-methoxy-5-nitropyridine	**1c6**	56
1-nitronaphthalene	**1d2**	41
	1d4	11

*) The last digit indicates position of the entering substituent

In the reaction of **1** with nitrobenzene and 1-nitronaphthalene two isomeric products of *ortho-* and *para*-substitution were produced. In the latter case the *o-/p-* ratio was about 4. When compared with the reaction of an open chain analogue, 2-phenylthiopropionitrile, it appears that the steric requirements of the cyclic carbanion of **1** are substantially smaller than its noncyclic analogue. The VNS reaction in 2-methoxy-5-nitropyridine proceeded selectively at C-6. The reason for such orientation was discussed earlier.[13]

The ring-opening VNS with **2** proceeds less efficiently. Yields of the products were moderate and in some cases, in spite of the ring-opening *β*-elimination, the intermediate σ-adducts underwent oxidation to give products of the oxidative nucleophilic substitution of hydrogen, ONSH. (Scheme 3, Table 2)

Scheme 3

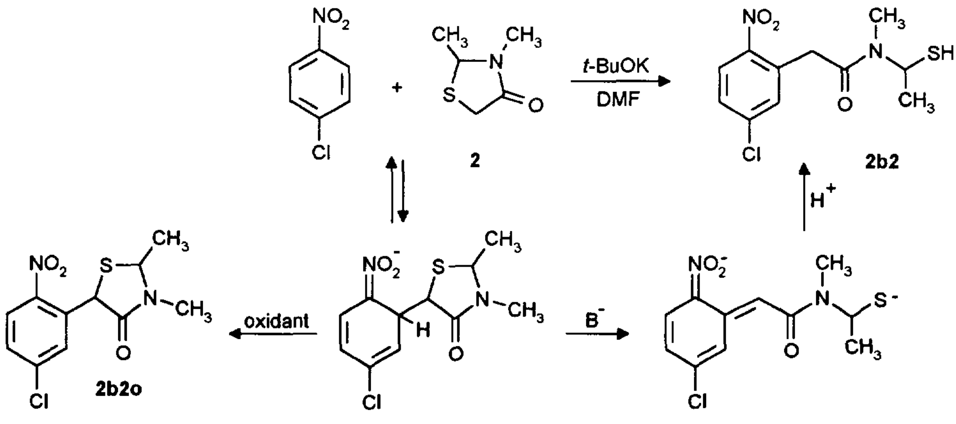


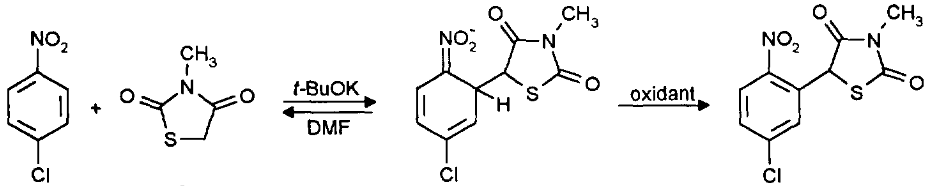
Table 2

nitroarene	product*, yield %				nitroarene recovered %
	VNS		ONSH		
nitrobenzene	**2a2**	18	**2a2o**	traces	-
p-chloronitrobenzene	**2b2**	18	**2b2o**	21	49
2-methoxy-5-nitropyridine	**2c6**	13	-	-	traces
1-nitronaphthalene	**2d2**	61	-	-	9
8-nitroquinoline	**2e7**	34	-	-	14

*) o - indicates oxidative product

Contrary to the reaction with **1** and **2** attempts to accomplish the ring opening VNS in the reaction of **3** with nitroarenes failed. When nitrobenzene and p-chloronitrobenzene were treated with **3** in the presence of *t*-BuOK/DMF, products of ONSH were formed in moderate yields. The oxidant was apparently oxygen since the final outcome of the reaction depended to some extent whether oxygen was present in the reaction mixture. (Scheme 4, Table 3)

