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# Studies on Thiazoline Derivatives (XVI) Synthesis of N-Alkyl-N'-cyano-N''-(3, 4-dimethyl-4-thiazoline-2-ylidene)guanidine

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N-Alkyl-N'-cyano-N''-(3, 4-dimethyl-4-thiazoline-2-ylidene)guanidine (3a-e) were prepared in two routes as outlined in Scheme 2. The structure of (3) was supported by elemental analysis, mass and NMR data. The IR spectra of (3) showed a characteristic absorption of  $\nu_{C\equiv N}$  at *ca*. 2130-2150 cm<sup>-1</sup>.

Treatment of (3) and (6), respectively, with conc.HCl gave N-(3, 4-dimethyl-4-thiazoline-2-ylidene) biuret (4). The UV spectrum having the absorption maxima in 2-PrOH at 235 nm and 298 nm resembled that of the known compound (8).

Furthermore, (3) in HCl-EtOH soln. was heated at  $80-90^{\circ}$  for 2-4 hr to give colourless crystals after neutralization. The products were identified as N-Alkyl-N'-ethoxycarbonyl-N''-(3, 4-dimethyl-4-thiazoline-2-ylidene)guanidine (5a, c) on the basis of NMR data and elemental analysis.

The discovery of the selective antagonist burimamide permitted the characterization of histamine  $H_2$ -receptor and furnished a class of drug with a completely novel pharmacological action. Burimamide has a side chain so selected that it may show great potency as a histamine  $H_2$ -receptor antagonist.

G.J.Durant *et al.*<sup>1)</sup> chemically modified burimamide into another antagonist metiamide, and found kidney damage and agranulccytosis in high dosage chronic toxicity tests with metiamide. They considered that these effects might be attributable to the presence of a thiourea group in the drug molecule, which led to the synthesis of cimetidine possessing a cyanoimino group (=N-C=N) instead of the thione sulfur (=S) of metiamide. Cimetidine is slightly more active than metiamide *in vivo* as an inhibitor of histamine-stimulated gastric acid secretion. (Scheme 1)

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During past several years, we have synthesized carbamoylamino and thiocarbamoylamino derivatives of thiazole, 2-thiazoline and thiazolidine in order to study structureactivity relationship<sup>2</sup>). Among these compounds, N,N'-dimethyl-N'-(4-methylthiazole-2yl)thiourea and N-Alkyl-N'-(3, 4-dimethyl-4-thiazoline-2-ylidene)thiourea (7) exhibited strong antiinflammatory and analgetic activities, but showed an oral toxity in rat. We wish to report here the synthesis of 2-guanidino-3, 4-dimethyl-4-thiazoline derivatives, in which the thiourea sulfur atom of (7) is replaced by a cyanoimino group (=N-C=N) as chemical modification of metiamide by G.J.Durant *et al.*<sup>1</sup>.



