

John J. D'Amico\*, Frederic G. Bollinger, Ching C. Tung and William E. Dahl

Monsanto Agricultural Products Company, Research Department, 800 N. Lindbergh Boulevard, St. Louis, Missouri 63167

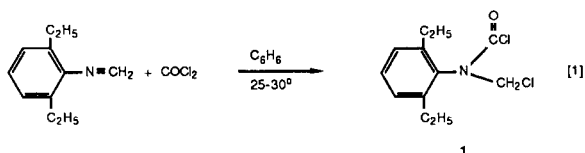
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The reaction of *N*-methylene-2,6-diethylbenzenamine with phosgene furnished the titled compound **1**. The reaction of **1** with the potassium salts of various thiazolethiols in an acetone medium afforded the expected *N*-substituted 2,6-diethylthiolcarbanilates **2-6**. Substituting the above thiazolethiols with the potassium salt of 2-mercaptobenzimidazole furnished a novel heterocyclic compound **7** in 98% yield. The reaction of **1** with the triethylamine salt of disubstituted-dithiocarbamic acids afforded an alternate method for the synthesis of bis(*N*-substituted-thiocarbonyl)sulfides **8** and **9**.

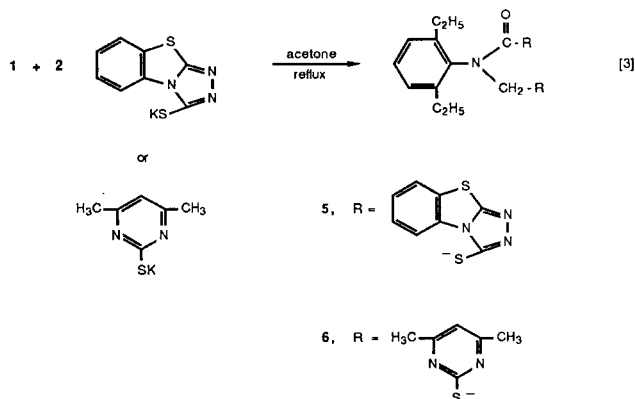
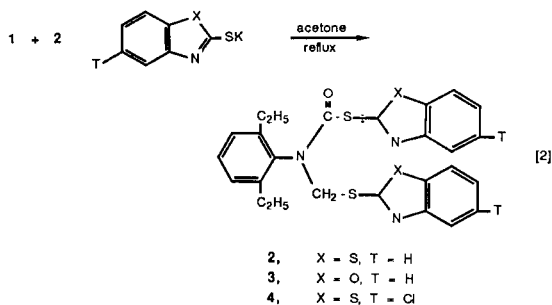
*J. Heterocyclic Chem.*, **24**, 945 (1987).

The purpose of this investigation was to prepare *N*-(chloromethyl)-2,6-diethylcarbaniloyl chloride (**1**) and to react **1** with various nucleophiles.

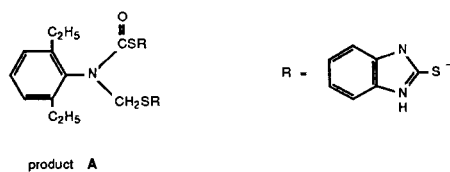
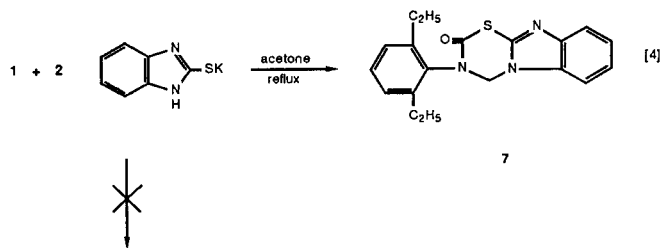
The key intermediate **1** was prepared in 74% yield by the reaction of *N*-methylene-2,6-diethylbenzenamine with phosgene.



