of this method to oxidize the sulfur quantitatively in all organic compounds is apparently not due to any particular type of sulfur linkage but rather to the physical properties of the compound. It will not give accurate results if the compound is volatile or sublimes. We believe that for all other organic compounds, it will serve as a simple, rapid and accurate method for determining sulfur.

SAINT PAUL, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF DACCA]

RING CLOSURE OF HYDRAZODITHIO- AND -MONOTHIO-DICARBONAMIDES WITH ACETIC ANHYDRIDE

BY PRAPHULLA CHANDRA GUHA

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Ring closure of hydrazodithio-dicarbonamide was first effected by Freund and Wischewiansky[1] by carbonyl chloride in toluene solution, and they assigned a triazole formula to the resulting compound. Later, Freund and his co-workers effected ring closure of the same hydrazo compound with hydrochloric acid and obtained two compounds, to both of which they assigned triazole formulas, one being dithio-urazole and the other iminothio-urazole. The constitution of the former has been established by the present author to be 5-amino-2-thiol-1,3,4-thiodiazole.[2] Arndt and Milde[3] found fault with the constitution of Freund and Imgart's iminothio-urazole and they have been successful in synthesizing the *real* iminothio-urazole by the action of very strong potassium hydroxide solution on the above hydrazo compound. Emil Fromm with E. Kayser, K. Briegleb and E. Fohrenbach[4] arrived at the conclusion that Freund and Imgart's iminothio-urazole is 2,5-diamino-1,3,4-thiodiazole.

With the object of studying the behavior of various organic acids and their anhydrides as ring-closing reagents towards hydrazodithio-dicarbonamide and its derivatives, the present investigation was undertaken. The action of acetic anhydride has been found to be very interesting in the sense that it not only brings about a closure of the ring when 2,5-di-imino-2,3,4,5-tetrahydro-1,3,4-thiodiazole is formed with the splitting up of 1 molecule of hydrogen sulfide, but this thiodiazole compound is also acetylated thus,

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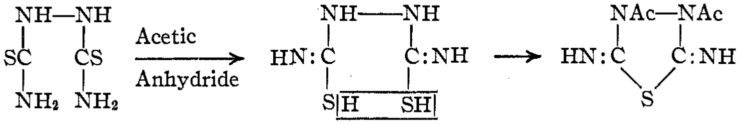
[1] Freund and Wischewiansky, *Ber.*, **26**, 2877 (1893).

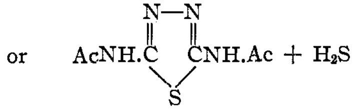
[2] Guha, THIS JOURNAL, **44**, 1502 (1922).

[3] Arndt and Milde, *Ber.*, **54**, 2089 (1921).

[4] Fromm, Kayser, Briegleb and Fohrenbach, *Ann.*, **426**, 313 (1922).



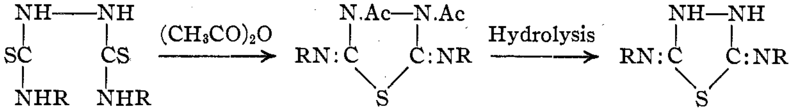
3,4-Diacetyl-2,5-di-imino-
2,3,4,5-tetrahydro-1,3,4-
thiodiazole



In the above process of ring closure, the hydrazo compound acts obviously in the dithiol form, as otherwise the formation of the thiodiazole compound is inexplicable. The di-acetyl compound loses its acetyl groups when hydrolyzed by boiling with hydrochloric acid, and the unsubstituted di-imino-tetrahydro-thiodiazole is generated.

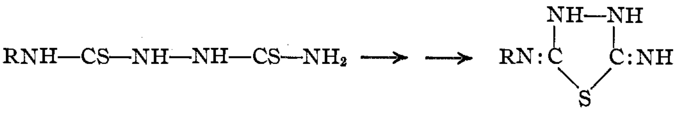
This method of ring closure is of special significance from the point of view of its applicability with all alkyl and aryl substituted hydrazo compounds. By the action of hydrochloric acid, Freund and Imgart could prepare this type of thiodiazole compounds only in the case of hydrazodithio-dicarbonamide and the corresponding methyl and ethyl substituted amides. However, by this new method, it has been found possible to prepare the thiodiazole compounds with all substituted and unsubstituted (alkyl and aryl) hydrazomono- and -dithio-carbonamides.

With the alkyl and aryl substituted hydrazo compounds the reaction takes exactly the same course as with the unsubstituted compound and a dialkyl or diaryl imino-thiodiazole compound is obtained in each case.