Scheme 2

- 48 -

As shown in Scheme 2, the title compounds were synthesized mainly by route A and identified by elemental analysis, UV, IR, NMR and Mass spectral data. Furthermore, in order to confirm their structures, synthesis through route B was carried out. The IR and MS spectra of (3a, b, c) were identical with those of compounds through route A. Route A is as follows. Intermediate N-cyano-N'-(3, 4-dimethyl-4-thiazoline-2-ylidene)-S-methylisothiourea (2) was synthesized from a mixture of 2-imino-3, 4-dimethyl-4-thiazoline (1) and dimethylcyanodithioimidocarbonate<sup>3)</sup> in EtOH. Then, to a hot solution of crude compound (2) in DMSO, an excess of alkylamine was added. For alkylamines with smaller number of carbons the mixture was stirred overnight at room temperature to give N-Alkyl-N'-cyano-N''-(3, 4-dimethyl-4-thiazoline-2-ylidene)guanidine (3) as colourless crystals. On the contrary, for alkylamines with greater number of carbons the mixture was heated in a sealed-tube at 105° for 24 hr to give (3) in good yield. On the other hand route B is as follows. An equimolar amount of (1) and S-methyl-N-alkyl-N'-cyanoisothiourea<sup>4</sup>) in acetonitrile or pyridine was heated in a 100 ml sealed-tube at 105° for overnight to give (3). As shown in Table 1 and 2, compounds (3) gave satisfactory analytical results and spectral data. The IR spectra of (3) showed  $\nu_{\rm NH}$  absorptions at 3255-3260 cm<sup>-1</sup> and 3075-3080 cm<sup>-1</sup>, and a characteristic absorption of  $\nu_{C=N}$  at ca. 2130–2150 cm<sup>-1</sup>. The UV spectra of (3a) showed absorption maxima at 233 nm, 260 nm and 313 nm. (Fig. 1) Each of the MS spectra of compounds (3a-e) showed a very intense molecular ion peak (M<sup>+</sup>), a peak at m/e 179 corresponding to [M+-RNH], a very intense peak or base peak at m/e 154 corresponding to loss of CN and gain of proton, and a characteristic peak of  $(M^+ - (RNH + = N -$ CN)] at m/e 139. (Scheme 3)

The compounds (3a, b) were very slightly soluble in CDCl<sub>3</sub> and DMSO-d<sub>6</sub>, but (3c) was readily soluble in above solvents. The NMR spectrum (CDCl<sub>3</sub>) of (3c) exhibited a doublet at  $\delta$  2.28 (3H, J=1.0Hz) due to C4-<u>CH<sub>3</sub></u> with a long-range coupling to C5-<u>CH</u> in the 4-thiazoline ring appearing at  $\delta$  6.25 (1H,d, J=1.0Hz), a singlet at  $\delta$  3.57 (3H) due to N-<u>CH<sub>3</sub></u> in the 4-thiazoline ring, and two singlets at  $\delta$  1.19 (s, 3H) and 1.25 (s, 3H) attributable to isopropyl group. A broad peak at  $\delta$  5.20-5.50 (1H) disappeared completely by the addition of D<sub>2</sub>O, which indicated the presence of <u>NH</u>.

On the other hand, the reaction of (2) with ethanolic NH<sub>3</sub> in a sealed-tube gave crystals (mp 247°) of a molecular formula of  $C_7H_9N_5S$ . The MS spectrum of this compound showed a very intense molecular ion peak at m/e 195, and a peak at m/e 179 (Rel. Intensity: 20%) corresponding to [M<sup>+</sup>-NH<sub>2</sub>]. The absorption at 3280 cm<sup>-1</sup>, 3180 cm<sup>-1</sup> and 3210 cm<sup>-1</sup> are attributed to  $\nu_{NH}$  and those at 2160 cm<sup>-1</sup> to  $\nu_{C=N}$ . Hydrolysis of the compound (6) (mp 247°) with conc. HCl gave (4) as reported below. The NMR spec-

<sup>3)</sup> A.Hantzch and M.Wolvekamp, Justus Lieigs Ann. Chem., 331, 265 (1904).

<sup>4)</sup> F.H.S.Curd et al., J.Chem. Soc. 1630 (1948); C.A. 43, 2947c (1949).

trum of (6) obtained in DMSO-d<sub>6</sub> showed a chemical shift for  $\underline{NH_2}$  at  $\delta$  7.04 which disappeared after D<sub>2</sub>O exchange. From above results it was confirmed that the reaction product (6) (mp 247°) by elimination of CH<sub>8</sub>S and addition of NH<sub>2</sub> was N-cyano-N'-(3, 4-dimethyl-4-thiazoline-2-ylidene)guanidine (6).

