identical with that of bufotenidine. No evidence for the presence of any bufagin-like substance in this secretion has been obtained.

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The Action of Perthiocyanic Acid on Amines

BY H. G. UNDERWOOD AND F. B. DAINS

In preparing dithiobiurets for another investigation, the action of perthiocyanic acid on various substances containing the amino group has been investigated. Glutz[1] has shown that perthiocyanic acid unites with aniline to form phenyldithiobiuret and Fromm[2] has pointed out that in the formation of phenyldithiobiuret an excess of aniline tends to increase the amount of thiocarbanilide formed along with the dithiobiuret. The reactions for the formation of dithiobiurets and dithioureas occur as follows

$$RNH_2 + C_2H_2N_2S_3 \longrightarrow RNHCSNHCSNH_2 + S \quad \text{(I)}$$

$$4RNH_2 + C_2H_2N_2S_3 \longrightarrow 2(RNH)_2CS + 2NH_3 + S \quad \text{(II)}$$

In this work fusions were carried out first at water-bath temperature and if no reaction was evident higher temperatures were employed. The ratio of the amine to perthiocyanic acid was usually 2:1. The results indicate that the nature of the reaction product depends upon the amine employed; thus there were formed (a) normal dithiobiurets, (b) thioureas, (c) fused side rings with certain substituted amines or (d) no reaction occurred.

Experimental

Synthesis of Dithiobiurets (I–VIII).—The new dithiobiurets listed in Table I (I–VIII) were prepared by fusing the amine (2 moles) with perthiocyanic acid (1 mole) on the water-bath. Di-*p*-bromophenylthiourea (IV) was obtained as a by-product in the preparation of *p*-bromophenyldithiobiuret. It is probable that dithioureas are also formed along with the other dithiobiurets but the small amounts formed did not warrant their separation.

TABLE I

Text no.	Compound	Formula	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
I	*m*-Tolyldithiobiuret	$C_9H_{11}N_3S_2$	159	18.66	18.63
II	*m*-Chlorophenyldithiobiuret	$C_8H_8ClN_3S_2$	164	17.11	16.96
III	*p*-Bromophenyldithiobiuret	$C_8H_8BrN_3S_2$	169	14.48	14.30
IV	α,β-Di-*p*-bromophenylthiourea	$C_{13}H_{10}BrN_2S$	184		
V	*p*-Iodophenyldithiobiuret	$C_8H_8IN_3S_2$	240	12.49	12.22
VI	α-Naphthyldithiobiuret	$C_{12}H_{11}N_3S_2$	235–236	16.09	15.93
VII	*m*-Aminophenyldithiobiuret[a]	$C_8H_{10}N_4S_2$	226	24.77	24.40
VIII	1-Methyl-1-*p*-tolyldithiobiuret	$C_{10}H_{13}N_3S_2$	236	17.55	17.51
IX	α,β-Di-*p*-xenylthiourea	$C_{25}H_{20}N_2S$	228	7.37	7.45
X	α,β-Dibenzylthiourea	$C_{15}H_{16}N_2S$	147–148	10.93	10.73
XI	4-Keto-2-thiotetrahydroquinazoline	$C_8H_6N_2OS$	285	15.72	15.61
XII	*o*-Phenylenethiourea	$C_7H_6N_2S$	298–299	18.66	18.84
XIII	Benzoxazole thiourea	$C_8H_7N_3OS$	205	21.74	21.57

[a] Only one amino group of *m*-diaminobenzene reacted.

Synthesis of Thioureas

α,β-Di-*p*-xenylthiourea (IX).—*p*-Xenylamine (0.1 mole) and perthiocyanic acid (0.05 mole) were heated for one hour at 150°. Only a small quantity of the reaction product was soluble in base. The main product insoluble in alkali was the thiourea which on recrystallization from hot water formed plate-like crystals melting at 228°,[3,4] yield 13 g.

α,β-Dibenzylthiourea (X).—The reaction was spontaneous on mixing benzylamine (0.05 mole) and perthiocyanic acid (0.05 mole), ammonia being evolved. The reaction mixture almost completely liquefied and then resolidified. To ensure complete reaction the product was warmed on the water-bath for one hour. Large plate-like crystals of dibenzylthiourea melting at 147–148°[5,6] were obtained from alcohol.

Reaction of Secondary Butylamine with Perthiocyanic Acid.—Secondary butylamine at room temperature gave an oily product which on distillation yielded secondary butyl thiourea and secondary butyl isothiocyanate.

Fused Ring Compounds

$\overline{C_6H_4NHCSNHC}O$, **4-Keto-2-thiotetrahydroquinazoline (XI).**—This product resulted when anthranilic acid or methyl anthranilate was heated at 180° for two hours. The reaction product was extracted with sodium hy-

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[1] Glutz, *Ann.*, **154**, 44 (1870).

[2] Fromm, *ibid.*, **275**, 20 (1893).

[3] Friebel and Rassow, *J. prakt. Chem.*, [2] **63**, 457 (1901).

[4] Zimmermann, *Ber.*, **13**, 1963 (1880).

[5] Werner, *J. Chem. Soc.*, **59**, 406 (1891).