Scheme 4



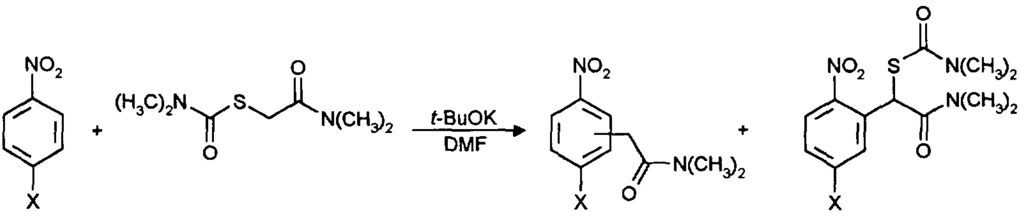
3 **3b2o**

Table 3

nitroarene	reaction conditions	product, yield %		nitroarene recovered %
nitrobenzene	argon	**3a4o**	18	34
nitrobenzene	oxygen	**3a4o**	34	47
p-chloronitrobenzene	argon	**3b2o**	21	39
p-chloronitrobenzene	oxygen	**3b2o**	29	18

Since the eventual VNS process with **3** should occur *via* base inducted *β*-elimination of *N*,*N*-dialkylmonothiocarbamate moiety, which to this point has not been used as a leaving group in this reaction, we have prepared a corresponding open chain analogue of **3** - *N*,*N*-dimethyl-[S-(*N*,*N*-dimethylcarbamoyl)]thioglycolamide **4**. The reaction of **4** with nitroarenes proceeded along the VNS pathway, although ONSH also took place to some extent. (Scheme 5)

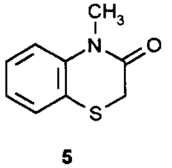
Scheme 5



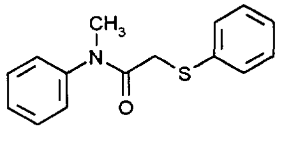
4

X= H **4a2, 18%, 4a4, 4%** **4a2o, 18 %**
X= Cl **4b2, 62%**

From these results it appears that the ring opening VNS reaction does proceed with 5-membered S-heterocycles. It is, however, limited to ring systems which show some conformational flexibility. The rigid, planar ring of **3**, when attached to the aromatic ring in the σ^H-adduct, is apparently unable to attain proper conformation for the β-elimination. This conclusion can be supported by the result of the experiments in which the ring opening VNS with 4-methyl-4*H*-benzo[1,4]thiazin-3-one **5**[14] was attempted. Because of the rigidity of the six-membered ring fused with the aromatic ring we have not observed VNS but the ONSH reaction exclusively whereas the open chain analogue *N*-phenyl-*N*-methyl-*S*-phenylthioglycolamide **6** reacted along the VNS pathway. (Table 4)



5



6

Table 4

nitroarene	C-H acid	product, yield %				C-H acid recovered %
		VNS		ONSH		
nitrobenzene	**5**	-		**5a2o**	16	-
		-		**5a4o**	6	
nitrobenzene	**6**	**6a2**	17	-		42
		6a4	18	-		
p-chloronitrobenzene	**5**	-		**5b2o**	24	-
p-chloronitrobenzene	**6**	**6b2**	55	-		32

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR spectra were taken on Varian Gemini 200 (200 MHz) spectrometer in CDCl$_3$. Chemical shifts are given in δ ppm referred to TMS. Silica gel (230-400 mesh, Merck) was used for column chromatography. Starting materials were commercial or prepared according to the described procedures. The mass spectra were obtained on AMD-604 (Intercta GmbH).

2,3-Dimethylthiazolidine-4-one (2): Methylamine (~ 2.0 g, 64 mmole) and acetaldehyde (~ 3.0 g, 68 mmole) were placed in a cooled sealed tube and left to reach room temperature. After one hour methyl thioglycolate (3.0 g, 28 mmole) was added and then the tube was heated at 60 °C for 15 h. The crude mixture was dissolved in ethyl acetate (50 ml), washed with diluted hydrochloric acid, water and dried. After the solvent was removed, the crude product was filtered through silica gel using ethyl acetate/hexane as eluent, and finally distilled under reduced pressure from bulb to bulb (15 Torr) to give 2,3-dimethylthiazolidine-4-one, yield 2.0 g, 15 mmole, 54%.

