CH_2Cl_2–hexanes to provide pure **7**.

L-**7** (from **8a** obtained via pyroglutamate): 93% yield; mp 110–111 °C; $[\alpha]_D$ = −19.93° (*c* = 4, CH_2Cl_2); NMR (300 MHz, $CDCl_3$) δ 1.80 (m, 4 H), 3.35 (m, 2 H), 4.10 (m, 1 H, *J* = 6 Hz), 4.85 (s, 2 H), 4.97 (dd, 1 H, *J* = 12 Hz), 5.8 (d, 1 H, *J* = 8 Hz), 7.38 (m, 10 H), 9.8 (s, 1 H); IR (Nujol) 3320, 3190, 1675, 1660 cm^{-1}.

L-**7** (from **8a** obtained via γ-ethyl ester): 88% yield; mp 112–114 °C; $[\alpha]_D$ = −21.6° (*c* = 2, CH_2Cl_2). Anal. Calcd for $C_{20}H_{23}N_2O_4Br$: C, 55.17; H, 5.29; N, 6.44. Found: C, 55.30; H, 5.47; N, 6.51.

D-**7** (from **8a** obtained via pyroglutamate): 62% yield; $[\alpha]_D$ = +20.1° (*c* = 4.6, CH_2Cl_2); mp 109–111 °C. The spectral data were identical with that obtained for L-**7**.

D-**7** (from **8a** obtained via γ-methyl ester): 83% yield; mp 115–7 °C; $[\alpha]_D$ = +22.3° (*c* = 2.3, CH_2Cl_2); IR (Nujol) 3320, 3180, 1680, 1655 cm^{-1}; exact mass calcd for $C_{20}H_{23}N_2O_4Br$ 434.0841, found 434.0841.

α-*N*-Carbobenzoxy-δ-*N*-(benzyloxy)cycloornithine (2a). General Procedure. A solution of 10 mmol of **7** and 20 mmol of anhydrous K_2CO_3 in 300 mL of acetone was refluxed for 12 h at which time analysis by TLC revealed the absence of starting material. The acetone was removed under reduced pressure, and the residue was passed through a silica gel column with CH_2Cl_2–ethyl acetate (4:1) as the eluent to provide **2a**. The final product was obtained after recrystallization from ethyl acetate–hexanes.

D-**2a** (from **8a** obtained via pyroglutamate): 91% yield; mp 68–71 °C; $[\alpha]_D$ = −51.0° (*c* = 1.4, CH_2Cl_2).

D-**2a** (from **8a** obtained via γ-methyl ester): 98% yield; mp 75–76 °C; $[\alpha]_D$ = −51.7° (*c* = 1.8, CH_2Cl_2).

L-**2a** (from **8a** obtained via pyroglutamate): 82% yield; mp 71–73 °C; $[\alpha]_C$ = +52.0° (*c* = 1.45, CH_2Cl_2); MS (CI with isobutane) *m/e* 355 (M + 1), 247 (M − 108); NMR (300 MHz, $CDCl_3$) δ 1.57 (d, 1 H, *J* = 5 Hz), 1.85 (m, 2 H), 2.37 (m, 1 H), 3.32 (m, 1 H), 3.41 (sextet, 1 H, *J* = 6 Hz), 4.17 (quintet, 1 H, *J* = 6 Hz), 4.9 (dd, 2 H, *J* = 10.5 Hz), 5.16 (s, 2 H), 5.8 (br s, 1 H), 7.4 (m, 10 H).

L-**2a** (from **8a** obtained via γ-ethyl ester): 95% yield; mp 70–71 °C; $[\alpha]_D$ = +51.6° (*c* = 1.8, CH_2Cl_2). Anal. Calcd for $C_{20}H_{22}N_2O_4$: C, 67.78; H, 6.21; N, 7.91. Found: C, 67.59; H, 6.26; N, 7.93.

α-*N*-(Bis(benzoyloxy)succinyl)-δ-*N*-(benzyloxy)cycloornithine (38). The dibenzoyltartarimide (DBT) derivatives of *N*-(benzyloxy)cycloornithine **38** were made from **2a** as described in the literature.[38]

L-**38** (obtained via pyroglutamate): mp 94–97 °C; $[\alpha]_D$ = +93.0° (*c* = 0.3, CH_2Cl_2); NMR (300 MHz, $CDCl_3$) δ 1.85 (m, 1 H), 2.03 (m, 2 H), 2.32 (dq, 1 H, *J* = 3 and 12 Hz), 3.39 (dd, 1 H, *J* = 5 and 11 Hz), 3.55 (dt, 1 H, *J* = 4 and 11 Hz), 4.83 (dd, 1 H, *J* = 6 and 12 Hz), 5.0 (s, 2 H), 6.06 (s, 1 H), 7.4 (m, 11 H), 8.1 (d, 4 H, *J* = 7 Hz).

L-**38** (prepared via γ-ester route): mp 95–98 °C; $[\alpha]_D$ = +95.4° (*c* = 1.0, CH_2Cl_2); NMR spectrum (same as that reported above); IR (Nujol) 1795, 1730, 1710, 1670 cm^{-1}; MS (CI with isobutane) *m/e* 543 (M + 1), 314.

D-**38** (obtained via pyroglutamate): mp 154–157 °C; $[\alpha]_D$ = +116.3° (*c* = 0.8, CH_2Cl_2); NMR (300 MHz, $CDCl_3$) δ 2.0 (m, 3 H), 2.32 (dq, 1 H, *J* = 3 and 12 Hz), 3.42 (dd, 1 H, *J* = 5 and 12 Hz), 3.56 (dt, 1 H, *J* = 4 and 11 Hz), 4.86 (dd, 1 H, *J* = 6 and 12 Hz), 5.0 (s, 2 H), 6.01 (s, 1.7 H), 6.07 (s, 0.3 H), 7.4 (m, 11 H), 8.1 (d, 4 H, *J* = 7 Hz).

