

Construction of the infrared standardization curves. Accurately weighed amounts of the four alcohols, acrolein, and the tertiary amine were added to 49 g. of the appropriate solvent to give the required percentage solution. The infrared spectra (Perkin-Elmer Model 21) of the solutions were obtained in a 0.5-mm. sodium chloride absorption cell with a reference of solvent in a 0.5-mm. cell. This method gave excellent resolution of the peaks due to oxygen-hydrogen stretching at 3.00 microns in the alcohols, carbon-oxygen double bond stretching at 5.85 microns in the aldehydes, and the carbon-hydrogen stretching at 3.50 microns in the amine. The percentage transmissions of the oxygen-hydrogen, carbon-oxygen double bond, and the carbon-hydrogen peaks were determined for the various concentrations, and these were plotted against concentration to give the standardized curves. The curves showed both positive and negative deviations from Beer's Law, but subsequent determinations indicated that the curves were accurate to $\pm 2\%$.

Methods used in this study. One-gram samples of the four alcohols and *N,N*-dimethylaniline were weighed in a weighing bottle. The solvent (49 g.) and the manganese dioxide were weighed on a triple beam balance and placed in a flask equipped with a condenser and a sidearm that permitted samples to be taken. The compound was transferred from the weighing bottle to the flask with a hypodermic syringe. The reaction mixture was stirred with a Teflon-covered stirring bar and a magnetic stirrer. At the desired time stirring was stopped, the rubber bulb capping the sidearm was removed, and a sample was taken with a hypodermic syringe and transferred to the infrared cell. The per cent transmission of the sample was then determined.

When the reaction was carried out in a nitrogen atmosphere, a hypodermic needle which extended below the surface of the reaction mixture was pushed through the rubber bulb on the sidearm. Nitrogen was then passed through the solution for 0.5 hr. to remove the air present. The condenser was equipped with a mercury bubbler which was then closed to prevent air from entering the system. Samples were taken with a hypodermic syringe through the rubber bulb covering the sidearm.

In those reactions carried out at elevated temperatures a flask with a sidearm and a thermometer well was used. The reaction mixture was prepared in the usual manner. The temperature was controlled to $\pm 0.2^\circ$ by a Thermocap Relay (Niagara Electron Laboratories) which was attached to a thermometer placed in the thermometer well of the flask, which was heated with a heating mantle. To ensure better

thermal conductivity some mercury was placed in the thermometer well. The samples were obtained in the same manner as above.

X-ray study. An attempt was made to detect traces of the suspected permanganate in the dioxide of Attenburrow; Ball, Goodwin, and Morton; Maxwell, Thirsk, and Butler (No. 3); Baker Analyzed (Commercial); Glemsir (No. 2); and the dioxide prepared from the pyrolysis of manganous nitrate, by x-ray diffraction. An x-ray diffraction pattern (Phillips Standard Unit with Cu radiation) was first taken of potassium permanganate and this was used as a standard. The lines on the x-ray pictures of the above dioxides did not show any similarity to the lines produced by the potassium permanganate. In many instances the lines were blurred and this is in agreement with the analysis reported by Maxwell, Thirsk, and Butler¹⁶ who obtained dark brown pictures. The x-ray information is limited since it is difficult to detect materials present in concentrations of less than 5%.¹⁷

Ultraviolet study in the visible range. An attempt was made to detect the suspected permanganate in the above manganese dioxides with an ultraviolet spectrophotometer (Beckman Model DU). A preliminary study was made on permanganate in a mineral oil suspension, and it was found that absorption occurred between 540 and 545 m μ . The samples were prepared by suspending 100 mg. of the dioxides in 2.97–3.00 g. of mineral oil. The dioxides failed to give any absorption in the permanganate region, but this could be due to the inability of the apparatus to detect traces of permanganate present in concentrations less than 2%.¹⁸

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(16) K. H. Maxwell, H. R. Thirsk, and G. Butler, *J. Chem. Soc.*, 4210 (1952).

(17) C. W. Bunn, *Chemical Crystallography*, The Clarendon Press, Oxford, 1946, pp. 125–6.

(18) Private communication, Dr. W. C. Purdy, Dept. of Chemistry, University of Maryland.

