crystallization of the residue from 95% EtOH gave 1.88 g (46%) of crude **10a**, mp 178.5–182°. Two more recrystallizations from 95% EtOH gave an analytical sample, mp 186–187°. The nmr spectrum ($CDCl_3$) had a sharp singlet at δ 3.66 (3 H, NCH_3), a broadened singlet at δ 3.42 [6 H, $(CH_3)_2N$], and a sharp singlet at δ 2.47 ppm (3 H, CH_3).

Anal. Calcd for $C_7H_{12}N_4S_2$: C, 38.86; H, 5.59; N, 25.90. Found: C, 39.09; H, 5.65; N, 25.83.

1,1-Dimethyl-3-(3-methyl-4-phenyl-4*H*-1,2,4-dithiazolin-5-ylidene)-2-thiourea (10b). A solution of **2b** (2.08 g) in MeCN (20 ml) was refluxed under N_2 for 7 hr. The solvent was evaporated and the residue was triturated with Et_2O to give 1.42 g of a yellow solid, mp 151–153°. This material consisted mainly of self-condensation products of **2b**.

A second crop of solid (0.20 g, mp 149–156°) was obtained from the Et_2O filtrate and was recrystallized from absolute EtOH to give 103 mg of pure **10b** as a white solid, mp 163–164°. The nmr spectrum ($CDCl_3$) had a multiplet at δ 7.16–7.66 (5 H, aromatic H), a doublet at δ2.92 and 3.29 [6 H, $(CH_3)_2N$], and a singlet at δ2.22 ppm (3 H, CH_3).

Anal. Calcd for $C_{12}H_{14}N_4S_2$: C, 51.77; H, 5.07; N, 20.13. Found: C, 51.69; H, 5.10; N, 20.17.

1,1-Dimethyl-3-(4-methyl-3-phenyl-4*H*-1,2,4-dithiazolin-5-ylidene)-2-thiourea (10c). A solution of **2a** (2.51 g) and benzonitrile (4 ml) in Me_2CO (10 ml) was refluxed for 2 hr, then the solvent was stripped. Addition of Et_2O to the residue gave 1.93 g of a solid, mp 153–172°. Recrystallization from 95% EtOH, then from EtOAc gave a material whose nmr spectrum indicated a 2:1 mixture of a self-condensation product of **2a** and the cycloadduct **10c**. Recrystallization from MeCN and then from C_6H_6–hexane gave several crops of the self-condensation product. Finally a solid was obtained from the combined mother liquors that was recrystallized from 95% EtOH to give pure **10c**, mp 194.5–195.5°. The nmr spectrum ($CDCl_3$) consisted of three singlets at δ 7.49 (5 H, aromatic H), 3.47 (3 H, NCH_3), and 3.41 ppm [slightly broadened, 6 H, $(CH_3)_2N$].

Anal. Calcd for $C_{12}H_{14}N_4S_2$: C, 51.77; H, 5.07; N, 20.13. Found: C, 52.01; H, 5.16; N, 19.98.

3-[5-(Bromomethyl)-3-methylthiazolidin-2-ylidene]-1,1-dimethyl-2-thiourea (7). A mixture of **3f** (2.0 g) and absolute EtOH (10 ml) was heated on a steam bath for 10 min and then cooled to room temperature. Filtration provided 8 mg of **8**, mp 243° dec. Cooling the filtrate to −20° precipitated 173 mg of **7**. The filtrate was concentrated and the residue was extracted successively with Et_2O, EtOAc, and Me_2CO. Evaporation of these extracts gave an additional 827 mg of **7** (50% total yield). An analytical sample was recrystallized from aqueous Me_2CO, mp 110.5–111.5°.

Anal. Calcd for $C_8H_{14}BrN_3S_2$: C, 32.43; H, 4.76; Br, 26.97; N, 14.18; S, 21.65. Found: C, 32.49; H, 4.71; Br, 26.88; N, 14.32; S, 21.58.

The nmr spectrum of **7** did not unambiguously confirm its structure because all the methylene signals fell in the area of the methylamino and dimethylamino absorptions; thus we also had to consider the isomeric 5-bromotetrahydro-1,3-thiazine derivative that would have resulted from reaction of the dithiazole sulfur with the terminal end of the olefin in **3f** (Scheme III). That the five-membered ring had in fact been formed was confirmed by dehydrohalogenating **7** to **9** (Scheme III) with KO-*t*-Bu in refluxing *t*-BuOH. The nmr spectrum of **9** contained a well-defined pattern characteristic of a methylallyl fragment, $CH_3\overset{|}{C}{=}\overset{|}{C}H$. Presumably the exocyclic double bond was formed initially but migrated into the ring under the basic conditions.