3-Methylthiazolidine-2,4-dione (3) was prepared by methylation of thiazolidine-2,4-dione with methyl iodide in DMF/K$_2$CO$_3$ system.

***N,N*-dimethyl-S-(N,N-dimethylcarbamoyl)]thioglycolamide (4):** A solution of potassium *N,N*-dimethylthiocarbamate (1.50 g, 10.0 mmole) and *N,N*-dimethylchloroacetamide (1.30 g, 10.7 mmole) in methanol (30 ml) was stirred at room temperature for 2 h. Precipitated potassium chloride was filtered off, the filtrate concentrated *in vacuo* and finally distilled under reduced pressure (0.05 Torr) from bulb to bulb to give 4, yield 1.70 g, 90%, semicrystalline at room temperature.

General procedure for the reaction of carbanions of 1-6 with nitroarenes: To a solution of *t*-BuOK (561 mg, 5 mmole) in DMF (8 ml) cooled to -20 ~ -90 °C a solution of the nitroarene (1 mmole) and C-H acid (1 mmole) in DMF (1 ml) was added dropwise. The reaction was carried out under argon for 5 to 20 min and the mixture was poured into water (50 ml) containing 10% hydrochloric acid (2 ml). The product was extracted with ethyl acetate, the extract was washed with water, dried and the solvent was evaporated. The residue was chromatographed using ethyl acetate-hexane as eluent. Solid products were crystallised. Spectral and analytical data are given below.

N,N-dimethyl-[S-(N,N-dimethylthiocarbamoyl)]acetamide **(4),** oil. ^{1}H NMR: 3.85 (s, 2H), 3.12 (s, 3H), 3.03 (bs, 6H), 2.98 (s, 3H). EI HRMS calcd. for $C_7H_{14}N_2O_2S$: 190.0776; found: 190.0075.

N-Methyl-N-phenyl-S-phenylthioglycolamide **(6),** Mp. 70-71 °C (hexane). ^{1}H NMR: 7.50-7.05 (m, 10H), 3.52 (s, 2H), 3.29 (s, 3H). Anal calcd. for $C_{15}H_{15}NOS$: C, 70.00; H, 5.88; N, 5.44%; found: C, 69.98; H, 5.88; N, 5.34%.

2-(2-Nitrophenyl)-5-mercaptopentanenitrile **(1a2),** oil. ^{1}H NMR: 8.27, 7.55 (AA'XX', 4H), 3.97 (t, *J*= 7.0 Hz, 1H), 2.7-2.5 (m, 2H), 2.2-1.7 (m, 4H), 1.36 (t, *J*= 8.0 Hz, 1H). Anal. calcd. for $C_{11}H_{12}N_2O_2S$: C, 55.91; H, 5.12; N, 11.86%; found: C, 55.90; H, 5.14; N, 11.91%.

2-(4-Nitrophenyl)-5-mercaptopentanenitrile **(1a4),** oil. ^{1}H NMR: 8.07 (dd, *J*= 8.1, 1.5 Hz, 1H), 7.65-7.85 (m, 2H), 7.50-7.60 (m, 1H), 4.73 (dd, *J*= 8.7, 4.9 Hz, 1H), 2.5-2.7 (m, 2H), 1.7-2.3 (m, 4H), 1.40 (t, *J*= 8.0 Hz, 1H). Anal. calcd. for $C_{11}H_{12}N_2O_2S$: C, 55.91; H, 5.12; N, 11.86%; found: C, 55.96; H, 5.18; N, 11.88%.