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Structure and Antimicrobial Activity of the 3-Aminorhodanines

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Some *N*-substituted derivatives of 3-aminorhodanine have been synthesized by the cyclization of the corresponding carboxymethyl dithiocarbazates and their structures confirmed by infrared and ultraviolet spectra. Within this series, the most active compounds in producing inhibition of the growth of *A. niger* are the *p*-haloanilinerhodanines.

The antimicrobial activity¹ of the 3-phenyl- (IA) and 3-benzylrhodanines (IB) suggested the investigation of other 3-substituted rhodanines. By the principle of isosterism,² the 3-anilinerhodanines (IC) would be expected to resemble the

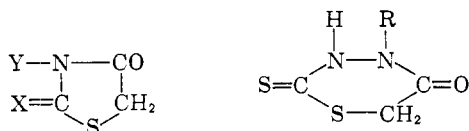
3-benzylrhodanines in activity. It was also anticipated that the presence of the amino group would perhaps lead to the possibility of salt formation and hence greater water solubility, since 3-amino-2,4-thiazolidine (ID) has been isolated as a hydrochloride salt.³

(1) F. C. Brown, C. K. Bradsher, E. C. Morgan, M. Tetenbaum, and P. Wilder, Jr., *J. Am. Chem. Soc.*, **78**, 384 (1956).

(2) H. Erlenmeyer, *Bull. soc. chim. biol.*, **30**, 792 (1948).

(3) H. W. Stephen and F. J. Wilson, *J. Chem. Soc.*, 2531 (1926).

3-Amino- (IE)^{4b,c} and 3-anilinothodaninane (IC)^{4a,c} were reported about fifty years ago; the former melts at 92°, the latter at 133.5–134°. By the same procedure, Mathes⁵ obtained compounds with the same melting points, but he formulated the products as derivatives of the six-membered 1,3,4-thiadiazine structure, IIA and IIB. Such compounds would be expected to tautomerize to the thioenol form and be soluble in base. Diacetyl derivatives of the compound melting at 92° have been pre-

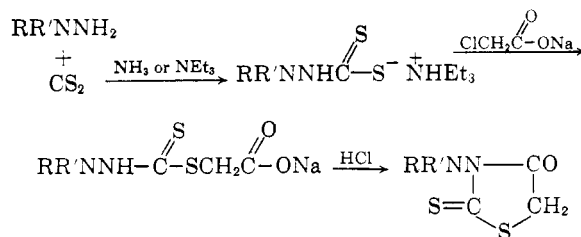


- IA. X = S; Y = C₆H₅
 IB. X = S; Y = CH₂C₆H₅
 IC. X = S; Y = NHC₆H₅
 ID. X = O; Y = NH₂
 IE. X = S; Y = NH₂
 IF. X = S; Y = N(CH₃)₂
 IIA. R = H
 IIB. R = C₆H₅

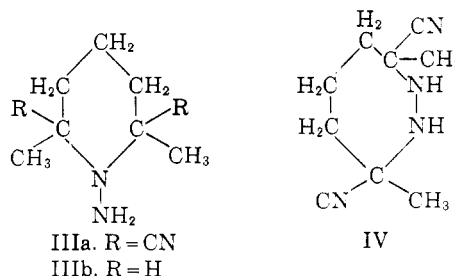
pared,⁶ but it is obvious that either structure (IE or IIA) would be expected to form a diacetyl derivative.

Chemical evidence in favor of the 3-aminorhodaninane structure has been reported recently,^{7,8} and includes the replacement of the amino group by hydrogen on treatment with nitrous acid, a reaction characteristic of an amino group attached to the nitrogen of a heterocyclic ring, the formation of two different benzylidene derivatives, one of which is considered to be a Schiff base and the other a 5-methylene derivative, and a dibenzylidene derivative. The compound assigned the structure of 3-aminorhodaninane, and melting at 91–92°, solidifies above the melting point and remelts at 100–101°. Sandstrom⁷ attributes this behavior to polymorphism.

