analyzed by immersing a thermometer in the refluxing liquid, observing the b.p. and comparing with the previously determined b.p.-composition curve for mixtures of the two isomers.[4] Superheating was negligible compared with the difference in b.p. of the isomers (11.9°). The barometric correction was 0.04 deg./mm. for both compounds.

Typical results are shown in Table I.

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[4] George L. Jones, Jr., Thesis, University of Virginia, 1950.

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The Preparation of Certain *s*-Trithianes[1,2]

BY IRWIN B. DOUGLASS AND WILLIAM R. HYDRO

In the course of recent work in this Laboratory[3] it was desired to find a method for the preparation of 2,4,6-tribenzyl-*s*-trithiane. The ordinary methods yielded chiefly a gummy, ill-smelling product but the procedure outlined below proved to be highly satisfactory. Fractional crystallization of the crude product from acetone yielded the α- and β-forms which structural theory would lead one to expect.

When the same procedure was applied to the preparation of 2,4,6-triphenyl-2,4,6-trimethyl-*s*-trithiane, a good yield was obtained in a much shorter time than by the best previous method.[4]

Experimental

2,4,6-Tribenzyl-s-trithiane (Trithiophenylacetaldehyde), $(C_6H_5CH_2CHS)_3$.—Dry hydrogen chloride was passed into 400 ml. of absolute alcohol contained in a three-neck flask fitted with mechanical stirrer and maintained at 0° or lower until 262 g. had been adsorbed. The solution was then cooled to −10 to −12° and hydrogen sulfide was passed in for 30 minutes following which the flow of hydrogen sulfide was continued while 132 g. of a 50% solution of phenylacetaldehyde in alcohol was added dropwise over a two- to three-hour period. The temperature was kept below −10° during the entire operation. The increase in weight due to hydrogen sulfide was 19 g.

After the last of the phenylacetaldehyde had been added the slurry of crystals was stirred for 15 min. longer and was then filtered. The filtrate was placed in the ice-chest overnight and then separated from the crystals which had formed. Concentration of the mother liquor and cooling further increased the yield. The combined crystals, after washing with cold alcohol, yielded 70 g. (73%) of practically odorless product melting 105–140°.

Separation of α- and β-Forms.—Ten grams of the dry reaction product was dissolved in 50 ml. of acetone and filtered while hot. The solution was covered and set aside to crystallize slowly. After several hours about 20 ml. of fresh acetone was added to the felted mass of crystals and the mixture was stirred and warmed. When the fine needles had dissolved the acetone solution was decanted from a residue of less soluble prismatic crystals. Cooling of the acetone solution and repeated recrystallization of the fine needles which separated gave the pure α-form with m.p. 122–123° (cor.).

Anal. Calcd. for $C_{24}H_{24}S_3$: C, 70.5; H, 5.92; S, 23.5; mol. wt., 408.6. Found: C, 70.1; H, 6.10; S, 22.5; mol. wt., 386.

Repeated recrystallization of the prismatic crystals from acetone gave the pure β-form with m.p. 168–169° (cor.).

Anal. Calcd. for $C_{24}H_{24}S_3$: C, 70.5; H, 5.92; S, 23.5; mol. wt., 408.6. Found: C, 70.4; H, 5.96; S, 23.6; mol. wt., 438.

Several separations, as above, indicated that the crude reaction mixture contained 14–22% of the higher melting β-form.

2,4,6-Triphenyl-2,4,6-trimethyl-*s*-trithiane, $(C_6H_5CSCH_3)_3$, **(Trithioacetophenone).**—One hundred fifty ml. of absolute alcohol was saturated with 99 g. of hydrogen chloride at 0 to 5° as previously described. Hydrogen sulfide was passed into the mixture for 30 min., the temperature was lowered to −10 to −12° and a solution of 25 g. of acetophenone dissolved in an equal weight of alcohol was added dropwise over a 2–3-hour period as described above.

The solution first turned a deep purple color and later began to precipitate white crystals. The mixture was stirred 15 min. after adding the last acetophenone and then filtered. After standing overnight additional crystals formed and on concentration of the liquors the yield was further increased. After washing the crude product in alcohol and drying 22.8 g. (80%) of white material was obtained which melted at 118–121°. Recrystallization of a portion gave a pure product melting at 121–122° and at the same temperature when mixed with an authentic sample of trithioacetophenone.

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[1] This note describes a portion of the work done on project NR 055 165 under contract N8onr77000 with the Office of Naval Research, United States Navy.

[2] Taken from a master's thesis presented by William R. Hydro.

[3] Douglass and Martin, *J. Org. Chem.*, **15**, 795 (1950).

[4] Reid, "A Study in the Chemistry of Thiones," Doctoral Thesis, Indiana University, Bloomington, Indiana, 1946.

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Reactions of Ethylene Thiourea

BY NELSON R. EASTON, ALEX HLYNSKY AND HAROLD FOSTER

Very few S-substituted-2-imidazolidinethiones have been reported in the literature. The preparation of S-carboxymethyl-2-imidazolidinethione hydrochloride has been accomplished by the reaction of ethylene thiourea with chloroacetic acid[1] and S-carboethoxymethy-2-imidazolidinethione has been prepared by the action of ethyl chloroacetate on ethylene thiourea in the presence of sodium ethoxide.[2] The synthesis of S-dodecyl-2-imidazolidinethione has also been reported.[3]

We have prepared the S-benzyl, S-*p*-nitrobenzyl, S-*p*-chlorobenzyl and S-*o*-chlorobenzyl derivatives by condensing the appropriate halide with ethylene thiourea[4] and the treatment of the resulting salt with ammonium hydroxide. Due to its instability, however, the benzyl derivative could not be obtained in an analytically pure state. Table I gives the melting points and analyses.

TABLE I

S-2-IMIDAZOLIDINETHIONES

	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	
Benzyl-	68–70	14.57	14.0, 14.1	
p-Nitrobenzyl-	158	17.70	17.70	
o-Chlorobenzyl-	63–64	12.36	12.35, 12.25	
p-Chlorobenzyl-	100–103	12.36	12.50	
Hydrochlorides				Yield, %
Benzyl-	173.4	12.25	12.32	82
p-Nitrobenzyl-	191	15.35	15.40	86
o-Chlorobenzyl-	214–215	10.63	10.54	97 crude
p-Chlorobenzyl-	172.5–175	10.63	10.67, 10.68	73

Experimental

Preparation of the S-Substituted-2-imidazolidinethione Hydrochlorides.—A mixture of 0.25 mole of ethylene thiourea and 0.25 mole of the halide in 90 ml. of ethanol was

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[1] Johnson and Edens, THIS JOURNAL, **64**, 2706 (1942).

[2] Wilson, Baird, Burr, Munra and Stephen, *J. Roy. Tech. Coll.* (*Glasgow*), **2**, no. 1, 56 (1929).

[3] Puetzen, U. S. Patent 2,156,193.

[4] Received through the kindness of Rohm and Haas Co., Philadelphia, Penna.