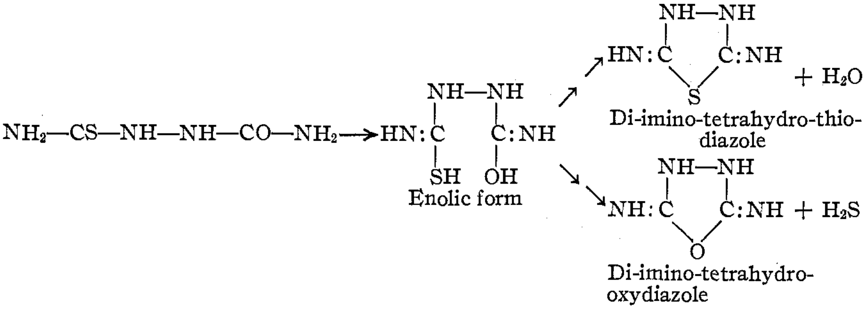
2,5-di-R-imino-2,3,4,5-
tetrahydro-1,3,4-thiodiazole

With the monosubstituted hydrazo compound, as expected, the monosubstituted imino-thiodiazole is obtained.



5-R-imino-tetra-
hydro-thiodiazole

The behavior of acetic anhydride toward hydrazomonothio-dicarbonamide, $NH_2—CS—NH—NH—CO—NH_2$, is interesting. Instead of giving a di-imino compound according to the general rule,

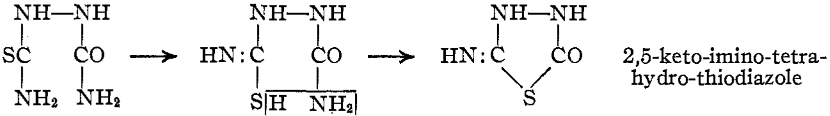


Enolic form

Di-imino-tetrahydro-thiodiazole

Di-imino-tetrahydro-oxydiazole

there is formed a keto imino-thiodiazole, thus,



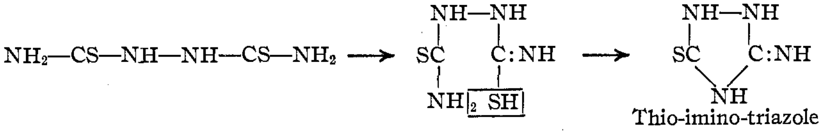
2,5-keto-imino-tetrahydro-thiodiazole

The oxygen atom does not lend itself to the ring formation in the enolic form, and this is effected by the elimination of a molecule of ammonia. That the atom of sulfur in the compound is a member of the ring is evident from the following facts: (1) it is insoluble in alkali, (2) the compound cannot be desulfurized by treatment with mercuric oxide, (3) it melts at 240°, whereas monothio-urazole as prepared by Arndt, Milde and Tscheuscher[5] melts at 206°.

The unsubstituted di-imino-tetrahydro-thiodiazole and the corresponding di-alkylimino (not aryl) compounds possess the characteristic property of combining with a molecule of hydrochloric acid to give soluble hydrochlorides, from which the free basic compounds can be obtained by the action of alkalies. The aqueous solutions of the hydrochlorides give beautiful yellow picrates, and mononitroso compounds with sodium nitrite.

The reasons for assigning a thiodiazole formula to this class of compounds are as follows.

The only plausible alternative formula of the unsubstituted parent compound, $C_2H_4N_4S$, is according to the following scheme of its formation, 2-thio-5-imino-tetrahydro-triazole.



Thio-imino-triazole

The compound so formed would possess a mercaptanic group (either real or potential) and in that case it should give all the characteristic reactions of a mercaptan, that is, it should be soluble in alkali to form mercaptides, should form compounds with mercuric chloride and nitrite, give a disulfide with mild oxidizing agents and also give thio-ethers with alkyl iodides, very

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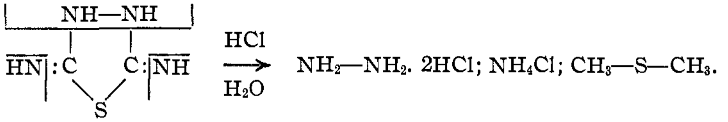
[5] Arndt, Milde and Tscheuscher, *Ber.*, **55**, 341 (1922).

readily.[2] As a matter of fact, it does not lend itself to any of the above reactions. Moreover, the position of the sulfur atom in the ring has been determined by treating the compound $C_2H_4N_4S$ and the diphenyl compound with mercuric oxide, when they were left quite unchanged.[6]

The decomposition of di-imino-tetrahydro-thiodiazole by the action of strong hydrochloric acid at high temperature and pressure gives hydrazine hydrochloride, ammonium chloride and methyl sulfide.



