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, $\underline{C_6H_4{-}N{=}CO}(NHCSNH_2)$.[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.

LAWRENCE, KANSAS RECEIVED JULY 1, 1935

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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).

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, $\underline{SCNH_2NC_6H_5C{=}NC_6H_5}$ (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, $\underline{\overset{1}{S}\overset{2}{C}HR\overset{3}{S}\overset{4}{C}(NR)\overset{5}{N}H\overset{6}{C}(NR)}$ 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, $\underline{SCHRSCHRNHCHR}$, 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.

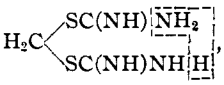
The following work shows that such rings can be synthesized by methods that give some definite proof of their constitution.

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,



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

The free base was not isolated in a pure condition. Excess alkali decomposes the salt yielding benzaldehyde, hydrogen sulfide and ammonia, while neutralization with 0.1 *N* alkali gave mixtures in which part of the nitrogen had been lost. The imino group was easily hydrolyzed to ammonia.

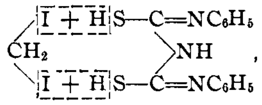
Phenylthiourea Derivative, 4,6-Diphenylimino-1,3,5-dithiazane.—The stability of the dithiazane ring is greatly increased by the presence of phenylimino rather than imino groupings. Phenylthiourea and methylene iodide were refluxed in alcoholic solution for four hours. The difficultly soluble hydroiodide salt when crystallized from hot water melted at 263°.

Anal. Calcd. for $C_{15}H_{14}IN_3S_2$: N, 9.83; S, 14.98. Found: N, 9.90; S, 15.04.

The Hydrobromide Salt.—A mixture of methylene bromide and phenyl thiourea was heated in an oil-bath at 120–130° for one-half hour. The mixture was treated with alcohol and the precipitated salt crystallized from hot water (m. p. 268°). The free base was obtained on neutralizing hot dilute solutions of the bromide or iodide salts with alkali. It crystallized from alcohol in the form of a light yellow powder of m. p. 107°.

Anal. Calcd. for $C_{15}H_{13}N_3S_2$: N, 14.04; S, 21.46; mol. wt., 299. Found: N, 13.98; S, 21.92; mol. wt., 297.

The dithiazane was decomposed by boiling with 15% potassium hydroxide, yielding hydrogen sulfide, phenyl isothiocyanate and aniline.

Thiazanes from Dithiobiurets.—Final proof of the dithiazane structure was shown as follows. 1,5-Diphenyldithiobiuret and methylene bromide were heated at 120°, giving a hydrobromide salt that melted at 263°. The free base was insoluble in alkali, melted at 109° and was shown by analysis and mixed melting point to be identical with the compound from phenylthiourea. Ring closure evidently occurred as follows,  , thus confirming the structure.

Benzoyl Derivative (5- or 6-Benzoyl).—The diphenyliminodithiazane was readily benzoylated in pyridine solution, yielding a product of m. p. 120–121°.

Anal. Calcd. for $C_{22}H_{22}N_3OS_2$: N, 8.77. Found: N, 8.71.

4,6-Di-*p*-tolylimino-1,3,5-dithiazane Hydrobromide.—*p*-Tolyl thiourea was heated with methylene dibromide at 130° for one-half hour. From the melt on crystallization from hot water was isolated a yellow salt, m. p. 283°.

Anal. Calcd. for $C_{17}H_{18}BrN_3S_2$: N, 10.29. Found: N, 10.18, 10.98.

The free base melted at 175°.

Anal. Calcd. for $C_{17}H_{17}N_3S_2$: N, 12.83. Found: N, 12.47, 12.58.

4,6-Di-*o*-tolylimino-1,3,5-dithiazane Hydrobromide.—The yellow hydrobromide salt melted at 236°.

Anal. Calcd. for $C_{17}H_{18}BrN_3S_2$: N, 10.29. Found: N, 10.29, 10.04.

The free base melted at 174°.

Anal. Calcd. for $C_{17}H_{17}N_3S_2$: N, 12.83. Found: N, 12.31, 12.35.