G.J.Durant *et al.*<sup>1)</sup> reported also the reaction of cyanoimino compounds with conc. HCl to give imino compounds. The compound (3) or (6) in conc.HCl was heated on a steam-bath for 2-3 hr to give yellow crystals, mp 200-225° (HCl salt). Neutralization of the HCl salt with NaHCO<sub>3</sub> soln. gave a free base (4) (mp 246°) (from DMF). The IR spectrum of (4) showed no absorption for  $\nu_{C=N}$  in the region of 2100 cm<sup>-1</sup>, but new absorptions for amide I at 1680-1690 cm<sup>-1</sup>. The MS spectrum of (4) showed a molecular ion peak at m/e 214 with very strong relative intensity and a peak at m/e 155 corresponding to 2-carbonylimino-3, 4-dimethyl-4-thiazoline cation. The compound (4) (mp 246°) evolved NH<sub>3</sub> gas when heated with 1N-NaOH soln. but the biuret test was negative. Then its deuterated derivative had a peak at m/e 217 (RI, 39%) which was m/e 3 more than the molecular ion peak of the undeuterated compound. The additional peaks at m/e 173 and m/e 155 corresponded to [M<sup>+</sup>-NDCO] and 2-carbonylimino-3, 4-dimethyl-4-thiazoline cation, respectively. The UV spectrum of (4) showed absorption maxima at 235 nm 298 nm. The spectral pattern and MS fragmentation of (4) resembled those of known compound, 2-(N-carbamoyl)imino-3, 4-dimethyl-4-thia-





-50 -



Scheme 4 Hydrolysis of (3)

zoline (8). As shown in Scheme 4, the product (4) was identified as N-(3, 4-dimethyl-4-thiazoline-2-ylidene)biuret.

W.K.Detweiler *et al.*<sup>5)</sup> reported that 2-amino-heterocyclic compounds reacted with nitrobiuret to give heterocyclic biurets and biuret test gave a colour.

The compound (3a) in ethanolic HCl was heated at 80–90° for 4 hr, and then neutralized with NaHCO<sub>3</sub> soln. to give colourless crystals which melted at 148° after recrystallization from EtOH. The elemental analysis gave a molecular formula of C<sub>10</sub>H<sub>16</sub> N<sub>4</sub>O<sub>2</sub>S. The MS spectrum of this compound showed a molecular ion peak at m/e 256 (base) and a very intense ion peak at m/e 211 for [M<sup>+</sup>-OC<sub>2</sub>H<sub>5</sub>]. The IR spectrum showed strong absorptions for  $\nu_{\rm NH}$  at 3315 cm<sup>-1</sup> and 3075 cm<sup>-1</sup>, no absorption for  $\nu_{\rm C=N}$ in the region of 2100 cm<sup>-1</sup> and a new absorption for amide I at 1630 cm<sup>-1</sup>. The NMR spectrum (CDCl<sub>8</sub>) of (5a) exhibited a triplet at  $\delta$  1.32 (3H, J=7.0Hz), a quartet at  $\delta$  4.17 (2H, J=7.0Hz) and a doublet at  $\delta$  3.04. The first two of these indicated the presence of OCH<sub>2</sub>CH<sub>8</sub>. The last due to CH<sub>8</sub>-NH showed a singlet after D<sub>2</sub>O exchange.

As shown in Scheme 5, treatment of (3a) with ethanolic HCl have a possibility to give compounds (5a') or (5a"). From above results the product (mp 148°) was uneqivocally identified as N-ethoxycarbonyl-N'-methyl-N"-(3, 4-dimethy1-4-thiazoline-2-ylidene)guanidine (5a). The formation of (5a) in the above reaction may be explained by pathway either *via* iminoester or carboxylic acid. In the former,  $C_2H_5OH$  may add to the nitril group of (3a) in the presence of acid catalyst to afford the iminoester derivative, which then the imino moiety is hydrolyzed to give oxo-derivative (5a). In the latter,  $H_2O$  may add to nitril group of (3a) to form amido-derivative. It is

<sup>5)</sup> W.K.Detweiler and E.D.Amstutz, J.Am.Chem.Soc. 73, 5451 (1951).

converted to the carboxilic acid derivative, whose carboxylic acid moiety is easily esterified to (5a). The compound (5c) was also prepared by the same procedure as (5a) from (3c) and it was characterized satisfactorily by elemental and spectral analysis.



