gave 16 (10.2 mg, 75%): mp 158–159° ($CHCl_3$–petroleum ether); mass spectrum *m/e* 379.757 (calcd for $C_6H_5{}^{79}Br_2{}^{81}BrSO_2$, 379.754); ir (KBr) 1600, 1465, 1422, 1380, 1333, 1240, 1205, 1175, 1100, 1015, 895, 850, 790, 735, and 722 cm^{-1}; nmr, see discussion.

Dehydrobromination of 16. Compound 16 (14.2 mg) was dissolved in CCl_4 (0.3 ml), DBN (1 drop) was added, and the solution was shaken at room temperature for 30 min. Ptlc on silica eluting with $CHCl_3$ gave **15** (7.5 mg, 70%) identical in all observed respects with the previous sample.

Registry No.—**8**, 33689-28-0; **9**, 51593-74-9; **10**, 38828-44-3; **11**, 38828-45-4; **12**, 51593-75-0; **13**, 38916-88-0; **14**, 51593-76-1; **15**, 51593-77-2; **16**, 51593-78-3.

References and Notes

(1) For a preliminary account of part of this work see P. J. Garratt and D. N. Nicolaides, *J. Chem. Soc., Chem. Commun.*, 1015 (1972).
(2) North Atlantic Treaty Organization Fellow, 1971–1972, on leave from the University of Thessaloniki, Greece.
(3) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).
(4) Mills and Nixon[3] believed in the individual identify of the separate Kekulé forms, and suggested that indan was an equilibrium mixture of the two forms.
(5) The π system of the aromatic ring will be represented by a circle when no specific bonding structure is implied.
(6) For an account of studies on the Mills–Nixon effect and on bond fixation in general, see G. M. Badger, *Quart. Rev., Chem. Soc.*, **5**, 147 (1951).
(7) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **42**, 756 (1946).
(8) In fact, as Cava discovered, Finkelstein had prepared a benzocyclobutene derivative before 1909. For a general discussion of early work in this field see M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.
(9) W. C. Lothrop, *J. Amer. Chem. Soc.*, **63**, 1187 (1941).
(10) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2255 (1958).
(11) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).
(12) E. Vogel, S. Korte, W. Grimme, and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **7**, 289 (1968). For a review of this type of system see B. Halton, *Chem. Rev.*, **73**, 113 (1973).
(13) M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, **92**, 1605 (1970).
(14) E. L. Motell, D. Lauer, and G. E. Maciel, *J. Phys. Chem.*, **77**, 1865 (1973).
(15) H. Günther, G. Jikeli, H. Schnickler, and J. Prestien, *Angew. Chem., Int. Ed. Engl.*, **12**, 762 (1973). There is a disagreement in assignment between the authors of ref 14 and 15.
(16) E. Carstensen-Oeser, B. Müller, and M. Dürr, *Angew. Chem., Int. Ed. Engl.*, **11**, 422 (1972). See also W. E. Billups, W. Y. Chow, K. H. Leavell, E. S. Lewis, J. L. Margrave, R. L. Sass, J. J. Shieh, P. G. Werness, and J. L. Wood, *J. Amer. Chem. Soc.*, **95**, 7878 (1973).
(17) R. Taylor, G. F. Wright, and A. J. Holmes, *J. Chem. Soc. B*, 780 (1967); R. Taylor, *ibid.*, 1559 (1968); 536 (1971); R. Taylor, M. P. David, and J. F. W. McOmie, *ibid.*, 162 (1972).
(18) A. Streitweiser, G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, **90**, 1357 (1968).
(19) In his discussion of these effects, Taylor tends to neglect changes in molecular structure other than those of strain. Thus, for example, when discussing the reactions of biphenylene and benzocyclobutene, the fact that reaction of biphenylene at position 1 introduces more cyclobutadiene character into the transition state than does reaction at position 2, a factor which does not arise in benzocyclobutene, does not appear to have been considered.
(20) R. A. Finnegan, *J. Org. Chem.*, **30**, 1333 (1965).
(21) R. D. Riecke, W. E. Rich, and T. H. Ridgeway, *J. Amer. Chem. Soc.*, **93**, 1962 (1971); R. D. Riecke and W. E. Rich, *ibid.*, **92**, 7349 (1972), and previous papers.
(22) A. R. Bassindale, C. Eaborn, and D. M. R. Walton, *J. Chem. Soc. B*, 12 (1969).
(23) The range of ^{13}C chemical shifts for a series of cyclobutene derivatives has been found to be small, and this indicates that this parameter may be a good indicator of ring strain, being insensitive to other effects; see A. J. Jones, P. J. Garratt, and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, **12**, 241 (1973), and unpublished results.
(24) Substituted derivatives of 10 have been prepared: S. W. Longworth and J. F. W. McOmie, *J. Chem. Soc., Chem. Commun.*, 623 (1972). See also K. P. C. Vollhardt and R. G. Bergman, *J. Amer. Chem. Soc.*, **95**, 7538 (1973).
(25) J. M. Conia and J. M. Denis, *Tetrahedron Lett.*, 2845 (1971).
(26) K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).
(27) P. J. Garratt and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, **94**, 7087 (1972).
(28) P. J. Garratt and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, **94**, 1022 (1972).
(29) For a valuable general discussion of thiophene chemistry, see S. Gronowitz, *Advan. Heterocycl. Chem.*, **1**, 1 (1963).
(30) S. B. Neoh, unpublished experiments.
(31) H. L. Coonradt, H. M. Hartough, and G. C. Johnson, *J. Amer. Chem. Soc.*, **70**, 2564 (1948).
(32) S.-O. Lawesson, *Ark. Kemi*, **11**, 373 (1957).
(33) It should be pointed out that benzocyclopropene (**5**) does add iodine across the tetrasubstituted double bond to give 1,6-diiodocycloheptatriene.[11] However, initial attack on this double bond provides a carbonium ion which cannot readily eliminate a proton to reestablish the benzenoid system. If the initial attack on **10** was at the ring junction, a similar argument could be applied, but such an attack appears unlikely in view of the relative stabilities of the carbonium ions formed.
(34) It could, however, be argued that delocalization in **10** would lead to a shortening of the 1,5 bond and thus to a decrease in strain in comparison to the bond-fixed structure.

