The acidic hydrogen in the nmr spectrum of 8 and the discovery that 8 was soluble in aqueous NaOH prompted the assignment of the salt structure to 7. We mentioned earlier that the iminodithiazoles formed salts with acids, and apparently 8 is acidic enough to protonate 1c. The ability of sulfur to stabilize both positive and negative charges is reflected in this facile rearrangement of a strongly basic molecule into an acidic isomer. The structure of 7 has also been studied by X-ray crystallography. Details of this study and that on molecule 4a will be published elsewhere.

Experimental Section[11,12]

Iminodithiazoles 1a–c were prepared and stored as hydrobromides as described previously.[1] The bases 1a–c were obtained by partitioning the appropriate HBr salt between aqueous Na_2CO_3 and CH_2Cl_2, drying the CH_2Cl_2 solutions ($MgSO_4$), and stripping the solvents at room temperature.

Self-Consensation of 5-(Dimethylamino)-3-(methylimino)-1,2,4-dithiazole (1a). A flask containing 1.12 g of 1a was heated under N_2 on a steam bath for 1 hr. The original solid melted, then the resulting oil slowly solidified. MeOH (45 ml) was added and the mix was boiled for a few minutes and then filtered while hot. Upon cooling to room temperature the solution deposited 0.79 g (78%) of crude 1a, mp 170–181°. Recrystallization from EtOAc and then from 2-butanone gave 0.50 g of 4a, mp 183–184°. The analytical sample had mp 185–186° (EtOAc).

Anal. Calcd for $C_{10}H_{18}N_6S_3$: C, 37.71; H, 5.70; N, 26.39; S, 30.20. Found: C, 37.81; H, 5.66; N, 26.29; S, 30.12.

The nmr spectrum (pyridine) consisted of singlets at δ 3.48 and 3.32 (CH_3N), a pair of singlets at δ 3.15 and 3.17 [$(CH_3)_2N$], and a broad singlet at δ 3.39 [$(CH_3)_2N$].

3-(Cyclohexylimino)-5-(dimethylamino)-1,2,4-dithiazole (1b) similarly gave 4b in *ca.* 60% yield, mp 195–197° (EtOAc).

Anal. Calcd for $C_{20}H_{34}N_6S_3$: C, 52.82; H, 7.54; N, 18.48. Found: C, 52.86; H, 7.63; N, 18.45.

Thermal Decomposition of 5-(Dimethylamino)-3-(phenylimino)-1,2,4-dithiazole (1c) to 7 and 8. A sample of 1c (1.77 g) was heated under N_2 for 1 hr at 115°. The resulting material was extracted with boiling 95% EtOH; the EtOH solution was filtered and evaporated and the residue was recrystallized from EtOAc to give 1.33 g of a mixture of yellow and white solids. Recrystallization from MeOH gave 0.90 g (51%) of 7, mp 152–154. Evaporation of the filtrate and recrystallization of the residue from C_6H_6 gave 0.19 g (11%) of 8, mp 186–188°.

An analytical sample of 8 was recrystallized from 2-butanone, mp 198.5–200° (whether 8 melts at 198–200° or 186–188° appears to depend on the recrystallization solvent).

Anal. Calcd for $C_{10}H_{11}N_3S_2$: C, 50.60; H, 4.67; N, 17.70. Found: C, 50.53; H, 4.58; N, 17.76.

An analytical sample of 7 was recrystallized from EtOAc, mp 152–154°.

Anal. Calcd for $C_{20}H_{22}N_6S_4$: C, 50.60; H, 4.67; N. 17.70. Found: C, 50.68; H, 4.59; N. 17.74.

Conversion of 1c to 8 in Refluxing Toluene. A solution of 1c (0.53 g) in toluene (5 ml) was refluxed for 4 hr. Chilling the solution resulted in the separation of 0.39 g (74%) of 8, mp 184–186°.

Conversion of 7 to 8 in Refluxing Toluene. A solution of 7 (329 mg) in toluene (4 ml) was refluxed for 3 hr. The solution was chilled and 8 (237 mg, 72%) was collected, mp 187°.

Synthesis of 8 from 2-Aminobenzenethiol (11). A cold solution of 0.02 mol of dimethylthiocarbamoyl isothiocyanate (5) in 25 ml of MeCN[1a] was treated dropwise with 2.5 ml of 11. After the addition the solution was refluxed for 1 hr (H_2S evolution) and then was chilled, whereupon 2.08 g (44%) of crude 8 separated as a white solid, mp 186–188° (plus a little high-melting solid). Recrystallization from 2-butanone gave pure 8, mp 198.5–200°.