Scheme 5 Hydrolysis of (3a) in HCl-EtOH

To our knowledge, the compounds (2-6) were new derivatives. Toxicity of the compound (3) was reduced relative to previously reported compounds, however antiinflammatory and analgetic effects were also reduced. Recently, American Cyanamide Co. reported that thiazolyl phenyl guanidines were useful against rhinovirus *in vitro*<sup>6</sup>).

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# Experimental

Melting points were taken on a Yanako micro melting point apparatus and are uncorrected. Infrared spectra were obtained with a Hitachi EPI-G3 spectrometer, ultraviolet spectra with a Shimadzu double beam spectro photometer UV-200s and nuclear magnetic resonance spectra with a Nihon Denshi JNM-NH 100 (100 MHz) with tetramethylsilane (TMS) as internal standard. Chemical shift are expressed in  $\delta$  (ppm). The coupling constants (J) is expressed in Hz. Abbreviation : s: singlet, d: doublet, q: quartet, m: multiplet, b: broad.

American Cyanamid Co., Beg, 850, 148; C.A. 88, 170131c (1978), A.R.Bruceand and L.H.Lee, S.African 7607, 539; C.A. 88, 190813e (1978).

# dimethylcyanodithioimidocarbonate

To a stirred mixture of crude NH<sub>2</sub>CN (0.41 mole) and CS<sub>2</sub> (0.41 mole) was added KOH (30 g) in EtOH (120 ml). After stirring for several hours, the crude product was collected on a filter, dried *in vacuo* over KOH to give 22 g of (KS)<sub>2</sub>C=NCN. Then, to an excess of CH<sub>3</sub>I (100 ml) was added (KS)<sub>2</sub>CN=CN with vigorous stirring at room temperature. After stirring for overnight, the reaction mixture was filtered, the filtrate was concentrated *in vacuo* to dryness and the residue was treated with activated charcoal in EtOH-H<sub>2</sub>O to give 10 g of (CH<sub>3</sub>S)<sub>2</sub>C=NCN.  $\nu_{C=N}$  2160 cm<sup>-1</sup>, NMR ( $\delta$  in CDCl<sub>3</sub>) 2.62 (s. CH<sub>3</sub>).

#### S-methyl-N-alkyl-N'-cyano-isothiourea

Alkylisothiocyanate (0.05 mole) in EtOH (100 ml) was stirred for 18 hr at room temperature. The filtrate was treated with  $CH_{3}I$  (0.05 mole) and the mixture was refluxed for 0.5 hr and kept at room temperature. After the solvent was evaporated *in vacuo* to dryness, the crude product was recrystallized from EtOH to give S-methyl-N-alkyl-N'-cyano-isothiourea. (Alkyl,  $CH_{3}$ , mp 187°,  $C_{2}H_{5}$ , mp 163°, ( $CH_{3}$ )<sub>2</sub>CH, mp 107°)

# N-cyano-N'-(3, 4-dimethyl-4-thiazoline-2-ylidene)-S-methylisothiourea (2)

Equimolar amounts of (1) (0.0137 mole) and dimethylcyanodithioimidocarbonate in EtOH (25 ml) was stirred at room temperature. The resulting white precipitate was collected on a filter and recrystallized from dimethylsulfoxide (or acetonitrile). MS: m/e 226 (M<sup>+</sup>, 40%), 179 (M<sup>+</sup>-SCH<sub>3</sub>, base), 154(7), 125(10), 99(8), 72(13), 56(10).

# N-Alkyl-N'-cyano-N"-(3, 4-dimethyl-4-thiazoline-2-ylidene)guanidine (3) method A

(3a): To a hot solution of (2) (0.0089 mole) in DMSO (40 ml), a commercial 40% CH<sub>3</sub>NH<sub>2</sub> in MeOH (10 g) was added. After stirring at room temperature for 24 hr, the crystallized precipitate was collected on a filter, washed with water, and dried to give 1.52 g of (3a). Compound (3a) is nearly insoluble in all common solvents.