Imino-1,2,4-dithiazoles. I. Alkylation

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A series of 5-(dialkylamino)-3-(substituted imino)-1,2,4-dithiazoles were alkylated with alkyl halides to give the 3,5-bis(dialkylamino)-1,2,4-dithiazolium halides **3a–h**. The scope and limitations of the reaction are discussed.

A number of 3,5-bis(substituted amino)-1,2,4-dithiazolium salts (**3**) are housefly (*Musca domestica L.*) sterilants.[1,2] The most active compounds have been those in which both of the exocyclic nitrogens were fully substituted, and we have employed two methods (paths a and b, Scheme I) for preparing these materials.[1,3,4] In each case the substituent NR^1R^2 was derived from the corresponding secondary amine; thus the accessibility of a given dithiazolium salt depended on the availability of the secondary amine. An obvious alternative synthesis would be the alkylation of iminodithiazoles **2** (path c, Scheme I). Alkylation on the imino nitrogen, as opposed to ring alkylation, would be expected, since an aromatic dithiazolium salt would result from the former process.

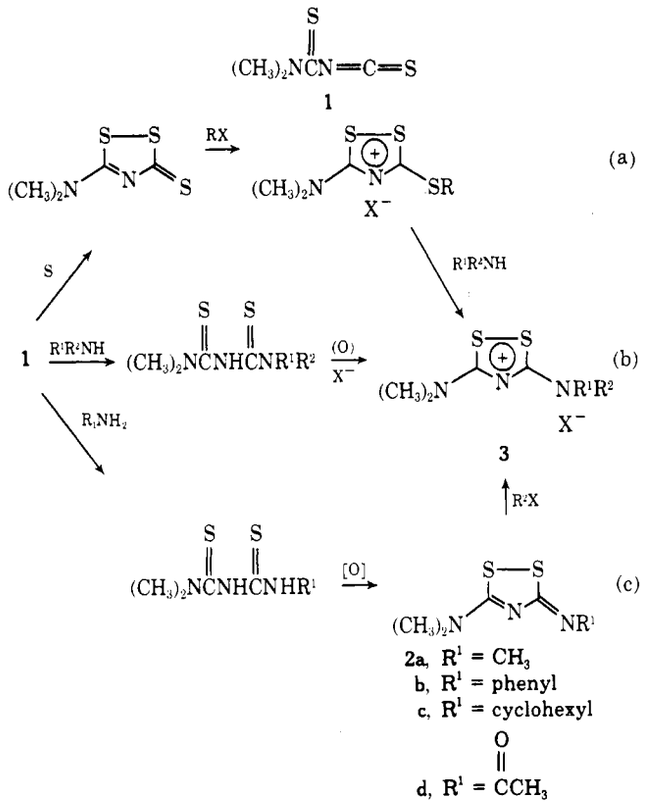
