Studies of Dithiobiurets. III. The Preparation and Properties of 3,5-Disubstituted 3*H*-1,2,4-Dithiazoles

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3,5-Disubstituted 3*H*-1,2,4-dithiazoles were prepared by the oxidation of dithiobiurets, *S*-benzylisodithiobiurets, and alkyl trithioallophanates, and then 3-acyl or carbamoylimino derivatives were obtained by the direct acylation or carbamoylation of the dithiazole salts. From the spectral data of these compounds, it is concluded that the carbonyl group affects the pseudoaromatic character of the dithiazole ring system.

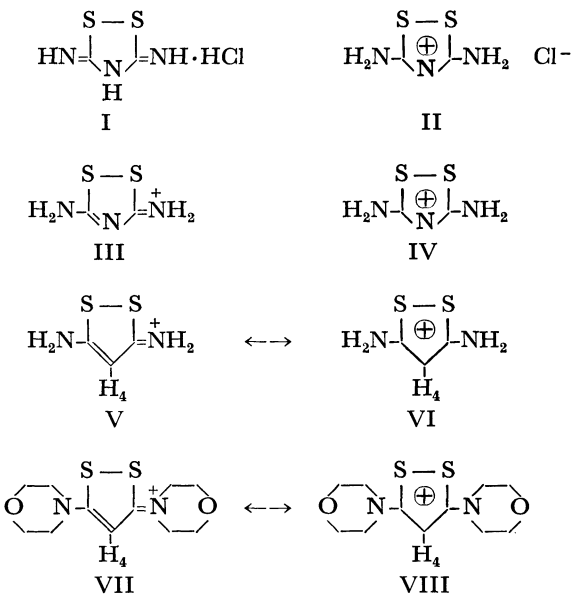
We previously reported that 2-acetylimino-5-dimethylamino-3*H*-1,2,4-dithiazole hydrothiocyanate was obtained by the thermal decomposition of 1,1-dimethyl-5-acetyldithiobiuret.[1] The free base which was prepared by the neutralization with potassium carbonate did not show any carbonyl absorption in the infrared spectrum in spite of the existence of the acetyl group, while its hydrochloride or sulfate showed a strong carbonyl absorption band at 1690 cm^{-1}.

In this investigation, we prepared many related compounds and obtained new information concerning their pseudoaromatic chartacteristics from their spectral properties. Indeed, 3-acylimino or carbamoylimino dithiazole derivatives showed the same behavior as 2-acetylimino-5-dimethylamino-3*H*-1,2,4-dithiazole, except in a few cases.

Dithiazole derivatives, prepared by the oxidation of dithiobiurets, are well known as thiurets. Their structure had been studied by mean of IR, UV, X-ray, *etc.*, and their pseudoaromatic ring system has been confirmed by many workers. Unsubstituted thiuret, prepared by the oxidation of dithiobiuret with hydrogen peroxide in hydrochloric acid, was first formulated as having a hydrochloride of diiminodithiazole structure I,[2] but this compound formed salt with only one equivalent of acid; therefore, Jensen, Baccaro and Buchardt[3] considered that the basic ion was the diaminodithiazolyl ion, II. Furthermore, they described that 1,2,4-dithiazole derivatives showed an strong infrared band at 1510—1540 cm^{-1} which is due to the aromatic ring system.

Foss and Tjomsland[4] obtained data denying the I structure by X-ray methods, but they suggested that the conjugation does not extend over the S–S bond, unlike the cases of 3-alkyl or phenyl-1,2-dithiolium salts.[5]

Hordvik and Sundsfjord[6] concluded, from their structural investigations of the hydrobromide and the hydrochloride, that the relative weight of the resonance form containing the S–S double bond should be smaller in the 3,5-diamino-1,2-dithiolium ion than in the unsubstituted 1,2-dithiolium ion. Prinzbach and Futterer[7] described, with regard to the ion structure of 1,2 and 1,3-dithiolium salts, that the positive charge is largely locarized on the exocyclic nitrogen atom; they concluded this from the chemical shift of the proton at the 4 position in the nmr spectra. That is, the chemical shifts for H-4 in the cases of the 3,5-diamino VI and dimorpholino VIII derivatives appear in a high field (6.52 and 6.46 ppm) in comparison with the substituted 1,2-dithiolium salts (8—9 ppm). Thus, it is clear that the 3,5-diamino-1,2,4-dithiazole salts are of the III structure because they have the same properties as 3,5-diaminodithiolium salts. This fact has already been confirmed by Jensen, Baccaro, and Buchardt.[3] On the other hand, a preliminary result of a X-ray structural determination of 3,5-diacetamino-1,2-dithiolium iodide[8] indicates that a partial bonding between sulfur and oxygen leads to a shortening of the S–S bond; consequently, the stability of the dithiolium cation increases upon acetylation.



Results and Discussion

Preparation of the Starting 3H-1,2,4-Dithiazole Salts. 1-Mono or disubstituted 2,4-dithiobiurets, which were the starting materials of this study, were prepared by known methods. The first of these is by the fusion of

1) I. Iwataki and A. Ueda, This Bulletin, in press.

2) P. W. Preisler and M. M. Bateman, *J. Amer. Chem. Soc.*, **69**, 2632 (1947).

3) K. A. Jensen, H. R. Baccaro, and O. Buchardt, *Acta Chem. Scand.*, **17**, 163 (1963).

4) O. Foss and O. Tjomsland, *ibid.*, **12**, 1799 (1958).

5) A. Hordvik and H. M. Kjoge, *ibid.*, **19**, 935 (1965).

6) A. Hordvik and L. Sundsfjord, *ibid.*, **19**, 753 (1965).

