ethanolamine were commercial materials. The aliphatic aldehydes were redistilled before use.

1,1-Bis(2-hydroxyethyl)hydrazine solution. Concentrated ammonium hydroxide (13.4 ml.) was added slowly to 161 g. (0.113 mole) of cold (0°), 5.25% commercial sodium hypochlorite solution. The temperature was held below 5° during the addition. To this cold solution was added 12.5 g. (0.113 mole) of diethanolamine. The solution was warmed to room temperature slowly (6 hr.) and used in the following preparations in which it is designated as hydrazine solution (A).

9-Anthraldehyde 1,1-bis(2-hydroxyethyl)hydrazone. The hydrazine solution (A) prepared as described above was concentrated to a volume of 50 ml. by heating on a steam bath under vacuum. Seventy-five milliliters of methanol were added and the solution filtered to remove the precipitated sodium chloride. Two grams of 9-anthraldehyde were added to 21.5 ml. of this solution and the mixture heated to reflux for 18 hr. The orange crystals which separated upon cooling to room temperature were collected, dried, and taken up in 100 ml. of ether. The ether solution was washed with a dilute sodium bisulfite solution twice, then once with water, and evaporated to dryness. Recrystallization of the orange crystalline residue from ethanol-water gave 2.8 g., 93.6%, of the orange crystals, m.p. 80–81°. A second recrystallization from ethanol-water produced no change in the melting point.

1-Hexanal 1,1-bis(2-hydroxyethyl)hydrazone. To the 1,1-bis(2-hydroxyethyl)hydrazine solution (A) prepared as described above were added 100 ml. of methanol and 7.5 g. (0.075 mole) of 1-hexanal. The mixture was warmed to 50–60° for 0.5 hr. and then allowed to stand at room temperature overnight. After concentration to 100 ml. on a steam bath under vacuum, the solution was saturated with sodium chloride and extracted twice with 125 ml. portions of ether. Removal of solvent and distillation of the residue gave 6.9 g., 45.5%, of the colorless product, b.p. 89–90° at 0.9 mm.

Benzaldehyde 1,1-bis(2-hydroxyethyl)hydrazone. Twice the quantity of 1,1-bis(2-hydroxyethyl)hydrazone (0.226 mole) solution (A) prepared as described above was concentrated to a volume of 300 ml. on a steam bath under vacuum. To this solution was then added 10.6 g. (0.1 mole) of freshly distilled benzaldehyde and 100 ml. of methanol. After refluxing for 2 hr. and standing at room temperature overnight, the mixture was concentrated to 275 ml. on a steam bath under vacuum and extracted twice with 175-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate. The ether was removed on a water bath and the residue distilled to give 11.55 g., 55.6% of the product, b.p. 161° at 0.1 mm.

Pyridine-2-carboxaldehyde 1,1-bis(2-hydroxyethyl)hydrazone. A solution of 1,1-bis(2-hydroxyethyl)hydrazone prepared as described above for solution (A) but with four times the quantities was concentrated to 400 ml. on a steam bath under vacuum and was made acidic to congo red with concd. hydrochloric acid. Seventeen and one-half grams of pyridine-2-carboxaldehyde were then added and the mixture heated to reflux for 15 min. Upon cooling to room temperature the solution was made basic to litmus and extracted twice with 200-ml. portions of chloroform. After drying 3 hr. over magnesium sulfate, the solvent was removed and the residue fractionated very slowly to yield 9.34 g., 27.3%, of the product, b.p. 188–193° at 0.5 mm. The viscous oil crystallized to give the solid product, m.p. 53–60°.

Attempted preparation of 4-acetamidobenzaldehyde 1,1-bis-(2-hydroxyethyl)hydrazone. A solution (A) of 1,1-bis(2-hydroxyethyl)hydrazine, prepared as described above, was concentrated on a steam bath under vacuum to 100 ml. The precipitated sodium chloride was then removed by filtration and the resulting liquid added to a solution containing 6.0 g. (0.0369 mole) of 4-acetamidobenzaldehyde in 100 ml. of ethanol. After refluxing gently for 1 hr. the mixture was cooled to room temperature and 200 ml. of water added. Upon standing 4 hr. in an ice bath the yellow crystals which had separated were collected by filtration and recrystallized from acetone-ethanol to give 0.2 g. of the product, m.p. 325°, with decomposition.

Benzaldehyde 1,1-bis(2-chloroethyl)hydrazone. Five and one-half grams (0.0263 mole) of benzaldehyde 1,1-bis(2-hydroxyethyl)hydrazone were mixed with 55 g. of phosphorus oxychloride and the mixture heated to reflux for 1 hr. The excess of liquid was removed by distillation on a steam bath under vacuum and the residue treated with 300 ml. of water. The solution was then extracted with 300 ml. of ether and the ether extract washed with 5% sodium bicarbonate solution. After drying over magnesium sulfate overnight the ether was removed on a steam bath and the product distilled carefully to yield 2.80 g., 43.5%, of product, b.p. 126° at 0.3 mm.