[6] Salkowski, *Ber.*, **24**, 2724 (1891).

droxide solution (10%) and filtered. Neutralization gave the quinazoline which was recrystallized from glacial acetic acid (m. p. 285°).[7]

***o*-Phenylenethiourea (XII)**.—*o*-Phenylenediamine and perthiocyanic acid were heated for two hours at 180° with evolution of ammonia. An extraction was made of the fusion mixture with dilute sodium hydroxide solution. The basic product, obtained on acidifying the alkaline filtrate, gave light yellow, almost colorless leaflets from alcohol melting at 298–299°.[8,9]

Fusion of *o*-Aminophenol with Perthiocyanic Acid (XIII).—*o*-Aminophenol was fused with perthiocyanic acid at 180° for one hour with evolution of hydrogen sulfide. Light orange colored leaflets, melting at 205°, were obtained on acidifying the sodium hydroxide extraction solution of the fusion product. The analyses and properties correspond to a benzoxazole thiourea, $C_6\underbrace{H_4—N{=}C}O$-(NHCSNH$_2$.)[10]

No Reaction.—Perthiocyanic acid failed to react to form dithiobiurets or dithioureas with *p*-nitroaniline, 2,6-dibromo-3-methylaniline, 2,5-dichloroaniline, glycine, phenylglycine, benzanilide and glutamic acid.

Summary

Perthiocyanic acid reacted with amines to form (a) normal dithiobiurets, (b) thioureas, (c) fused rings or (d) no reaction occurred, depending upon the nature of the amine employed.

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(7) Rupe, *Ber.*, **30**, 1098 (1897).

(8) Lellmann, *Ann.*, **221**, 9 (1893).

(9) Billeter and Steiner, *Ber.*, **20**, 231 (1887).

(10) Deck and Dains, THIS JOURNAL, **55**, 4986 (1933).

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Some Dithiazane Rings

BY H. G. UNDERWOOD AND F. B. DAINS

The formation of thiazolidines and of *m*-thiazanes from thioureas and ethylene dibromide or trimethylene dibromide has been fully investigated. With the methylene dihalides and thioureas the only ring compound listed is one described by Foerster[1] as the methylene ether of thiocarbanilide, $\underbrace{\mathrm{SCNH_2NC_6H_5C}}{=}\mathrm{NC_6H_5}$ (from methylene iodide and diphenyl thiourea). Further examples of such ethers are described later in our paper. It has been shown in our work, however, that six-membered rings of the type 1,3,5-dithiazanes, $\underbrace{\overset{1}{\mathrm{S}}\overset{2}{\mathrm{C}}\mathrm{HR}\overset{3}{\mathrm{S}}\overset{4}{\mathrm{C}}\mathrm{(NR)}\overset{5}{\mathrm{N}}\mathrm{H}\overset{6}{\mathrm{C}}}\mathrm{(NR)}$ can be formed by the action of methylene halides on thiourea, monoaryl thiourea or 1,5-diaryldithiobiurets. To date derivatives of the dithiazanes have been confined to the thialdine, $\underbrace{\mathrm{SCHRSCHRNHC}}\mathrm{HR}$, the 2,4,6-trimethyldithiazane formed by the action of hydrogen sulfide on aldehyde ammonia, or an N-methyl derivative from methylamine and thioacetic aldehyde.[2,3,4] The structure of these thialdins has not been confirmed by direct experiment.

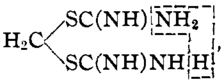
The following work shows that such rings can be synthesized by methods that give some definite proof of their constitution.

Experimental

4,6-Diimino-1,3,5-dithiazane Hydroiodide.—Dixon and Taylor[5] had heated methylene diiodide in alcohol solution with thiourea. The free base (m. p. 198°) from the salt was assumed to be the methylene ether of dithiourea, $CH_2(SC{=}NHNH_2)_2$, on the basis of a sulfur determination. In repeating this work the methylene iodide (1 mole) was heated in alcohol solution with thiourea (2 moles) for two hours and filtered hot; the salt that separated was purified by crystallization from hot water. Since the free base (m. p. 202–209°) failed to give concordant results on analysis for nitrogen, due seemingly to hydrolysis and loss of ammonia, the stable hydriodide salt was examined.

Anal. Calcd. for $C_3H_5N_3S_2{\cdot}HI$: N, 15.27. Found: N, 15.08, 15.22, 15.16.

The results correspond to the dithiazane structure and not to the monohydriodide salt of methylene dithiourea (N, 19.16) or the dihydroiodide salt (N, 13.37). The mechanism of this reaction is evidently as follows; a mol of ammonia is lost from the methylene thiourea,



$$\mathrm{H_2C}\begin{cases}\mathrm{SC(NH)}\boxed{\mathrm{NH_2}}\\ \mathrm{SC(NH)NH}\boxed{\mathrm{H}}\end{cases}$$

, thus closing the ring which in the form of a salt is stable.

Benzal Chloride and Thiourea, 4,6-Imino-2-phenyl-1,3,5-dithiazane.—Abel[6] heated benzal chloride with thiourea and obtained a compound $C_9H_{10}ClN_3S_2$ for which he gives no structural formula or melting point. In this work thiourea and benzal chloride in excess were heated in an oil-bath, the temperature not being allowed to rise above 150°. Unless care is used the temperature goes to 190° and a resin results. The solid residue was difficultly soluble in hot water and was further purified by solution in alcohol and precipitation with ether. The salt melted at 236° and was formed as follows

$$C_6H_5CHCl_2 + 2CS(NH_2)_2 \longrightarrow C_9H_9N_3S_2{\cdot}HCl + NH_4Cl$$

Anal. Calcd. for $C_9H_{10}ClN_3S_2$: N, 16.15; S, 24.69; Cl, 13.65. Found: N, 16.23, 15.95; S, 24.45, 24.25; Cl, 13.11, 13.22.

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(1) Foerster, *Ber.*, **21**, 1872 (1888).

(2) Marckwald, *ibid.*, **19**, 1826 (1886).

(3) Nord, *ibid.*, **52**, 1208 (1919).

(4) Delépine, *Bull. soc. chim.*, [3] **15**, 889 (1896).

(5) Dixon and Taylor, *J. Chem. Soc.*, **109**, 1255 (1916).

(6) Abel, *Am. Chem. J.*, **13**, 118 (1891).