Dehydrohalogenation of 7 to 3-(3,5-Dimethylthiazol-2-ylidene)-2,2-dimethyl-2-thiourea (9). A solution of **7** (0.444 g) in *t*-BuOH (15 ml) containing KO-*t*-Bu (from 59 mg of K) was refluxed for 1.25 hr, then allowed to stand at room temperature overnight. The solvent was stripped, the residue was extracted with $CHCl_3$, and the $CHCl_3$ solution was washed with brine, dried, and stripped to give 0.257 g of **9** as a white solid, mp 209–215°. Recrystallization from EtOH and then from MeCN provided an analytical sample, mp 213–216°.

Anal. Calcd for $C_8H_{13}N_3S_2$: C, 44.62; H, 6.08; N, 19.51. Found: C, 45.10; H, 6.24; N, 19.56.

The nmr spectrum of **9** ($CDCl_3$) contained, in addition to a CH_3N singlet at δ 3.55 and a broadened $(CH_3)_2N$ singlet at δ 3.38, doublets (J = 1.5 Hz) at δ 2.21 (3 H) and 6.56 ppm (1 H) corresponding to the methyl and vinyl hydrogens on the thiazoline ring.

Registry No.—**2a**, 51568-05-9; **2b**, 40229-20-7; **2c**, 51568-06-0; **2d**, 40034-37-5; **6**, 33885-76-6; **7**, 51568-07-1; **9**, 51705-85-2; **10a**, 51568-08-2; **10b**, 51568-09-3; **10c**, 51568-10-6; methyl iodide, 74-88-4; benzyl chloride, 100-44-7; allyl bromide, 106-95-6; ethyl bromoacetate, 105-36-2.

References and Notes

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(7) In a private communication, Dr. Iwataki has confirmed the identity of his degradation product with our sample of **5**.
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(15) 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. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.
(16) Mention of a proprietary product or company does not imply endorsement by the U. S. Department of Agriculture.

Imino-1,2,4-dithiazoles. II. Dipolar Additions

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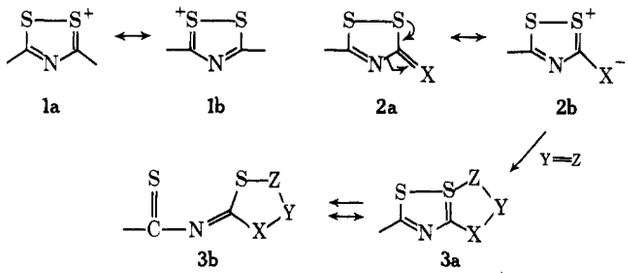
The sulfur atoms of imino-1,2,4-dithiazoles tend to donate electrons into the system, resulting in nucleophilic imino nitrogens and electrophilic ring sulfurs. This combination allows the iminodithiazoles to undergo 1,3-dipolar additions with such species as activated acetylenes, isothiocyanates, and carbon disulfide.

Much of the chemistry of 1,2,4-dithiazole derivatives appears to result directly from the ability of the ring sulfurs to donate p electrons into the ring to provide the 6-π electron dithiazolium system **1**. Thus the zwitterionic form **2b** presumably contributes significantly to the structures of 1,2,4-dithiazole-3-thiones (**2a**, X = S) and 3-imino-1,2,4-dithiazoles (**2a**, X = NR). A consequence of the electron density on the exocyclic heteroatom is the nucleophilicity of that atom, as has been demonstrated by alkylation of both the iminodithiazoles[1] and dithiazo-