Acknowledgment. We are indebted to Dr. John Ruth for the mass spectra.

Registry No.—1a, 51568-05-9; 1b, 51568-06-0; 1c, 40229-20-7; 4a, 51593-18-1; 4b, 51593-19-2; 5, 30013-32-2; 7, 46458-54-2; 8, 6423-79-6; 11, 137-07-5.

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(10) Farbenfabriken Bayer A.-G., Netherlands Appl. 6,500,844 (July 26, 1965); *Chem. Abstr.*, **64**, 4191*f* (1966).
(11) Melting points are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer and infrared spectra were obtained on a Perkin-Elmer Model 137 Infracord. Mass spectra were recorded on a Consolidated Electrodynamics Corp. Model 21-110B high-resolution spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.
(12) Mention of a proprietary product or company does not imply endorsement by the U. S. Department of Agriculture.

Imino-1,2,4-dithiazoles. IV.[1] Alkylation as a Probe of No-Bond Resonance

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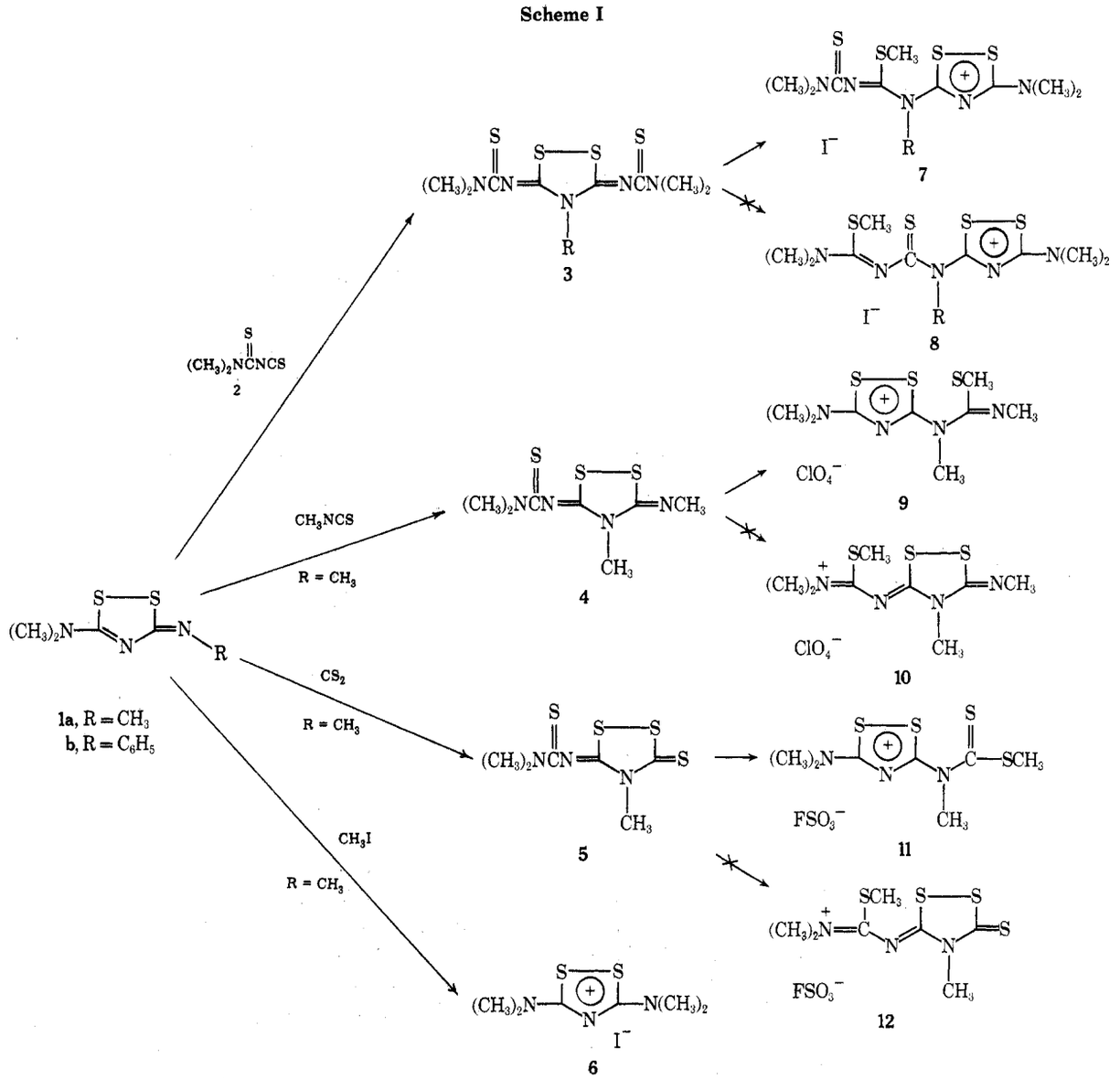
1,2,4-Dithiazoles containing strong no-bond resonance interactions react with alkylating agents at a ring sulfur, resulting in cleavage of the S–S bond. In cases where the no-bond interactions are weak, however, alkylation of the imino nitrogen may occur.