7) H. Prinzbach and E. Futterer, Advances in Heterocyclic Chemistry, **7**, 39 (1966), Academic Press, New York, N. Y.

8) A. Hordvik and H. M. Kjoge, *Acta Chem. Scand.*, **19**, 523 (1965).

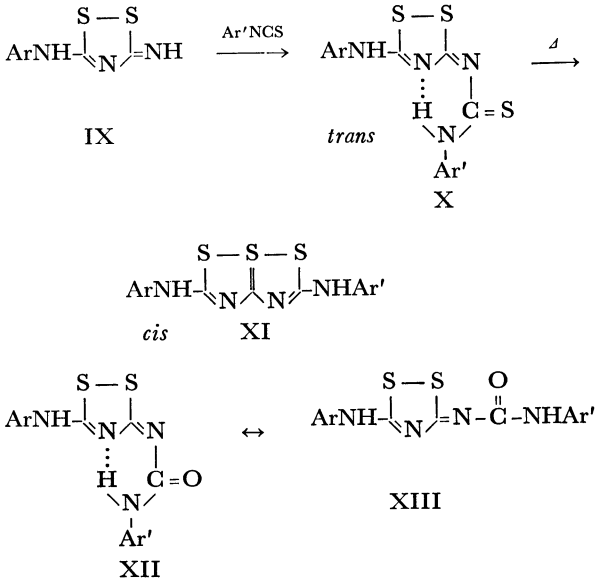
arylamines with perthiocyanic acid.[9] The second method is that of Dixit[10] whereby perthiocyanic acid is treated with aliphatic amines in water. He described that 1-alkyl-2,4-dithiobiurets were obtained in good yields at an ordinary temperature, but most of the 1,1-disubstituted derivatives could not be obtained by this method. The third method is the action of amines on methyl trithioallophanate. Bousquet obtained 1-aryl-2,4-dithiobiurets by the reaction of potassium trithioallophanate with anilines.[11] Aliphatic amines reacted with it, but no pure product could be obtained. On the other hand, methyl trithioallophanate which has been prepared from the potassium salt with dimethyl sulfate reacted with dialkylamines at an ordinary temperature to give 1,1-dialkyl-2,4-dithiobiurets. 1,1,5-Trisubstituted-2,4-dithiobiurets were also obtained from dialkylthiocarbamoylisothiocyanates.[12] The dithiobiurets thus prepared were oxidized with chlorine in an alcohol or chloroform solution to give the corresponding 3*H*-1,2,4-dithiazole hydrochlorides in good yields.

5-Alkylamino-*3*-imino or *5*-alkylamino-*3*-alkylimino dithiazole salts were prepared by Dixit's method[13] by means of the oxidative debenzylation of S-benzylisodithiobiurets which had previously been obtained by the reaction of S-benzylisothioureas and alkylisothiocyanates without going through dithiobiurets. Generally, free bases of 5-substituted amino-3-iminodithiazole salts are unstable and decompose to substituted cyanothioureas under alkaline conditions, even at low temperatures,[14] but 3-alkylimino derivatives are stable and can be isolated as free bases.[13]

Acylation of the Imino Group. Salts of the dithiazole derivatives react with acid anhydride in acetone or benzene at ordinary temperatures in the presence of 2 mole equivalents of tertiary amines to give the corresponding 3-acylimino derivatives. Higher fatty acid anhydrides, such as capric or palmitic anhydride, are less reactive and require heating. Acid halides also react with the salts, but the yields are always very low. In these cases, the acylation will occur on sulfur atoms and results in ring opening and decomposition. Acetic and propionic anhydrides react with them without tertiary amines, and keeping only at room temperature gives the corresponding acetylated or propionylated derivatives in good yields. 3-Acyliminodithiazoles are thermally unstable under alkaline conditions. When the reaction is carried out at a higher temperature, the primary product is formed first, but it is decomposed later by excess tertiary amine.

*Preparation of 3-acylimino-5-alkylthio-3*H*-1,2,4-dithiazoles.* Hydroiodides of 5-alkylthio derivatives were prepared by the method of Allen and Shelton from alkyl trithioallophanates.[15] The subsequent treatment of these salts with acid anhydrides, as described above, afforded the corresponding acylated compounds.

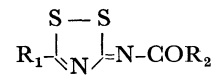
Spectral Properties. The dithiazole derivatives which were prepared by the above methods showed characteristic behavior in the infrared spectra. The frequencies of the carbonyl and C=N stretching bands of the related compounds are shown in Table 1. Most of the free bases of the 3-acylimino or carbamoylimino derivatives do not show carbonyl absorption in the region normally expected for amide groups, but a pair of absorptions appears at 1550—1600 cm^{-1}. These two bands have equal intensities, and one of them may be assigned to the C=N stretching band. All the 3-acylimino derivatives form salts with mineral acids, and the infrared spectra of the corresponding salts show an carbonyl absorption in the ordinary region, like mesoionic compounds (cf. Table 2).