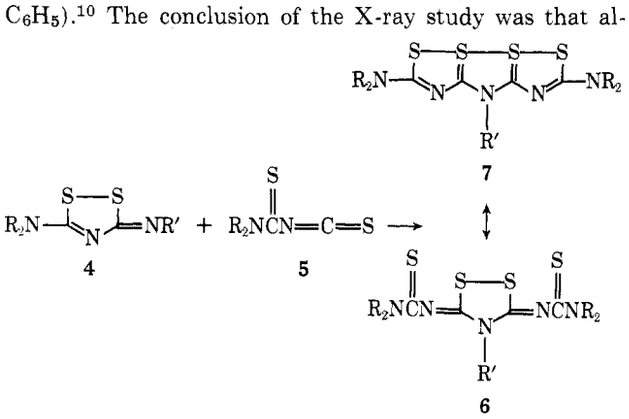


1a 1b 2a 2b

3b 3a

lethiones.[2] A second consequence is the electrophilicity of the ring carbons; thus the ring can be attacked and opened by a variety of nucleophiles in synthetically useful reactions.[3] Finally, the ring sulfurs, in donating electron density into the π system, also become electrophilic and can accept electrons in empty orbitals. The electron-rich exocyclic heteroatom and electrophilic ring sulfur can thus undergo 1,3-dipolar additions with selected unsaturated reactants Y=Z to form the adduct **3**. In most cases a bond reorganization occurs, probably simultaneously with the dipolar addition,[4] so that the final product is better represented by the monocyclic form **3b** than by **3a**. In some, and perhaps many, cases however, an interaction of the no-bond resonance type[5] exists between the ring and thione sulfurs of **3b** so that **3a** may be considered a minor resonance contribution. In the extreme cases of the thiothiophthenes and their analogs, **3a** provides the better description of the structure.

Vialle[6] has described dipolar additions of acetylenes to dithiazole-3-thiones and to iminodithiazoles, and similar reaction with the related 1,2-dithiole-3-thiones have been examined in some detail.[7] Recently we obtained adducts from iminodithiazoles and nitriles.[1] Goerdeler and Ulmen[8] described the reactions of some iminodithiazoles **4** with thiocarbamoyl isothiocyanates **5** to give the 1,1′-(1,2,4-dithiazolidine-3,5-diylidene)bisthioureas **6**; we encountered this reaction independently[9] and reported X-ray crystal determinations of two of the structures (**6**, R = CH_3 and C_6H_5).[10] The conclusion of the X-ray study was that al-



7

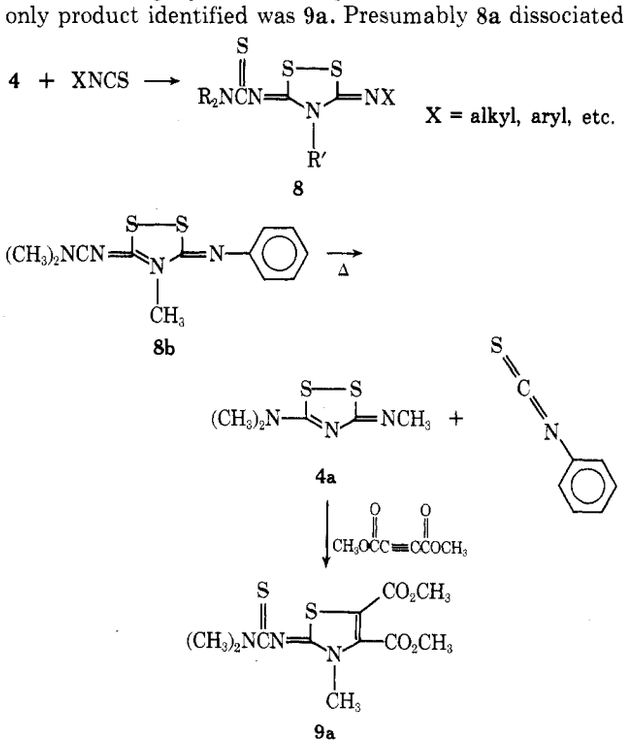
4 5 6

though structure **6** describes the system better than does **7**, the molecules are planar with all four sulfurs collinear, and the inner and outer sulfur atoms are separated by only *ca.* 2.75 Å. Thus the molecules possess a certain degree of no-bond resonance as implied by structure **7**.

Our interest in the 1,2,4-dithiazole system developed from the activity of a series of 1,2,4-dithiazolium salts as insect sterilants.[11] Interestingly, **6b** and **6c** (Table I) also had sterilant activity against houseflies (*Musca domestica* L.), and we decided to prepare a series of these compounds and to further elaborate the system by treating the iminodithiazoles **4** with other types of 1,3-dipolarophiles, including other isothiocyanates, dimethyl acetylenedicarboxylate, and carbon disulfide. Dipolar additions of iminodithiazoles to CS_2 have not been studied previously.[12] We also obtained adducts from two 5-(dialkylamino)-1,2,4-dithiazole-3-thiones (**10**) and dimethyl acetylenedicarboxylate; in general, however, the thiones undergo dipolar additions less readily than the iminodithiazoles.