Evidently, the 2 carbon atoms are very firmly attached to the sulfur atom.

Experimental Part

Reaction between Acetic Anhydride and Hydrazodithio-dicarbonamide and its Alkyl Derivatives

Hydrazodithio-dicarbonamide and Acetic Acid. Formation of 3,4-Diacetyl-2,5-di-imino-2,3,4,5-tetrahydro-1,3,4-thiodiazole.—Five g. of the hydrazo compound was heated under a reflux condenser with an excess of acetic anhydride for about 15 minutes when white, insoluble, needle-shaped crystals were obtained. The reaction mixture was poured into 300 cc. of cold water and the crystalline precipitate was separated by filtration, washed several times with water and sucked dry. The compound thus obtained was further purified by crystallization from glacial acetic acid or from a large quantity of boiling water. It was dried in a steam-oven and was found to be insoluble in alkali; m. p., above 315°; yield, about 4 g.

Analyses. Calc. for $C_6H_8O_2N_4S$: C, 36.00; H, 4.00; N, 28.00; S, 16.00. Found: C, 36.35; H, 4.46; N, 27.91; S, 16.61.

HYDROLYSIS.—Three g. of this diacetyl compound was boiled with about 20 cc. of conc. hydrochloric acid (sp. gr., 1.16) for about 5 minutes, when a clear solution was obtained, which when evaporated on the water-bath gave white, needle-shaped crystals, which were further purified by recrystallizing twice from water; m. p., 241°; yield, 1.4 g.

Analyses. Calc. for $C_2H_4N_4S.HCl + H_2O$: C, 14.08; H, 4.10; Cl, 20.82; S, 18.77. Found: C, 14.39; H, 4.44; Cl, 21.31; S, 19.01.

The Free Base.—To an aqueous solution of the hydrochloride was added a solution of sodium carbonate in slight excess. The solution was evaporated to dryness and the solid residue was extracted with absolute alcohol. The alcoholic solution on concentration gave a white crystalline substance, melting at 210–211°. It was very soluble in water.

Analysis. Calc. for $C_2H_4N_4S$: S, 27.59. Found: 27.38.

2,5-Diamino-tetrahydro-thiodiazole gave with nitrous acid a chocolate-colored precipitate, which was soluble in alkali with the formation of a deep red solution. The yellow crystalline picrate darkened in color at 250° and did not melt even at 265°.

Dimethyl Derivative and Acetic Anhydride.—Three and a half g. of the diacetyl compound was obtained from 4 g. of the hydrazo compound. It crystallized from water in white needles, melting at 219°.

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[6] See Busch and Wolpert, *Ber.*, **34,** p. 304.

Analyses. Calc. for $C_8H_{12}O_2N_4S$: N, 24.56; S, 14.04. Found: N, 24.29; S, 14.22.

HYDROLYSIS.—The clear solution obtained by boiling with conc. hydrochloric acid was evaporated to dryness and the residue crystallized from water; m. p., 235°.

Analyses. Calc. for $C_4H_8N_4S.HCl + H_2O$: Cl, 17.88; S, 16.16. Found: Cl, 17.34; S, 16.73.

The free base was obtained as a white crystalline precipitate when sodium carbonate solution was added to a solution of the hydrochloride. It was crystallized from absolute alcohol and was sparingly soluble in water; m. p., 180°.

Analyses. Calc. for $C_4H_8N_4S$: C, 33.33; H, 5.55; N, 38.85. Found: C, 33.66; H, 5.81; N, 38.59.

NITROSO DERIVATIVE.—The golden yellow nitroso derivative was purified by crystallizing from dil. alcohol; it melted at 151°.

Analysis. Calc. for $C_4H_7(NO)N_4S$: N, 40.66. Found: 40.69.

The beautiful yellow crystalline picrate melted at 205°.

Allyl Derivative and Acetic Anhydride.—The compound was crystallized from water; m. p., 113°.

Analyses. Calc. for $C_{12}H_{16}O_2N_4S$: N, 20.00; S, 11.42. Found: N, 19.59; S, 10.96.

HYDROLYSIS.—Formation of the hydrochloride.

Analyses. Calc. for $C_8H_{12}N_4S.HCl + H_2O$: N, 22.36; S, 12.77. Found: N, 22.41: S, 13.10.