Behringer and Weber[16] obtained a trans form of 5-anilino-3-(N-phenyl)thiocarbamoylimino-3H-1,2,4-dithiazole X when IX was treated with phenylisothiocyanate, then it was converted to the *cis* form XI by heating. They confirmed those structures by studying the UV spectra. On the other hand, they also prepared carbamoyl derivatives; in those cases, they presumed that the carbamoyl groups were present in the tautomeric form, as is shown (XII and XIII). However, 5-dimethylamino-3-carbamoylimino derivatives showed an infrared absorption band of the carbonyl group in a region similar to that of the corresponding acyl derivatives, unlike the cases of 5-alkylamino or anilino-3-carbamoylimino derivatives. The difference between 5-dimethylamino and 5-monoalkyl or arylamino derivatives was further confirmed by studying the UV spectra. The UV spectra of the related compounds are shown in Table 3 and Fig. 1—3. Fig. 1 shows the spectra of the starting dithiazole

9) E. Fromm, *Ann.*, **275**, 20 (1893), A. E. S. Fairfull and D. A. Peak, *J. Chem. Soc.*, **1955**, 796.
10) S. N. Dixit, *J. Indian Chem. Soc.*, **38**, 44 (1961).
11) E. W. Bousquet and H. G. Guy, U. S. 2410862 (1946).
12) L. A. Spurlock and P. E. Newallis, *J. Org. Chem.*, **33** 2073 (1968). J. Goerdeler and H. Ludke, *Ber.*, **103**, 3393 (1970).
13) S. N. Dixit and V. K. Verma, *Indian J. Chem.*, **1** 487 (1963), S. N. Dixit, *J. Indian Chem. Soc.*, **39**, 407 (1962), C. P. Joshua and V. K. Verma, *ibid.*, **38**, 988 (1961), S. N. Dixit, *ibid.*, **40**, 153 (1963).
14) V. L. Nirenburg and I. Ya. Postouskii, *Zhur. Obshchei Khim.*, **28**, 198 (1958).
15) R. E. Allen, R. S. Shelton, and M. G. Van Campen, *J. Amer. Chem. Soc.*, **76**, 1158 (1954).
16) H. Behringer and D. Weber, *Chem. Ber.*, **97**, 2567 (1964).

Table 1. Infrared spectra of 3,5-disubstituted 3*H*-1,2,4-dithiazoles



S. No.	R_1	R_2	C=O	C=N	Kind of salts and Mp (°C)		C=O	C=N or NH (cm^{-1})
(1)	$N(CH_3)_2$	CH_3	1600	1570	HCl	215[a)]	1690	1600
(2)	$N(CH_3)_2$	C_2H_5	1600	1560	HSCN	183—184[a)]	1685	1610
(3)	$N(CH_3)_2$	*n*-C_3H_7	1590	1570	HSCN	152—153	1690	1600
(4)	$N(CH_3)_2$	*n*-C_5H_{11}	1600	1570	HCl	92— 94	1690	1610
(5)	$N(CH_3)_2$	*n*-C_9H_{19}	1590	1560	HCl	115—117	1690	1610
(6)	$N(CH_3)_2$	$CH{=}CH{-}CH_3$	1590	1540	HCl	166—169[a)]	1670	1605
(7)	$N(CH_3)_2$	C_6H_5	1580	1530	HCl	148—149	1655	1605
(8)		CH_3	1570	1540	HSCN	159—160	1685	1580
(9)		CH_3	1560	1540	HSCN	157—159	1680	1590
(10)		CH_3	1560	1550	HCl	196—197[a)]	1695	1600
(11)	$N(C_6H_5)(CH_3)$	CH_3	1570	1540	HSCN	160—162[a)]	1660	1600
(12)	$N(C_6H_5)H$	CH_3	1590	1585	HCl	194—195[a)]	1690	1620
(13)	$N(C_6H_5)(COCH_3)$	CH_3	1690 1590	1585	HCl	180—181	1690 1680	1590
(14)	$N(CH_3)(COCH_3)$	CH_3	1670 1590	1575	HCl	142—145[a)]	1680 1670	1600
(15)	SCH_3	CH_3	1570	1560	HSCN	143—144[a)]	1690	(1520)
(16)	SC_2H_5	CH_3	1580	1570	HSCN	112—113[a)]	1700 1680	(1510)
(17)	$SCH_2C_6H_5$	CH_3	1560	1555	HSCN	132—135[a)]	1680	(1510)
(18)	$N(CH_3)_2$	$NHCH_3$	1610	1590	HCl	230[a)]	1680 1670	1600
(19)	$N(CH_3)_2$	NHC_6H_5	1590	1550	HCl	212—214[a)]	1705	1705
(20)	NHC_6H_5	$NHCH_3$	1720	1610	HSCN	171—172[a)]	1680 1660	1600
(21)	NHC_6H_5	NHC_6H_5	1690	1630	HCl	202—203[a)]	1700	1630

a) Decomp.

Table 2. Infrared spectra of mesoionic compounds

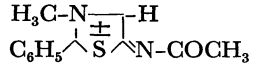
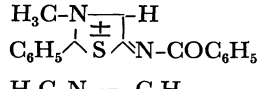
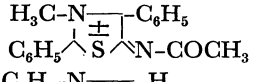
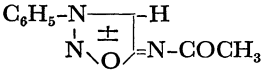
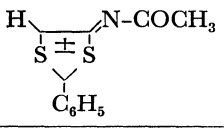
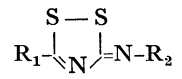
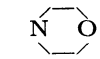
S. No.	Compounds	C=O	Kind of salts	C=O	Ref.
(1)		1560	HCl	1660	17)
(2)		1580 1560	HCl	1750 1650	17)
(3)		1550	HCl	1660	17)
(4)		1640	HCl	1720	18)
(5)			HCl	1670	19)