The reaction of **1** with the potassium salts of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 5-chloro-2-mercaptobenzothiazole, 10-mercapto-2,3-azinomethylbenzothiazole or 4,6-dimethylpyrimidinethiol in spectral grade acetone afforded the following expected products: 2-benzothiazolyl-*N*-(2-benzothiazolylthiomethyl)-2,6-diethylthiolcarbanilate (**2**), 2-benzoxazolyl-*N*-(2-benzoxazolylthiomethyl)-2,6-diethylthiolcarbanilate (**3**), 5-chloro-2-benzothiazolyl-*N*-(5-chloro-2-benzothiazolylthiomethyl)-2,6-diethylthiolcarbanilate (**4**), *S*-triazole[3,4-*b*]benzothiazol-3-yl-2,6-diethyl-*N*-(*s*-triazolo[3,4-*b*]benzothiazol-3-ylthiomethyl)thiolcarbanilate (**5**) and 4,6-dimethyl-2-pyrimidinyl-*N*-(4,6-dimethyl-2-pyrimidinylthiomethyl)thiolcarbamate (**6**), respectively. The chemical analysis and the nmr spectral data are in agreement for our proposed structures **2-6**. (Table I).



However, when the potassium salt of 2-mercaptobenzimidazole was reacted with **1** under the same reaction conditions as in reactions 2 and 3 the expected product **A** was not obtained but instead furnished a heterocyclic compound, 3-(2,6-diethylphenyl)-3,4-dihydro-2*H*-[1,3,5]thiadiazino[3,2-*a*]benzimidazol-2-one (**7**) in 98% yield. The electron mass spectrum for **7** furnished the molecular weight



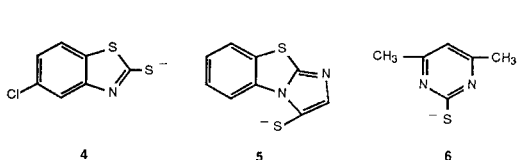
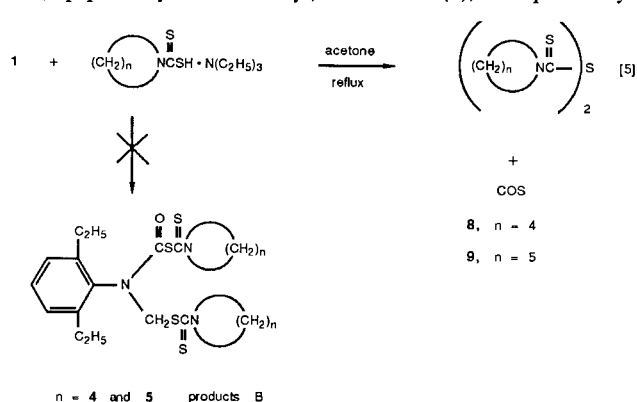
in the form of  $M^+$  at  $m/e$  337. Moreover, the chemical analysis and nmr spectral data for **7** are in complete agreement for our proposed structure.

Table I

No.	mp°	% Yield	nmr, $\delta$ , ppm CDCl <sub>3</sub> -Me <sub>4</sub> Si	Empirical formula	% C		% H		% N		% S	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
2	107-108 [a]	97	1.23 (t, 6, 2CH <sub>3</sub> CH <sub>2</sub> ) 2.67 (q, 4, CH <sub>3</sub> CH <sub>2</sub> ) 5.67 (s, 2, NCH <sub>2</sub> ) 7.01-8.00 (m, 11, ArH)	C <sub>26</sub> H <sub>23</sub> N <sub>3</sub> OS <sub>4</sub> [c]	59.85	59.92	4.44	4.28	8.05	7.90	24.58	24.67
3	141-142 [b]	51	1.24 (t, 6, 2CH <sub>3</sub> CH <sub>2</sub> ) 2.72 (q, 4, 2CH <sub>3</sub> CH <sub>2</sub> ) 5.60 (s, 2, NCH <sub>2</sub> ) 7.10-7.90 (m, 11, ArH)	C <sub>26</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	63.78	64.05	4.74	4.65	8.58	8.88	13.10	12.90
4	161-162 [d]	68	1.20 (t, 6, 2CH <sub>3</sub> CH <sub>2</sub> ) 2.65 (q, 4, 2CH <sub>3</sub> CH <sub>2</sub> ) 5.70 (s, 2, NCH <sub>2</sub> ) 7.00-7.90 (m, 9, ArH)	C <sub>26</sub> H <sub>21</sub> Cl <sub>2</sub> N <sub>3</sub> OS <sub>4</sub>	52.87	53.09	3.58	3.68	7.12	7.03	21.72	21.69
5	106-107 [e]	78	Insoluble in all solvents even dimethylsulfoxide	C <sub>28</sub> H <sub>23</sub> N <sub>7</sub> OS <sub>4</sub>	55.89	55.75	3.85	3.88	16.29	16.04	21.31	21.29
6	159-160 [b]	75	1.22 (t, 6, 2CH <sub>3</sub> CH <sub>2</sub> ) 2.13 (s, 6, CH <sub>3</sub> C=) 2.45 (s, 6, CH <sub>3</sub> C=) 2.73 (m, 4, 2CH <sub>3</sub> CH <sub>2</sub> ) overlapping q 5.57 (s, 2, NCH <sub>2</sub> ) 6.52 (s, 1, CH=CCH <sub>3</sub> ) Hindered Rotation 6.88 (s, 1, CH=CCH <sub>3</sub> ) Hindered Rotation 7.00-7.37 (m, 3, ArH)	C <sub>24</sub> H <sub>23</sub> N <sub>5</sub> OS <sub>2</sub>	61.65	61.52	6.25	6.32	14.97	14.83	13.71	13.48