Thiocarbamoyl isothiocyanates **5** reacted readily with iminodithiazoles **4** at room temperature to give **6a–p** (Table I) as stable, yellow solids. The adducts **8a–k** in Table II were prepared from **4** and other isothiocyanates; in general these isothiocyanates reacted less readily than did **5** and the reaction mixtures were usually refluxed for *ca.* 1 hr in MeCN or $CHCl_3$. These products are also relatively high-melting solids, but in contrast to **6** are colorless or very nearly so. Goerdeler and Ulmen[8] obtained an adduct from **4** (R = isopropyl; R′ = phenyl) and phenyl isocyanate that apparently dissociated in solution since its infrared spectrum contained an NCO band. The isothiocyanate adducts **8** are stable compounds whose infrared spectra do not contain N=C=S bands; the only exception found was **8h**. A sample of **8h** that had been standing at room temperature for 1.5 years was reexamined; its melting point (166–170°) had changed very little from the original 168.5–170.5°, but its infrared spectrum contained a moderately strong band at 2040 cm^{-1}. Two recrystallizations (EtOH) gave material that again melted at 168.5–170.5° whose ir spectrum contained no absorptions in the NCS region. Infrared spectra of some of the other isothiocyanate adducts including **8b**, **8c**, and **8f** were also reexamined after *ca.* 1.5 years, but no evidence of deterioration was found in any of these samples.

Thermal dissociation of one of the stable isothiocyanate adducts could be demonstrated, however, by heating **8b** in the presence of dimethyl acetylenedicarboxylate. At 81° (refluxing MeCN) **8b** was recovered unchanged, but at 140° (refluxing xylene) decomposition occurred, and the only product identified was **9a**. Presumably **8a** dissociated



4 + XNCS → 8 X = alkyl, aryl, etc.

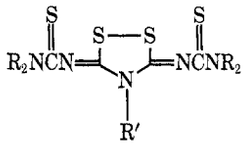
8b → 4a + phenyl isothiocyanate

4a + $CH_3OCC{\equiv}CCOCH_3$ → 9a

into phenyl isothiocyanate and **4a**, and **4a** reacted with the acetylenic ester to provide **9a**. Interestingly, the yield of **9a** was higher from this reaction than from the direct reaction of **4a** and dimethyl acetylenedicarboxylate. In contrast to the iminodithiazoles, 5-(dimethylamino)-1,2,4-dithiazole-3-thione (**13a**) appeared unreactive toward isothiocyanates and no adducts were isolated.

Vialle[6] has reported that 5-aryl-1,2,4-dithiazole-3-

Table I
Adducts from 5-(Dialkylamino)-3-(substituted imino)-1,2,4-dithiazoles and Dialkylthiocarbamoyl Isothiocyanates