2-(5-Chloro-2-nitrophenyl)-5-mercaptopentanenitrile **(1b2),** oil. ^{1}H NMR: 8.06 (d, *J*= 8.07 Hz, 1H), 7.76 (d, *J*= 2.3 Hz, 1H), 7.52 (dd, *J*= 8.7, 2.3 Hz, 1H), 4.75 (dd, *J*= 8.8, 4.9 Hz, 1H), 1.75-1.50 (m, 2H), 2.25-1.80 (m, 4H), 1.41 (t, *J*= 8.0 Hz, 1H). Anal. calcd. for $C_{11}H_{11}N_2O_2ClS$: C, 48.80; H, 4.10; N, 10.35%; found: C, 49.01; H, 4.18; N, 10.35%.

2-(6-Methoxy-3-nitro-2-pyridyl)-5-mercaptopentanenitrile **(1c6),** oil. ^{1}H NMR: 8.37 (d, *J*= 9.1 Hz, 1H), 6.85 (d, *J*= 9.1 Hz, 1H), 4.99 (dd, *J*= 7.7, 6.4 Hz, 1H), 4.13 (s, 3H), 2.70-2.55 (m, 2H), 2.25-1.80 (m, 4H), 1.42 (t, *J*= 8.0 Hz, 1H). Anal calcd for $C_{11}H_{13}N_3O_3S$: C, 49.42; H, 4.90; N, 15 72%; Found: C, 49.56; H, 4.92; N, 15.71%.

2-(1-Nitro-2-naphthyl)-5-mercaptopentanenitrile **(1d2),** Mp. 65-67 °C (EtOH). ^{1}H NMR: 8.09 (d, *J*= 8.6 Hz, 1H), 8.0-7.9 (m, 1H), 7.80-7.60 (m, 4H), 4.05 (t, *J*= 7.5 Hz, 1H), 2.65-2.50 (m, 2H), 2.25-1.70 (m, 4H), 1.38(t, *J*= 8.0 Hz, 1H). Anal. calcd for $C_{15}H_{14}N_2O_2S$: C, 62.91; H, 4.93; N, 9.79%; found: C, 62.90; H, 4.77; N, 9.78%.

2-(1-Nitro-4-naphthyl)-5-mercaptopentanenitrile **(1d4),** oil. ^{1}H NMR: 8.60-8.50 (m, 1H), 8.17 (d, *J*= 8.0 Hz, 1H), 8.12-8.00 (m, 1H), 7.86-7.70 (m, 3H), 4.67 (dd, *J*= 8.6, 5.3 Hz, 1H), 2.80-2.50 (m, 2H), 2.40-1.80 (m, 4H), 1.38 (t, *J*= 8.0 Hz, 1H). Anal. calcd. for $C_{15}H_{14}N_2O_2S$: C, 62.91; H, 4.93; N, 9.79%; found: C, 63.06; H, 4.71; N, 9.53%.

N-(1-Mercaptoethyl)-N-methyl-(2-nitrophenyl)acetamide **(2a2),**oil. ^{1}H NMR: 8.12 (dd, *J*=8.0, 1.5 Hz, 1H), 7.65-7.28 (m, 3H), 6.20-6.00 & 5.65-5.50 (2 x m, 1H), 4.15 & 4.08, 3.98 (s & AB *J*= 15 Hz, 2H), 3.09 &2.94 (2 x s, 3H), 2.21 (dd, *J*=5.7, 0.8 Hz, 1H), 1.65 &1.48 (d & dd, *J*= 6.6 & *J*= 7.1, 0.8 Hz, 3H). Anal. calcd. for $C_{11}H_{14}N_2O_3S$: C, 51.95; H, 5.55; N, 11.02%; found: C, 52.07; H, 5.57; N, 11.04%.