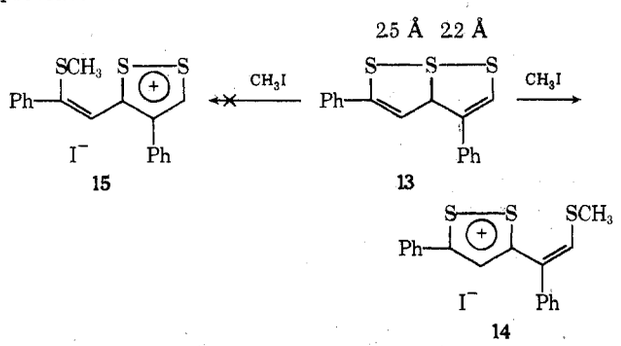
5-(Dialkylamino)-3-(substituted imino)-1,2,4-dithiazoles (1) undergo 1,3-dipolar additions with a variety of substrates, including various isothiocyanates and carbon disulfide (Scheme I).[2] The products, *e.g.*, 3–5, contain three or more sulfur atoms capable of interacting in the "no-bond resonance" sense, and X-ray structure determinations of 3a and 3b established that indeed all four sulfurs in these molecules are colinear with S–S distances of *ca.* 2.2 and 2.8 Å between the inner, and inner and outer, sulfurs, respectively.[3,4] The former distance is slightly longer than normal for a S–S single bond; the latter is considerably less than twice the sulfur van der Waals radius (*ca.* 3.5 Å), but is too long to be considered a *bona fide* single bond. Thus an interaction between the inner and outer sulfurs is apparent, but the magnitude of the interaction appears to be less than that in the true thiothiophthenes.[5]

Scheme I



No X-ray studies were undertaken on compounds **4** and **5**, but we have assumed that S–S interactions in these systems would resemble those of **3**.[6]

Klingsberg observed that the more tightly bound of the two terminal sulfur atoms of unsymmetrically substituted thiothiophthenes was the more reactive with respect to alkylation. For example, reaction of **13** with methyl iodide provided **14** instead of **15**. The shorter S–S bond was



cleaved with concurrent normalization of the longer bond.[5,7] Because of the long distances and apparently weak interactions between the nonbonded sulfur atoms of **3–5**, and because of the desirability of establishing experimental criteria other than X-ray determinations for assessing no-bond resonance interactions,[5] we have examined alkylations of representatives of systems **3–5**. In the absence of no-bond resonance, **3** and **4**, and perhaps also **5**, would be expected to be alkylated on their exocyclic thione sulfurs to give **8**, **10**, and **12**, respectively. If however, the formal S–S bonds of the dithiazole ring are to be cleaved, products **7**, **9**, and **11** should result.