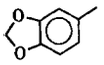
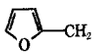
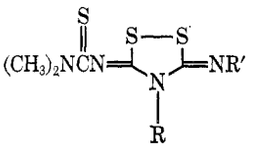
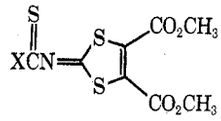
Registry no.	Compd	R	R′	Yield, %	Mp, °C	Recrystn solvent	Empirical formula	Anal., % Calcd C, H, N Found C, H, N
39656-37-6	**6a**	CH_3	CH_3	73	254	C_5H_5N	$C_9H_{15}N_5S_4$	33.62, 4.70, 21.78 33.66, 4.73, 21.72
39656-38-7	**6b**	CH_3	C_6H_5	73	199	C_6H_6	$C_{14}H_{17}N_5S_4$	43.83, 4.47, 18.26 44.02, 4.59, 18.09
51593-13-6	**6c**	CH_3	4-$C_6H_4NO_2$	55	192	C_5H_5N	$C_{14}H_{16}N_6O_2S_4$	39.23, 3.76, 19.61 39.38, 3.80, 19.79
51593-14-7	**6d**	CH_3	4-$C_6H_4OCH_3$	86	193–194	EtOH–DMF	$C_{15}H_{19}N_5OS_4$	43.56, 4.63, 16.93 43.79, 4.75, 17.02
51593-15-8	**6e**	CH_3	4-C_6H_4Cl	89	200.5–201.5	$CHCl_3$	$C_{14}H_{16}ClN_5S_4$	40.23, 3.86, 16.75 40.24, 3.82, 16.67
51593-43-2	**6f**	CH_3	3-C_6H_4Cl	85	194–195	C_5H_5N	$C_{14}H_{16}ClN_5S_4$	40.23, 3.86, 16.75 40.36, 3.92, 16.71
51593-16-9	**6g**	CH_3	3,4-$C_6H_3Cl_2$	84	195–195.5	$CHCl_3$	$C_{14}H_{15}Cl_2N_5S_4$	37.16, 3.34, 15.48 37.14, 3.32, 15.60
51593-17-0	**6h**	CH_3		75	186	DMF	$C_{15}H_{17}N_5O_2S_4$	42.13, 4.01, 16.38 42.22, 3.50, 16.41
51592-60-0	**6i**	CH_3		80	236 dec	C_5H_5N	$C_{13}H_{17}N_5OS_4$	40.28, 4.42, 18.07 40.45, 4.50, 17.91
51592-61-1	**6j**	CH_3	$(CH_3)_2N$	85	159–160	CH_3CN	$C_{10}H_{18}N_6S_4$	34.26, 5.17, 23.98 34.26, 5.25, 24.07
51592-62-2	**6k**	CH_3	Cyclohexyl	31	197–198	C_6H_6	$C_{14}H_{23}N_5S_4$	43.15, 5.95, 17.98 43.38, 6.02, 18.41
51592-63-3	**6l**	CH_3	4-C_6H_4F	51	189–189.5	C_6H_5Cl	$C_{14}H_{16}FN_5S_4$	41.87, 4.02, 17.44 41.65, 3.97, 17.30
51592-64-4	**6m**	$(CH_2)_4$	C_6H_5	12	186–188.5	$CHCl_3$	$C_{18}H_{21}N_5S_4$	49.63, 4.86, 16.08 49.71, 4.96, 16.02
51593-00-1	**6n**	CH_3	4-$C_6H_4CF_3$	28	187–187.5	MeCN	$C_{15}H_{16}F_3N_5S_4$	39.90, 3.57, 15.51 40.14, 3.63, 15.43
51593-01-2	**6o**	CH_3	3-$C_6H_4CF_3$	72	194–195	MEK	$C_{15}H_{16}F_3N_5S_4$	39.90, 3.57, 15.51 40.06, 3.71, 15.37
51593-02-3	**6p**	CH_3	3,5-$C_6H_3(CF_3)_2$	69	193.5–194.5	MeCN	$C_{16}H_{15}F_6N_5S_4$	36.99, 2.91, 13.48 37.09, 3.06, 13.39

Table II
Adducts from 5-(Dimethylamino)-3-(substituted imino)-1,2,4-dithiazoles and Miscellaneous Isothiocyanates



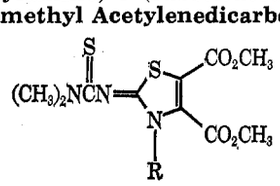
Registry no.	Compd	R	R′	Yield, %	Mp, °C	Recrystn solvent	Empirical formula	Anal., % Calcd C, H, N Found C, H, N
51593-03-4	**8a**	CH_3	CH_3	89	210–211	MEK	$C_7H_{12}N_4S_3$	33.84, 4.87, 22.56 33.79, 4.88, 22.68
51593-04-5	**8b**	CH_3	C_6H_5	87	185–185.5	MEK	$C_{12}H_{14}N_4S_3$	46.42, 4.54, 18.05 46.36, 4.52, 18.21
51593-05-6	**8c**	C_6H_5	CH_3	68	166–167	EtOAc	$C_{12}H_{14}N_4S_3$	46.42, 4.54, 18.05 46.34, 4.44, 18.20
51593-06-7	**8d**	C_6H_5	C_6H_5	75	142–142.5	CH_3CN	$C_{17}H_{16}N_4S_3$	54.81, 4.33, 15.04 55.13, 4.38, 15.31
51593-07-8	**8e**	C_6H_5	$SO_2C_6H_5$	82	171–172.5	CH_3CN	$C_{17}H_{16}N_4O_2S_4$	46.77, 3.69, 12.83 46.86, 3.77, 11.91
51593-08-9	**8f**	CH_3	$SO_2C_6H_5$	77	215–216	C_5H_5N	$C_{12}H_{14}N_4O_2S_4$	38.48, 3.77, 14.96 38.49, 3.78, 14.99
51593-09-0	**8g**	C_6H_5	O=CN$(CH_3)_2$	61	168.5–170.5	MeOH	$C_{14}H_{17}N_5OS_3$	45.75, 4.66, 19.06 45.65, 4.72, 19.04
51593-10-3	**8h**	C_6H_5	$CO_2C_2H_5$	71	172.5	MEK–DMF	$C_{14}H_{16}N_4O_2S_3$	45.63, 4.38, 15.20 45.83, 4.44, 15.13
51593-11-4	**8i**	$N(CH_3)_2$	$SO_2C_6H_5$	82	144–145	CH_3CN	$C_{13}H_{17}N_5O_2S_4$	38.69, 4.25, 17.25 38.55, 4.30, 17.25
51593-12-5	**8j**	Cyclohexyl	CH_3		224	Toluene	$C_{12}H_{20}N_4S_3$	45.53, 6.37, 17.70 45.54, 6.58, 17.65