(3b): To a hot solution of (2) (0.0044 mole) in DMSO (20 ml), a commercial 70%  $C_2H_5NH_2$  aq. soln. (3 g) was added. The mixture was worked up by the same procedure as (3a) to give 0.25 g of (3b). NMR ( $\delta$  in DMSO-d<sub>6</sub>, very sparingly soluble) 1.14 (t, J=7.0Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>), 3.20-3.48 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>), 3.55 (s, 3H, CH<sub>3</sub>N-), 2.26 (d, J=1.0Hz, 3H, C4-CH<sub>3</sub>), 6.49 (b, 1H, C5-CH), NH (not appear).

(3c): The mixture of (2) (0.0044 mole) in DMSO (24 ml) and isopropylamine (2 g) was heated in a 100 ml sealed-tube at 105° for 24 hr. After standing for 1 hr at room temperature, H<sub>2</sub>O was added. Then the precipitated crystals were collected on a filter and dried to give crude 0.72 g of (3c). NMR ( $\delta$  in DMSO-d<sub>6</sub>) 3.56 (s, 3H, CH<sub>3</sub>N-),

2. 27 (d, J=1.0Hz, 3H, C4–<u>CH<sub>3</sub></u>) 6. 53 (d, J=1.0Hz, 1H, C5–<u>CH</u>) 1. 24 and 1. 17 (s, 6H, (<u>CH<sub>3</sub></u>)<sub>2</sub>CH), 4. 00–4. 50 (m, 1H, (CH<sub>3</sub>)<sub>2</sub>CH), 6. 60–6. 80 (b, 1H, <u>NH</u>, This signal disappeared by the addition of  $D_2O_2$ ).

(3d) : To a 100 ml sealed-tube was added (2) (0.0177 mole) and n-butylamine (6.5 g) in DMSO (20 ml). The solution was heated at 105° for 48 hr. After standing at room temperature for several hours, the crude product were collected on a filter, washed with DMSO, dried, and recrystallized from EtOH to give 1.9 g of (3d). NMR ( $\delta$  in CDCl<sub>3</sub>) 2.28 (d, J=1.0Hz, 3H, C4-<u>CH<sub>3</sub></u>), 3.58 (s, 3H, <u>CH<sub>3</sub>-N-</u>), 6.26 (d, J=1.0Hz, 1H, C5-<u>CH</u>), 0.94 (t, 3H, <u>CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>), 3.36-3.60 (m, 2H, CH<sub>3</sub><u>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>). 1.20-1.70 (m, 4H, CH<sub>3</sub>CH<sub>2</sub>(<u>CH<sub>2</sub>)<sub>2</sub></u>), 5.40-5.70 (b, 1H, NH, This signal disappeared by the addition of D<sub>2</sub>O.)</u></u>

(3e): This was prepared by the same procedures as (3d) from (2). method B

(3a): The mixture of (1) (0.005 mole) in acetonitrile (5 ml) and N-cyano-N', S-dimethylisothiourea (0.005 mole) was heated in a sealed-tube at 105° for 15 hr. The crystallized precipitate was collected on a filter and treated with an activated charcoal in pyridine. MS: m/e 209 (base), 179 (58), 154 (24).

(3b) and (3c): These were prepared by the same procedures as (3a) from N-cyano-N', S-dimethylisothiourea. (3b) MS: m/e 223 (base), 179 (53), 170 (29), 154 (80).