D-**38** (prepared via γ-ester): mp 170–172 °C; $[\alpha]_D$ = +119.1° (*c* = 0.7, CH_2Cl_2); NMR as above with the exception of only one 2 H singlet at 6.01 ppm; IR (Nujol) 1800, 1733, 1715, 1680 cm^{-1}; MS (CI with isobutane) *m/e* 543 (M + 1), 314.

Acknowledgment. We are pleased to acknowledge the NIH for support of this work.

Registry No. **2**, 125049-95-8; (*R*)-**2a**, 125049-95-8; (*S*)-**2a**, 125050-20-6; **2b**, 125049-92-5; **2c**, 125050-11-5; (*Z*)-**4a**, 125050-02-4; (*E*)-**4a**, 125050-03-5; (*Z*)-**4b**, 125050-07-9; (*E*)-**4b**, 125050-08-0; (*Z*)-**4b** (*N*-hydroxysuccinimide ester), 125050-09-1; (*E*)-**4b** (*N*-hydroxysuccinimide ester), 125050-10-4; **6**, 125050-15-9; D-**7**, 125050-16-0; L-**7**, 125050-19-3; D-**8a**, 125076-26-8; L-**8a**, 124620-51-5; D-**8b**, 125049-87-8; L-**8b**, 125137-57-7; **8c**, 125050-04-6; (*R*)-**14**, 125049-81-2; (*S*)-**14**, 89969-27-7; **15**, 125049-82-3; **16**, 125049-83-4; L-**17a**, 81470-51-1; D-**17a**, 125134-29-4; D-**17b**, 125049-85-6; L-**17b**, 125049-86-7; L-**19a**, 1119-33-1; D-**19a**, 45025-26-1; L-**20a**, 125076-24-6; D-**20a**, 125076-25-7; L-**20b**, 57732-63-5; D-**20b**, 23577-92-6; **22**, 125049-96-9; **23**, 125049-97-0; **24**, 125049-98-1; **25**, 125049-99-2; (*Z*)-**26**, 125050-00-2; (*E*)-**26**, 125050-01-3; (*Z*)-**27**, 125050-05-7; (*E*)-**27**, 125050-06-8; **28**, 125049-88-9; **29**, 125049-90-3; **30**, 125049-91-4; **31**, 125049-93-6; **32**, 125049-94-7; **34**, 125050-12-6; **35**, 125050-13-7; **35** (*N*-hydroxysuccinimide ester), 125076-27-9; **36**, 125050-14-8; L-**37**, 125050-17-1; D-**37**, 125050-18-2; (*S*)-**38**, 125076-07-5; (*R*)-**38**, 125050-21-7; L-CbzGluOH, 1155-62-0; D-GbzGluOH, 63648-73-7; $H_2C{=}CHCH_2OCOGluOH$, 125049-84-5; $CbzNHOCH_2Ph$, 15255-86-4; $H_2C{=}CHCH_2OCONHOCH_2Ph$, 125049-89-0.

2-Amino-5-imino-4,5-dihydrothiazoles: Synthesis by Reaction of Isocyanides with 2-Amino-3-aza-1-thiabutadienes and Base-Induced Rearrangement into Imidazolines or Diazolidines

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The reaction of isocyanides R^3NC with 2-amino-3-aza-1-thiabutadienes **3** gives the 2-amino-5-imino-4,5-dihydrothiazoles **4**. The rearrangement of **4** (R^2 = H) was induced by 1,5-diazabicyclo[4.3.0]non-5-ene and leads to 4*H*-imidazoline-5-thiones **5** or 4-thioxo-1,3-diazolidines **6** according to the nature of the substituent R^1. The tautomeric form **5** is the only one obtained when R^1 is an alkyl group. Diazolidine **6** appears in the tautomeric mixture or is the single form observed when R^1 is the benzoyl or an aryl group. Structural assignments of **5** and **6** and the tautomeric equilibrium investigation are based on ^{13}C NMR spectral data. The same structures **5** and **6** (R^2 = H) are observed in the solid state by single-crystal X-ray analysis.

Isocyanides are stable nucleophilic carbenes that provide [1 + 4] cycloaddition reactions with conjugated electron-deficient heterodienes. It has been shown that these reactions are useful for the synthesis of functionalized

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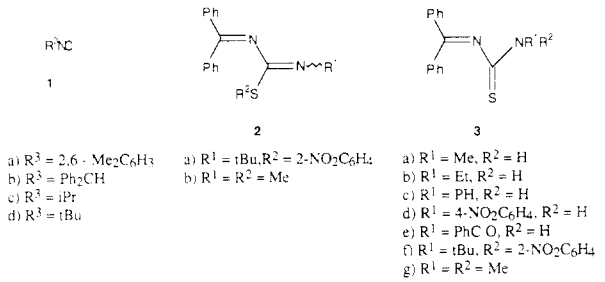
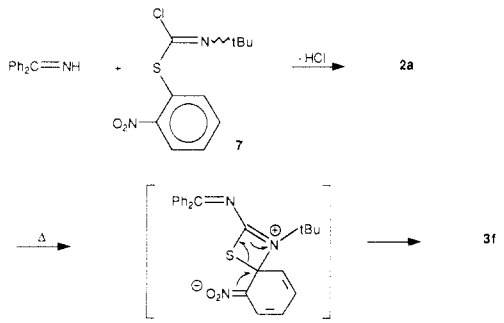
Chart I



Scheme I



five-membered ring systems.[1,2]

In connection with this work, we have recently examined the reactivity of isocyanides **1** toward various 1,3-diaza-4,4-diphenyl-2-(methylthio)butadienes (e.g. **2b**). We have shown that the use of protic acid (HCl or HI) greatly enhances the rate of the reactions. The expected [1 + 4] cycloadducts were isolated in good yields but 2-amino-4,5-dihydrothiazoles **4** and 4*H*-imidazoline-5-thiones **5** (R^2 = H) were sometimes obtained, probably through a thiazolium salt as common intermediate.[3] In this acidic medium, compounds **4** did not rearrange into their isomers **5**.