The *free base* was crystallized from dil. alcohol. It was sparingly soluble in water; m. p., 151°.

Analysis. Calc. for $C_8H_{12}N_4S$: S, 16.33. Found: 16.63.

Phenyl Derivative and Acetic Anhydride.—On being heated with acetic anhydride, the hydrazo compound yielded the diacetyl-thiodiazole compound mixed with a small quantity of phenyl mustard oil which was detected by its characteristic odor. The reaction mixture gave a heavy oil when poured into water. The supernatant acid liquor was decanted, a fresh quantity of water was added to the oily residue, and the mixture stirred thoroughly with a glass rod and made slightly alkaline by the addition of sodium carbonate solution. The oily product soon solidified, and was separated by filtration. The trace of adhering mustard oil was removed by washing the crystals with ether. The substance was crystallized from a mixture of benzene and alcohol; m. p., 224°.

Analyses. Calc. for $C_{18}H_{16}O_2N_4S$: C, 61.38; H, 4.54; S, 9.09. Found: C, 61.80 H, 4.30; S, 9.35.

HYDROLYSIS.—When the acetyl compound was boiled with conc. hydrochloric acid, it dissolved within 2–3 minutes. On further heating the solution became turbid, and soon a semisolid pasty mass was deposited, which solidified into a hard brittle mass as it cooled. It was crystallized from a large quantity of absolute alcohol; m. p., 247°.

Analyses. Calc. for $C_{14}H_{12}N_4S$: C, 62.69; S, 12.00. Found: C, 62.34; S, 12.48.

The *p*-Tolyl Derivative and Acetic Anhydride.—The oily product obtained in this case could not be solidified by the processes applied in the case of the phenyl compound. The semisolid mass was dissolved in alcohol, boiled for an hour with animal charcoal, filtered and the clear alcoholic solution was poured in a thin stream into a large quantity of water with constant stirring. It was allowed to stand for 24 hours, when a solid deposit was collected from the bottom and walls of the beaker. The process was repeated thrice and finally the solid compound was crystallized from dil. alcohol; m. p., 235°.

Analysis. Calc. for $C_{20}H_{20}O_2N_4S$: S, 8.42. Found: 8.39.

2,5-Ditolylimino-2,3,4,5-tetrahydro-1,3,4-thiodiazole

HYDROLYSIS.—The 2,5-ditolyl compound was prepared and purified as was the corresponding diphenylimino compound; m. p., 249–250°.

Analysis. Calc. for $C_{16}H_{16}N_4S$: S, 10.81. Found: 11.30.

Monophenyl Derivative and Acetic Anhydride.—The compound was crystallized from dil. alcohol; m. p., 144°.

Analysis. Calc. for $C_{12}H_{12}O_2N_4S$: S, 11.60. Found: 11.91.

HYDROLYSIS.—The hydrochloride was crystallized from water; m. p., 144°.

Analyses. Calc. for $C_8H_8N_4S.HCl + H_2O$: Cl, 14.45; S, 13.03. Found: Cl, 14.91; S, 12.83.

It gave a yellow crystalline picrate; m. p., 226°.

The *free base* was purified by crystallization from dil. alcohol and was obtained as dull yellow leaflets; m. p., 215°.

Analyses. Calc. for $C_8H_8N_4S$: N, 29.17; S, 16.66. Found: N, 29.32; S, 16.42.

p-Bromophenyl-hydrazodithio-dicarbonamide.—This new hydrazo-thiocarbonamide was prepared by boiling for 3–4 hours under a reflux condenser, on a water-bath, 1 molecular proportion of hydrazine sulfate dissolved in the minimum quantity of warm water, to which was added a mixture of 1 molecular proportion of sodium carbonate and 2 molecular proportions of p-bromophenyl mustard oil dissolved in 5 times its weight of alcohol. Crystals of the hydrazo compound began to separate from the solution after an hour's heating. A large quantity of water was added to the reaction mixture and the crystalline precipitate was separated by filtration. It was dissolved in dil. sodium hydroxide solution, precipitated by dil. hydrochloric acid, and was finally crystallized from alcohol; m. p., 213°.

Analysis. Calc. for $C_{14}H_{12}N_4Br_2S_2$: S, 13.91. Found: 13.6.

p-Bromophenyl Derivative and Acetic Anhydride.—The method used was the same as with the phenyl compound. The diacetyl derivative melted at 229°.

Analyses. Calc. for $C_{18}H_{14}O_2N_4Br_2S$: Br, 31.37; S, 6.27. Found: Br, 31.89; S, 6.23.