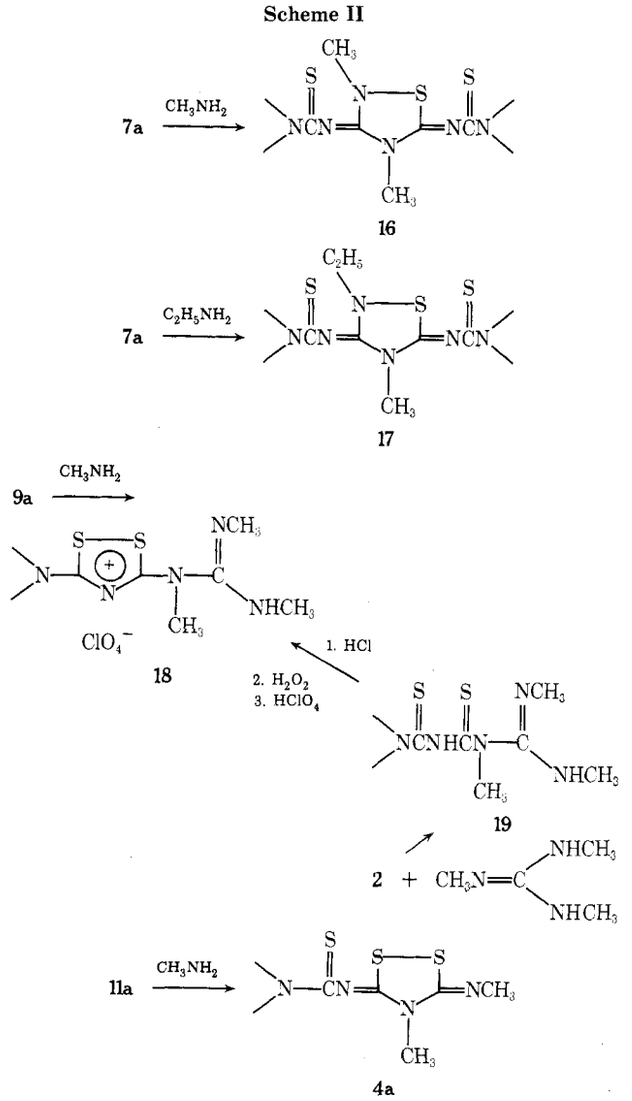
Results

Compound **3a** was alkylated by methyl iodide in dimethylformamide at 90–100° to give **7a** (X = I). The phenyl analog **3b** was similarly converted to **7b** with methyl iodide in refluxing acetonitrile. Methiodide **7a** was recrystallized without incident from water, as was **7b** from methanol, but attempted recrystallization of **7b** from pyridine resulted in dealkylation to regenerate **3b**. An attempted recrystallization of **7b** from acetic acid also resulted in decomposition; in this case 5-(dimethylamino)-3-(phenylimino)-1,2,4-dithiazole hydriodide (**1b**·HI) was obtained. Dithiazole **4** was recovered unchanged from methyl iodide in refluxing acetonitrile, but methylation was accomplished by warming **4** in dimethyl sulfate. The crude methyl sulfate salt was converted to the perchlorate **9** with $HClO_4$. Thione **5** was recovered unchanged from

methyl iodide in refluxing acetone; with methyl iodide in refluxing acetonitrile some alkylation of **5** occurred but the product was contaminated with 3,5-bis(dimethylamino)-1,2,4-dithiazolium iodide (**6**). The latter product undoubtedly resulted from thermal loss of CS_2 from **5** to generate **1a**[2] and subsequent N-alkylation of **1a** with methyl iodide.[8] Successful alkylation of **5** to **11** was easily achieved with methyl fluorosulfate in methylene chloride at room temperature.

The nmr spectra of the products confirmed that S- and not N-alkylation had occurred in each case. That alkylation had occurred on the ring sulfurs and not on the exocyclic thione sulfurs was verified for **3a**, **4**, and **5** as follows (Scheme II). Each of the alkylation products **7**, **9**, and **11** was treated with methylamine. Elemental analyses and nmr spectra of the resulting products demonstrated that the net change in each case was the replacement of CH_3S by CH_3NH. Thus only **7**, **9**, and **11**, and not **8**, **10**, and **12**, could have provided the observed products, **16**, **18**, and **4**, respectively. This method does not distinguish between position 2 and the 3-thione sulfur as the alkylation site of **5**, but does eliminate the exocyclic thione sulfur.