# Acid hydrolysis of (3).

(3a) (0.0096 mole) in conc.HCl (30 ml) was heated on a steam-bath for 2-3 hr. The pale-yellow solution was condensed *in vacuo*. The crude product (HCl salt) was dissolved in H<sub>2</sub>O and neutralized with a saturated NaHCO<sub>3</sub>aq. soln.. After stirring for 0.5 hr the free-base was collected on a filter and recrystalized from DMF to give N-(3, 4-dimethy1-4-thiazoline-2-ylidene)biuret (4). The HCl salt : mp. 220-225° (from Et-OH). Anal. calcd. for C<sub>7</sub>H<sub>11</sub>N<sub>4</sub>OSCl MW. 250.708 : C, 33.54% ; H, 4.42 ; N, 22.35. found C, 33.82% ; H, 4.55 ; N, 21.99. MS : m/e 214 (39%, M<sup>+</sup>), 171(21), 155 (base), 128(8), 100(4), 86(7), 71(6), 56(20). Each of (3a, b, c) or (6) derived from route A and B was hydrolized by the same procedures as described above. The infrared spectra of these products were identical with that of (4).

# **Deuteration of (4)**

(4) (50 mg) in DMSO-d<sub>6</sub> (1.5 ml) and  $D_2O$  was heated on a steam-bath for 5 hr. The hot solution was filtered. After standing at room temperature for several minutes, the crystalized precipitate was collected on a filter, and dried. mp 249°. MS: m/e 217 (38%), 185(8), 173(17), 155(base), 129(7), 128(7), 114(4), 100(6), 86(9), 71(12), 56(30).

# Ethanolic HCl hydrolysis of (3)

(3a) (0.005 mole) in ethanolic hydrochloride (20 ml) was heated at 80° for 4 hr and then concentrated *in vacuo*. The crude product was dissolved in H<sub>2</sub>O, filtered, neutrized with saturated sodium bicarbonate aq. soln. After standing for 0.5 hr the crystals were collected on a filter and recrystallized from EtOH or EtOH-H<sub>2</sub>O to give 0.3 g of N-ethoxycarbonyl-N'-methyl-N"-(3, 4-dimethyl-4-thiazoline-2-ylidene)guanidine (5a). NMR ( $\delta$  in CDCl<sub>3</sub>) 3.04 (d, J=5.0Hz, 3H, CH<sub>3</sub>NH, This signal changed to a singlet by the addition of D<sub>2</sub>O), 1.32 (t, J=7.0, 3H, CH<sub>3</sub>CH<sub>2</sub>O), 4.17 (q, J=7.0, 3H, CH<sub>3</sub>CH<sub>2</sub>O), 3.56 (s, 3H, CH<sub>3</sub>-N-), 2.24 (d, J=1.0, 3H, C4-CH<sub>3</sub>), 6.12 (d, J=1.0, 1H, C5-CH), 8.65 -9.08 (b, 1H, NH. This signal disappeared by the addition of D<sub>2</sub>O.) MS: m/e 256 (base), 223(8), 211(87), 210(66), 185(67), 178(24), 168(44), 155(61), 154(86), 153(19), 151 (31), 149(13), 139(14), 128(70), 113(19), 106(16), 86(18), 83(77).

(5c): This was prepared by the same procedures as (5a) from (3c). MS: 284(50%, M<sup>+</sup>), 269(11, M<sup>+</sup>-CH<sub>3</sub>), 251(13), 239(26, M<sup>+</sup>-OC<sub>2</sub>H<sub>5</sub>), 227(30), 155(34), 154(base), 138(9), 129(20), 128(21), 114(17), 113(21). Anal. calcd. for  $C_{12}H_{20}N_4O_2S$  (see Table 1) S:11.27 %, found, S:11.43%.

# N-cyano-N'-(3, 4-dimethyl-4-thiazoline-2-ylidene)guanidine (6)

The mixture of (2) (0.0265 mole) in ethanolic NH<sub>3</sub> in a 100 ml sealed-tube was heated at 105° for 48 hr. After standing for room temperature, the crystallized precipitate was collected on a filter and recrystallized from DMF-H<sub>2</sub>O to give 3.2 g of (6). NMR ( $\delta$  in DMSO-d<sub>6</sub>) 2.26 (d, J=1.0Hz, 3H, C4-CH<sub>3</sub>), 3.54 (s, 3H, CH<sub>3</sub>-N-), 6.47 (d, J=1.0, 1H, C5-CH) 7.04 (b, 2H, NH. This signal disappeared by the addition of D<sub>2</sub>O.)