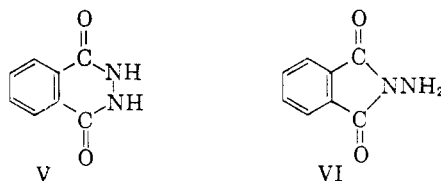
It seemed probable that evidence concerning the structure could be obtained from the infrared and ultraviolet absorption spectra of the compounds. Starting with hydrazine or substituted hydrazines and using general methods previously described, we obtained eleven compounds whose infrared and ultraviolet spectra were measured. In the synthesis, the dithiocarbazate salt was prepared from the hydrazine and carbon disulfide in the presence of a base and was treated with the salt of chloroacetic acid. The cyclization was usually effected with hot hydrochloric acid. One of the compounds (IF) was prepared from 1,1-dimethylhydrazine and must necessarily have the 3-amino structure.



Overberger and Marks,⁹ on the basis of infrared and chemical studies, assigned the structure of 1-amino-2,6-dicyano-2,6-dimethylpiperidine (IIIA) to the compound they had previously reported as 3,7-dicyano-3,7-dimethylhomopiperidazine (IV). They attribute a peak at 6.18–6.25 μ (1618–1600 cm.⁻¹) to the NH₂ bending frequency, and twin peaks in the 3 μ (3300 cm.⁻¹) region to NH₂ stretching. They also point out that these bands are present in 1-amino-2,6-dimethylpiperidine (IIIB). Spectral evidence was confirmed by chemical evi-



A similar structure assignment, but one in which both possible isomers have been isolated and characterized by chemical evidence, is that of phthalhydrazide (V) and *N*-aminophthalimide (VI).¹⁰ Both of these compounds were synthesized and their infrared spectra determined to discover bands which



might be characteristic of the two structures. Bands at 3335 cm.⁻¹ and at 1605 cm.⁻¹, similar to those found by Overberger and Marks and assigned to NH stretching and NH bending, are present in the *N*-aminophthalimide spectrum but are absent from that of phthalhydrazide (see Fig. 1).

A similar band at 3335 cm.⁻¹ and a shoulder at 1590 cm.⁻¹ in the cyclization product of carboxymethyl dithiocarbamate indicate that it has the structure of 3-aminorhodaninane (IE) rather than that of 1,3,4-thiadiazine (IIA). Likewise, 3-anilinothodaninane (IC) and its phenyl substituted deriva-

(4) (a) R. Andreasch, *Monatsh.*, **27**, 1211 (1906); (b) R. Andreasch, *Monatsh.*, **29**, 399 (1908); (c) B. Holmberg, *J. prakt. Chem.*, [2], **81**, 451 (1910).

(5) R. A. Mathes, *J. Org. Chem.*, **17**, 877 (1952).

(6) Z. P. Sytnik, S. V. Natanson, M. V. Deichmeister, and L. D. Zhilina, *Zhur. Obshchei Khim.*, **22**, 705 (1952).

(7) J. Sandstrom, *Arkiv Kemi*, **8**, 487 (1955).

(8) H. Ueda and M. Ohta, *Nippon Kagaku Zasshi*, **77**, 385 (1956); *Chem. Abstr.*, **52**, 401 (1958).

(9) C. G. Overberger and B. S. Marks, *J. Am. Chem. Soc.*, **77**, 4097 (1955).

(10) H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 16 (1937).

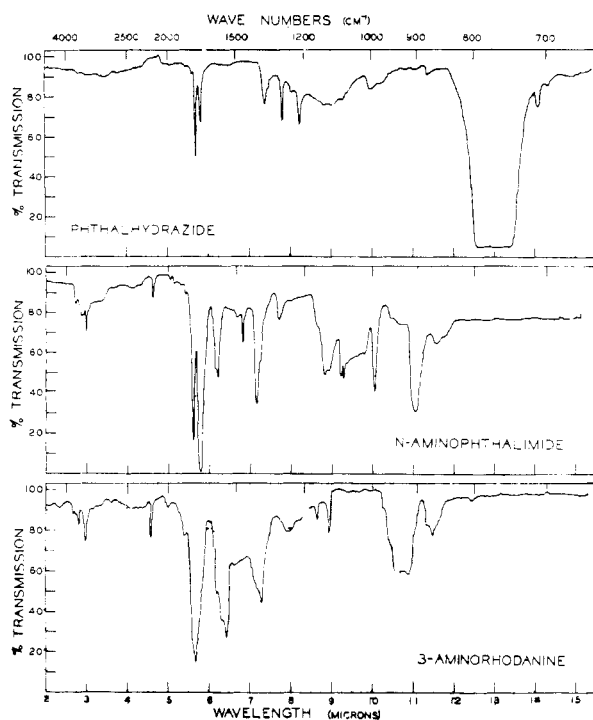


Fig. 1. Infrared absorption spectra

tives show bands in the same region. The absence of these bands in the spectrum of 3-dimethylaminorhodanine is further confirmation of the correctness of their assignment.