We report herein a new preparation of a series of dihydrothiazoles **4** from the [1 + 4] cycloaddition of isocyanides **1** with 2-amino-3-aza-1-thiabutadienes **3**. We also describe the base-induced rearrangement of **4** (R^2 = H) into 2-aminoimidazoline-5-thiones **5** or 2-imino-4-thioxo-1,3-diazolidines **6**, depending on the nature of the substituent R^1. A mechanism is suggested for this new rearrangement.

4-Amino-3-aza-1-thiabutadienes have been extensively investigated as 4π components of hetero-Diels–Alder reactions.[4,5] However, to our knowledge, there is no literature report related to the participation of 2-amino-3-aza-1-thiabutadienes in similar cycloadditions. Furthermore, only a few examples could be found involving the [1 + 4] cyclization process of such heterodienes. They have been reported by Burger et al. in the conversion of 3-aza-4,4-bis(trifluoromethyl)-2-phenyl-1-thiabutadiene to dihydrothiazole derivatives, in the presence of isocyanides,[6]

Scheme II

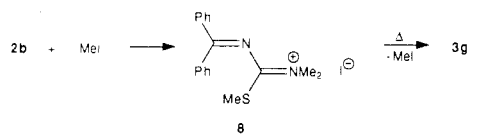
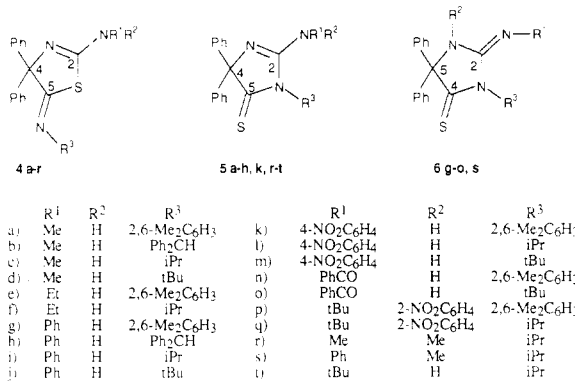


Table I. Reactions of Isocyanides 1 with 3. Preparation of Dihydrothiazoles 4

educts		reaction conditions			
azathia-butadiene	iso-cyanide	1/3 ratio	solvent	reflux time,[b] h	product yield,[a] %
3a	**1a**	1.2	THF	360	70 **4a**[c,d]
3a	**1b**	1.4	THF	120	62 **4b**
3a	**1c**	1.5	MeCN	69	76 **4c**[c]
3a	**1d**	1.5	MeCN	69	86 **4d**
3b	**1a**	1.2	THF	320	69 **4e**[e]
3b	**1c**	2	MeCN	144	59 **4f**[f]
3c	**1a**	1.2	THF	196	80 **4g**
3c	**1b**	1.5	THF	93	71 **4h**
3c	**1c**	2	THF	89	74 **4i**
3c	**1d**	2	MeCN	17	83 **4j**
3d	**1a**	1.3	MeCN	20	81 **4k**
3d	**1c**	2.1	THF	22	84 **4l**
3d	**1d**	2	MeCN	21	86 **4m**
3e	**1a**	1.2	CH_2Cl_2	22	61 **4n**
3e	**1d**	2	CH_2Cl_2	19	63 **4o**
3f	**1a**	1.3	MeCN	47	92 **4p**
3f	**1c**	2.5	MeCN	4	77 **4q**
3g	**1c**	1.5	MeCN	154	70 **4r**

[a] Isolated product yield based on **3**. [b] Time required for the entire conversion of the starting heterodiene. [c] Small quantity of this compound has already been obtained from the reaction of **1** with protonated 2-(methylthio)diazabutadiene (**2b**, HI)[3]. [d] 10% of **5a** was also isolated. [e] 8% of **5e** was also isolated. [f] 20% of **5f** was also isolated.

Chart II



and methyl propiolate,[7] phenylacetylene,[7] or trimethylsilyl cyanide.[8]

Results and Discussion

Preparation of 2-Amino-3-aza-1-thiabutadienes 3. Compounds **3a–e** were obtained in high yields by the addition of diphenylmethylenamine to isothiocyanates R^1NCS[3,9] (Chart I). The diazadiene **2a** was prepared by the reaction of diphenylmethylenamine with the imino chloro sulfide **7**, according to a known procedure.[3] In refluxing toluene **2a** led to **3f** via an intramolecular nu-

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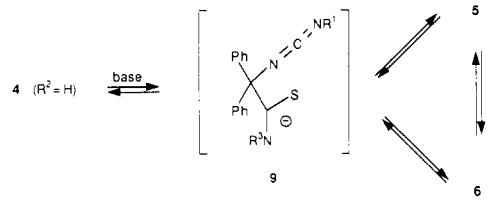
Scheme III



cleophilic aromatic substitution (Scheme I). This thermal [1,3] S to N migration of the 2-nitrophenyl group is similar to the Smiles rearrangement.[10] The ortho position of the nitro group in the rearranged product **3f** was proved by ^{13}C NMR spectral data (Experimental Section). Alkylation of **2b** with MeI gave the salt **8**, which was thermolyzed in refluxing toluene to afford **3g** (Scheme II).