TABLE 3. UV SPECTRA OF 3,5-DISUBSTITUTED 3*H*-1,2,4-DITHIAZOLES



S. No.	R_1	R_2	λ_{max}^{EtOH} mμ (log ε)	$\lambda_{max}^{EtOH+HCl}$ mμ (log ε)	
(1)	$N(CH_3)_2$	$COCH_3$	297.7 (4.25)	312.6 (3.90)	272.1 (4.00)
(2)	$N(CH_3)_2$	COC_2H_5	297.8 (4.32)	311.9 (3.89)	273.1 (4.22)
(3)	$N(CH_3)_2$	CO-*n*-C_3H_7	299.1 (4.32)	313.4 (3.90)	273.9 (4.23)
(4)	$N(CH_3)_2$	CO-*n*-C_5H_{11}	298.7 (4.31)	313.1 (3.86)	273.0 (4.21)
(5)	$N(CH_3)_2$	COC_6H_5	319.5 (4.19) 253.6 (4.20)	319.5 (4.12)	284.2 (4.51) 254.3 (4.37)
(6)	$N(C_6H_5)CH_3$	$COCH_3$	299.5 (4.31)	321.2 (3.87)	277.4 (4.23)
(7)		$COCH_3$	301.2 (4.33)	319.8 (4.12)	275.2 (4.30)
(8)		$COCH_3$	300.1 (4.37)	314.2 (4.02)	273.5 (4.25)
(9)	$N(C_6H_5)H$	$COCH_3$	314.7 (4.22) 244.0[a] (4.16)	345.9 (4.03)	281.9 (4.16)
(10)	SCH_3	$COCH_3$	340.1[a] (3.91) 307.2 (4.20)	332.3 (3.99)	301.8 (4.18)
(11)	$N(CH_3)_2$	$COOC_2H_5$	285.7 (4.37)	301.2 (3.91)	265.6 (4.31)
(12)	$N(CH_3)_2$	*t*-C_4H_9	290.0[a] (4.16) 258.0 (4.39)	294.0[a] (4.19)	266.0 (4.46)
(13)	$N(CH_3)_2$	C_6H_5	299.9[a] (3.95) 257.9 (4.36)	318.4[a] (4.17)	285.7 (4.33)

a) shoulder

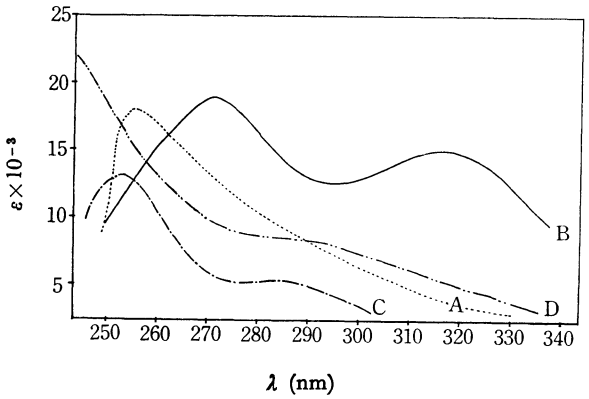


Fig. 1. UV spectra of 5-alkylamino or anilino-3-imino-3H-1,2,4-dithiazole salts.
A ····· 5-dimethylamino-3-imino-, hydrochloride.
B ——— 5-anilino-3-imino-, hydrochloride.
C —·—· 5-methylamino-3-imino-, hydrobromide.
D —··— 5-anilino-3-imino-.

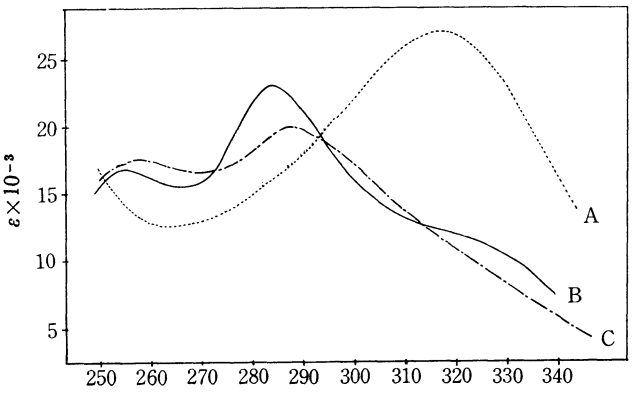


Fig. 2. UV spectra of 5-anilino or dimethylamino-3-(N-phenyl)carbamoylimino or benzoylimino-3*H*-1,2,4-dithiazoles.
A ····· 5-anilino-3-(*N*-phenyl)carbamoylimino-.
B ——— 5-dimethylamino-3-benzoylimino-.
C —·—· 5-dimethylamino-3-(*N*-phenyl)carbamoylimino-.

salts. The spectrum of 5-dimethylamino-3-(N-phenyl)carbamoylimino derivative is very similar to the corresponding 3-benzoylimino derivative and differs a little from the spectrum of the 5-anilino-3-(N-phenyl)carbamoylimino derivative. From this fact, it is obvious that the carbamoyl group of the 5-dimethylamino compound has the same conformation as the corresponding acyl derivatives and is located at the *cis* position, because the interaction between S and O can occur only at the *cis* form. Actually, all the acylimino derivatives will be in the *cis* form, because the intramolecular hydrogen bonding can not arise in the acyl series. The spectra of 3-(*N*-methyl)-carbamoylimino-5-substituted amino dithiazoles are shown in Fig. 3. The 5-monoalkylamino and 5-anilino derivatives gave similar spectra. They contain two amino protons, namely, *a* and *b*; the *a* proton is able to shift to the imino nitrogen at the 3 position by resonance, as is shown in XV, and then XV isomerizes to the trans structure, such as XVI or XVII.