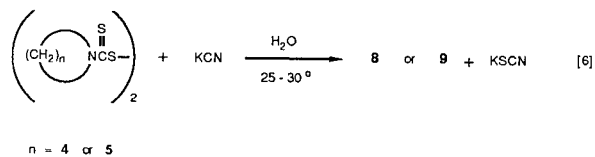
[a] Recrystallization from ethanol-ethyl acetate (3:1). [b] Recrystallization from ethanol. [c] Calcd. M.W. 531.7. Found: 532 (acetone). [d] Recrystallization from ethyl acetate. [e] Recrystallization from chloroform-ethanol (3:1).

It was anticipated that the reaction of the triethylamine salt of pyrrolidine or piperidinethiocarbamic acids with **1** would have afforded products **B**. However, our postulate was not substantiated for the products isolated in this reaction were bis(1-pyrrolidinylthiocarbonyl) sulfide (**8**) and bis(1-piperidinylthiocarbonyl) sulfide (**9**), respectively.



No.	mp°	% Yield	nmr, $\delta$ , ppm CDCl <sub>3</sub> -Me <sub>4</sub> Si	Empirical formula	% C		% H		% N		% S	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
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3	141-142 [b]	51	1.24 (t, 6, 2CH <sub>3</sub> CH <sub>2</sub> ) 2.72 (q, 4, 2CH <sub>3</sub> CH <sub>2</sub> ) 5.60 (s, 2, NCH <sub>2</sub> ) 7.10-7.90 (m, 11, ArH)	C <sub>26</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub>	63.78	64.05	4.74	4.65	8.58	8.88	13.10	12.90
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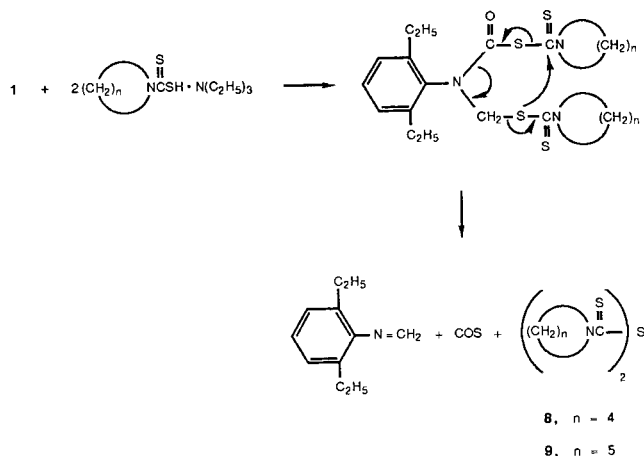
Proof of structure for **8** and **9** isolated in reaction 5 was established by the conventional reaction 6. A mixture melting point of **8** or **9** derived by reactions 5 and 6 was not depressed and their nmr spectra were superimposable. Evidence for the liberation of carbonyl sulfide in reactions 5



was obtained by the formation of the triethylamine salt of diisopropylthiocarbamic acid when the gas was allowed to bubble through a solution containing di-isopropylamine and triethylamine at 0-10°. The identification of the liberated carbonyl sulfide lends support for the proposed pathway depicted in Scheme I.