Ethylidene Dibromide and Monophenyl Thiourea: 2-Methyl-4,6-diphenylimino-1,3,5-dithiazane Hydrobromide.—Molar quantities of ethylidene dibromide and monophenyl thiourea were heated at 160° for four hours. From the reaction product was isolated and purified by crystallization from hot water the hydrobromide salt of 2-methyl-4,6-diphenylimino-1,3,5-dithiazane melting at 248°.

Anal. Calcd. for $C_{16}H_{16}BrN_3S_2$: N, 10.66. Found: N, 10.60, 10.52.

The free base melted at 181°.

Anal. Calcd. for $C_{16}H_{15}N_3S_2$: N, 13.48. Found: N, 13.37, 13.30.

2-Phenyl-4,6-phenylimino-1,3,5-dithiazane.—Monophenyl thiourea (35 g.) and benzal chloride (30 g.) were heated on a paraffin bath. The reaction began at 100° and the flask was removed from the bath, the temperature rising to 150°. The solid residue was crystallized from water–alcohol and melted at 232°.

Anal. Calcd. for $C_{21}H_{18}ClN_3S_2$: N, 10.21; S, 15.57; Cl, 8.61. Found: N, 10.22; S, 15.60; Cl, 8.52.

The free base melted at 145°.

Anal. Calcd. for $C_{21}H_{17}N_3S_2$: N, 11.19; mol. wt., 375. Found: N, 10.69; mol. wt., 368.

Further evidence as to the dithiazane structure was shown by its synthesis from 1,5-diphenyldithiobiuret which was heated with benzal chloride at 150° until evolution of hydrogen chloride ceased. A hydrochloride was obtained melting at 232°, which by mixed melting point and analysis proved to be identical with the product from benzal chloride and monophenyl thiourea.

Anal. Calcd. for $C_{21}H_{18}ClN_3S_2$: N, 10.21. Found: N, 9.91, 10.02.

2-Phenyl-4,6-di-*p*-tolylimino-1,3,5-dithiazane Hydrochloride.—Benzal chloride and *p*-tolyl thiourea gave the corresponding 2-phenyl-4,6-di-*p*-tolylimino-1,3,5-dithiazane hydrochloride which was obtained as a light yellow powder melting at 222°.

Anal. Calcd. for $C_{23}H_{22}ClN_3S_2$: N, 9.55. Found: N, 9.46.

The Action of Methylene Iodide on Disubstituted Thioureas.—This was tried in order to see whether a dithiazane ring could be made with the loss of a RNH_2. The results show that not to be the case, but instead evidence was obtained of the formation of the methylene ethers of the thioureas. Foerster[1] heated methylene iodide with thiocarbanilide in alcoholic solution and obtained a base (m. p. 68°). It was analyzed as the platinum salt which gave figures corresponding to the methylene ether of diphenylthiourea. On repeating his work a gummy base was obtained which gave an impure platinum salt and a product melting at 68–69°, which proved to be phenyl thiourethan.

Methylene Ether of Di-*p*-tolyl Thiourea.—Molar quantities of di-*p*-tolyl thiourea and methylene iodide were heated in acetone solution for a period of four hours. The reaction product was found to contain unchanged thiourea, tolyl mustard oil, toluidine and a basic compound that melted at 151° when crystallized from alcohol.

Anal. Calcd. for $C_{16}H_{16}N_2S$: N, 10.41; mol. wt., 268. Found: N, 10.77, 10.83; mol. wt., 271.

These results point to a methylene ether and not a dithiazane derivative or a methylene dithio ether, $CH_2(SC{=}NC_6H_5NHC_6H_5)_2$, which has nearly the same percentage composition but a molar weight of 468.

1,5 - Diphenyl - 2 - thiolmethyl - 4 - thiolmethylenedipseudodithiobiuret Hydroiodide and Base.—A corresponding methylene ether was obtained from 1,5-diphenyl-2-thiolmethylpseudodithiobiuret ($C_6H_5N{=}C(SCH_3)NHCSNHC_6H_5$) when heated with methylene iodide alone at 120° or in alcoholic solution. This was obtained as the difficultly soluble hydroiodide salt (m. p. 275°) together with phenyl mustard oil.

Anal. Calcd. for $C_{16}H_{16}IN_3S_2$: N, 9.52. Found: N, 9.53, 9.58.

The light yellow base melted at 125°.

