anate (37 mmol) was refluxed for 1 hr, cooled, and poured into H_2O. The product was collected by filtration and recrystallized to give **19a** or **19b** (Table VI).

Registry No.—**4a**, 51568-05-9; **4b**, 40229-20-7; **4c**, 37423-15-7; **4d**, 51592-87-1; **4e**, 51592-88-2; **4f**, 51592-89-3; **4g**, 51592-90-6; **4h**, 51592-91-7; **4i**, 51592-92-8; **4j**, 51592-93-9; **4k**, 51568-06-0; **4l**, 51592-94-0; **4m**, 51592-95-1; **4n**, 51592-96-2; **4o**, 51592-97-3; **4p**, 51592-98-4; **5** (R = Me), 30013-32-2; **5** [R_2 = $(CH_2)_4$], 51592-99-5; **13a**, 29220-04-0; **13b**, 36884-35-2; **18**, 31354-33-3; CH_3NCS, 556-61-6; C_6H_5NCS, 103-72-0; $C_6H_5SO_2NCS$, 1424-53-9; $(CH_3)_2NCONCS$, 16011-79-3; $C_2H_5O_2CNCS$, 16182-04-0; $CH_3O_2CC{\equiv}CCO_2CH_3$, 762-42-5; CS_2, 75-15-0. 75-15-0.

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Imino-1,2,4-dithiazoles. III. Thermal Decomposition of 5-(Dialkylamino)-3-(substituted imino)-1,2,4-dithiazoles

James E. Oliver*

Agricultural Environmental Quality Institute, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Maryland 20705

Judith L. Flippen

Naval Research Laboratory, Washington, D. C. 20390

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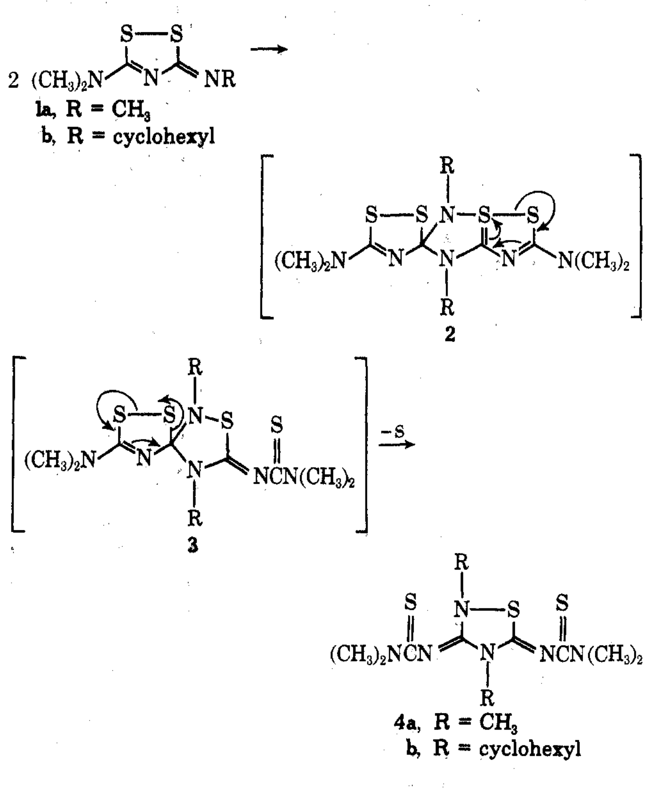
5-(Dialkylamino)-3-(substituted imino)-1,2,4-dithiazoles decompose thermally *via* pathways that differ depending on the substituent on the imino nitrogen. The alkylimino compounds appear to decompose *via* a dimeric cycloadduct, whereas the phenyliminodithiazole decomposes by attack on a ring sulfur by the benzene ring.

We have studied a variety of amino-substituted 1,2,4-dithiazole derivatives as insect sterilants[1] including a number of 5-(dialkylamino)-3-(substituted imino)-1,2,4-dithiazoles **1a–c**. The latter compounds are prepared as mineral acid salts, and as such are thermally stable, high-melting solids. Conversion to the free bases can be effected with Na_2CO_3 (but not always $NaHCO_3$); the free bases can react with alkyl halides[2] and with a variety of 1,3-dipolarophiles.[3] While attempting some alkylations of 5-(dimethylamino)-3-(methylimino)-1,2,4-dithiazole (**1a**), we observed that it did not react with relatively unreactive alkyl halides, but instead gave a decomposition product $C_{10}H_{16}N_6S_3$ (**4a**), corresponding to the combination of two molecules of **1a** with the loss of one atom of sulfur; elemental sulfur was indeed isolable from the reaction mixture. The same decomposition product was conveniently prepared simply by heating **1a** for 1 hr at 100°, and the analog **4b** was obtained similarly from **1b**.