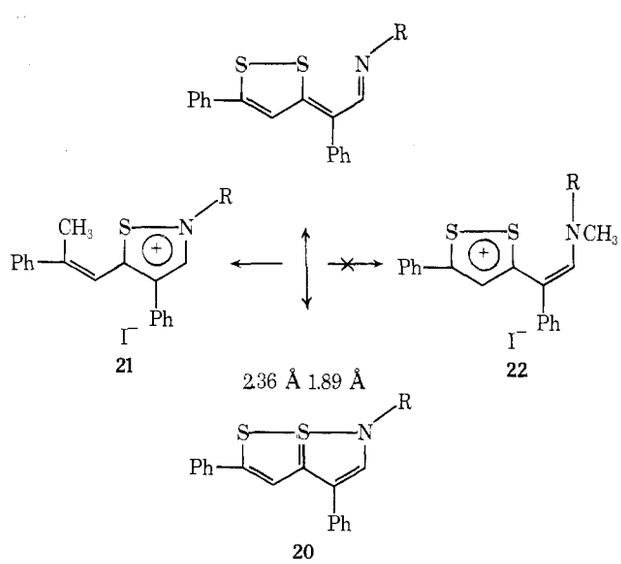
Scheme II



Identification of the methylamine derivatives **16**, **18**, and **4** was straightforward. Compound **4**, isolated from **11** and CH_3NH_2, was identical with the material prepared from **1a** and CH_3NCS.[2] The thiadiazole derivative **16**, obtained from **7a** and CH_3NH_2, was recently identified as a self-condensation product of **1a**.[1] Recalling that **7b** could, under at least one set of conditions, be converted to **1b**, we felt it necessary to establish that **16** was actually formed from **7a** by the direct displacement of methyl mercaptan rather than *via* the sequence **7a** → **1a** → **16** [a control experiment demonstrated that under the conditions for the conversion of **7a** to **16** (excess $MeNH_2$–CH_2Cl_2), **1a** HCl was also converted to **16**]. Accordingly, we treated **7a** with ethylamine; if the reaction proceeded *via* **1a** the previously observed product **16** should again be obtained, but if the amine displaced methyl mercaptan as expected, the ethyl derivative **17** should result. In fact **17** was the isolated product; its ir spectrum was essentially identical with that of **16**, but its nmr spectrum clearly differed from that of **16** by the substitution of an ethyl for a methyl absorption. The structure of the remaining methylamine product, **18**, was confirmed by treating 1,2,3-trimethylguanidine with dimethylthiocarbamoyl isothiocyanate (**2**), oxidizing the resulting dithiobiuret with hydrogen peroxide, and converting the dithiazolium chloride thus formed to the perchlorate **18** with perchloric acid.

Discussion

In each of the three systems investigated, alkylation occurred on one of the more tightly bonded sulfurs with concurrent rupture of the "normal" S–S single bond. This is consistent with Klingsberg's generalization concerning the methylation of unsymmetrically substituted thiothiophthenes (*e.g.*, **13** → **14**) and of their nitrogen isosteres (*e.g.*, **20** → **21**).[5,7] In either of the possible methiodides from thiothiophthene **13** the positive charge would be stabilized by an aromatic dithiolium ring; for the N isostere **20** there is a choice between a dithiolium cation (**22**) and an isothiazolium ion (**21**) with the latter being the observed product. Our systems **4** and **5** lack similar options; each can give only a single dithiazolium-stabilized cation, namely the observed products **9** and **11**, respectively. Thus it might be argued that formation of the stable dithiazolium system provides the driving force for cleavage of the dithiazole S–S bond. Compound **3a**, however, has the option of forming either of two dithiazolium cations, **7** or **8**, but in this case too, the S–S bond of the 1,2,4-dithiazole ring was cleaved. It is not obvious that **7** should be a particu-

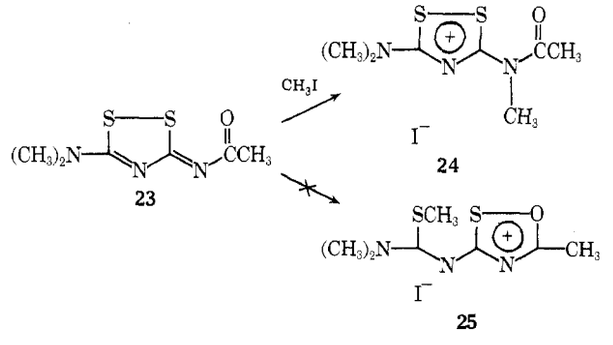


larly more favorable cation than **8**, or, for that matter, that **21** should be more favorable than **22**.[9]

Klingsberg suggested that steric hindrance of the more weakly bound sulfur of **13** might be responsible for the alkylation of the more tightly bound sulfur.[5] A noteworthy feature of the conversion of **3** to **7** is that the less sterically accessible sulfur was alkylated.[10] Thus it seems that neither steric considerations nor cation stabilities can completely rationalize the course of alkylation of thiothiophthenes and related compounds. Perhaps some subtlety in the hybridization of the more tightly bound sulfur is responsible for that atom's nucleophilicity.

From the considerations outlined above, we conclude that although the X-ray study of **3a** and **3b** left some doubt as to the importance of no-bond interactions in these systems, the interactions are in fact sufficiently strong to dictate the chemical properties of those and related compounds. In contrast to systems **3–5**, we recently observed that the acetylimino-1,2,4-dithiazole **23** reacted with methyl iodide to produce the N-methylated dithiazolium iodide **24**.[8] Although no X-ray study of **23** itself was undertaken, Hordvik and coworkers[11-13] determined the crystal structures of several closely related compounds. Their results imply that **23** should have an S–S bond length of 2.05–2.10 Å and an S–O distance of *ca.* 2.6 Å. These figures correspond to a "close approach" of oxygen and sulfur with the S–S bond little influenced by the proximal sulfur.[14] If **23** had followed the alkylation pattern of **20**, S-alkylation should have occurred to produce the oxathiazolium salt **25**. The fact that **23** reacted with methyl iodide as a normal iminodithiazole in spite of the presumed interaction between sulfur and oxygen implies a fringe area of no-bond resonance wherein the interaction is no longer strong enough to influence the chemical properties of the compounds.