Preparation and Rearrangement of Dihydrothiazoles 4. 3-Aza-1-thiabutadienes **3** were converted into 2-amino-5-imino-4,5-dihydrothiazoles **4a–r** by treatment with isocyanides **1** (Table I). The reactions were carried out in refluxing MeCN but THF was also used as solvent in order to avoid or minimize the rearrangement of primary [1 + 4] cycloadducts **4**, $R^2 = H$.[11]

4a–o rearrangement to 2-amino-4*H*-imidazoline-5-thiones **5** or (and) 2-imino-4-thioxo-1,3-diazolidines **6** (Chart II) proceeded smoothly in the presence of an excess of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). An acceleration was observed when the solvent polarity was increased, this rearrangement being faster in MeCN than in THF or CH_2Cl_2.[11] Generally, **4** in acetonitrile under reflux was quantitatively converted to **5** or (and) **6**. In some cases, an equilibrium was reached between **4** and the rearranged products **5** and **6** (Table II, entries 4, 8, 10, 13, and 15). The reversibility of the reaction was proved by heating a solution of pure **5d** or **6j** and DBN in MeCN. The equilibrium mixtures described in Table II (entries 4 and 10) were obtained. Other bases like DABCO or NaH can also induce the rearrangement of **4** in MeCN or THF.

The base-induced rearrangement of the dihydrothiazoles **4** very likely takes place via a ring cleavage initiated by the aza anion formation. The cyclization of the ambident anion **9** provides **4**, **5** or **6** after protonation (Scheme III). According to this mechanism, cycloadducts **4p–r** were found unaltered after being refluxed for a long time in MeCN containing DBN or isocyanides **1a** and **1c**. The reversible formation of **9** is consistent with the previously reported cleavage of some 2-amidate-5-dimethyliminium-4,5-dihydrothiazoles.[12] These dipolar cyclic compounds were shown to be in equilibrium with the corresponding α-dimethylthiocarbamoyl carbodiimides.[13]

Tautomeric Equilibrium Investigation. Structures **5** and **6** were established via ^{13}C NMR spectroscopy (Table III). For imidazolines **5**, the carbon of the thione function appeared at very low field (δ(C-5) = 211–217 ppm). It appeared at 202–207 ppm (δ(C-4)) for the diazolidines **6**. This bis-phenyl substituted carbon also exhibited a downfield chemical shift for **5** (δ(C-4) = 87–90 ppm) relative to **6** (δ(C-5) = 78–81 ppm). In any case, the multiplicities of the NMR signals for the thione carbon and for the quaternary carbons of the equivalent 4- or 5-phenyl groups proved to be decisive in assigning structures **5** and **6** when $R^2 = H$. The quaternary aromatic carbons appeared as a triplet for **5** and as a multiplet for **6**, owing to the coupling with the proton on the N-1. For the thione carbon, imidazolines **5** showed a singlet (or a doublet when $R^3 = CHPh_2$, iPr; $^3J(CNCH) = 3–3.5$ Hz) while diazolidines **6** exhibited a doublet ($^3J(CCNH) = 4–5$Hz) or a doublet of doublets. The C-2 displayed the expected multiplicities, with a low or without any coupling constant $^2J(CNH)$.

In the ^1H NMR spectra, the *HNCH* coupling was generally observed for the 2-amino group of imidazolines **5a–f** (Experimental Section). Mass spectra of compounds **4–6** showed the same fragmentations ($M^{\bullet+} - R^3NCS$; $M^{\bullet+} -$ PhNHCN when $R^1 = Ph$).

In order to obtain authentic 2-aminoimidazoline-5-thione and 2-imino-4-thioxodiazolidine, we treated **5c** and **6i** with NaH then MeI, in THF at room temperature. The N-alkylation of **5c** provided exclusively **5r**. The N-alkylation of **6i** gave a mixture of imidazoline **5s** (25%) and diazolidine **6s** (75%), which were separated by fractional crystallization.[14] The same results were obtained from **4c** or **4i** as starting products. The carbon-13 chemical shifts for **5r**, **5s**, and **6s** agreed with those observed when $R^2 = H$ (Table III). The ^{13}C NMR spectrum of the previously prepared **5t**[3] was also in agreement with the assigned structure.

In some cases (**g**, **h**, **k**) both tautomeric forms **5** and **6** were observed by NMR spectroscopy, in $CDCl_3$ solution (Table II, entries 7, 8, and 11). At 30–40 °C, a slow chemical exchange process on the NMR time scale can occur for the proton attached to the nitrogen atoms and the ^{13}C NMR signals were broadened. At a lower tem-

Table II. DBN-Induced Rearrangement of Dihydrothioazoles 4 into 5 and 6 in Refluxing MeCN

		reaction conditions		results			
				products distribution[b,c]			
entry	dihydrothiazole	DBN/4 ratio	time,[a] h	4	5	6	yield,[d] %
1	**4a**	1.1	2		100		86 **5a**[e]
2	**4b**	1.2	4		100		87 **5b**
3	**4c**	1.1	2		100		87 **5c**[e]
4	**4d**	1.1	2	65	35		22 **5d**
5	**4e**	1.2	2		100		82 **5e**
6	**4f**	1.1	2		100		81 **5f**
7	**4g**	1.2	2		70	30	85 **5g + 6g**
8	**4h**	1.2	4	45	52	3	45 **5h + 6h**
9	**4i**	1.2	4			100	82 **6i**
10	**4j**	1.2	3	35		65	55 **6j**
11	**4k**	1.2	3		20	80	85 **5k + 6k**
12	**4l**	1.1	3			100	72 **6l**
13	**4m**	1.1	3	25		75	53 **6m**
14	**4n**	1.2	2			100	80 **6n**
15	**4o**	1.2	3	35		65	54 **6o**

[a] Time necessary to reach the equilibrium rearrangement or time required for the complete transformation of **4**. [b] The distribution between **4** and **5** or(and) **6** was calculated on the basis on the ^1H NMR spectrum of the crude mixture. [c] The distribution between **5** and **6** was estimated on the basis on the ^{13}C NMR spectrum of the mixture **5 + 6** at −55 °C. [d] Isolated product yield based on starting **4**. [e] Already obtained from the reaction of **1** with protonated 2-(methylthio)diazabutadiene (**2b**, HI)[3].