In an accompanying paper[3] we pointed out that three characteristics of iminodithiazoles are (1) nucleophilic imino nitrogens; (2) electrophilic ring sulfurs; (3) electrophilic ring carbons.[3] The first and second of these characteristics provide the basis for the reactivity of **1** in 1,3-dipolar additions.[3] The first and third could also serve to make **1** act as dipolarophiles, and the report[4] of additions across the exocyclic C=S bond of closely related 1,2,4-dithiazole-3-thiones is consistent with this suggestion. Thus a self-condensation with one molecule of **1a** acting as a 1,3-dipole and another molecule acting as a dipolarophile was considered. The spiro structure **2** would result from this kind of addition. Intermediates of this nature, con-


1a, R = CH_3
b, R = cyclohexyl

2

3

4a, R = CH_3
b, R = cyclohexyl

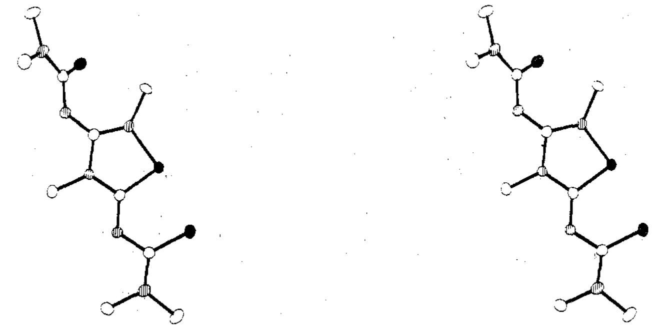
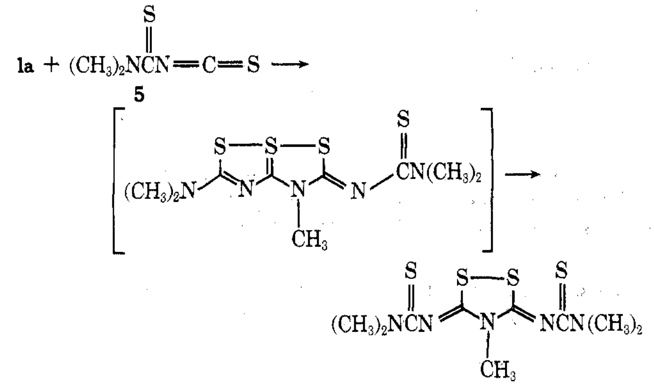


Figure 1. A stereodrawing of molecule 4a. The sulfur atoms are solids and the nitrogen atoms are vertically lined.

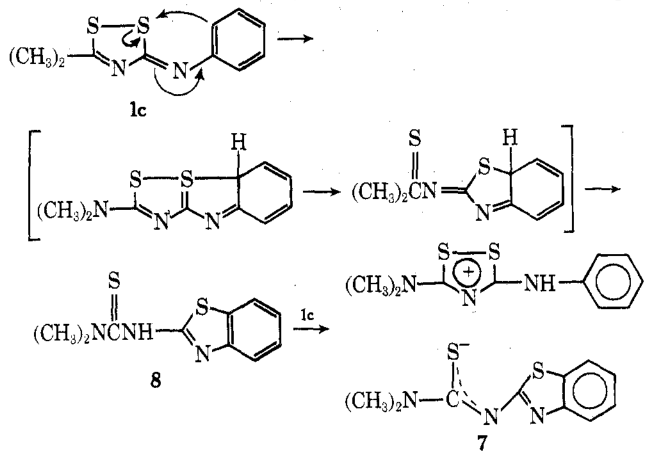
taining tetravalent sulfur, normally undergo bond reorganizations, apparently simultaneously with the dipolar addition;[5] thus structure 3 would presumably better represent the initial adduct. Structure 3, in the sense that C-3 of the dithiazole ring is tetrahedral, resembles the postulated initial adducts from dithiazoles and dithiazolium salts with various nucleophiles.[6] These adducts typically extrude the adjacent ring sulfur as elemental sulfur, again with the appropriate bond reorganization. Loss of sulfur from 3 would give 4. Although this series of events is consistent with the formation of 4, their actual chronology must remain speculative.