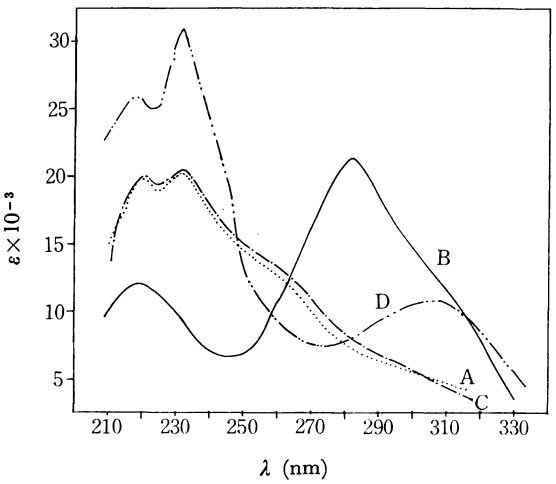
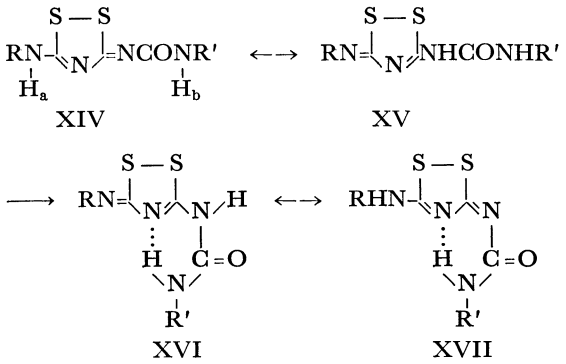


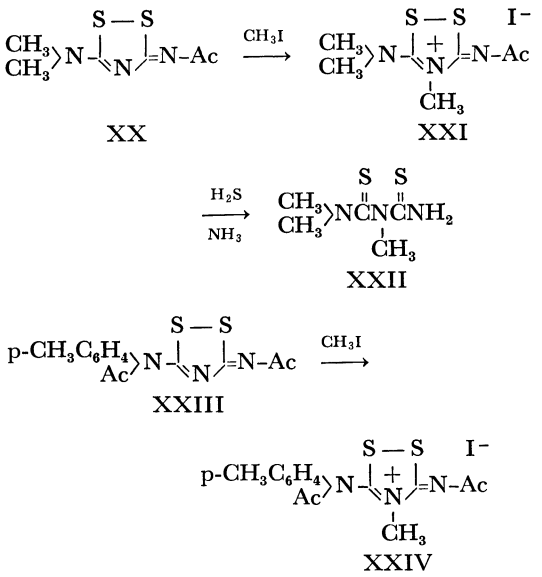
Fig. 3. UV spectra of 3-(*N*-methyl)carbamoylimino-3*H*-1,2,4-dithiazole derivatives.
A ····· 5-methylamino-.
B ——— 5-dimethylamino-.
C —·—· 5-ethylamino-.
D —··— 5-anilino-.

The presence of the *b* proton facilitates the formation of the stable *trans* conformation by intramolecular hydrogen bonding. On the other hand, as the 5-dimethylamino derivative does not contain the *a* proton, the resonance between XIV and XV does not occur and the *cis* compound is formed as in the cases of the acylation.



All the acylimino derivatives showed an absorption at about 290 mμ similar to the *N*-acyl sydnonimines,[19] and their salts showed a charge separation between the dithiazole ring and the exocyclic acylimido group.

A carbonyl group which combines with the 3-imino group facilitates the formation of a dithiazolyl cation, as is shown by XVIII and XIX; as a result, the dithiazole ring may be stable, like other heteroaromatic compounds.



5-Alkyl or arylamino-3-acyliminodithiazoles were easily reacted with methyl iodide to give the methiodides in good yields. In these cases, the methylation occurred at the 4 position because, by the treatment of an alcoholic solution of a dithiazole with alkaline sulfide, it is smoothly reduced to a 3-methylated dithiobiuret. For instance, XX reacted with methyl iodide to form XXI, when kept at only room temperature, and was then reduced to XXII with hydrogen sulfide and ammonia in a hot ethanolic solution. Diacetyl derivatives such as XXIII also reacted with methyl iodide to give the corresponding methiodide XXIV. The methiodides thus obtained showed an infrared absorption band of the carbonyl group at 1670 cm^{-1}, and they decomposed upon treatment with alkali, even with sodium bicarbonate. These results suggest that the positive charge may be localized on the nitrogen atom at the 4 position and that the dithiazole ring may be unstable.

Experimental

The melting points are uncorrected. The ultraviolet spectra were recorded on a Shimadzu model MPS-50L apparatus. The infrared spectra were recorded on a JASCO model IR-G spectrophotometer in Nujol mull.

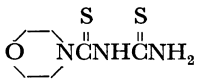
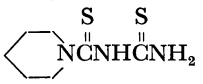
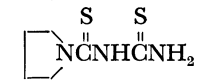
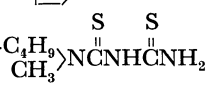
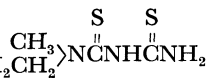
Formation of 1-Substituted 2,4-Dithiobiuret from Amines and Methyl Trithioallophanate. To a suspended solution of methyl trithioallophanate (0.1 mol) in 50 m*l* of ethanol, the amine (0.2 mol) was added at an ordinary temperature. When the reaction mixture was warmed with stirring, the methyltrithioallophanate gradually went into the solution. The resulting solution was stirred for 1 hr at 30—40°C and poured into 300 m*l* of 1 N-hydrochloric acid. The precipitate was then filtered off and recrystallized from ethanol. In this manner, the following dithiobiurets were prepared.

Di-*n*-propyl, di-*i*-propyl and di-*n*-butyl amines all failed to react with methyl trithioallophanate.