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(11) Isocyanides **1a** and **1c** can induce the rearrangement of **4** into **5** or **6**. In these cases, the dihydrothiazoles **4** should be prepared in refluxing THF where this rearrangement proceeds much more slowly than in MeCN.

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(14) The NMR spectra of **5r** exhibit the equivalence of the two *N*-methyl groups (^1H, δ 2.82 s; ^{13}C, δ 41.7 q q). Structures **5s** and **6s** were proved by the multiplicity of the ^{13}C NMR signal for the quaternary carbon of the *N*-phenyl group (**5s**, δ 146.4 m; **6s**, δ 147.2 t).

Table III. Selected ^{13}C NMR Chemical Shifts at 75.469 MHz for 5 and 6 in $CDCl_3$ Solutions (δ (ppm) from Internal TMS (mult)[a] (J, Hz))

no.	C-2	C-4	C-5	C_{arom},[b]
5a	154.6 q (4)[c]	89.1 br	213.0 s	143.6 t
5b	155.9 m	87.9 br	214.8 d (2.2)[c]	143.7 t
5c[d]	155.4 br	87.7 br	213.8 br	142.7 br
5d	157.0 br	87.2 br	217.1 br	144.0 br
5e	153.6 t (4)[c]	89.0 m	213.0 s	143.6 t
5f	154.2 br	87.5 br	213.1 br	143.2 t
5g[d,e]	149.9 s	89.9 m	211.7 s	142.6 t
5h[d,e]	150.7 d (5.3)[c]	88.8 m	212.8 d (3.3)[c]	142.8 t
5k[d,e]	149.4 s	90.1 m	210.9 s	143.6 t
5r	163.3 m	88.4 m	215.2 d (5.5)[c]	142.6 t
5s	160.0 m	88.8 m	214.9 d (6)[c]	142.7 t
5t[f]	152.1 d (5.5)[c]	88.3 m	213.3 d (3.3)[c]	143.5 t
6g[d,e]	148.7 d (5)[g]	202.3 d (5.3)[h]	79.1 m	141.5 m
6h[d,e]	147.2 br	203.8 br	78.7 m	141.7 m
6i	149.0 dd (4.5, 5.5)[c,g]	202.9 dd (4.5, 5.5)[c,h]	78.3 m	142.1 m
6j	151.2 d (4.1)[g]	205.8 d (4.4)[h]	78.1 m	142.6 m
6k[d,e]	149.1 d (5.7)[g]	202.2 d (6)[h]	79.7 m	141.6 m
6l	149.5 d (4.9)[c]	203.0 dd (2.8, 5.7)[c,h]	78.8 m	141.6 m
6m	151.5 s	205.9 br	78.5 m	142.2 m
6n	159.2 s	203.2 br	81.2 m	140.6 m
6o[d]	162.2 d (2.8)[g]	207.1 d (5.8)[h]	80.0 m	140.6 m
6s	144.3 br	202.8 d (4.4)[c]	83.6 br	138.9 t

[a] Values are given at 30–40 °C, unless otherwise indicated. [b] Quaternary carbons of the equivalent 4- or 5-phenyl groups. [c] $^3J(CNCH)$. [d] Data obtained at −55 °C. [e] In a mixture of tautomers **5** and **6** (at 30–40 °C this compound exists in fast equilibrium with the other tautomeric form and the signals broaden). [f] Previously prepared via the reaction of **1c** with protonated 1-*tert*-butyl-4,4-diphenyl-2-(methylthio)-1,3-diazabuta-1,3-diene[3]. [g] $^2J(CNH)$. [h] $^3J(CCNH)$.

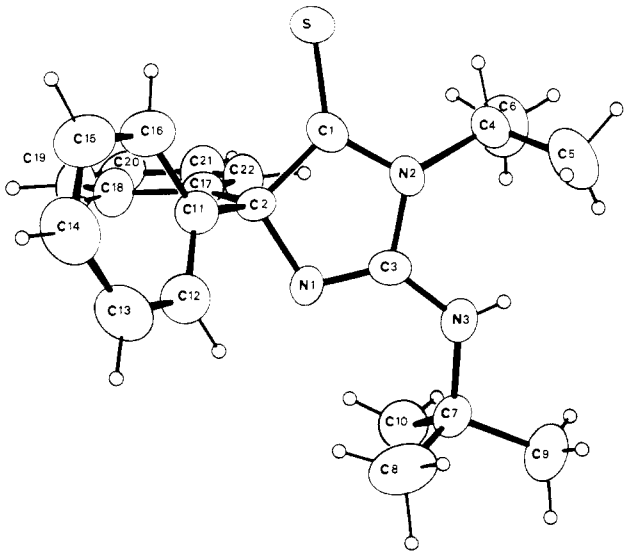

Figure 1. X-ray crystallographic structure of **5t**.