Table III
Adducts from 5-(Dialkylamino)-1,2,4-dithiazole-3-thiones and Dimethyl Acetylenedicarboxylate



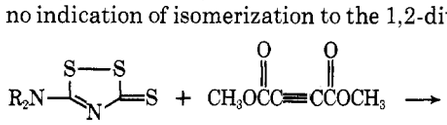
Registry no.	Compd	X	Yield, %	Mp, °C	Recrystn solvent	Empirical formula	Anal., % Calcd C, H, N Found C, H, N
51592-74-6	**14a**	$(CH_3)_2N$	55	131–132	Hexane–EtOAc	$C_{10}H_{12}N_2O_4S_3$	37.48, 3.78, 8.74 37.47, 3.64, 8.57
51592-75-7	**14b**		51	124.5–125	EtOH	$C_{13}H_{16}N_2O_4S_3$	43.32, 4.47, 7.77 43.16, 4.57, 7.60

Table IV
Adducts from 5-(Dimethylamino)-3-(substituted imino)-1,2,4-dithiazoles and Dimethyl Acetylenedicarboxylate

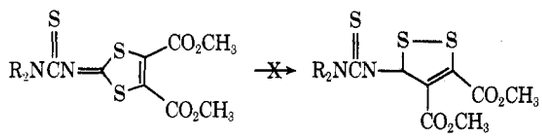


Registry no.	Compd	R	Yield, %	Mp, °C	Recrystn solvent	Empirical formula	Anal., % Calcd C, H, N Found C, H, N
51592-76-8	**9a**	CH_3	12	155–156	Hexane–EtOAc	$C_{11}H_{15}N_3O_4S_2$	41.63, 4.76, 13.24 41.43, 4.59, 12.97
51592-77-9	**9b**	C_6H_5	47	133–134	MeOH	$C_{16}H_{17}N_3O_4S_2$	50.65, 4.52, 11.07 50.74, 4.58, 11.11
51592-78-0	**9c**	4-C_6H_4Cl	53	180–181.5	EtOH	$C_{16}H_{16}ClN_3O_4S_2$	46.43, 3.90, 10.15 46.29, 4.09, 10.18
51635-65-5	**9d**	1-Adamantyl	83	231 dec	Toluene	$C_{20}H_{27}N_3O_4S_2$	54.90, 6.22, 9.60 55.08, 6.34, 9.62

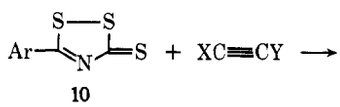
thiones (10) react with certain acetylenes to give initially the 1,3-dithiole derivatives 11 and that 11 can rearrange to the 1,2-dithiole isomers 12. We have obtained single 1:1 adducts from two 5-(dialkylamino)-1,2,4-dithiazole-3-thiones (13, R = Me_2N and piperidinyl, Table III) and dimethyl acetylenedicarboxylate; their nmr spectra contain only sharp singlets for the ester methyls, indicating the symmetrical 1,3-dithiole derivatives 14. We have seen no indication of isomerization to the 1,2-dithioles 15.



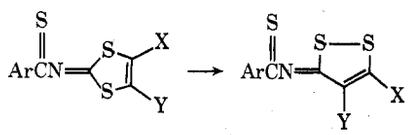
13a, R = CH_3
b, R = $(CH_2)_5$



14 15

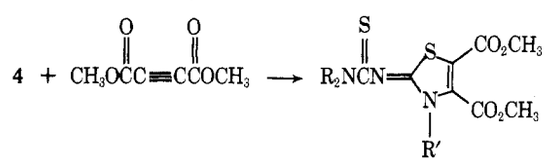


10



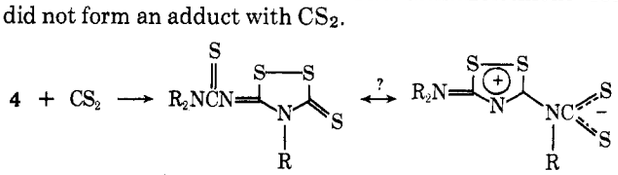
11 12

A few 5-(dialkylamino)-3-alkyl- (or aryl-) imino-1,2,4-dithiazoles were treated directly with dimethyl acetylenedicarboxylate to give thiocarbamoyliminothiazoles 9a–d. Similar reactions between 5-aryl-3-imino-1,2,4-dithiazoles have previously been described[6a] and require no further comment here. New adducts are contained in Table IV.



