ium ion process cannot be ruled out, particularly in view of Rylander's[11] recent demonstration of the existence and stability of the tropylium ion in the gas phase.

Equation 3 accounts for the observed small amounts of benzene and ethylene. The absence of benzene in Run 2 (Table I), where a large excess of butane was present, is consistent with such a bimolecular process.

EXPERIMENTAL

Bicyclo[2.2.1]heptadiene was generously supplied by the Shell Chemical Corp. and was distilled before use.

Apparatus. A 1.8 cm. o.d. by 50 cm. long horizontal Pyrex furnace with a volume of 85.5 ml. and fitted with a concentric thermocouple well was used in the pyrolyses. Liquid reactants were introduced through a vertically attached tube by means of a graduated dropping funnel. The gas streams were passed in through a flow meter which was calibrated against pure *n*-butane and could be adjusted to give a residence time of 10 sec. in the furnace.

Method. In the diazomethane-*n*-butane experiments, a 500-ml. flask was used as a diazomethane generator. After flushing the system with *n*-butane, the diazomethane generator (containing 2 g. of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and 50 ml. of cold 50% potassium hydroxide solution) was slowly warmed to 70° with a water bath. When the bath reached 50° the Dry Ice trap was attached. At the peak of diazomethane generation, a minor explosion was usually observed in the generating flask.

Except in Runs 3 and 5, the products were stored at −80° until analyzed by GLPC. All GLPC analyses were performed with a Perkin Elmer Vapor Fractometer Model 154B. Low boiling materials were chromatographed at 30° on a 4-m. type "A" column packed with di-*n*-decyl phthalate on Celite. The analyses in Table I were obtained on a 2-m. type "B" column packed with ethyl hexyl sebacate on Celite at 80°. In order to show the sharpness of the separations attained, retention times at 30° and 80° for all the compounds studied are given in Table III. Comparative retention times were obtained on authentic specimens of all products and known mixtures were used for quantitative calibration. Areas were measured with a planimeter and only small corrections were necessary to convert area per cent to weight per cent.

A high purity specimen of CHT was obtained by distillation of the pyrolyzate from Run 6 through a spinning band Podbielniak column. GLPC analysis of a fraction boiling at 117° is given in Table IV along with the product analysis for its pyrolysis at 478° (Run 7).

TABLE III

GLPC Retention Times[a]

Component	Type "A" Column, 30°	Type "B" Column, 80°
Air	1.65 (1.75)	0.65 (0.7)
n-Butane	3.9 (4.05)	0.9 (1.1)
Isopentane	8.0 (8.6)	1.7 (1.85)
n-Pentane	10.4 (11.1)	2.3 (2.5)
CPD	21.9 (23.2)	3.9 (4.25)
Benzene	—	11.4 (12.2)
BCH	—	13.3 (14.1)
Toluene	—	26.4 (29.3)
CHT	—	30.5 (32.0)

[a] In minutes. Helium was used as the carrier gas at a flow rate of about 120 ml./min. The first number denotes the appearance of the initial rise of the peak. The retention time for the peak maximum is given in parentheses. Deviations from these average values occurred when very large or very small amounts of the component were present.

TABLE IV

Data on the Purity and Pyrolysis of CHT

Component	Mole %, CHT[a]	Mole %, Run 7[a,b]
CHT	98.67	0.87
Toluene	0.0	96.48
CPD	0.43[c]	0.89
Benzene	0.89[c]	1.76

[a] Analyses at 80° on a type "B" column. [b] A trace of ethylene was identified by mass spectrometry in the material collected in a liquid nitrogen trap. [c] Carried over during fractionation because of a vapor pocket in the top of the Podbielniak column.

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General Electric Research Laboratory
Schenectady, N. Y.

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Condensation of Rhodanine with Pyridine and Quinoline Aldehydes

Frederick J. Allan, G. Graham Allan[1], and James B. Thomson[2]

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5-Substituted rhodanines (I), which contain the toxiphoric dithiocarbamate chromophore —NCSS— have been the subject of scrutiny as fungicides and mildew-proofing agents.[3-9] Among the most effective were those obtained by condensation of rhodanine with the heterocyclic aldehydes of the furan and thiophen series.[8] Since carbonyl derivatives of

(1) Present Address; Electrochemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

(2) Present Address; Royal College of Science and Technology, Glasgow, Scotland.

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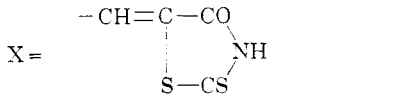
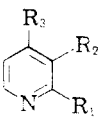
pyridine and quinoline aldehydes have been reported to possess antibacterial properties,[10–13] we have prepared substituted 5-methylene-rhodanines from the unsubstituted aldehydes of the pyridine series and two of the quinoline series for fungicidal and antibacterial evaluation.