The Free Base.—The best method for its crystallization was that of adding 30 cc. of hot water to 90 cc. of a hot saturated alcoholic solution of the compound. Crystals appeared on cooling; m. p., 241°.

Analyses. Calc. for $C_{14}H_{10}N_4Br_2S$: Br, 37.66; S, 7.51. Found: Br, 37.29; S, 7.84.

m-Chlorophenyl-hydrazodithio-dicarbonamide.—The method of preparation was that used for the corresponding p-bromo compound; m. p., 170°.

Analyses. Calc. for $C_{14}H_{12}N_4Cl_2S_2$: Cl, 19.14; S, 17.25. Found: Cl, 19.51; S, 16.83.

2,5-Dichlorophenylimino-2,3,4,5-tetrahydro-1,3,4-thiodiazole

Reaction with Acetic Anhydride. *The Free Base.*—The diacetyl compound could not be isolated in the pure state. The impure pasty mass was excessively soluble in all ordinary solvents, such as methyl and ethyl alcohols, acetone, ether, chloroform, carbon tetrachloride, carbon disulfide, acetic ether, benzene, toluene, etc. However, the deacetylated thiodiazole could be obtained very easily from the impure pasty mass, and was crystallized from 60% methyl alcohol; m. p., 186–187°.

Analyses. Calc. for $C_{14}H_{10}N_4Cl_2S$: Cl, 21.07; S, 9.50. Found: Cl, 20.93; S, 9.11.

Hydrazodi-α-naphthyl-dithio-dicarbonamide.—The method of preparation was identical with that for the bromophenyl compound. The substance began to shrink at 235° and melted at 265°.

Analysis. Calc. for $C_{22}H_{18}N_4S_2$: S, 15.92. Found: S, 16.22.

Reaction with Acetic Anhydride.—The compound was obtained in shining white crystals from ethereal solution by the addition of a large quantity of benzene. It was soluble in ether but not so in benzene and alcohol; m. p., 270°.

Analysis. Calc. for $C_{26}H_{20}O_2N_4S$: S, 7.08. Found: 7.47.

2,5-Dinaphthylimino-tetrahydro-thiodiazole.—On boiling the acetyl compound with conc. hydrochloric acid, it did not go into solution as in the case of the phenyl, tolyl, and similar compounds; only a soft white product was obtained, which solidified into a brittle mass on cooling. To ensure complete hydrolysis, this was powdered and boiled again with hydrochloric acid. Finally, it was crystallized from dil. pyridine. It was insoluble in water, alcohol, ether, acetone or benzene; m. p., 275–276°.

Analyses. Calc. for $C_{22}H_{16}N_4S$: C, 71.74; H, 4.35; S, 8.70. Found: C, 72.17; H, 4.94; S, 8.45.

Hydrazomonothio-dicarbonamide and Acetic Anhydride.—On heating this hydrazo compound for some time with acetic anhydride it went into solution; on further heating, the acetyl compound was precipitated as a yellowish-white, crystalline powder, which was crystallized from water; m. p., 295°.

The Free Base.—The hydrochloride was obtained when the above acetyl compound was boiled with conc. hydrochloric acid; m. p., 107–108°. The free base was obtained from the hydrochloride by the addition of sodium carbonate solution, as white, shining leaflets which were further purified by crystallization from alcohol; m. p., 240°. It was insoluble in alkali.

Analyses. Calc. for $C_2H_3ON_3S$: C, 20.51; H, 2.56; S, 27.35. Found: C, 20.19; H, 2.31; S, 27.70.

The author takes this opportunity of expressing his sincere thanks to Sir P. C. Rây, Dr. J. C. Ghosh and Mr. S. N. Bose for the kind interest they have taken during the progress of the work.

Summary

It is shown that acetic anhydride converts hydrazodithio-dicarbonamide into a diacetyl derivative of 2,5-di-imino-2,3,4,5-tetrahydro-1,3,4-thiodiazole from which it is easy to remove the acetyl groups.

This new method of closing the thiodiazole ring is of special significance because it is applicable also to all alkyl and aryl hydrazodithio-carbonamides. Hydrazomonothio-dicarbonamide, however, behaves differently. Instead of losing either hydrogen sulfide or water and forming a di-imino-thiodiazole or oxydiazole it loses ammonia and gives a keto-imino-thiodiazole.

A description is given of a number of alkyl and aryl thiodiazoles that were obtained in this way, and an account of their most important reactions.

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