			Tat	le 1 Pł	iysical	propert	ies					
	Formula	mp °C	UV · 2-PrOH	Analysi	s(%)	Calcd.			IR	KBr disl	R	
Compd. No.	MW	(recrys. solvent)	$\begin{array}{c} \lambda & \underline{-} & \underline{-} & \underline{-} \\ max & nm \\ (\varepsilon) \end{array}$	c	H	(found) N	>3000		-2000	max 1600	-1500	$-1400 \text{ cm}^{-1}$
(9)	C <sub>7</sub> H <sub>9</sub> N <sub>5</sub> S	247	234(7900)	43.06	4.65	35.87	3380sh	2900sh	2160vs	1655sh	1560sh	1500 – 1450 br
	195.248	$(DMF-H_2O)$	310(19900)	(43.05)	4.56	35.76)	3280m		2125 s	1638 s	1555sh	1410 s
							3180 s			1605sh	1530sh	
							3120m					
(3a)	C <sub>8</sub> H <sub>11</sub> N <sub>5</sub> S	>300	233(5200)	45.91	5.30	33.47	3250vs	2910m	2140vs	1600sh	1580sh	
	209.275	(pyridine)	260(5600)	(45.87	5.37	33.23)	3075 s				1575 s	
			313(21500)								1510br	
(3b)	C <sub>9</sub> H <sub>13</sub> N <sub>5</sub> S	268	236(5800)	48.41	5.87	31.36	3260vs	2975m	2140vs		1570m	1487m
	223.302	(pyridine)	260(6600)	(48.29)	5.78	31.26)	3085 s	2925m			1525br	1460 w
			313(23300)									
(3c)	$C_{10}H_{15}N_5S$	208	235(5800)	50.61	6 37	29.51	3250sh	2950m	2140vs	1600sh	1580sh	1475br
	237.329	(EtOH)	260(6600)	(50.64)	6.34	29.59)	3213 <b>m</b>	2900m			1570m	1440br
			313(23500)				<b>3080m</b>				1520br	1400m
(3q)	$C_{11}H_{17}N_sS$	233	235(5900)	52.56	6.82	27.86	3255vs	2940m	2140vs	1600sh	1578sh	1490 s
	251.356	(EtOH)	263(6700)	(52.52	6.63	27.74)	3080 s	2910m			1570 s	1460sh
			313(23600)					2840sh			1560sh	1420br
											1510 s	
(3e)	C <sub>19</sub> H <sub>33</sub> N <sub>5</sub> S	148	235(5600)	62.77	9.15	19.26	3400br	2940sh	2150vs	1600m	1580vs	1490 s
	363. 572	(EtOH)	262(6600)	(63.08	9.06	19.28)	3240vs	2905vs			1515 s	1455sh
			313(23200)				3075sh	2840 <sup>ws</sup>			1508sh	1420vs
(4)	$C_7H_{10}N_4O_2S$	246	235(900)	39.24	4.71	26.15	<b>3300m</b>			1690sh	1585br	1490m
	214.247	(DMF)	298(8100)	(39.19)	4.74	25.58)	3140br			1680m	1505sh	1455sh
										1615br		1440m
(5a)	$C_{10}H_{16}N_4O_2S$	148	245(8000)	46.86	6.29	21.86	3315vs	2975 m		1640sh	1585vs	1480m
	256.328	(EtOH)	313.5(21300	)(46.89	6.23	21.87)	3075 s	2940m		<b>1630vs</b>	1550sh	1450br
								2885 w		1600sh	1520br	1418 w
											1510sh	

- 56 -

No.23 (1978)