We have found that 5-(dimethylamino)-3-(alkyl- or arylimino)-1,2,4-dithiazoles (**2**) are smoothly alkylated by reactive alkyl halides to give the dithiazolium salts **3a–h** shown in Table I. Yields were good to excellent with methyl iodide, benzyl chloride, allyl bromide, and ethyl bromoacetate. That alkylation occurred on the imino nitrogen as expected was confirmed in two cases by comparing the products with dithiazolium salts previously prepared by the standard methods: **3a** had been synthesized earlier by oxidation of 1,1,5,5-tetramethyl-2,4-dithiobiuret

Table I
Dithiazolium Salts *via* Alkylation of Iminodithiazoles

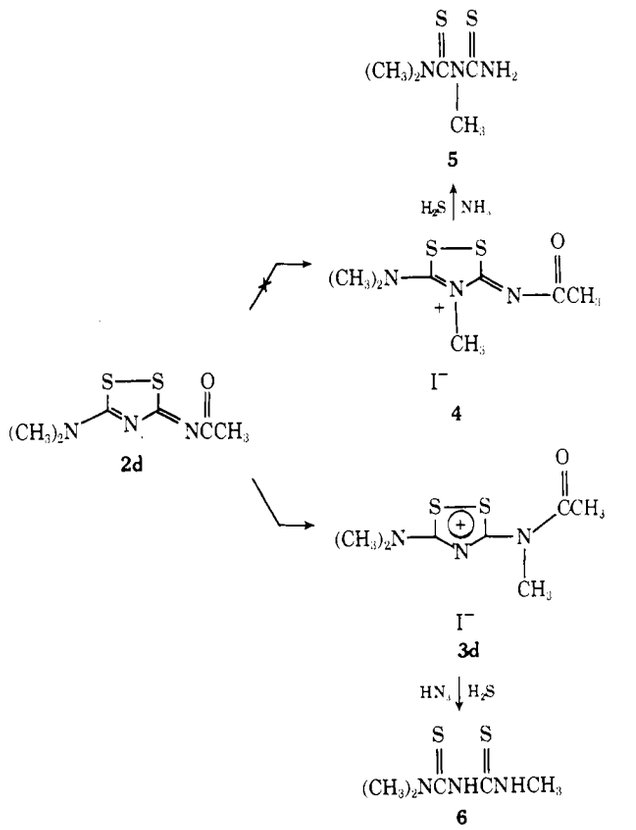
Registry no.	Salt	R^1	R^2	X^-	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Recrystn solvent
50312-97-5	**3a**	CH_3	CH_3	I	267.5–269 dec	91	Reference 2						
51567-98-7	**3b**	C_6H_5	CH_3	I	175 dec	85	34.83	3.72	11.08	34.94	3.62	10.92	HOAC
51567-99-8	**3c**	Cyclohexyl	CH_3	I	211–212	91	34.28	5.23	10.90	34.33	5.15	10.83	EtOH
51568-00-4	**3d**	$COCH_3$	CH_3	I	211.5–212.5 dec	90	Reference 5						EtOH
51568-01-5	**3e**	CH_3	$C_6H_5CH_2$	Cl	217–218 dec	60	47.75	5.34	13.92	47.63	5.45	13.82	*i*-PrOH
51568-02-6	**3f**	CH_3	$CH_2CH{=}CH_2$	Br	97.5	41	32.22	4.73	14.08	32.35	4.66	14.33	
51568-03-7	**3g**	C_6H_5	$C_6H_5CH_2$	Cl	169–170	51	*a*						
51568-04-8	**3h**	C_6H_5	$CH_2CO_2C_2H_5$	Br	195 dec	91	41.58	4.49	10.39	41.97	4.52	10.31	*i*-PrOH–MEK