All of the compounds investigated have bands between 1745–1760 cm^{-1} , which are indicative of the presence of the carbonyl group. A band between 1470–1525 cm^{-1} is within the range ascribed to the thiureide group.¹¹ A band in the 1250 cm^{-1} region, which is usually comparable in intensity with the carbonyl group band, is present in all the 3-aminorhodanines, while another band which is usually less intense is found between 1092–1155 cm^{-1} , most frequently between 1100–1130 cm^{-1} . These bands are in the general region assigned to the C=S group, but further work is necessary before either band is definitely identified with this group.¹²

Ultraviolet spectra of the 3-aminorhodanines were compared with those of rhodanine, 3-benzylrhodanine and 3-*p*-bromobenzylrhodanine. Values of λ and $\log \epsilon$ are recorded in Table I. The two peaks characteristic of rhodanine, at 250.5 $\text{m}\mu$ and at 294 $\text{m}\mu$, are present at approximately the same wave

length in all cases except 3-aminorhodanine, for which the shorter wave-length peak is missing. Any shifting of wave length in the 3-anilino- and 3-*p*-bromobenzylrhodanines is toward shorter wave length, which is opposite to what might be expected if a six-membered ring, which should be less strained than the five-membered ring, were present.¹³ Values of $\log \epsilon$ are of the same order of magnitude for all the compounds investigated. There is an increase in the value of $\log \epsilon$ with an increase in the atomic weight of the halogen in the 3-*p*-haloanilino- and 3-*p*-bromobenzylrhodanines.

TABLE I
ULTRAVIOLET SPECTRA OF RHODANINE DERIVATIVES

R	λ , $\text{m}\mu$	\log ϵ_{max}	λ , $\text{m}\mu$	\log ϵ_{max}
H ^a	250.5	4.12	294	4.24
C ₆ H ₅ CH ₂	259	4.24	295	4.24
<i>p</i> -BrC ₆ H ₄ CH ₂	258	4.23	295	4.24
NH ₂	—	—	290.5	4.36
(CH ₃) ₂ N	253.3	4.24	294.5	4.21
C ₆ H ₅ NH	250.4	4.25	287	4.23
<i>p</i> -FC ₆ H ₄ NH	250	4.11	289	4.17
<i>p</i> -ClC ₆ H ₄ NH	248	4.37	290.5	4.23
<i>p</i> -BrC ₆ H ₄ NH	249	4.41	290.2	4.25
<i>p</i> -IC ₆ H ₄ NH	245.5	4.62	288.5	4.33
<i>p</i> -CH ₃ C ₆ H ₄ NH	250	4.16	289	4.17
<i>p</i> -CH ₃ OC ₆ H ₄ NH	251	4.25	289.5	4.29
<i>o</i> -ClC ₆ H ₄ NH	247.5	4.08	288	4.08
2,5-Cl ₂ C ₆ H ₃ NH	246.5	4.30	290.5	4.22

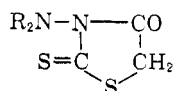
^a S. Menczel, *Z. Physik. Chem.*, **125**, 198 (1927) gives the following values for the maxima of rhodanine; $\lambda = 250.5$, $\log \epsilon = 4.17$; $\lambda = 291.2$, $\log \epsilon = 4.32$.