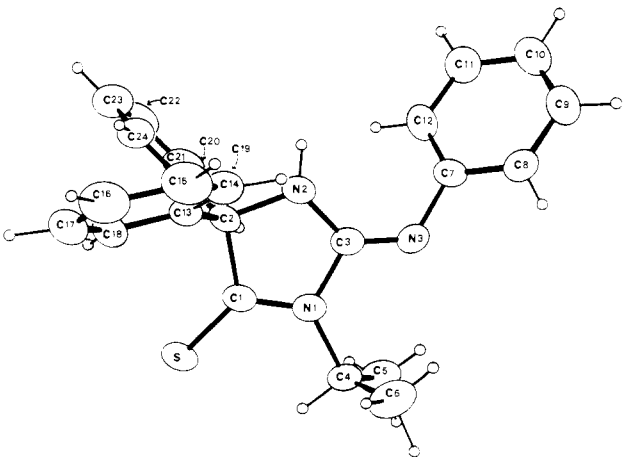

Figure 2. X-ray crystallographic structure of **6i**.

perature (−55 °C), the ^{13}C NMR spectra showed well-resolved signals both for **5** and **6** (Table III). The syn–anti isomerization was probably fast for the imino form **6**, R^1 being an aryl group.[15]

The tautomeric structures **5t** and **6i**, uniquely observed in solution, were also present in the crystal state as shown by a single-crystal X-ray analysis (Figures 1 and 2).

It is interesting to emphasize that **5** was only observed when R^1 is an alkyl group while **6** was generally the single or the major form when R^1 is benzoyl or aryl group. The presence of the conjugated system $R^1N{=}C$ is probably one of the driving factors of this equilibrium.

For identical reasons, we can postulate that the 2-amino-4,5-dihydrothiazole structure was the exact tautomeric form in solution of compounds **4a–m**, which possess an alkyl or aryl group R^1 (Table IV). The ^{13}C NMR spectra of cycloadduct **4o** exhibited a moderate resolution, in particular for the three endocyclic carbon atoms. The 2,5-diiminothiazolidine structure probably exists in fast equilibrium with the tautomeric form **4o** but we did not study this equilibrium. For steric reasons, the plane of the o-nitrophenyl group of **4p** and **4q** cannot lie

Table IV. Selected ^{13}C NMR Chemical Shifts at 75.469 MHz for Some Dihydrothiazoles 4[a]

no.	C-2 (J, Hz)[b]	C-4	C-5 (J, Hz)[b]	C_{arom},[c]
4a	154.9 q (3)	88.9 m	177.0 s	143.8 t
4c	155.1 q (3)	88.5 m	168.0 d (10)	144.9 t
4d	156.4 q (4)	90.7 m	161.2 s	145.5 t
4g	152.7 s	85.8 m	173.8 s	142.9 t
4i	152.0 s	85.9 m	164.9 d (9)	143.9 t
4j	153.8 s	87.3 m	158.5 s	144.6 t
4o	158.6 br	82.3 m	159.1 br	143.3 m
4p	152.9 s	91.0 m	176.1 s	143.4 t and 144.7 t
4q	152.6 s	90.6 m	167.6 d (9)	144.7 t and 145.3 t
4r	155.8 m	88.7 m	166.8 d (9.8)	145.2 t

[a] Values are given in ppm referenced to Me_4Si and were obtained in $CDCl_3$ solutions, at 30–40 °C. [b] $^3J(CNCH)$. [c] Quaternary carbons of the 4-phenyl groups.

(15) Kalinowski, H. O.; Kessler, H. *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; John Wiley: New York, 1973; Vol. 7, p 295.

in the dihydrothiazole plane. Consequently, the two phenyl groups on C-4 are diastereotopic and give different ^{13}C NMR signals.

In summary, we have prepared 3-aza-1-thiabutadienes **3** and described their subsequent use in [1 + 4] cycloaddition reactions with isocyanides. These reactions provide kinetic 2-amino-5-imino-4,5-dihydrothiazoles **4**. Treatment of **4** with base leads to rearrangement to stable tautomeric isomers **5** or (and) **6**. The nature of the R^1 substituent is a factor determining the tautomeric equilibrium. X-ray crystallographic studies support the ^{13}C NMR solution structure assignments.

Experimental Section

Melting points are uncorrected. NMR spectra (internal standard Me_4Si) were taken in $CDCl_3$ on Bruker WP 80 (^1H) and AM 300 WB (^{13}C) spectrometers. The mass spectra were obtained on a Varian MAT 311 spectrometer by the Centre de Mesures Physiques. Infrared spectra were recorded as suspensions in Nujol with a Perkin-Elmer 1420 spectrophotometer. Elemental analyses were performed by the analytical laboratory, Centre National de la Recherche Scientifique.

Synthesis of 2-Amino-4,4-diphenyl-1-thia-3-azabuta-1,3-dienes 3. The known compounds **3a–c**[3,9] and **3e**[9b] were prepared as previously described[3] by the addition of diphenylmethylenamine to isothiocyanates R^1NCS, in Et_2O solution. The yields were around 80–95%. A slightly modified procedure was used to obtain **3d**: Diphenylmethylenamine (5.4 g, 30 mmol) was added to a solution of 4-nitrophenyl isothiocyanate (3.6 g, 20 mmol) in THF (40 mL). The mixture was maintained at room temperature for 3 days. Evaporation of the solvent and trituration of the residue with Et_2O gave crystalline **3d** (6.55 g, 90% yield): mp 155 °C (from $MeOH/CHCl_3$); IR 3195, 1625, 1590 cm^{-1}. Anal. Calcd for $C_{20}H_{15}N_3O_2S$: C, 66.48; H, 4.15; N, 11.63; S, 8.86. Found: C, 65.79; H, 4.17; N, 11.62; S, 9.01.

The imino chloro sulfide **7** (40 mmol) was prepared by the addition of 2-nitrobenzenesulfenyl chloride to isocyanide **1d**, in THF solution (60 mL), according to a known procedure.[2,16] We added dropwise a mixture of diphenylmethylenamine (7.25 g, 40 mmol) and NEt_3 (5 g, 50 mmol) dissolved in THF (40 mL). An exothermic reaction was accompanied by crystallization of the triethylammonium chloride. After stirring at room temperature for 6 h, the precipitate was filtered off and the filtrate was concentrated to a oil. The crude diazadiene **2a** was isolated by crystallization from Et_2O (15 g, 90% yield).