In summary, a wide variety of compounds are known that display no-bond resonance interactions between an exocyclic heteroatom and a dithiole or dithiazole ring. They range from the symmetrically substituted thiothiophthenes with identical S–S bond lengths, through compounds in which the external heteroatoms are more distant but still control certain chemical properties of the system, to cases where the primary manifestation of the interaction is simply a close approach of the heteroatom as revealed by X-ray studies.



Experimental Section[16,17]

3-(Dimethylamino)-5-[[*N*-(dimethylthiocarbamoyl)-1-(methylthio)formimidoyl]methylamino]-1,2,4-dithiazolium Iodide (7a). A mixture of **3a**[2] (2.21 g) and CH_3I (1.5 ml) in DMF (20 ml) was warmed on a steam bath for 0.5 hr, and then the resulting solution was diluted with Et_2O. Crude **7a** was collected and recrystallized from H_2O, mp 249–250° dec (2.19 g, 69%). An analytical sample was recrystallized from EtOAc–EtOH.

Anal. Calcd for $C_{10}H_{18}IN_5S_4$: C, 25.91; H, 3.91; N, 15.11. Found: C, 25.63; H, 3.73; N, 14.85.

3-(Dimethylamino)-5[[*N*-(dimethylthiocarbamoyl)-1-(methylthio)formimidoyl]anilino]-1,2,4-dithiazolium Iodide (7b). A mixture of **3b**[2] (0.50 g) and CH_3I (0.4 ml) in MeCN (10 ml) was refluxed for 1.5 hr. Evaporation of solvent and trituration with EtOAc gave 0.57 g (83%) of **7b**, mp 173–175°. Recrystallization from MeOH gave 0.41 g, mp 174.5–175.5.

Anal. Calcd for $C_{15}H_{20}IN_5S_4$: C, 34.28; H, 3.84; N, 13.33. Found: C, 34.41; H, 3.87; N, 13.11.

Decomposition of 7b to 5-(Dimethylamino)-3-(phenylimino)-1,2,4-dithiazole Hydriodide (1b·HI) with Acetic Acid. A sample of **7b** was dissolved in hot HOAc; upon cooling a white solid, mp 218° dec, separated. This material was identified as **1b** HI by its ir and nmr spectra, and by conversion with $HClO_4$ to the corresponding perchlorate, which was compared with an authentic sample.[18]

Decomposition of 7b to 3b with Pyridine. During an attempted recrystallization of **7b**, a sample (0.67 g) was heated in pyridine (10 ml) until a clear yellow-orange solution resulted (*ca.* 3 min). Upon cooling the solution, 0.17 g of **3b** separated, mp 192–193°.

3-(Dimethylamino)-5-[methyl[*N*-methyl-1-(methylthio)formimidoyl]amino]1,2,4-dithiazolium Perchlorate (9a). A mixture of **4a** (5.18 g) and dimethyl sulfate (30 ml) was heated on a hot plate until a clear solution resulted. The solution was chilled, and 70% $HClO_4$ (1.85 ml) was added. Ethyl acetate was added and **9a** was collected by filtration (6.86 g, 91%, mp 195–197°). Recrystallization from HOAc raised the melting point to 202.5–203.5°.

Anal. Calcd for $C_8H_{15}ClN_4O_4S_3$: C, 26.47; H, 4.17; N, 15.44. Found: C, 26.73; H, 4.02; N, 15.42.

3-(Dimethylamino)-5-[methyl[(methylthio)thiocarbamoyl]-amino]-1,2,4-dithiazolium Fluorosulfate (11). Thione **5**[2] (0.37 g) was suspended in CH_2Cl_2 (6 ml). Methyl fluorosulfate (0.16 ml) was added, and the mixture was stirred under N_2 at room temperature. Within 15 min a clear solution developed. After another 0.5 hr, a few drops of MeOH were added to decompose any excess methyl fluorosulfate, and then the solvent was stripped to give a yellow solid that was triturated with EtOAc and collected, mp 210–212° (0.54 g, 100%). A portion was recrystallized from HOAc, mp 220–221°.

Anal. Calcd for $C_7H_{12}FN_3O_3S_5$: C, 23.00; H, 3.31; N, 11.50. Found: C, 23.13; H, 3.40; N, 11.45.