(2c)	C <sub>12</sub> H <sub>20</sub> 284. 33	₀N₄O₂S 32 (	116 EtOH-H <sub>2</sub> O)	248() 314()	8700) 21700)	50.68 (50.63	3 7.0 3 6.9	919 019	. 70 . 56)	3575 3500		955m 925m			1650sl 1630v	n 15 s 15	90sh 80br	147 143	0 s		
										3440 3325 3125 3125	s s E s	<b>H</b> 006			1615n	12	35br	140	5vs		
(2)	C <sub>6</sub> H <sub>10</sub> ]	N4S2	224-7	290(	6400)	42.4(	5 4.4	5 24	. 76	3425	br 2	910m	216(	)sh		15	86m	149	5sh		
	226. 3	24 (	(DMSO)	336(	23600)	(42.8	5 4.4	9 24	. 78)	3088	В		214(	SV(		15	50sh	148	u O		
																15	25sh	146	2m		
																15	15sh				
						abb sh:	reviati shoul	ion der, v	w : we	ak, t	br : br	oad, 1	n : me	diun	l,s : s	trong	vs:	Verv	stro	D.C.	1
																I				I	
			L	able 2 N	Aass sp	ectral	data r	n/e (	Relati	ve Ir	itensit	y:%	~								
frag.	N + N	HJ +1	+ HJ)+M			2	Na +	н		Ν̈́Η	CH <sub>3</sub> -1 =C=N	Ĩ~s	;H <sub>3</sub>	СН	°-N-		<b>.</b>		ن= ۲	-CH3	ſ
compd.No.	-N1 - TA1						2				)	1	· <del>.</del>		HN≯S				<b>ר</b> גע		
(9)	↓ 195						↓ 179	176	170 1	68	55  ↓ 15	<u>→</u> =	53 139	129	↓ 128	127 1	13 8	82	72	56	ł
	(base)						(20)	$\overline{)}$	$\frac{)}{(-)}$	<u>ි</u>	10)(4	2 2	(8)	ଚ	9	(16)	18)	14) (4	<del>D</del> C	4)(34	G
(3a)	209						179	176	170 1	68 1:	55 15	<u>=</u>	53 139	129	128	127  1	13 8	6 82	72	56	
	(base)						(20)	(10)	$\frac{)}{(-)}$	19)	17)(3	<u>0</u> ೧	29)(24		(38)	(16)	27)(	16)(2	3)(2	0)(34	G
(3 P)	223	208				18	2 179	176	170 1	68 1:	55 15		53 139	129	128	127 1	13 8	6 82	72	56	
	(base)	(2)				9	(77)	$\underbrace{]}{}$	(39)	$\frac{0}{1}$	12) (8,	<u>ຕ</u> ຊ	35) (55	0 (15	(43)	8	47)(	13)((1	<u>8</u>	1)(42	୍
(3 C)	237	222				204 19	7 179	176	170 1	68 1:	55 15	<del></del>	53 139	129	128	127 1	13 8	82	72	56	
	(54)	(2)				(7)	1)(96)	$\underbrace{]}{}$	((01)	$\frac{2}{1}$	35) (be	ise) ((	52) (59	6)	(34)	6	24) (	2 2		4)(21	
(3 q)	251	236			222	210 20	9 179	176	170 1	68 1	55 15		53 139	129	128	127 1	13 8	6 82	72	56	
	(22)	(6)			(41)	(20) (4)	3)(96)	(12)	(22)(	<u>ි</u> බ	18) (ba	() (:	23) (19	(15)	(37)	<u>)</u> 9	17)(0	8 (8	<u></u> 0	5)(33	<u>_</u>
(3e)	363	348 334(19	) 320(23) 3	306(21)	222	20	9 179	176	170 1	68 1	55 15	<b>1</b>	53 139	129	128	127 1	13 8	6 82	72	56	
	(62)	(10)292(19	) 280(27) 2	278(18)	(base)	<u> </u>	2)(92)	(11)		3 3	18)(9;	<u>୦</u> ର	22)(13	(20)	(33)	<u> </u>	13)	<u>マ</u>	0	1)(30	9
		264(33	) 250(31) 2	237(30)	236(25)																

— 57 —



Fig. 1 UV absorption spectra of (6), (3a), and (4) in 2-PrOH (Merck).