[a] Could not be purified by recrystallization, but the structure was confirmed by nmr.

Scheme I
Synthesis of 3,5-Bis(dialkylamino)-1,2,4-dithiazolium Salts



Scheme II



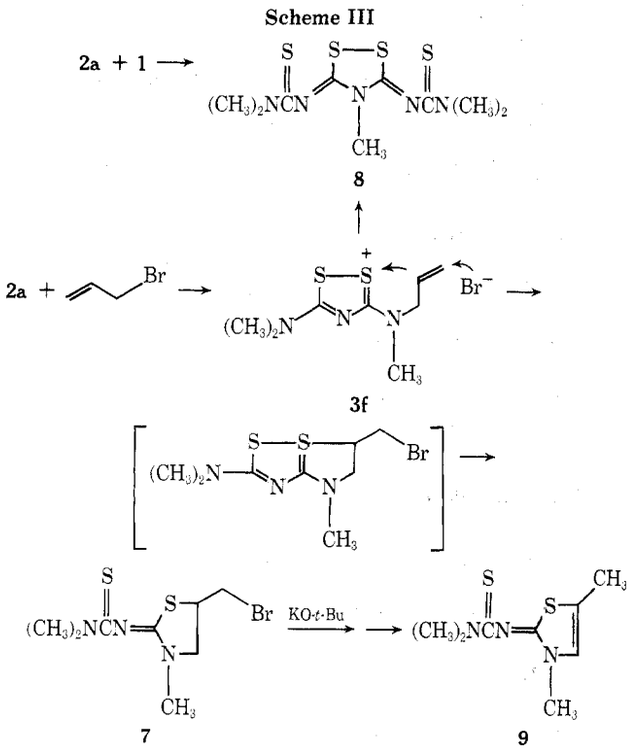
with iodine,[2] and **3b**, when treated with 1 equiv of perchloric acid, yielded the corresponding perchlorate which had been prepared earlier by the reaction of 3-(dimethylamino)-5-(ethylthio)-1,2,4-dithiazolium perchlorate with *N*-methylaniline.[3]

Iwataki[5] recently described the alkylation of 3-(acetylimino)-5-(dimethylamino)-1,2,4-dithiazole (**2d**) with methyl iodide, and assigned the 4-methyldithiazolium structure 4 (Scheme II) to the product. He degraded his dithiazolium iodide with H_2S–NH_3 to a trimethyldithiobiuret which he described as the 1,1,3 isomer **5**. Since this result was contrary to ours, we repeated his procedure; our dithiazolium iodide appeared to be identical with Iwataki's, but upon treatment of this salt with H_2S–NH_3 we obtained a quantitative yield of 1,1,5-trimethyl-2,4-dithiobiuret (**6**, identical with an authentic sample[6]) instead of the 1,1,3 isomer **5**. We therefore concluded that alkylation had in fact occurred on the imino nitrogen.[7]