9

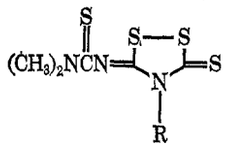
Several of the imino-1,2,4-dithiazoles also formed 1:1 adducts with carbon disulfide (Table V). The reaction was rather dependent on the nature of the substituent on the imino nitrogen; alkyliminodithiazoles reacted very quickly and sometimes exothermically at room temperature whereas the aryliminodithiazoles reacted only when heated in refluxing CS_2. 5-(Dimethylamino)-3-(carbethoxyimino)- and 5-(dimethylamino)-3-(2,2-dimethylhydrazono)-1,2,4-dithiazoles did not form adducts. Similarly, the adducts from the alkylimino compounds were fairly stable thermally, whereas that from the phenyliminodithiazole dissociated upon attempted recrystallization. Adduct 16a was not alkylated by methyl iodide in refluxing acetone; perhaps this low reactivity favors the thione structure 16 over the zwitterionic form 17. The dithiazolethione 13a did not form an adduct with CS_2.



16 17

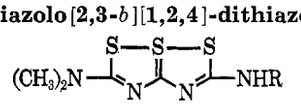
5-(Dimethylamino)-3-imino-1,2,4-dithiazole 18 reacted with methyl and phenyl isothiocyanate to provide the 3,4-diaza-6a-thiothiophthenes 19 (R = CH_3 and C_6H_5,

Table V
Adducts from 5-(Dimethylamino)-3-(substituted imino)-1,2,4-dithiazoles and Carbon Disulfide



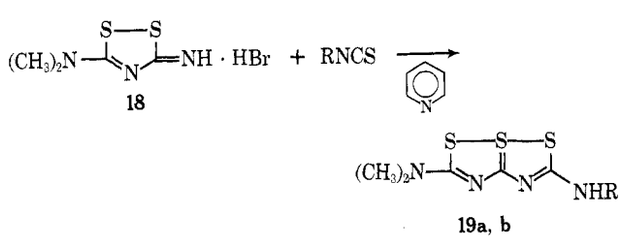
Registry no.	Compd	R	Yield, %	Mp, °C	Recrystn solvent	Empirical formula	Anal., % Calcd C, H, N Found C, H, N
51592-79-1	**16a**	CH_3	93	200–201		$C_6H_9N_3S_4$	28.06, 3.01, 16.71 28.36, 3.27, 16.88
51592-80-4	**16b**	C_6H_5	91	116–117.5		$C_{11}H_{11}N_3S_4$	42.14, 3.54, 13.40 42.03, 3.39, 13.28
51592-81-5	**16c**	4-$(CH_3O)C_6H_4$	80.5	116–118 dec	CS_2	$C_{12}H_{13}N_3S_4O$	41.96, 3.81, 12.23 41.98, 3.90, 12.29
51592-82-6	**16d**	CH_2-(2-furyl)	94	168–170	C_6H_6	$C_{10}H_{11}N_3OS_4$	37.83, 3.49, 13.24 37.96, 3.36, 13.17
51592-83-7	**16e**	*n*-C_3H_7	68.5	156–158	CS_2	$C_8H_{13}N_3S_4$	34.38, 4.69, 15.04 34.52, 4.76, 14.92
51592-84-8	**16f**	Cyclohexyl	81	152	C_6H_6	$C_{11}H_{17}N_3S_4$	41.35, 5.36, 13.15 41.59, 5.56, 13.19

Table VI
1,2,4-Dithiazolo[2,3-*b*][1,2,4]-dithiazole-4-S^{IV}



Registry no.	Compd	R	Yield, %	Mp, °C	Recrystn solvent	Empirical formula	Anal., % Calcd C, H, N Found C, H, N
51592-85-9	**19a**	CH_3	60	252–253 dec	DMF	$C_6H_{10}N_4S_3$	30.75, 4.30, 23.91 30.90, 4.32, 24.01
51592-86-0	**19b**	C_6H_5	65	203–204	HOAc	$C_{11}H_{12}N_4S_3$	44.57, 4.08, 18.90 44.56, 3.89, 19.11

Table VI). Similar reactions have been described by Behringer and Weber[13] and were not considered dipolar



18 **19a, b**

additions, although dipolar additions followed by tautomerism would have been consistent with the observed products.