Formation of 3,5-Disubstituted 3H-*1,2,4-Dithiazoles, Oxidation of 1,1-Disubstituted 2,4-Dithiobiurets.* 2,4-Dithiobiurets were easily oxidized to the related dithiazole salts with many oxidizing reagents, for example, iodine, bromine, hydrogen peroxide, ferric chloride and sodium hypochlorite in an acidic medium.

17) T. Shiba and H. Kato, This Bulletin, **44**, 1864 (1971).
18) H. V. Daeniker and J. Druey, *Helv. Chim. Acta*, **45**, 2426 (1962).
19) M. Ohta and M. Sugiyama, This Bulletin, **36**, 1437 (1963).

Table 4. Formation of *l*-substituted 2,4-dithiobiurets

Dithiobiuret prepared	Yield %	Mp °C	Mol. formula	Nitrogen, % Found	Nitrogen, % Reqd	Sulfur, % Found	Sulfur, % Reqd
	65	138[a)]	$C_6H_{11}N_3OS_2$	20.27	20.49	31.45	31.22
	57	138—139	$C_7H_{13}N_3S_2$	20.57	20.69	31.64	31.53
	89	188[a)]	$C_6H_{11}N_3S_2$	22.35	22.22	33.71	33.86
	48	69— 72	$C_7H_{15}N_3S_2$	20.61	20.49	31.32	31.22
	43	137—138*	$C_5H_{11}N_3OS_2$	21.49	21.72	33.34	33.16

a) Decomp.

A small quantity (0.1 mol) of the dithiobiuret was dissolved in 50 m*l* of chloroform or ethanol, and an excess of chlorine gas was passed through the solution with stirring at an ordinary temperature. The hydrochloride thus precipitated was filtered and washed with acetone. It was almost pure and could be used in the next reaction without recrystallization. All of the 1,1-disubstituted 2,4-dithiobiurets were oxidized in a similar manner.

*Oxidation of 1-Alkyl-4*S*-benzyliso-2,4-dithiobiurets.* 5-Methylamino, 5-isopropylamino, and 5-*n*-butylamino-3*H*-1,2,4-dithiazole hydrobromides were prepared by Dixit's method.[13)]

The isodithiobiuret (0.1 mol) was dissolved in 50 m*l* of chloroform, and then bromine (0.11 mol) was stirred in 40°C. The precipitate was filtered and washed with acetone. The yield was 80—90%: 5-methylamino-3-imino-3*H*-1,2,4-dithiazole hydrobromide, mp 232—233°C (decomp.) (Ref. 13, mp 228°C), 5-isopropylamino-3-imino-, mp 215—218°C (decomp), 5-*n*-butylamino-3-imino-, mp 189—193°C (decomp.).

Formation of 1,1,5-Trisubstituted 2,4-Dithiobiurets. Freshly-prepared dimethylthiocarbamoyl isothiocyanate[12)] (0.1 mol) was dissolved in 50 m*l* of acetone, and then the amine (0.1 mol) was added at an ordinary temperature. The solution was stirred for 1 hr, the solvent was removed *in vacuo*, and the crystalline residue was recrystallized from ethanol. The yield was almost quantitative. In this manner, the following new dithiobiurets were prepared:
1,1-dimethyl-5-*t*-butyl-2,4-dithiobiuret, mp 102—103°C. Found: C, 43.84; H, 7.76; N, 19.18; S, 29.22%. Required for $C_8H_{17}N_3S_2$: C, 43.55; H, 7.76; N, 18.84; S, 28.88%.
1,1-dimethyl-5-phenyl-, mp 83—84°C. Found: C, 50.21; H, 5.44; N, 17.57; S, 26.78%. Required for $C_{10}H_{13}N_3S_2$; C, 50.08; H, 5.81; N, 17.37; S, 26.88%.

*Formation of 1,1-Dimethyl-5-t-butylimino-*3H*-1,2,4-dithiazole.* 1,1-Dimethyl-5-*t*-butyl-2,4-dithiobiuret (11 g, 0.05 mol) was dissolved in 50 m*l* of ethanol, and then bromine (8 g) was added at 0°C. The precipitate was filtered and dissolved in 300 m*l* of water; subsequent neutralization with potassium carbonate gave 10 g (91%) of the dithiazole. The substance was recrystallized from ethanol as pale yellow prisms. Mp 76—77°C. Found: C, 43.94; H, 6.61; N, 19.10; S, 29.54%. Required for $C_8H_{15}N_3S_2$: C, 44.24; H, 6.91; N, 19.35; S, 29.49%.

1,1-Dimethyl-5-phenylimino-3*H*-1,2,4-dithiazole was prepared by the same procedure. Mp 89—90°C. Found: C, 50.33; H, 4.58; N, 17.81; S, 26.86%. Required for $C_{10}H_{11}N_3S_2$: C, 50.63; H, 4.64; N, 17.72; S, 27.00%.

*Formation of 5-Alkylthio-3-imino-*3H*-1,2,4-dithiazole Hydroiodide.* Alkyl trithioallophanate were oxidized by the known method.[15)] The yield was always quantitative, and the following hydroiodides were thus prepared: 5-methylthio-3-imino-3H-1,2,4-dithiazole hydroiodide, mp 161—163°C (Ref. mp 157°C), 5-ethylthio-, mp 143—144°C (Ref. mp 143—145°C), 5-benzylthio-, mp 133—134°C. Found: C, 29.61; H, 2.34; N, 7.53; S, 26.38; I, 34.55%. Required for $C_9H_9IN_2S_3$: C, 29.32; H, 2.45; N, 7.61; S, 26.09; I, 34.51%.