Dipolar addition of **1a** across the C=S bond of dimethylthiocarbamoyl isothiocyanate (**5**) provides the bis(thiocarbamoylimino)dithiazole **6**.[3,7] The latter compound is of interest because of the nonbonded interactions between the ring and thione sulfurs, as was demonstrated by an X-ray crystallographic determination of its structure.[7,8] The resemblance of **4a** and **6** is striking; **4a** corresponds to replacement of a ring sulfur of **6** by NCH_3, and the similarity of the nmr and mass spectra of **4a** to those of **6** supported our structural assignment. To further examine nonbonded interactions between heteroatoms in compounds related to **6**, and to confirm the structure of **4a**, an X-ray crystal determination was performed on **4a**.

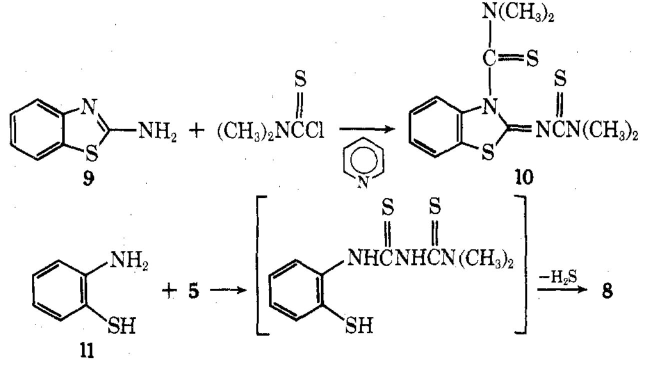


The molecule **4a** crystallizes in the monoclinic space group $P2_1/c$ with a = 9.922 (8), b = 12.052 (11), c = 13.359 (12) Å, and B = 104.9 (1)°. There are four molecules per unit cell corresponding to a calculated crystal density of 1.37 g/cm³. The structure was solved by the symbolic addition procedure for centrosymmetric crystals[9] and the results are displayed in Figure 1. Full-matrix least-squares of the atomic coordinates and thermal parameters is in progress. Molecule **6**, with four colinear sulfur atoms, exhibits strong intramolecular S···S attractions which stabilize the planar structure.[7,8] Substitution of the NCH_3 moiety for a central sulfur atom in **6** has disrupted the intramolecular attractions between the sulfur atoms and molecule **4a** is nonplanar.

5-(Dimethylamino)-3-(phenylimino)-1,2,4-dithiazole (**1c**) also decomposed when heated above its melting point (88°), but in contrast to **1a** and **1b**, no elemental sulfur was observed from **1c**. When **1c** was heated at 115° for 1 hr, two products, **7** and **8**, were formed that could be separated by fractional crystallization. Heating **1c** for longer periods or at higher temperatures gave predominantly **8**. Each of the products analyzed correctly for $C_{10}H_{11}N_3S_2$ (isomeric with **1c**), but the nmr spectrum of **7** contained two different dimethylamino signals, indicating that **7** was in fact $C_{20}H_{22}N_6S_4$. Refluxing **1c** for several hours in toluene converted it cleanly to **8**, and under the same conditions **7** was also converted cleanly to **8**. The mass spectrum of **7** corresponded to the sum of the mass spectra of **1c** and **8**, and indeed, **7** (a bright yellow solid) could be produced by simply combining equal portions of **1c** (very pale yellow) and **8** (white) and recrystallizing from MeOH.



The nmr spectrum of **8** consisted of a dimethylamino singlet at δ 3.35, *four* aryl hydrogens, and an exchangeable hydrogen at δ 12.7 ppm, indicating that cyclization onto the ring had occurred. The benzothiazole structure shown seemed mechanistically probable and was consistent with the nmr and mass spectra (m/e 108.0029, 17%, $C_6H_4S^+$). A search of the literature revealed a recent patent[10] in which **8** had been described as having been prepared from 2-aminobenzothiazole (**9**) and dimethylthiocarbamoyl chloride in pyridine. However, the reported melting point, 241–242°, did not agree with our melting point of 198.5–199.5° for **8**. We attempted to repeat the preparation and did isolate a product whose melting point was 228–231°; however, its nmr spectrum contained two dimethylamino signals, indicating that 2 mol of the thiocarbamoyl chloride had reacted with **9** to give, presumably, **10**. Confirmation of the benzothiazole structure for **8** was finally realized by condensing the thiocarbamoyl isothiocyanate **5** with 2-aminobenzenethiol (**11**). The product from this reaction had mp 198.5–200° and was identical with **8** in all respects.



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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(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

James E. Oliver

Agricultural Environmental Quality Institute, Insect Chemosterilants Laboratory,
Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Maryland 20705

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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]