There are definite limitations to the alkylation reaction, perhaps the most serious one being the lability of the iminodithiazoles. Thus, with relatively unreactive alkyl halides such as bromocyclohexane, decomposition of the iminodithiazoles occurred, and the desired dithiazolium salts were not obtained. The thermal decompositions of selected iminodithiazoles were studied in some detail and are described in an accompanying communication.[8]

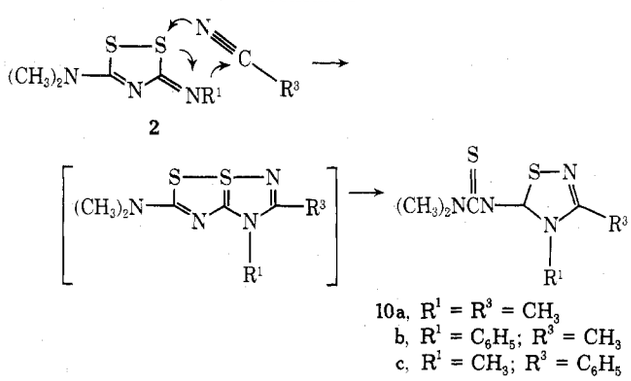
Another limitation is the ability of certain functionalized dithiazolium salts to undergo subsequent reactions. For example, **2a** reacted with allyl bromide to give the dithiazolium bromide **3f**; however, when **3f** was warmed in ethanol, decomposition occurred, and the thiazoline derivative **7** was isolated along with a trace of the bis(thiocarbamoylimino)dithiazole **8**. A probable pathway for the formation of **7** is shown in Scheme III and is related to the base-catalyzed decomposition of the acylimino dithiazole to a thiazolidinone described by Iwataki and Ueda.[9] Dithiazole 8 is a cycloadduct of **2a** and **1**,[10] but how these two species arose from **3f** remains uncertain.

Scheme III



A similar decomposition appeared to occur when **2a** was treated with ethyl bromoacetate; in this case, however, the HBr salt of **2a** rapidly precipitated from solution in 42% yield. The other products have not been characterized, but presumably the carbonyl oxygen of the initially formed dithiazolium salt interacted with the charged ring to facilitate elimination of the HBr. In contrast, **2b** reacted smoothly with ethyl bromoacetate to give the dithiazolium bromide **3b**, which was purified without difficulty.

Scheme IV



10a, $R^1 = R^3 = CH_3$
b, $R^1 = C_6H_5$; $R^3 = CH_3$
c, $R^1 = CH_3$; $R^3 = C_6H_5$

Still another side reaction was observed when certain alkylations of the methylimino- and phenyliminodithiazoles (**2a** and **2b**) were attempted in acetonitrile. In these cases 1,3-dipolar additions between the iminodithiazole and the nitrile occurred, and the 1,2,4-thiadiazole derivatives **10a** and **10b** were isolated. The methylimino dithiazole **2a** also reacted with benzonitrile to give **10c** (Scheme IV). Dipolar additions of iminodithiazoles with isothiocyanates[11,12] and with acetylenes[13] have been observed, and we have described some additional examples in an accompanying paper,[14] but additions of these compounds to nitriles appear not to have been recorded in the literature. The previously mentioned decomposition of the iminodithiazoles competes with these dipolar additions, and the adducts were usually contaminated with decomposition products. Although a moderate yield of **10a** was obtained by heating **2a** with a large excess of acetonitrile (250 ml for 3.3 g of **2a**), this reaction appears to be of little synthetic value for less readily available nitriles.