*Acylation of 5-Substituted Amino or Alkylthio-3-imino-*3H*-1,2,4-dithiazole Salts.* *(A) With Tertiary Amine*: The dithiazole salt (0.05 mol) and the required acid anhydride (0.1 mol) were mixed in 50 m*l* of acetone, and then triethylamine (0.1 mol) was stirred in at room temperature. The exothermic reaction was observed, and the temperature was raised to 30—40°C. The mixture was stirred for 1 hr at this temperature, and then poured into water and made alkaline with potassium carbonate. The resulting precipitate was filtered off, washed with water, and recrystallized from methanol or ethanol.

(B) Without Tertiary Amine: The dithiazole salt (0.05 mol) and the acid anhydride (0.2 mol) were heated at 50—60°C for 1 hr with stirring; the mixture was then poured into water, and the precipitate was filtered off, washed with water, and recrystallized from methanol or ethanol.

(C) With Acyl Halides Instead of Acid Anhydrides: Into a mixture of the dithiazole salt (0.05 mol) and the acyl halide (0.05 mol) in 50 m*l* of acetone, pyridine (0.05 mol) was stirred at room temperature, that temperature was maintend for 20 min. The mixture was then poured into water, and the precipitate was collected and then recrystallized from alcohol, acetone, *n*-hexane, *etc.* The results are summarized in Table 5.

*Formation of 5-Anilino-3-acetylimino-*3H*-1,2,4-dithiazole.* A mixture of 5-anilino-3-imino-3*H*-1,2,4-dithiazole (1.1 g) and 1-acetylimidazole (0.6 g) in 10 m*l* of tetrahydrofuran was allowed to stand for 1 week at room temperature. The solution was then poured into water, and the precipitate was collected. Recrystallization from alcohol gave 1 g of yellow needles, melting at 191—192°C with decomposition. Found: C, 47.92; H, 3.51; N, 16.64; S, 25.72%. Re-

quired for $C_{10}H_9N_3OS_2$: C, 47.81; H, 3.59; N, 16.73; S, 25.50%. This substance was converted to a diacetyl derivative with acetic anhydride and pyridine. The melting points and infrared spectra were identical.

Formation of 3-Acetylimino-5-dimethylamino-4-methyl-3H-*1,2,4-dithiazolium Iodide, XX.* 3-Acetylimino-5-dimethylamino-3H-1,2,4-dithiazole (3 g) and methyl iodide (10 m*l*) were refluxed in acetone (20 m*l*) for 1 hr and then allowed to stand at room temperature for 2 days. The resulting precipitate was filtered off, washed with acetone, and recrystallized from ethanol, affording the methiodide (4.2 g, 85%) as pale yellow needles. Mp 208—209°C with decomposition. Found: C, 24.36; H, 3.52; I, 36.73; N, 12.32; S, 18.89%. Required for $C_7H_{12}IN_3OS_2$: C, 24.35; H, 3.48; I, 36.81; N, 12.17; S, 18.55%. IR: 1670 cm^{-1} (C=O).

3-Acetylimino-4-methyl-5-(*N-p*-tolyl)acetamido-3*H*-1,2,4-dithiazolium iodide XXIII was prepared by the same procedure as a yellow powder. The yield was 65%. Mp 190—191°C with decomposition. Found: C, 35.91; H, 3.10; I, 28.95; N, 9.42; S, 14.85%. Required for $C_{13}H_{14}IN_3O_2S_2$: C, 35.86; H, 3.22; I, 29.20; N, 9.66; S, 14.71%. IR: 1690, 1680 cm^{-1} (C–O).

Reduction of 3-Acetylimino-5-dimethylamino-4-methyl-3H-*1,2,4-dithiazolium Iodide, XXII.* Into a suspended solution of the methiodide (2.8 g) in 10 m*l* of ethanol and 20 m*l* of 28%-aqueous ammonia, hydrogen sulfide was passed for 1 hr

Table 5. 5-Substituted amino or alkylthio-3-acylimino-3*H*-1,2,4-dithiazoles prepared