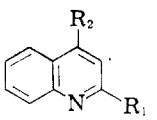


I



II

a. R_1 = CHO; R_2 = R_3 = H
b. R_2 = CHO; R_1 = R_3 = H
c. R_3 = CHO; R_1 = R_2 = H
d. R_1 = X; R_2 = R_3 = H
e. R_2 = X; R_1 = R_3 = H
f. R_3 = X; R_1 = R_2 = H



III

a. R_1 = CHO; R_2 = H
b. R_2 = CHO; R_1 = H
c. R_1 = X; R_2 = H
d. R_2 = X; R_1 = H

Condensation of rhodanine with pyridine-2-carboxaldehyde (IIa), pyridine-3-carboxaldehyde (IIb), pyridine-4-carboxaldehyde (IIc), quinoline-2-carboxaldehyde (IIIa), and quinoline-4-carboxaldehyde (IIIb) proceeds with great facility to yield the adducts (IId), (IIe), (IIf), (IIIc), and (IIId), respectively. The aldehyde-rhodanine derivatives were prepared using ammonia–ammonium chloride or acetic acid–sodium acetate as condensing agents.[14–17] These products, unlike other rhodanine-aldehyde condensation products, exhibit a characteristic insolubility in the common organic solvents, have high melting points (with decomposition) and can be crystallized from dimethylformamide. We ascribe these properties to the amphoteric nature of the adducts which permits intermolecular salt formation between the basic nitrogen of the pyridine ring and the acidic imino group of the rhodanine moiety. Substitution of the hydrogen atom of the imino group of the rhodanine ring in adducts (IIe) and (IIf) by a phenyl radical, to yield 3-phenyl-5(3-pyridylmethylene)- and 3-phenyl-5-(4-pyridylmethylene)rhodanine, with consequent blocking of possible intermolecular ionic bonding, restores the normal solubility pattern of rhodanine-aldehyde adducts, lowers the melting point and eliminates decomposition on melting.

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EXPERIMENTAL[18]

5-(2-Pyridylmethylene)rhodanine (IId). A solution of 2.0 g. (0.019 mole) of pyridine-2-carboxaldehyde and 2.6 g. (0.020 mole) of rhodanine in 15 ml. of ethanol and 13 ml. of concentrated ammonium hydroxide was heated on the steam bath. A solution of 13 g. of ammonium chloride in 20 ml. of hot water was added and heating continued for 30 min. The reaction mixture was allowed to stand overnight at 0° when crystals had separated. Recrystallization from ethanol gave 2.1 g. (yield 51%) of IId as bright yellow needles, m.p. 243–245° (dec.).

Anal. Calcd. for $C_9H_6N_2OS_2$: C, 48.62; H, 2.72; N, 12.6; S, 28.85. Found: C, 48.51; H, 2.70; N, 12.2; S, 28.7.

The following five compounds were similarly prepared.

5-(3-Pyridylmethylene)rhodanine (IIe), fine bright yellow needles (3.1 g., yield 75%) from dimethylformamide, m.p. 318–320° (dec.).

Anal. Calcd. for $C_9H_6N_2OS_2$: C, 48.62; H, 2.72; N, 12.6; S, 28.85. Found: C, 48.40; H, 2.80; N, 12.3; S, 28.50.

5-(4-Pyridylmethylene)rhodanine (IIf), fine yellow needles (2.9 g., yield 65%) from dimethylformamide, m.p. 320–322° (dec.).

Anal. Calcd. for $C_9H_6N_2OS_2$: C, 48.62; H, 2.72. Found: C, 48.41; H, 2.58.

5-(2-Quinolylmethylene)rhodanine (IIIc), bright yellow needles (560 mg., yield 69%) from aqueous acetone decomposing at 270°.

Anal. Calcd. for $C_{13}H_8N_2OS_2$: C, 57.31; H, 2.96; N, 10.29; S, 23.55. Found: C, 57.1; H, 2.8; N, 10.0; S, 23.2.

5-(4-Quinolylmethylene)rhodanine (IIId), yellow needles (500 mg., yield 59%) from dimethylformamide, m.p. 318–320° (dec.).

Anal. Calcd. for $C_{13}H_8N_2OS_2$: C, 57.31; H, 2.96. Found: C, 57.0; H, 2.8.

3-Phenyl-5-(3-pyridylmethylene)rhodanine. A mixture of 2.0 g. (0.019 mole) of pyridine-3-carboxaldehyde, 4.0 g. (0.019 mole) of 3-phenylrhodanine, and 4.0 g. of freshly fused sodium acetate in 15 ml. of acetic acid, to which 1 ml. of acetic anhydride had been added, was refluxed for 30 min. and allowed to cool. The yellow crystals which separated were recrystallized from ethanol to yield 1.5 g. (yield 27%) of *3-phenyl-5-(3-pyridylmethylene)rhodanine* as long yellow needles, m.p. 235–237°.

Anal. Calcd. for $C_{15}H_{10}N_2OS_2$: C, 60.37; H, 3.38. Found: C, 60.22; H, 3.2.

3-Phenyl-5-(4-pyridylmethylene)rhodanine was prepared in a similar manner and was recrystallized from ethanol as golden yellow needles (3.2 g., yield 54%), m.p. 245–246°.

Anal. Calcd. for $C_{15}H_{10}N_2OS_2$: C, 60.37; H, 3.38; N, 9.39; S, 21.5. Found: C, 60.22; H, 3.2; N, 9.05; S, 21.2.

DEPARTMENT OF CHEMISTRY
PAISLEY TECHNICAL COLLEGE
PAISLEY, SCOTLAND

(18) Melting points are uncorrected.

Reaction of Nitroacetamide with Hypobromite

S. K. BROWNSTEIN

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When nitroacetamide is heated in an aqueous solution of sodium hypobromite, dibromonitro-