Experimental Section[15,16]

Alkylation of Iminodithiazoles to Give Dithiazolium Salts 3a–h. The dithiazoles **2a–c** were prepared and stored as HBr salts.[1] Typically, 0.01 mol of a given hydrobromide was shaken with aqueous Na_2CO_3 and CH_2Cl_2, and the CH_2Cl_2 solution was separated and dried. The CH_2Cl_2 was stripped at room temperature and replaced with Me_2CO (25 ml) and the resulting solution was refluxed for 1–2 hr with 0.01 mol of the alkyl halide. The mixture was chilled, and the product was collected by filtration. In the case of **3g** the Me_2CO was evaporated and **3g** was crystallized by triturating the residue with warm Et_2O. The yield of **3e** was low when **2a** was treated with benzyl chloride in Me_2CO, but improved substantially when benzyl chloride was employed as the solvent: 1.75 g of **2a** and 10 ml of benzyl chloride were heated at 50° for 15 min, during which time **3e** began to precipitate from solution. Et_2O (10 ml) was added, the mixture was chilled, and crude **3e** (1.78 g, mp 204–210° dec) was collected by filtration.

Conversion of 3d to 1,1,5-Trimethyl-2,4-dithiobiuret (6). The procedure was that described by Iwataki:[5] 1.25 g of **3d** was dissolved in a solution of 28% NH_3 (7.2 ml) and absolute EtOH (3.6 ml), then H_2S was bubbled through the solution. An exothermic reaction occurred, a yellow color developed, and a white solid separated. The temperature was maintained at 30–35° while H_2S addition was continued for 50 min. The solid was removed by filtration, giving 0.43 g (67%) of 1,1,5-trimethyl-2,4-dithiobiuret (**6**), mp 125–127°, whose ir and nmr spectra were identical with those of a sample prepared previously from **1** and $MeNH_2$, mp 123–124°.[6] When the filtrate was acidified with HCl a tan solid (0.08 g, mp 108–113°) separated; extraction of the acidic filtrate with $CHCl_3$ yielded 0.13 g of solid, mp 108–117°. The ir spectra of each of these two solids were identical with that of pure **6**. Thus the total yield of **6** from **3d** was quantitative. We did not observe the acetyldithiobiuret (mp 161–162°) described by Iwataki as a minor product from this reaction.

1,1-Dimethyl-3-(3,4-dimethyl-4*H*-1,2,4-dithiazolin-5-ylidene)-2-thiourea (10a). A solution of 3.2 g of **2a** in MeCN (250 ml) was refluxed overnight under N_2. Evaporation of the solvent and re-

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

(1) J. E. Oliver, S. C. Chang, R. T. Brown, J. B. Stokes, and A. B. Borkovec, *J. Med. Chem.*, **14**, 772 (1971).
(2) J. E. Oliver, R. T. Brown, R. L. Fye, and A. B. Borkovec, *J. Agr. Food Chem.*, **21**, 753 (1973).
(3) J. E. Oliver, R. T. Brown, and N. L. Redfearn, *J. Heterocycl. Chem.*, **9**, 447 (1972).
(4) W. R. Diveley, U. S. Patent 3,166,564 (1965); *Chem. Abstr.*, **62**, 914*g* (1965).
(5) I. Iwataki, *Bull. Chem. Soc. Jap.*, **45**, 3572 (1972).
(6) J. E. Oliver, S. C. Chang, R. T. Brown, and A. B. Borkovec, *J. Med. Chem.*, **14**, 772 (1971).
(7) In a private communication, Dr. Iwataki has confirmed the identity of his degradation product with our sample of **5**.
(8) J. E. Oliver and J. L. Flippen, *J. Org. Chem.*, **39**, 0000 (1974).
(9) I. Iwataki and A. Ueda, *Bull. Chem. Soc. Jap.*, **45**, 3220 (1972).
(10) J. E. Oliver and J. B. Stokes, *Int. J. Sulfur Chem., Part A*, **2**, 105 (1972).
(11) J. E. Oliver, J. L. Flippen, and J. Karle, *J. Chem. Soc., Chem. Commun.*, 1153 (1972).
(12) J. Goerdeler and J. Ulmen, *Chem. Ber.*, **105**, 1568 (1972).
(13) J. M. Buchshriber, D. M. McKinnon, and M. Ahmed, *Can. J. Chem.*, **47**, 2039 (1969).
(14) J. E. Oliver and R. T. Brown, *J. Org. Chem.*, **39**, 2228 (1974).
(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-