Infrared spectra were determined using a Baird double beam recording spectrophotometer against the 3.419 μ band for polystyrene and were run in carbon tetrachloride, chloroform, or potassium bromide as indicated in the Table. Ultraviolet spectra were made with a Beckman DK 3 recording spectrometer in spectral grade chloroform.

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Action of Grignard Reagents on Heterocyclic Compounds. IV.[1] Action of Grignard Reagents on Some Substituted Rhodanines

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Recently, substituted rhodanines that contain the toxiphoric dithiocarbamate chromophore —NCS_2— have received much attention as fungicides and mildew proofing agents,[2] and antimicrobal compounds.[3] It was thus of interest to prepare some differently substituted rhodanines which might be of use in this field. Mustafa, *et al.*[4] have allowed benzylidenerhodanine to react with Grignard reagents and they have stated that Grignard reagents add to the double bond of the lateral chain. The infrared measurements of their products (IId and IIe) are in favor of the constitution pro-

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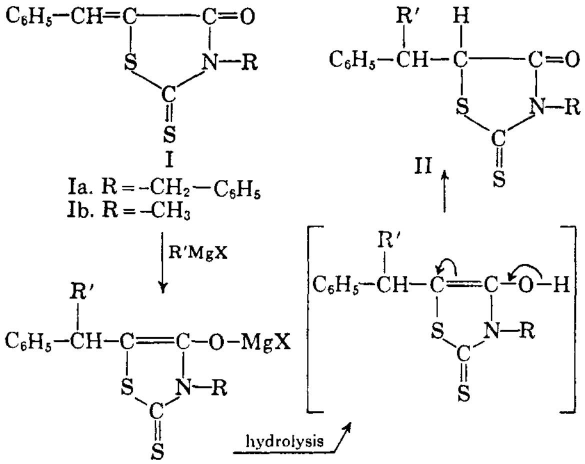
posed (*cf.* Table I). We have now allowed the benzylidene derivatives of *N*-methyl- and *N*-benzylrhodanine to react with arylmagnesium halides. The following scheme is proposed for such a reaction:



IIa. R = C_6H_5—CH_2, R' = C_6H_5
IIb. R = C_6H_5—CH_2, R' = α-$C_{10}H_7$
IIc. R = CH_3, R' = $C_{10}H_7$(α)
IId. R = H, R' = C_6H_5 and
IIe. R = H, R' = CH_3

Similar 1,4-additions have been found in the case of 3-methyl-4-benzylideneisoxazolone[5] and 2-phenyl-4-benzylidene-2-imidazoline-5-one.[1] The constitution of II is mainly based on: i) similarity with the above mentioned reactions, ii) analytical data which show that one mole of the Grignard reagents only add to one mole of I, and iii) infrared spectra of the starting material and the products which show the persistance of the carbonyl stretching frequency (*cf.* Table I).

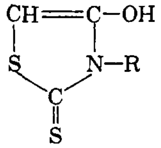
TABLE I[a]

INFRARED SPECTRA OF REACTANT AND PRODUCTS

Compound	C=O	C=C conjugated with C=O and aromatic ring	C=S in $\underset{\text{S}}{\underset{\|}{\text{C}}}$—N—$\underset{\text{O}}{\underset{\|}{\text{C}}}$—
Rhodanine	1754 1724		1408
Benzylidene-rhodanine I, R=H	1724	1612	1408
IId	1739		1408
IIe	1739		1408
N-Benzyl-rhodanine	1709		1412
Benzylidene-*N*-benzyl-rhodanine Ia	1709	1587	1420
IIa	1724		1408
IIb	1724		1428
N-Methyl-rhodanine	1724		1408
Benzylidene-*N*-methyl-rhodanine Ib	1709	1600	1418
IIc	1724		1428

[a] Infrared measurements were carried out using a Perkin-Elmer Infracord Model 137, and are measured in cm.$^{-1}$

It is also to be noticed that rhodanine itself, *N*-methyl- or N-benzylrhodanine are obtained unchanged on treatment with Grignard reagents. This fact may be attributed to the possible enol form of such a compound. (*cf.* III).



III

An infrared investigation of several rhodanine derivatives (*cf.* Table I) was carried out. In all cases two main bands were observed, namely a carbonyl stretching frequency ranging from 1709–1754 cm.$^{-1}$, and a thiocarbonyl stretching frequency in CO—N—C=S structure ranging from 1408–1428 cm.$^{-1}$ The thiocarbonyl stretching frequency is slightly shifted towards longer wave lengths than that described by Bellamy[6] for thioureides (1513–1471 cm.$^{-1}$). This may be attributed to the fact that rhodanines are cyclic structures.

Rhodanine and benzylidenerhodanine are sparingly soluble in carbon tetrachloride and their infrared measurements were carried out in chloroform. The rest of the infrared measurments of the other compounds were carried out in carbon tetrachloride. The authors believe that the presence of these bands together with the shift of the thiocarbonyl stretching frequency discussed before can be taken as a criterion for the presence of such a cyclic structure. In the case of the infrared spectra of the benzylidene derivatives another strong band appears in the region of 1587–1612 cm.$^{-1}$ which is attributed to carbon-carbon double bond conjugated with a carbonyl group and an aromatic nucleus.