Anal. Calcd. for $C_{16}H_{15}N_3S_2$: N, 13.48. Found: N, 13.44.

Benzal chloride failed to give ethers of this type. Heated with thiocarbanilide or di-*p*-tolyl thiourea at 160° it gave only the triphenyl or tritolyl guanidine.

2 - Phenylimino - 3 - thioformanil - tetrahydrothiazole.—While 1,5-diphenyldithiobiuret with methylene iodide gave a dithiazane ring, with ethylene dibromide, a thiazole is formed. An alcoholic solution of the thiobiuret and ethylene dibromide with an excess of ammonium hydroxide was allowed to stand for several days, when light yellow crystals of the thiazole separated (m. p. 165°).

Anal. Calcd. for $C_{16}H_{15}N_3S_2$: N, 13.41. Found: N, 13.39.

Hydrolysis with alcoholic potassium hydroxide gave phenyl mustard oil and 2-phenylaminothiazolidine.

Thiazolidone Synthesis.—The action of chloroethyl acetate on 1,5-diphenyl-2-thiolmethylpseudodithiobiuret was studied in order to note the influence of the two groups upon the constitution of the possible thiazolidone. Heating the two components in alcoholic solution gave a thiazolidone $\underbrace{SC(NCSCH_3NC_6H_5)NC_6H_5COCH_2}$, melting at 127° with the structure phenyl-4-thiazolidone-thiolmethylpseudothiourea. This was shown by the fact that the 5-benzal derivative melting at 157° (N, calcd. 9.79; found, 9.86) on hydrolysis yielded the known 5-benzal-3-phenyl thiazoledione identified by melting point and analysis.

Anal. Calcd. for $C_{17}H_{15}N_3OS_2$: N, 12.26. Found: N, 12.17.

α,α-Phenylmethyl-β-thiazolidone Thiourea.—This compound was readily formed by heating the phenylmethyldithiobiuret with chloroethyl acetate or chloroacetyl chloride with one mol of pyridine in acetone solution for four hours (m. p. 222°).

Anal. Calcd. for $C_{11}H_{11}N_3OS_2$: N, 15.85. Found: N, 15.92, 15.95.

Hydrolysis of the 5-benzal derivative (m. p. 274°) with 50% sulfuric acid gave 5-benzal-2,4-thiazoledione, thus proving that the thiourea grouping was at position 2.

Anal. Calcd. for $C_{18}H_{16}N_3OS_2$: N, 11.86. Found: N, 11.37, 11.38.

Summary

Methylene dihalides reacted with thiourea, monoaryl thioureas and 1,5-diaryldithiobiurets to form dithiazanes while α,β-diaryl thioureas formed methylene ethers or products of hydrolysis.

LAWRENCE, KANSAS RECEIVED JULY 1, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Densities of Adsorbed Gases. I. Carbon Dioxide on Charcoal[1]

BY THOS. DE VRIES

It is possible, by the use of Polanyi's theory,[2] to calculate from an adsorption isotherm, the isotherms for other temperatures. It is also possible to calculate the average density of the adsorbed layer. An experimental method was developed to determine the density of adsorbed carbon dioxide, and the agreement between observed and calculated densities lends confirmation to the reasonableness of the underlying assumptions. The density of water on silica gel at 25° has been determined by Ewing and Spurway.[3] No other densities of adsorbed vapors have been recorded in the literature. In this paper an apparatus and technique are described which gave results with a precision of 3 to 5% for the density of carbon dioxide adsorbed on activated coconut charcoal. In brief the method consisted in using helium as the displaced fluid to determine, before and after carbon dioxide adsorption, the unoccupied volume in a tube containing charcoal. A temperature of 30.00° was chosen which is just under the critical temperature of carbon dioxide.

Experimental

Carbon dioxide was prepared according to the method of Lowe and Guthmann,[4] and thoroughly dried by passing over anhydrous magnesium perchlorate. Helium was

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[1] Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, April 22–26, 1935.

[2] Polanyi, *Verh. d. Deutsch. Phys. Ges.*, **18**, 55 (1916); Berényi, *Z. physik. Chem.*, **94**, 628 (1920).

[3] Ewing and Spurway, THIS JOURNAL, **52**, 4635 (1930).

[4] Lowe and Guthmann, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 440 (1932).