Table II records the results of antimicrobial testing. The compounds did not inhibit the growth of *E. coli*. and the slight inhibition of the growth of *B. subtilis* which several compounds showed does not appear to be of significant interest. However, in case of *A. niger*, the slow decrease of inhibition as the concentration was reduced seems noteworthy. Thus the four 3-*p*-haloanilino- and 3-*p*-bromobenzylrhodanines gave a range of inhibition between 70–84% at 250 p.p.m. and between 42–54% at 10 p.p.m. With a twenty-five fold decrease in concentration the per cent inhibition decreases only 50–67% and the concentration required to inhibit 50% of the growth of the organism would be of the order of magnitude of 10 p.p.m. In their greater activity against fungi than against bacteria, the 3-anilino- and 3-*p*-bromobenzylrhodanines resemble the previously reported 3-phenylrhodanines more closely than they do the 3-benzylrhodanines.¹

(13) Corresponding peaks of the less strained 2-thionc-4-keto-1,3-thiazane at 258.5 $\text{m}\mu$ ($\log \epsilon = 4.15$) and 309 $\text{m}\mu$ ($\log \epsilon = 4.16$) and of the strainfree ethyl acetyldithiocarbamate at 258.5 $\text{m}\mu$ ($\log \epsilon = 4.16$) and 309.5 $\text{m}\mu$ ($\log \epsilon = 4.11$) have been found by R. A. Potter, Ph.D. dissertation, Duke University, Durham, N. C.

(11) H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangle, *Infrared Determination of Organic Structures*, D. Van Nostrand Co., Inc., New York, 1949.

(12) Bands ascribed to C=S have been reported near 1110 cm^{-1} for thiolactams [R. Meeke and R. Meeke, *Chem. Ber.*, **89**, 343 (1956)], 1207–1225 cm^{-1} for thioketones [N. Lozač and G. Guillouzo, *Bull. soc. chim. France*, 1221 (1957)], 1210–1230 cm^{-1} for thioesters [R. Felumb, *Bull. soc. chim. France*, 890 (1957)], 1346–1395 cm^{-1} for 4-substituted thiosemicarbazones and 1338–1395 cm^{-1} for 1-substituted 2-tetrazoline-5-thiones [E. Lieber, C. N. R. Rao, C. N. Pillai, J. Ramachandran, and R. D. Hites, *Can. J. Chem.*, **36**, 801 (1958)].

TABLE II
 % INHIBITION OF GROWTH OF *A. niger*


R	250 P.P.M.	200 P.P.M.	100 P.P.M.	50 P.P.M.	25 P.P.M.	10 P.P.M.	Lowest Concentration Giving Complete Inhibition of	
							<i>B. subtilis</i>	<i>E. coli</i>
H	44%						200	>250
CH ₃	30%						250	>250
$ \begin{array}{c} \text{R}-\text{C}_6\text{H}_4-\text{NHN}-\text{CO} \\ \quad \\ \text{S}=\text{C} \quad \text{CH}_2 \\ \quad \quad \\ \quad \quad \text{S} \end{array} $								
H	14%						200	>250
<i>p</i> -F	76	72	64	60	55	50	200	>250
<i>p</i> -Cl	80 ^a	73	64	72	68	54	200	>250
<i>p</i> -Br	84	68 ^a	64 ^a	62 ^a	52 ^a	42 ^a	200	>250
<i>p</i> -I	70	64	52	46	42	42	>250	>250
<i>p</i> -CH ₃	56	61	48				200	>250
<i>p</i> -CH ₃ O	41						200	>250
<i>o</i> -Cl	66	55	42				>250	>250
2,5-Cl ₂	39						>250	>250

^a Average of two separate tests.

EXPERIMENTAL

All melting points are uncorrected and were taken on a Fisher-Johns hot stage.

Hydrazines. The hydrazines used in this work were commercially available or prepared by the reduction of the corresponding diazonium salts. The hydrochlorides of *p*-chlorophenylhydrazine, *o*-chlorophenylhydrazine, and *p*-tolylhydrazine were synthesized according to the directions of Bullock and Hand.¹⁴ *p*-Iodophenylhydrazine, melting at 95–102° (lit.¹⁵ 103°) and *p*-methoxyphenylhydrazine, melting at 35–40° (lit.¹⁶ 65°), were obtained by method A of the same authors in yields of 80% and 73%, respectively. *p*-Fluorophenylhydrazine hydrochloride, which melted at 208–210° after three crystallizations from hot water (lit.¹⁷ 216°), was prepared in 64% crude yield by method B.¹⁷ The hydrazines were usually obtained as the hydrochlorides and were neutralized with sodium hydroxide solution. If the free base was a solid at room temperature, it was isolated; if not, an ether extract of the aqueous mixture was dried and used without further treatment.