Conversion of 7a to 1,1′-(2,4-Dimethyl-1,2,4-thiadiazolidine-3,5-diylidene)bis(3,3-dimethyl-2-thiourea) (16). A solution of **7a** (0.31 g) in CH_2Cl_2 (6 ml) was treated with 6 ml of a 2.4 *M* solution of CH_3NH_2 in CH_2Cl_2. After standing at room temperature overnight the solution was washed with H_2O and aqueous, Na_2CO_3, dried, and concentrated to give 0.20 g of oily residue. This material was dissolved in a small volume of EtOAc, and the resulting solution was diluted with a few drops of hexane over *ca.* 3 hr. A light yellow solid was deposited that was collected, washed with MeOH, and then recrystallized from 2-butanone to give *ca.* 40 mg of **16**, mp 177–188°. The ir and nmr spectra of this material were identical with those of authentic **16**.[1]

Conversion of 7a to 1,1′-(2-Ethyl-4-methyl-1,2,4-thiadiazolidine-3,5-diylidene)bis(3,3-dimethyl-2-thiourea) (17). A solution of **7a** (0.665 g) in CH_2Cl_2 (5 ml) was treated with 10 ml of a 0.89 *M* solution of $CH_3CH_2NH_2$ in CH_2Cl_2. After standing at room temperature overnight the solution was washed with H_2O and aqueous Na_2CO_3, dried over $MgSO_4$, and concentrated. The residual sticky solid (0.48 g) was recrystallized twice from EtOAc to give pure **17**, mp 180–182°.

Anal. Calcd for $C_{11}H_{20}N_6S_3$: C, 39.73; H, 6.06; N, 25.28. Found: C, 39.86; H, 6.04; N, 25.31.

Conversion of 9 to 3-(Dimethylamino)-5-(1,2,3-trimethylguanidino)-1,2,4-dithiazolium Perchlorate (18). A solution of **9** (2.15 g) in absolute EtOH (45 ml) containing 0.5 g of 40% $MeNH_2$ was heated for 0.5 hr on a steam bath, and then was allowed to stand at room temperature for 2 days. Filtration provided 0.48 g of **18**, mp 251–254°. Recrystallization from HOAc plus a few drops of H_2O gave pure **18**, mp 261°.

Anal. Calcd for $C_8H_{16}ClN_5O_4S_2$: C, 27.78; H, 4.66; N, 20.25. Found: C, 28.07; H, 4.58; N, 20.06.

Preparation of 18 from 1,2,3-Trimethylguanidine. 1,2,3-Trimethylguanidine is an extremely strong base, and its hydriodide[19] could not be neutralized satisfactorily with aqueous KOH or with $NaOCH_3$ in CH_3OH. A solution of the hydriodide (0.01 mol) in warm H_2O was therefore stirred for 0.5 hr with a small excess of Ag_2O, and then the AgI and excess Ag_2O were removed by filtration. The filtrate was concentrated to *ca.* 15 ml on a rotary evaporator, and then was added to a solution of dimethylthiocarbamoyl isothiocyanate (**2**, 0.01 mol) in MeCN.[20] The resulting

solution was cooled and treated dropwise with concentrated HCl (0.01 mol) and 30% H_2O_2 (0.01 mol) in that order. Dilution with Me_2CO resulted in the separation of a white solid, mp *ca.* 255°, that was identified as trimethylguanidine hydrochloride. Upon cooling the filtrate another crop of a white solid was obtained, mp 225°. This material was recrystallized from EtOAc–HOAc, mp 226–227° dec, then was converted to **18** with 70% $HClO_4$. The resulting perchlorate had mp 263–265° dec and was identical with the product from **9** and CH_3NH_2.

Conversion of 11 to 1,1-Dimethyl-3-[4-methyl-5-(methylimino)-1,2,4-dithiazolidin-3-ylidene]-2-thiourea (4). A mixture of **11** (0.286 g) and absolute EtOH (5 ml) was treated with 40% CH_3NH_2 (0.2 ml) at room temperature. After 2.5 hr crude **4** (0.131 g) was collected by filtration, mp 187–192°. Recrystallization from HOAc and then from 2-butanone gave material, mp 200–204°, whose ir and nmr spectra were identical with those of authentic **4**.

Registry No.—**1b** HI, 51593-20-5; **3a**, 39656-37-6; **3b**, 39656-38-7; **4a**, 51593-03-4; **5**, 51592-79-1; **7a**, 51593-21-6; **7b**, 51593-22-7; **9a**, 51593-24-9; **11**, 51593-26-1; **16**, 51593-18-1; **17**, 51593-27-2; **18**, 51593-29-4; 1,2,3-trimethylguanidine hydriodide, 51593-30-7.