1-*tert*-Butyl-4,4-diphenyl-2-[(2-nitrophenyl)thio]-1,3-diazabuta-1,3-diene (2a): mp 111 °C ($CHCl_3$/petroleum ether); ^1H NMR δ 1.25 (s, 9 H), 7.4–7.9 (m, 14 H); IR 1615, 1526 cm^{-1}. Anal. Calcd for $C_{24}H_{23}N_3O_2S$: C, 69.06; H, 5.51; N, 10.07; S, 7.67. Found: C, 68.65; H, 5.51; N, 10.10; S, 7.80.

A solution of **2a** (2.1 g, 5 mmol) in toluene (15 mL) was refluxed for 3 days. Removal of the solvent under reduced pressure gave a solid material, which was fractionated by extraction with $CHCl_3$ (10 mL). Small quantities of the insoluble 2-nitrophenyl disulfide were filtered off (0.09 g). Evaporation of the filtrate and subsequent crystallization of the residue from Et_2O gave **3f** (1.42 g, 68% yield). The ^{13}C NMR spectrum proved the ortho position of the nitro group for **3f** (the 10 aromatic carbons display the expected multiplicities, with $^3J(CCCH)$ = 6–8 Hz).

2-[*tert*-Butyl(2-nitrophenyl)amino]-4,4-diphenyl-1-thia-3-azabuta-1,3-diene (3f): mp 180 °C (MeCN); ^1H NMR δ 1.66 (s, 9 H), 7.36–7.96 (m, 14 H); ^{13}C NMR δ 29.9 (qm, ^1J = 127 Hz, CH_3), 64.1 (m, CMe_3), 124.9 (dd), 128.2 (dm), 128.5 (dd), 130.1 (dd), 131.0 (dt), 131.8 (dd), 133.5 (dd) (7 aromatic carbons, ^1J = 168 Hz), 136.3 (t), 139.3 (m), 148.1 (m) (quaternary aromatic carbons), 166.8 (m, C-4), 192.9 (s, C-2); IR 1610, 1582, 1520 cm^{-1}. Anal. Calcd for $C_{24}H_{23}N_3O_2S$: C, 69.06; H, 5.51; N, 10.07; S, 7.67. Found: C, 69.01; H, 5.38; N, 9.97; S, 7.81.

Methyl iodide (4.3 g, 30 mmol) was added to a solution of diazadiene **2b**[3] (2.7 g, 10 mmol) in Et_2O (50 mL). The yellowish precipitate that slowly formed at ambient temperature was filtered and washed with dry ether (3.6 g, 88% yield). This crude salt **8** was used without further purification: ^1H NMR δ 2.42 (s, 3 H), 3.64 (s, 3 H), 3.67 (s, 3 H), 7.66 (s, 10 H).

A solution of **8** (3.7 g, 9 mmol) in toluene (30 mL) was refluxed for 3 days. The solvent was evaporated in vacuo and ether was added to the residue to give crystalline **3g** (2.3 g, 96% yield).

2-(Dimethylamino)-4,4-diphenyl-1-thia-3-azabuta-1,3-diene (3g): mp 155 °C (MeOH); ^1H NMR δ 3.11 (s, 3 H), 3.30 (s, 3 H), 7.38–7.45 (m, 10 H). Anal. Calcd for $C_{16}H_{16}N_2S$: C, 71.64; H, 5.97; N, 10.44; S, 11.94. Found: C, 71.86; H, 6.00; N, 10.58; S, 12.08.

Reactions of 3-Aza-1-thiabutadienes 3 with Isocyanides 1. General Procedure. Isocyanide was added to a solution of **3** (5 mmol in 15 mL of solvent). Excess isocyanide, nature of the solvent, and reflux time are indicated in Table I. The reaction mixture was concentrated under reduced pressure and the residue was triturated with Et_2O or MeOH (petroleum ether for **4n**, **4o**). Crude dihydrothiazole **4** was collected by filtration then purified by recrystallization from the solvent given below. Cycloadducts **4** and **5** (**a**, **e**, **f**) were separated by crystallization from Et_2O or MeOH (yields and ^{13}C NMR spectra, see Tables I and IV; **4a**, **4c**, see previous paper[3]).

4,5-Dihydro-4,4-diphenyl-5-[(diphenylmethyl)imino]-2-(methylamino)thiazole (4b): mp 171 °C (Et_2O/CH_2Cl_2); ^1H NMR δ 2.85 (s, 3 H), 3.82 (br, NH), 5.07 (s, 1 H), 7.1–7.5 (m, 20 H). Anal. Calcd for $C_{29}H_{25}N_3S$: C, 77.85; H, 5.59; N, 9.39; S, 7.15. Found: C, 77.81; H, 5.59; N, 9.46; S, 7.44.

5-(*tert*-Butylimino)-4,5-dihydro-4,4-diphenyl-2-(methylamino)thiazole (4d): mp 132 °C (Et_2O/petroleum ether); ^1H NMR δ 1.30 (s, 9 H), 2.82 (s, 3 H), 5.25 (br, NH), 7.15–7.5 (m, 10 H). Anal. Calcd for $C_{20}H_{23}N_3S$: C, 71.21; H, 6.82; N, 12.46; S, 9.49. Found: C, 70.99; H, 6.86; N, 12.31; S, 9.49.