3-Aminorhodanine. This compound was prepared by the procedure of Sandstrom⁷ and was obtained as yellow spears, melting at 92–93°. On tapping the glass cover plate after the first melting, crystals appeared in the drop of liquid which solidified and remelted at 102–103°. An ethanol solution of the compound could be seeded with a crystal melting at 102–103° and yielded flat crystals with the higher melting point; an ethanol solution of the higher melting crystals could be seeded with the spearlike crystals to give the lower melting form. The analytical sample was recrystallized from 95% ethanol and melted at 94.5–94.6° (lit.⁷ 91–92° for needles; 100–101° for flat crystals).

Anal. Calcd. for C₅H₁₀N₂O₂S₂: C, 24.31; H, 2.72. Found: C, 24.37; H, 2.71.

(14) M. W. Bullock and J. J. Hand, *J. Am. Chem. Soc.*, **78**, 5854 (1956).

(15) A. Neufeld, *Ann.*, **248**, 93 (1888).

(16) J. Altschul, *Ber.*, **25**, 1842 (1892).

(17) I. M. Hunsberger, E. R. Shaw, J. Fugger, R. Ketcham, and D. Lednicer, *J. Org. Chem.*, **21**, 394 (1956).

The following derivatives, described by Sandstrom, were obtained: 3-amino-5-benzylidenerhodanine, melting at 192–195° (lit.⁷ 198–200°); 3-benzylideneaminorhodanine, melting at 134–135° (lit.⁷ 137–138°); 5-benzylidene-3-benzylideneaminorhodanine, melting at 168–172° (lit.⁷ 172–173°); and, by treatment with nitrous acid, rhodanine, melting at 167–168°. The melting point of rhodanine was not depressed on admixture with an authentic sample.

3-Dimethylaminorhodanine. 1,1-Dimethylhydrazine (20 g.) was added to 50 ml. absolute ethanol and mixed with 50 ml. of absolute ethanol which had been saturated with ammonia. The mixture was cooled with an ice bath and stirred while 20 ml. of carbon disulfide was added dropwise. Stirring was continued 2 hr. after the addition was complete. The solid which separated was filtered, washed with a mixture of ethanol and ether, and dried giving 41 g. salt and added to an aqueous solution of sodium chloroacetate prepared by the neutralization of 25 g. chloroacetic acid with sodium carbonate. The mixture was stirred for 1 hr. and poured into 70 ml. of hot 25% hydrochloric acid. When the solution was cooled, no crystals were obtained, but the addition of 20% NaOH until the pH of the solution was 4 gave a white solid which was soluble in excess base. The yield of carboxymethyl 3,3-dimethyldithiocarbamate was 31 g. (61%) and after three recrystallizations from water, the analytical sample melted at 141–142.5°.

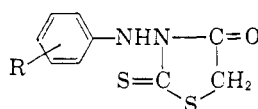
Anal. Calcd. for C₅H₁₀N₂O₂S₂: C, 30.91; H, 5.19; N, 14.49. Found: C, 31.19; H, 5.49; N, 14.57.

To a solution of 10 g. of the acid in 25 ml. ether and 25 ml. dioxane, 5.4 ml. of phosphorus tribromide was added carefully. The mixture was refluxed 2 hr. and poured onto ice. An oil separated which was dissolved in ethanol. After the ethanol solution had been treated with Norit, water was added to it until turbidity just appeared. The yield of 3-dimethylaminorhodanine was 3.2 g. (36%) which melted at 96–98°. After three recrystallizations the analytical sample melted at 104–104.5°.

Anal. Calcd. for C₅H₁₀N₂O₂S₂: C, 34.07; H, 4.57; N, 15.90. Found: C, 34.23; H, 4.65; N, 15.90.