N-(1-Mercaptoethyl)-N-methyl-(5-chloro-2-nitrophenyl)acetamide **(2b2),** Mp. 93-96 °C (ethyl acetate-hexane). ^{1}H NMR: 8.10 (d, *J*= 8.8 Hz, 1H), 7.43 (dd, *J*= 8.8, 2.3 Hz, 1H), 7.32 (d, *J*= 2.3 Hz, 1H), 6.18-6.00 & 5.60-5.45 (2 x m, 1H), 4.12 & 4.05, 3.96 (bs & AB *J*=15.8 Hz, 2H), 3.10 & 2.94 (2 x s, 3H), 2.20 (dd, *J*=5.8, 0.9 Hz, 1H), 1.67 &1.48 (d & dd, *J*= 6.7 & *J*= 7.0, 0.9 Hz, 3H). Anal. calcd. for $C_{11}H_{13}N_2ClO_3S$: C, 45.75; H, 4.54; N, 9.70%; found: C, 46.02; H, 4.54; N, 9.69%.

2,3-Dimethyl-5-(5-chloro-2-nitrophenyl)-4-thiazolidinone **(2b2o)** - first pair of enantiomers, Mp. 176-178 °C (ethyl acetate-hexane) ^{1}H NMR: 7.96 (d, *J*= 8.6 Hz, 1H), 7.47 (dd, *J*= 8.6, 2.2, 1H), 7.40 (d, *J*= 2.2 Hz, 1H), 5.66 (s, 1H), 4.75 (q, *J*= 6.0 Hz, 1H), 3.02 (s, 3H), 1.63 (d, *J*= 6.0 Hz, 3H). Anal. calcd.for $C_{11}H_{13}N_2ClO_3S$: C, 46.07; H, 3.87; N, 9.77%; found: C, 46.07; H, 3.63; N, 9.54%.

second pair of enantiomers, oil. ^{1}H NMR: 8.00-7.92 (m, 1H), 7.46-7.38 (m, 2H), 5.67 (d, *J*= 2.0 Hz, 1H), 4.78 (dq, *J*= 6.1, 2.0 Hz, 1H), 3.02 (s, 3H), 1.64 (d, *J*= 6.0 Hz, 3H). EI HRMS calcd for $C_{11}H_{13}N_2ClO_3S$: 286.01789; found: 286.01763.

N-(1-Mercaptoethyl)-N-methyl-(6-methoxy-3-nitro-2-pyridyl)acetamide **(2c6),** oil. ^{1}H NMR: 8.38 (d, *J*= 9.1 Hz, 1H), 6.77 (d, *J*= 9.1 Hz, 1H), 6.20-6.05 & 5.65-5.45 (2 x m, 1H), 4.37 & 4.28, 4.24 (bs & AB *J*=16.0 Hz, 2H), 4.02 (s, 3H), 3.09 & 2.96 (2 x s, 3H), 2.22 (dd, *J*=5.7, 0.9 Hz, 1H), 1.66 &1.50 (d & dd, *J*= 6.6 & *J*= 7.1, 0.9 Hz, 3H). Anal. calcd. for $C_{11}H_{15}N_3O_4S$: C, 46.30; H, 5.30; N, 14.73%; found: C, 46.40; H, 5.55; N, 14.62%.

N-(1-Mercaptoethyl)-N-methyl-(1-nitro-2-naphthyl)acetamide **(2d2),** oil. ^{1}H NMR: 7.97 (d, *J*= 8.6 Hz, 1H), 7.93-7.52 (m, 4H), 7.44 (d, *J*= 8.6 Hz, 1H), 6.22-6.04 & 5.54-5.40 (2 x m, 1H), 3.96 & 3.85 (2 x bs, 2H), 2.99 & 2.96 (2 x s, 3H), 2.25 & 1.97 (2 x d, *J*= 5.6 & *J*= 5.2 Hz, 1H), 1.56 & 1.47 (2 x d, *J*= 6.8 & *J*= 6.8 Hz, 3H).

^{1}H NMR at 50°C: 7.97 (d, *J*= 8.6 Hz, 1H), 7.91-7.50 (m, 4H), 7.44 (d, *J*= 8.6 Hz, 1H), 6.21-5.89 (m, 1H), 3.85 (s, 2H), 2.98 (s, 3H), 2.21 (d, *J*= 5.2 Hz, 1H), 1.56 & 1.48 (2 x d, *J*= 6.8 & *J*= 7.0 Hz, 3H). Anal. calcd. for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30; N, 9.21%; found: C, 59.05; H, 5.43; N, 8.96%.