It is also to be mentioned here that *N*-methylrhodanine and *N*-benzylrhodanine have been prepared by a method similar to that described for rhodanine itself.[7] The benzylidene derivatives were prepared by a method similar to that described for isoxazolones.[8]

EXPERIMENTAL[9]

General procedure for the reaction of substituted rhodanines with Grignard reagents. To an ethereal solution of Grignard

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(6) L. J. Bellamy, *The Infrared Spectra of Complex Molecules.* Metheum, London, 1956, p. 294.

(7) C. Ernest Redemann, Roland N. Lake, and Gordon A. Alles, *Org. Syntheses,* Coll. Vol. III, 763 (1955).

(8) *The Chemistry of Penicillin,* Princeton University Press, Princeton, N. J., 1949, p. 738.

(9) The analyses were carried out by Alfred Bernhardt, Mülheim, Ruhr Germany. The melting points were not corrected.

TABLE II

PRODUCTS FROM THE REACTION OF SUBSTITUTED RHODANINES WITH GRIGNARD REAGENTS

Compound Number	Solvent of Crystallization	M.P.	Yield,[c] %	Formula[d]	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
IIa	B	88–89	38	$C_{23}H_{19}ONS_2$	70.92	71.07	4.8	4.78	3.5	3.49	16.4	16.31
IIb	B	164–165	40	$C_{27}H_{21}ONS_2$	73.8	74.12	4.78	4.66	3.1	3.07	14.5	14.43
IIc	B	187–188	45	$C_{21}H_{17}ONS_2$	69.4	70.03	4.6	4.64	3.8	3.51	17.6	16.71
IId	A	163–164	75	$C_{16}H_{13}ONS_2$	64.2	64.49	4.3	4.36	4.69	4.8	21.4	21.4
IIe	A	140–141	50	$C_{11}H_{11}ONS_2$	55.69	55.44	4.63	4.55	5.90	5.76	27.0	26.06

[a] Solvent, petroleum ether (b.p. 70–80°). [b] Solvent, benzene–methyl alcohol mixture. [c] Calculated for the pure product. [d] All crystals were colorless.

reagent (3 moles), was added a solution of the substance (Ia or Ib) (1 mole) in benzene. The reaction mixture was refluxed for 2 hr. and left overnight. It was then hydrolyzed with saturated ammonium chloride solution, dried over anhydrous sodium sulfate, and evaporated on a water bath nearly to dryness. The oily residue thus obtained was triturated with petroleum ether (b.p. 40–60°) and allowed to cool. The product was filtered off and recrystallized from a suitable solvent (*cf.* Table II).

Preparation of N-benzylrhodanine.[10] The procedure adopted here is similar to that described for rhodanine,[7] using benzylamine instead of ammonia. The yield is almost quantitative, m.p. 94–96°.

Anal. Calcd. for $C_{10}H_9ONS_2$: N, 6.27; S, 27.8. Found: N, 6.28; S, 28.52.

Preparation of benzylidene-N-benzylrhodanine (Ia).[11] N-Benzylrhodanine (2 g.) was dissolved in hot alcohol (80 ml.), then benzaldehyde (4 ml.) and pyridine (2.5 ml.) were added. The reaction mixture was left at room temperature for 0.5 hr. and then cooled in ice. Water was then added until the solution became turbid. After a short time, the solid so obtained was recrystallized from benzene. The yield was almost quantitative, m.p. 158–159°.

This compound was also prepared according to Andreasch[12] and the melting point was the same as described here and not 219° as stated in the reference.

Anal. Calcd. for $C_{17}H_{13}ONS_2$: C, 65.6; H, 4.18; N, 4.5; S, 20.57. Found: C, 65.99; H, 3.97; N, 4.23; S, 20.27.

Preparation of N-methylrhodanine.[13] The procedure adopted for this compound was similar to that described for rhodanine,[7] using methylamine gas instead of ammonia. The yield was almost quantitative and the product was recrystallized from benzene-petroleum ether (b.p. 40–60°), m.p. 69–70°.

Anal. Calcd. for $C_4H_5ONS_2$: C, 32.69; H, 3.40; N, 9.52; S, 43.5. Found: C, 33.36; H, 3.5; N, 9.05; S, 40.92.

Preparation of benzylidene-N-methylrhodanine (Ib).[14] The procedure was similar to that described for Ia. It was recrystallized from benzene in an almost quantitative yield as yellow crystals, m.p. 167–168°.

Anal. Calcd. for $C_{11}H_9ONS_2$: C, 56.18; H, 3.83; N, 5.95; S, 27.14. Found: C, 56.92; H, 3.71; N, 5.81; S, 26.39.

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(11) Andreasch, *Beil*, **27**, 273 (1937).
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(13) Andreasch, *Beil*, **27**, 243 (1937).
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4-[*N*,*N*-Bis(2-haloethyl)amino]benzaldehyde Derivatives

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N-Phenyldiethanolamine has been converted to 4-[*N*,*N*-bis(2-chloroethyl)-amino]benzaldehyde in one step in 58% yield by reaction with phosphorus oxychloride in dimethylformamide. This synthesis offers advantages over that previously described[1]

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