Preparation of the 3-anilnorhodanines. One-tenth mole of the phenylhydrazine was dissolved in 150 ml. of anhydrous ether and 20 ml. of triethylamine added. The flask was sur-

TABLE III



R	M.P., °C.	Yield, %	Formula	Analyses					
				Calcd.			Found		
				C, %	H, %	N, %	C, %	H, %	N, %
H ^a	133-134 ^b	38 ^c	C ₉ H ₈ N ₂ O ₂						
<i>p</i> -F	135-137	23	C ₉ H ₇ FN ₂ O ₂	44.62	2.91	11.56	44.40	2.88	11.24
<i>p</i> -Cl	108.5-110.5	17.5	C ₉ H ₇ ClN ₂ O ₂ ^d	41.77	2.73	10.83	41.82	2.78	10.72
<i>p</i> -Br	137.5-138.5	17	C ₉ H ₇ BrN ₂ O ₂	35.64	2.33	9.24	35.62	2.44	8.54
<i>p</i> -I	163-164.5	21	C ₉ H ₇ IN ₂ O ₂	30.87	2.01	8.00	30.87	1.84	8.19
<i>p</i> -CH ₃	157-158	21	C ₁₀ H ₁₀ N ₂ O ₂	50.39	4.23	11.76	50.27	4.28	12.42
<i>p</i> -CH ₃ O	114.5-116	22	C ₁₀ H ₁₀ N ₂ O ₂ S ₂	47.22	3.96	11.02	47.24	3.89	10.66
<i>o</i> -Cl	138.5-140	42 ^c	C ₉ H ₇ ClN ₂ O ₂	41.77	2.73	10.83	41.86	2.69	10.86
2,5-Cl ₂ ^e	189-190 ^d	6 ^c	C ₉ H ₆ Cl ₂ N ₂ O ₂ ^f	36.87	2.06		36.97	2.09	

^a Prepared by the method of B. Holmberg, *J. prakt. Chem.*, [2] 81, 451 (1910). ^b Lit. 133.5-134° (Holmberg). ^c Crude yield. ^d Cl: Calcd., 13.70; found, 13.73. ^e This compound was obtained by treatment with PBr₃ as in the preparation of 3-dimethylaminorhodanine. ^f Cl: Calcd., 24.18; found, 24.32.

rounded by an ice bath and 10 ml. carbon disulfide added slowly while the mixture was stirred. At first an oil formed and then the solid dithiocarbamate precipitated. If necessary, seeds were obtained by dissolving a small amount of the oil in ether or ethanol and cooling or scratching the solution. Stirring was continued until the solid precipitated, which usually occurred within an hour's time. The solid was filtered, washed with ether and dried, unless evidence of decomposition (odor of hydrogen sulfide) was noticed. The solid was dissolved in 200 ml. water, using heat if necessary, and a solution of 0.1 mole sodium chloroacetate in 50 ml. water, prepared by neutralizing chloroacetic acid with sodium carbonate, was added. The mixture was stirred at room temperature until either the solid dissolved or a gum started forming in the flask or a noticeable amount of hydrogen sulfide was evolved. This required from 30 min. to 4 hr. The mixture was then poured into 100 ml. of hot 24% hydrochloric acid; heating was continued during the addition and for 20 min. afterwards or until a yellow oil or solid separated. On cooling, the product was usually a gum. If cyclization was incomplete, a white solid was present in the gum which could be removed by washing with aqueous sodium bicarbonate. The gum was washed thoroughly with water and recrystallized from absolute ethanol using Norit. Data on yields after one recrystallization (unless otherwise noted), melting points of analytical samples, and analyses are reported in Table III. The yields are not necessarily the maximum obtainable, as the purpose of this work was the preparation of small quantities of pure compounds for biological testing.

N-Aminophthalimide was prepared by the method of Drew and Hatt¹⁰ and melted at 192-199° (lit.¹⁰ 200-205°) after two recrystallizations from ethanol. After the first

melting, needles slowly formed in the liquid drop and a second melting was observed at 338°.

Phthalhydrazide was obtained in 52% yield by heating equimolar quantities of phthalic anhydride, hydrazine sulfate, and sodium acetate in dilute acetic acid for 4 hr. After two recrystallizations from ethanol, white crystals, melting at 330-333° (lit.¹⁰ 341-344°) were obtained.

The infrared spectra of *N*-aminophthalimide, phthalhydrazide, 3-aminorhodanine, 3-dimethylaminorhodanine, 3-anilino-rhodanine, and its *p*-chloro, *p*-bromo, and 2,5-dichloro derivatives were measured in chloroform solutions using a Perkin-Elmer Model 21 spectrophotometer; the others were obtained with an Infracord using KBr plates. The ultraviolet spectra were obtained with ethanol solutions of the compounds, using a Spectracord. The antimicrobial testing procedure was identical with that previously reported.¹

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