N-(1-Mercaptoethyl)-N-methyl-(8-nitro-7-quinoyl)acetamide **(2e7),** Mp. 123-126 °C. ^{1}H NMR: 9.00 (dd, *J*= 4.3, 1.6 Hz, 1H), 8.23 (dd, *J*= 8.4, 1.6 Hz, 1H) 7.95 (d, *J*= 8.7 Hz, 1H), 7.59 (d, *J*= 8.7 Hz, 1H), 7.53 (dd, *J*= 8.3, 4.3 Hz, 1H), 6.20-6.02 & 5.52-5.36 (2 x m, 1H), 3.97 &3.86 (2 x bs, 2H), 3.00 & 2.96 (2 x s, 3H), 2.24 & 1.97 (2 x d, *J*= 6.5, *J*= 6.0 Hz, 1H), 1.56 & 1.48 (2 x d, *J*= 6.8 & *J*= 7.0 Hz, 3H). Anal. calcd. for $C_{14}H_{15}N_3O_3S$: C, 55.07; H, 4.95; N, 13.36%; found: C, 55.18: H, 5.01: N, 13.52%.

3-Methyl-5-(4-nitrophenyl)-2,4-thiazolidinedione **(3a4o),** Mp. 129-130 °C (Ethanol). ^{1}H NMR: 8.27, 7.63 (AA'XX', 4H), 5.41 (s, 1H), 3.19 (s, 3H). Anal. calcd. for $C_{10}H_8N_2O_4S$: C, 47.61; H, 3.20; N, 11.11%; found: C, 47.72; H, 3.13; N, 11.15%.

3-Methyl-5-(2-nitro-5-chlorophenyl)-2,4-thiazolidineone **(3b2o),** Mp. 176-178 °C. ^{1}H NMR: 8.11 (d, *J*= 8.8 Hz, 1H), 7.50 (dd, *J*= 8.8, 2.0 Hz, 1H), 7.43 (d, *J*= 2.0 Hz, 1H), 5.96 (s, 1H), 3.24 (s, 3H). Anal. calcd. for $C_{10}H_7N_2ClO_4S$: C, 41.89; H, 2.46; N, 9 77%; found: C, 42.03; H, 2.27; N, 9.69%.

***N,N-Dimethyl-(2-nitrophenyl)acetamide* (4a2),** oil. ^{1}H NMR: 8.09 (dd, J= 8.1, 1.4 Hz, 1H), 7.64-7.30 (m, 3H), 4.06 (s, 2H), 3.15 (s, 3H), 2.98 (s, 3H). Anal. calcd. for $C_{10}H_{12}N_2O_3$: C, 57.68; H, 5.81; N, 13.46%; Found: C, 57.40; H, 5.89; N, 13.17%.

***N,N-Dimethyl-(4-nitrophenyl)acetamide* (4a4),** Mp. 87-89 °C (ethyl acetate-hexane). ^{1}H NMR: 8.19, 7.43 (AA'XX', 4H), 3.81 (s, 2H), 3.06 (s, 3H), 3.00 (s, 3H). Anal. calcd. for $C_{10}H_{12}N_2O_3$: C, 57.68; H, 5.81; N, 13.46%; found: C, 57.56; H, 5.81; N, 13.48%.

***N,N-dimethyl-[S-(N,N-dimethylcarbamoyl)]-(2-nitrophenyl)thioglycolamide* (4a2o),** oil. ^{1}H NMR: 8.00-7.88 (m, 2H), 7.67-7.56 (m, 1H), 7.48-7.37 (m, 1H), 6.34 (s, 1H), 3.21 (s, 3H), 3.03 (s, 3H), 2.98 (bs, 6H). Anal. calcd. for $C_{13}H_{17}N_3O_4S$: C, 50.15; H, 5.50; N, 13.50%; found: C, 50.23; H, 5.75; N, 13.47%.