Experimental Section[14,15]

Alkyl and aryl isothiocyanates were commercial samples. Dimethylthiocarbamoyl isothiocyanate was prepared in MeCN from dimethylthiocarbamoyl chloride and KSCN and was used without isolation;[11a] carbethoxy isothiocyanate was similarly obtained from $ClCO_2Et$. Benzenesulfonyl isothiocyanate was synthesized according to Hartke.[16] 5-(Dialkylamino)-3-(substituted imino)-1,2,4-dithiazoles (4) were prepared and stored as hydrochloride or hydrobromide salts as described previously.[11a] A few previously unreported iminodithiazoles were prepared and used without complete characterization; however, their method of preparation and the characterization of their adducts with the described dipolarophiles confirmed the assigned structures.

Reactions of Iminodithiazoles (4) with Dialkylthiocarbamoyl Isothiocyanates. The iminodithiazole hydrochloride or hydrobromide (0.01 mol) was shaken with CH_2Cl_2 and saturated aqueous Na_2CO_3. The organic phase was dried and the filtered CH_2Cl_2 solution was added to a solution of the thiocarbamoyl isothiocyanate (from 0.01 mol of the corresponding thiocarbamoyl chloride and KSCN) in MeCN at room temperature. In most cases the products (**6a–p**) precipitated from solution within a few minutes. In a few cases the solvent was stripped and the residue was recrystallized. Data are in Table I.

Reactions of Iminodithiazoles with Miscellaneous Isothiocyanates. The iminodithiazoles were obtained as free bases as described above, and extracted into CH_2Cl_2 or $CHCl_3$. If CH_2Cl_2 was used, the solution was dried and stripped and MeCN (25 ml per 0.01 mol) was added to the residue. An equivalent of the appropriate isothiocyanate was added, and the solution was refluxed for 1 hr. The products were collected from the chilled solutions by filtration. Alternatively, $CHCl_3$ extracts containing the iminodithiazoles were dried and treated directly with the desired isothiocyanate. After refluxing for 1 hr, the products were isolated by filtration or by concentrating the solutions. Data for adducts **8a–k** are collected in Table II.

Reactions of Iminodithiazoles with Dimethyl Acetylenedicarboxylate. The iminodithiazoles were extracted into CH_2Cl_2; the CH_2Cl_2 solutions were dried, filtered, and treated with 1 equiv of dimethyl acetylenedicarboxylate. The solutions (which rather quickly assumed dark colors) were stirred overnight at room temperature and then evaporated and the residue was triturated with MeOH or EtOH to give adducts **9a–d** (Table IV).

Reactions of 5-(Dialkylamino)-1,2,4-dithiazole-3-thiones with Dimethyl Acetylenedicarboxylate. The appropriate thione and 1 equiv of dimethyl acetylenedicarboxylate were combined in CH_2Cl_2 (30 ml per 0.01 mol) and the mix was either refluxed for 1 hr or stirred for *ca.* 6 hr at room temperature. The CH_2Cl_2 was then evaporated and the residue was recrystallized to give **14a** and **14b** (Table III).

Reactions of Iminodithiazoles with Carbon Disulfide. The iminodithiazoles were extracted into CH_2Cl_2; the CH_2Cl_2 solutions were dried and stripped, and the residues were treated with CS_2 (25–30 ml per 0.01 mol). If no immediate reaction was observed, the solutions were refluxed for 1 hr and then chilled, and the products (**16a–f**, Table V) were collected by filtration. The methyliminodithiazole reacted exothermically, and an ice bath should be applied if the reaction is run on a scale larger than *ca.* 1 g.

Reaction of 5-(Dimethylamino)-3-imino-1,2,4-dithiazole Hydrobromide (18) with Isothiocyanates. A suspension of **18** (15 mmol) in pyridine (50 ml) containing phenyl or methyl isothiocy-

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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(14) 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. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.
(15) Mention of a proprietary product or company does not imply endorsement by the U. S. Department of Agriculture.
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Imino-1,2,4-dithiazoles. III. Thermal Decomposition of 5-(Dialkylamino)-3-(substituted imino)-1,2,4-dithiazoles

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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-