S. No.	R_1	R_2	Method	Yield %	Mp °C		Anal. C	H	N	S
(1)	$N(CH_3)_2$	C_2H_5	B	82	89— 90	Found	38.73	5.36	19.44	29.73
						Calcd	38.71	5.07	19.35	29.49
(2)	$N(CH_3)_2$	n-C_3H_7	B	65	85— 84	Found	41.87	5.35	18.06	28.00
						Calcd	41.55	5.62	18.18	27.70
(3)	$N(CH_3)_2$	n-C_5H_{11}	A	64	69— 70	Found	46.18	6.74	16.20	24.98
						Calcd	46.33	6.56	16.22	24.71
(4)	$N(CH_3)_2$	n-C_9H_{19}	A	31	73— 74	Found	53.29	8.11	12.98	20.18
						Calcd	53.33	7.94	13.33	20.32
(5)	$N(CH_3)_2$	n-$C_{15}H_{31}$	A	23	83— 84	Found	60.15	9.34	10.63	15.87
						Calcd	60.15	9.27	10.52	16.04
(6)	$N(CH_3)_2$	C_3H_5	A	16	141—142	Found	41.87	4.79	18.40	27.90
						Calcd	41.92	4.80	18.34	27.95
(7)	$N(CH_3)_2$	C_6H_5	A	75	209—210	Found	50.22	4.13	16.02	24.14
						Calcd	49.81	4.15	15.85	24.15
(8)	$N(CH_3)_2$	C_6H_4-p-Cl	C	16	204—205	Found	44.16	3.28	13.97	21.13
						Calcd	44.07	3.34	14.02	21.37
(9)	$N(CH_3)_2$	CH_2Cl	A	86	151—152	Found	30.16	3.52	17.40	27.35
						Calcd	30.32	3.37	17.68	26.95
(10)	$N(CH_3)_2$	CF_3	A	11	146—147	Found	28.02	2.65	16.60	24.99
						Calcd	28.02	2.33	16.34	24.90
(11)	$N(CH_3)_2$	OC_2H_5	C	34	129—130	Found	36.16	4.97	17.70	27.62
						Calcd	36.05	4.72	18.03	27.47
(12)	$N(CH_3)C_6H_5$	CH_3	A	83	145—146	Found	49.94	4.07	15.88	23.97
						Calcd	49.81	4.15	15.85	24.15
(13)		CH_3	A	71	161—162	Found	39.36	4.34	16.97	25.99
						Calcd	39.18	4.44	17.14	26.12
(14)		CH_3	A	74	101—102	Found	44.34	5.47	17.25	26.05
						Calcd	44.34	5.34	17.28	26.33
(15)		CH_3	A	88	169—170	Found	41.69	4.78	18.29	27.66
						Calcd	41.92	4.80	18.34	27.95
(16)	$N(CH_3)COCH_3$	CH_3	A	38	158—159[a]	Found	36.37	3.86	18.03	27.63
						Calcd	36.36	3.90	18.18	27.71
(17)	$N(i$-$C_3H_7)H$	CH_3[b]	A	55	167—168	Found	38.69	5.15	19.32	29.33
						Calcd	38.71	5.07	19.36	29.49
(18)	$N(n$-$C_4H_9)COCH_3$	CH_3	A	45	163—164	Found	43.97	5.41	15.14	23.56
						Calcd	43.96	5.49	15.38	23.44
(19)	$N(C_6H_4$-p-$CH_3)COCH_3$	CH_3	A	74	178—179	Found	50.72	4.19	13.71	20.92
						Calcd	50.81	4.23	13.68	20.85
(20)	SCH_3	CH_3	A	71	111—112[a]	Found	32.48	3.51	12.91	43.57
						Calcd	32.73	3.64	12.73	43.64
(21)	SC_2H_5	CH_3	A	64	173—174[a]	Found	28.98	2.65	13.49	46.91
						Calcd	29.13	2.91	13.59	46.60
(22)	$SCH_2C_6H_5$	CH_3	A	53	128—129	Found	46.74	3.92	9.78	34.04
						Calcd	46.81	3.55	9.93	34.04

a) Decomp. b) Diacetyl compound could not be obtained.

at 40°C. The methiodide was then gradually fed into the solution, which thereby turned yellow. The solution was then cooled and acidified with concentrated hydrochloric acid. The white solid was filtered off, washed with water, and recrystallized from ethanol. Thus, 1,1,3-trimethyl-2,4-dithiobiuret (0.65 g) was obtained, while from the mother liquor, 1,1,3-trimethyl-5-acetyl-2,4-dithiobiuret (0.09 g) was obtained. The latter compound was obtained by the acetylation of the dithiobiuret. Their IR, tlc, and mp were identical. 1,1,3-trimethyl-2,4-dithiobiuret: mp 100—102°C. Found: C, 33.60; H, 6.11; N, 23.39; S, 36.48%. Required for $C_5H_{11}N_3S_2$: C, 33.90; H, 6.21; N, 23.73; S, 36.16%. 1,1,3-triemethyl-5-acetyl-2,4-dithiobiuret: mp 161—162°C. IR: 1720 cm^{-1} (C=O).

Formation of 5-*Methylamino*-3-(*N-methyl*)*carbamoylimino*-3H-1,2,4-*dithiazole.* To a suspended solution of 3-imino-5-methylamino-3H-1,2,4-dithiazole hydrobromide (2.3 g) and methyl isocyanate (0.6 g) in 20 m*l* of tetrahydrofuran, triethylamine (1 g) was added at room temperature. The solution was stirred for 1 hr, and poured into water, and then the precipitate was filtered off. Recrystallization from dimethylformamide gave 1 g of white crystals, melting at 229—230°C. Found: C, 29.38; H, 3.99; N, 27.23; S, 31.49%. Required for $C_5H_8N_4OS_2$: C, 29.41; H, 3.92; N, 27.45; S, 31.37%. IR: 1670 cm^{-1} (C=O). The following new 3-(*N*-substituted)carbamoyliminodithiazoles were prepared by the same method. 5-Ethylamino-3-(*N*-methyl)carbamoylimino-: mp 223—224°C. Found: C, 29.81; H, 4.62; N, 25.38; S, 29.39%. Required for $C_6H_{10}N_4OS_2$: C, 33.03; H, 4.59; N, 25.69; S, 29.36%. IR: 1680 cm^{-1} (C=O). 5-Anilino-3-(*N*-methyl)carbamoylimino-: mp 162—163°C with decomposition. Found: C, 45.23; H, 3.85; N, 20.91; S, 24.02%. Required for $C_{19}H_{10}N_4OS_2$: C, 45.11; H, 3.76; N, 21.05; S, 24.06%. 5-Dimethylamino-3-(*N*-methyl)carbamoylimino-: mp 218°C with decomposition. Found: C, 33.15; H, 4.92; N, 25.68; S, 29.57%. Required for $C_6H_{10}N_4OS_2$: C, 33.03; H, 4.59; N, 25.69; S, 29.36%. 5-Dimethylamino-3-(*N*-phenyl)carbamoylimino-: mp 183.5°C with decomposition. Found: C, 46.88; H, 4.57; N, 20.05; S, 22.46%. Required for $C_{11}H_{12}N_4OS_2$: C, 47.17; H, 4.29; N, 20.00; S, 22.86%.

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