***N,N-Dimethyl-(5-chloro-2-nitrophenyl)acetamide* (4b2),** Mp. 116-119 °C (ethyl acetate-hexane). ^{1}H NMR: 8.07 (d, J= 8.7 Hz, 1H), 7.41 (dd, J=8.7, 2.3 Hz, 1H), 7.34 (d, J= 2.3 Hz, 1H), 4.04 (s, 2H), 3.15 (s, 3H), 2.98 (s, 3H),. Anal. calcd. for $C_{10}H_{11}N_2O_3Cl$: C, 49.49; H, 4.57; N, 11.55%; found: C, 49.43; H, 4.49; N, 11.59%.

***4-Methyl-2-(2-nitrophenyl)-4H-benzo[1,4]thiazin-3-one* (5a2o),** Mp. 133-134 °C (ethyl acetate-diethyl ether). ^{1}H NMR: 8.04 (dd, J= 7.9, 1.5 Hz, 1H), 7.62-7.00 (m, 7H), 5.49 (s, 1H), 3.57 (s, 3H). Anal. calcd. for $C_{15}H_{12}N_2O_3S$: C, 59.98; H, 4.03; N, 9.33%; found: C, 59.87; H, 3.95; N, 9.29%.

***4-Methyl-2-(4-nitrophenyl)-4H-benzo[1,4]thiazin-3-one* (5a4o),** Mp. 190-191 °C (methanol-ethyl acetate). ^{1}H NMR: 8.13, 7.50 (AA'XX', 4H), 7.56-7.00 (m, 4H), 4.74 (s, 1H), 3.54 (s, 3H). Anal. calcd. for $C_{15}H_{12}N_2O_3S$: C, 59.98; H, 4.03; N, 9.33%; found: C, 59.78; H, 3.96; N, 9.34%.

***5-Chloro-2-(2-nitrophenyl)-4-methyl-4H-benzo[1,4]thiazin-3-one* (5b2o),** Mp. 156-157 °C (methanol-ethyl acetate). ^{1}H NMR: 8.02 (d, J= 8.8 Hz, 1H), 7.5-7.0 (m, 6H), 5.7 (s, 1H), 3.55 (s, 3H). Anal. calcd. for $C_{15}H_{11}N_2O_3ClS$: C, 53.81; H, 3.31; N, 8.37%; found: C, 53.88; H,3.12; N, 8.24%.

***N-Methyl-N-phenyl-(2-nitrophenyl)acetamide* (6a2),** Mp. 86-88 °C (hexane-diethyl ether). ^{1}H NMR: 8.07 (dd, J=8.0, 1.3 Hz, 1H), 7.60-7.20 (m, 8H), 3.76 (s, 2H), 3.30 (s, 3H). Anal. calcd for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.22, N, 10.37%; found: C, 66.55 H, 5.20; N, 10.65%.

***N-Methyl-N-phenyl-(4-nitrophenyl)acetamide* (6a4),** Mp. 92-92 °C (isopropanol). ^{1}H NMR: 8.11, 7.24 (AA'XX', 4H), 7.50-7.38 (m, 3H), 7.20-7.10 (m, 2H), 3.55 (s, 2H), 3.30 (s, 3H). Anal. calcd. for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.22; N, 10.37%; found: C, 66.59; H, 5.24; N, 10.46%.

***N-Methyl-N-phenyl-(5-chloro-2-nitrophenyl)acetamide* (6b2),** Mp. 102-104 °C (methanol). ^{1}H NMR: 8.04 (d, J= 8.7 Hz, 1H), 7.57-7.20 (m, 7H), 3.74 (s, 2H), 3.30 (s, 3H). Anal. calcd. for $C_{15}H_{13}N_2O_3Cl$: C, 59.12; H, 4.30; N, 9.20%; found: C, 59.04; H, 4.12; N, 9.05%.

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