Scheme 1



## EXPERIMENTAL

The nmr spectra were obtained with a Varian T-60 nmr spectrometer. The chemical shifts are reported in  $\delta$  using tetramethylsilane as reference. All melting points were taken upon a Fischer-Johns block and are uncorrected. The electron impact spectrum for 7 was determined with a Varian-MAT CH-7A mass spectrometer operating at an ionizing potential of 70 eV using a direct insertion probe technique with a source temperature of 250°.

## N-(Chloromethyl)-2,6-diethylcarbaniloyl Chloride (1).

To a stirred solution (1 kg) containing 1.25 moles of 12.5% phosgene in benzene, 101 g (1.0 mole) of freshly prepared *N*-methylene-2,6-diethylbenzenamine was added dropwise at 20-25° over a 0.5 hour period. The reaction mixture was stirred at 25-30° for 2 days, then slowly heated to reflux and held at reflux for 2 hours to expel the excess phosgene. The benzene was removed *in vacuo* at a maximum temperature of 75° at 10 mm. The residue was distilled *in vacuo*. The product, an amber liquid, bp 125°/0.65 mm ( $n_D^{25} = 1.5429$ ), was obtained in 74% yield; nmr (deuteriochloroform):  $\delta$  1.22 (t, 6, 2  $\text{CH}_3\text{CH}_2$ ), 2.60 (q, 4, 2,  $\text{CH}_3\text{CH}_2$ ), 5.30 (s, 2,  $\text{NCH}_2$ ), 7.10-7.40 (m, 3, ArH).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{15}\text{Cl}_2\text{NO}$ : C, 55.40; H, 5.81; Cl, 27.26; N, 5.39. Found: C, 55.68; H, 5.64; Cl, 27.38; N, 5.35.

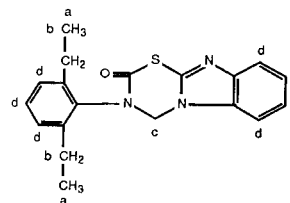
2-Benzothiazolyl-*N*-(2-benzothiazolylthiomethyl)-2,6-diethylthiolcarbanilate (2), 2-Benzoxazolyl-*N*-(2-benzoxazolylthiomethyl)-2,6-diethylthiolcarbanilate (3), 5-Chloro-2-benzothiazolyl-*N*-(5-chloro-2-benzothiazolylthiomethyl)-2,6-diethylthiolcarbanilate (4), *s*-Triazol[3,4-*b*]benzothiazol-3-yl-2,6-diethyl-*N*-(*s*-triazolo[3,4-*b*]benzothiazol-3-ylthiomethyl)thiolcarbanilate (5) and 4,6-Dimethyl-2-pyrimidinyl-*N*-(2,6-diethylphenyl)-*N*-(4,6-dimethyl-2-pyrimidinylthiomethyl)thiolcarbamate (6).

A stirred charge containing 0.2 mole of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 5-chloro-2-mercaptobenzothiazole, 10-mercapto-2,3-azinomethylbenzothiazole [2] or 4,6-dimethylpyrimidinethiol, 13.2 g (0.2 mole) of 85% potassium hydroxide and 400 ml of spectral grade acetone was heated at reflux for 30 minutes. After cooling to 30°, 26 g (0.1 moles) of 1 was added in one portion. The stirred reaction mixture was heated at reflux for 5 hours and thereafter at 25-30° for 24 hours. After cooling to 5°, 700 g of ice water was added and stirring was continued at 0-10° for 30 minutes. The solid was collected by filtration, washed with water until neutral and air-dried at 25-30°. The data are summarized in

Table I.

3-(2,6-Diethylphenyl)-3,4-dihydro-2*H*-[1,3,5]thiadiazino[3,2-*a*]benzimidazol-2-one (7).

The procedure was the same as described for 2-6 except 30 g (0.2 mole) of 2-mercaptobenzimidazole was employed as the nucleophile. Crude 7, mp 128-129°, was obtained in 98% yield. After recrystallization from ethyl alcohol it melted at 138-139°; nmr (deuteriochloroform):  $\delta$  1.24 (t, 6, a), 2.67 (q, 4, b), 4.87 (s, 2, c), 7.10-8.16 (m, 7, d); electron impact ms: *m/e* (relative intensity) 337 (72)  $\text{M}^+$ , 188 (58), 187 (23), 162 (22), 161 (82), 160 (32), 146 (100), 130 (18), 118 (71) and 91 (22).