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(4) J. L. Flippen, *J. Amer. Chem. Soc.*, **95**, 6073 (1973).
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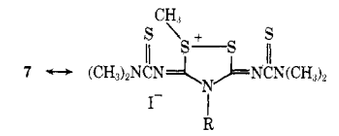
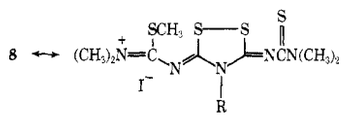
(6) The exocyclic thiocarbonyl groups influence the lengths of the dithiazole S–S bonds (see ref 13). We cannot presently assess whether the two thiocarbonyls of **3** influence the S–S bond length twice as much as the single thiocarbonyls influence the S–S bond lengths of **4** and **5**.
(7) E. Klingsberg, *J. Org. Chem.*, **33**, 2915 (1968).
(8) J. E. Oliver and A. B. DeMilo, *J. Org. Chem.*, **39**, 2225 (1974).
(9) A referee has suggested that structures **7** and **8** each show the same bond flipping with respect to **3**, with the same S–S bond broken and the same new S–S bond formed in either case. Thus, he contends, the course of the reaction (*i.e.*, the alkylation of **3**) cannot be diagnostic for no-bond resonance in the starting material. Our feeling is that had **8** been the observed alkylation product, this assessment would have been correct. However, structures **7** and **8**, as they appear in Scheme I, are after the fact (*i.e.*, allowing no-bond interactions) resonance structures of **7a** and **8a**. In the absence of no-bond interactions, **7a** and **8a** are the alkylation products that would have to be considered, and **8a** would be the expected product. The fact is that a ring sulfur, and not a thione sulfur, was alkylated; thus it seems imperative to assume that the course of the reaction was indeed influenced by no-bond interactions.

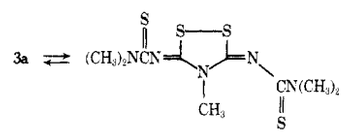


7a



8a

(10) In the solid state, all four sulfurs of **3a** are collinear (ref 3 and 4), and the inner sulfurs are clearly less accessible than the thiocarbonyl sulfurs. In solution, isomerization around a C=N bond could occur (**3a** → **26**); this would help to expose a ring sulfur but it appears unlikely that it would completely reverse the relative accessibilities of the two sulfurs.



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(11) A. Hordvik and E. Sletten, *Acta Chem. Scand.*, **20**, 2043 (1966).
(12) A. Hordvik and H. M. Kjøge, *Acta Chem. Scand.*, **20**, 1923 (1966).
(13) G. Eide, A. Hordvik, and L. J. Saethre, *Acta Chem. Scand.*, **26**, 2140 (1972).
(14) An external heteroatom interacting in the no-bond sense with a dithiole or dithiazole ring has the effect of lengthening the S–S bond of that ring: the stronger the no-bond interaction, the longer the S–S bond (ref 4 and 15). Thus the distance between bonded sulfurs can serve as a measure of no-bond resonance as well as the distance between nonbonded atoms.
(15) F. Leung and S. C. Nyburg, *Can. J. Chem.*, **49**, 167 (1971).
(16) Melting points are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer and infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.
(17) Mention of a proprietary product or company does not imply endorsement by the U. S. Department of Agriculture.
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Keto–Enol Tautomerism in the Thiophene Analogs of Anthrone. III. Synthesis and Properties of 4,8-Dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophen-4-one

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The remaining member, 4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophen-4-one (**11**), of the thieno analogs of anthrone–anthrol has been synthesized from the known 1,3-dichloro-4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (**15**) by reduction of one of the carbonyl groups to the ketol **16** followed by replacement of the hydroxyl group and subsequent dechlorination of the dichloro ketone **17** by means of copper in boiling propionic acid. Nuclear magnetic resonance, infrared, and ultraviolet spectroscopy indicated the presence of only the keto tautomer **11**. Interaction of **11** with potassium *tert*-butoxide followed by reaction with deuterium oxide results in the replacement of one of the methylene group hydrogen atoms by deuterium; 4,9-dihydronaphtho[2,3-*c*]thiophen-4-one (**22**) behaved similarly and incorporated deuterium. Similar treatment of 4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene (**20**), 3,3'-dithienylmethane (**21**), and 3-benzylthiophene gave no evidence of anion formation.

If both of the benzene rings in 9-anthrone are replaced by thiophene nuclei, six analogous keto–enol systems **1–12** result (Table II). The syntheses of the systems **1–10** were reported in a recent publication[1a] and the present report describes the synthesis and some of the properties of the remaining member of the series, **11**.

A spectroscopic examination of the position of the keto–enol equilibria in the systems **1–10** showed that the mode