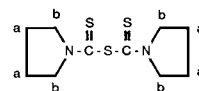
Anal. Calcd. for  $\text{C}_{15}\text{H}_{19}\text{N}_3\text{OS}$ : C, 67.63; H, 5.68; N, 12.45; O, 4.74; S, 9.50. Found: C, 67.43; H, 5.82; N, 12.23; O, 4.90; S, 9.56.

Bis(1-pyrrolidinylthiocarbonyl)sulfide (8) and Bis(1-piperidinylthiocarbonyl)sulfide 9.

## Method I.

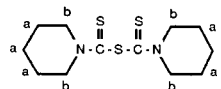
To a stirred slurry comprising 0.2 mole of triethylamine salt of pyrrolidine or piperidine dithiocarbamic acid [3] and 400 ml of spectral grade acetone, 26 g (0.1 mole) of 1 was added in one portion. The stirred reaction mixture was heated at reflux for 5 hours and therefore at 25-30° for 18 hours. During the heating period carbonyl sulfide was liberated. After cooling to 0°, 700 g of ice water and 50 ml of heptane were added and stirring continued at 0-10° for 30 minutes. The solid was collected by filtration, washed successively with 500 ml of water and 50 ml of heptane and air-dried at 25-30°. Crude 8, mp 110-115°, and crude 9, mp 118-119°, were obtained in 81% and 52% yield, respectively. After recrystallization from ethyl acetate 8 and 9 melted at 117-118° and 120.5-121.5°, respectively.

Compound 8; nmr (deuteriochloroform):  $\delta$  1.70-2.50 (m, 8, a), 3.60-4.20 (m, 8, b).



Anal. Calcd. for  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}_2$ : C, 46.11; H, 6.19; N, 10.76; S, 36.94. Found: C, 46.34; H, 6.27; N, 10.70; S, 36.88.

Compound 9; nmr (deuteriochloroform):  $\delta$  1.50-1.90 (m, 12, a), 3.90-4.15 (m, 8, b).



Anal. Calcd. for  $\text{C}_{12}\text{H}_{20}\text{N}_2\text{S}_2$ : C, 49.96; H, 7.24; N, 9.71; S, 33.34. Found: C, 49.86; H, 7.19; N, 9.74; S, 33.12.

## Method II [4].

A slurry containing 0.1 mole of bis(1-pyrrolidinylthiocarbonyl)disulfide or bis(1-piperidinylthiocarbonyl)disulfide, 7.4 g (0.11 mole) of 96% potassium cyanide and 600 ml of water was stirred at 25-30° for 5 hours. The solid was collected by filtration, washed with 1 liter of water and air-dried at 25-30°. Crude 8, mp 114-116°, and crude 9, mp 115-117°, were obtained in 99% and 87% yield, respectively. After recrystallization from ethyl acetate 8 and 9 melted at 117-118° and 121-122°, respectively.

ly. A mixture melting point with **8** or **9** derived by Method I was not depressed and their nmr spectral data were superimposable.

Compound **8**.

*Anal.* Calcd. for  $C_{10}H_{16}N_2S_3$ : C, 46.11; H, 6.19; N, 10.76; S, 36.94. Found: C, 46.34; H, 5.99; N, 10.71; S, 36.75.

Compound **9**.

*Anal.* Calcd. for  $C_{12}H_{20}N_2S_3$ : C, 49.96; H, 7.24; N, 9.71; S, 33.34. Found: C, 49.80; H, 7.20; N, 9.70; S, 33.12.

REFERENCES AND NOTES

- [1] Presented at 21st Midwest Regional ACS Meeting, Organic Division, Kansas City, MO., November 1986.
- [2] E. B. Knott and L. A. Williams, U. S. Patent 2,861,076 (1958); *Chem. Abstr.*, **53**, 9251i (1959).
- [3] E. Morita and J. J. D'Amico, *Rubber Chem. Technol.*, **44**, 881 (1971).
- [4a] J. V. Braun and F. Stechele, *Ber.*, **36**, 2275 (1903); [b] A. D. Cummings and H. E. Simmons, *Ind. Eng. Chem.*, **20**, 1173 (1928); [c] A. Cambron, *Can. J. Res.*, **2**, 341 (1930).