4,5-Dihydro-5-[(2,6-dimethylphenyl)imino]-4,4-diphenyl-2-(ethylamino)thiazole (4e): mp 201 °C (MeOH); ^1H NMR δ 1.12 (t, J = 7 Hz, 3 H), 1.81 (s, 6 H), 3.33 (q, 2 H), 4.45 (br, NH), 6.91 (s, 3 H), 7.2–7.75 (m, 10 H). Anal. Calcd for $C_{25}H_{25}N_3S$: C, 75.18; H, 6.26; N, 10.52; S, 8.02. Found: C, 75.17; H, 6.36; N, 10.34; S, 7.84.

4,5-Dihydro-4,4-diphenyl-2-(ethylamino)-5-(isopropylimino)thiazole (4f): mp 140 °C (MeOH); ^1H NMR δ 1.17 (t, J = 7 Hz, 3 H), 1.20 (d, J = 7 Hz, 6 H), 3.07 (m, 1 H), 3.40 (q, 2 H), 4.25 (br, NH), 7.2–7.55 (m, 10 H). Anal. Calcd for $C_{20}H_{23}N_3S$: C, 71.21; H, 6.82; N, 12.46; S, 9.49. Found: C, 71.11; H, 6.88; N, 12.28; S, 9.42.

4,5-Dihydro-5-[(2,6-dimethylphenyl)imino]-4,4-diphenyl-2-(phenylamino)thiazole (4g): mp 212 °C (MeCN); ^1H NMR δ 1.82 (s, 6 H), 6.55 (br, NH), 6.9 (s, 3 H), 7.1–7.7 (m, 15 H); MS calcd for $C_{29}H_{25}N_3S$, m/e 447.1769 (M^+), found 447.1789; m/e (rel intensity) 447 (6), 329 (5), 316 (7), 297 (5), 284 (100), 283 (54), 224 (25).

4,5-Dihydro-4,4-diphenyl-5-[(diphenylmethyl)imino]-2-(phenylamino)thiazole (4h): mp 170 °C, then 187 °C (MeCN); ^1H NMR δ 5.15 (s, 1 H), 7.25–7.5 (m, 25 H); MS calcd for $C_{34}H_{27}N_3S$, m/e 509.1926 (M^+), found 509.1912; m/e (rel intensity) 509 (40), 342 (25), 316 (20), 311 (20), 284 (100), 224 (55), 193 (25). Anal. Calcd: C, 80.15; H, 5.30; N, 8.25; S, 6.28. Found: C, 80.22; H, 5.38; N, 8.19; S, 6.61.

4,5-Dihydro-4,4-diphenyl-2-(phenylamino)-5-(isopropylimino)thiazole (4i): mp 213 °C (MeOH); ^1H NMR δ 1.25 (d, J = 7 Hz, 6 H), 3.15 (m, 1 H), 7.0–7.55 (m, 15 H); MS, m/e (rel intensity) 385 (15) (M^+), 343 (15), 316 (25), 284 (100), 267 (25), 224 (60). Anal. Calcd for $C_{24}H_{23}N_3S$: C, 74.80; H, 5.97; N, 10.90; S, 8.31. Found: C, 74.84; H, 6.15; N, 10.80; S, 8.28.

5-(*tert*-Butylimino)-4,5-dihydro-4,4-diphenyl-2-(phenylamino)thiazole (4j): mp 181 °C (MeOH); ^1H NMR δ 1.22 (s, 9 H), 7.2–7.5 (m, 15 H); MS calcd for $C_{25}H_{25}N_3S$, m/e 399.1769 (M^+), found 399.1772; calcd for $C_{20}H_{16}N_2$, m/e 284.1313 (M^+ – tBuNCS), found 284.1317; m/e (rel intensity) 399 (2), 316 (15), 284 (100), 224 (50). Anal. Calcd: C, 75.18; H, 6.28; N, 10.52; S, 8.02. Found: C, 74.91; H, 6.32; N, 10.52; S, 8.11.

4,5-Dihydro-5-[(2,6-dimethylphenyl)imino]-4,4-diphenyl-2-[(4-nitrophenyl)amino]thiazole (4k): mp 204 °C (MeCN); ^1H NMR δ 1.84 (s, 6 H), 6.90 (s, 3 H), 7.15–8.05 (m, 14 H). Anal. Calcd for $C_{29}H_{24}N_4O_2S$: C, 70.73; H, 4.87; N, 11.38; S, 6.50. Found: C, 70.98; H, 4.85; N, 11.26; S, 6.23.

(16) Morel, G.; Marchand, E.; Nguyen Thi, K. H.; Foucaud, A. *Tetrahedron* **1984**, *6*, 1075. Morel, G.; Marchand, E.; Haquin, C.; Foucaud, A. *J. Org. Chem.* **1986**, *51*, 4043.

4,5-Dihydro-4,4-diphenyl-2-[(4-nitrophenyl)amino]-5-(isopropylimino)thiazole (4l): mp 208 °C (MeOH); ^{1}H NMR δ 1.22 (d, J = 7 Hz, 6 H), 3.27 (m, 1 H), 7.3–8.3 (m, 14 H). Anal. Calcd for $C_{24}H_{22}N_4O_2S$: C, 66.97; H, 5.11; N, 13.02; S, 7.44. Found: C, 66.87; H, 5.08; N, 12.98; S, 7.30.

5-(*tert*-Butylimino)-4,5-dihydro-4,4-diphenyl-2-[(4-nitrophenyl)amino]thiazole (4m): mp 235 °C (MeCN); ^{1}H NMR δ 1.30 (s, 9 H), 7.35–8.35 (m, 14 H). Anal. Calcd for $C_{25}H_{24}N_4O_2S$: C, 67.56; H, 5.40; N, 12.61; S, 7.20. Found: C, 67.78; H, 5.43; N, 12.70; S, 6.92.

2-(Benzoylamino)-4,5-dihydro-5-[(2,6-dimethylphenyl)imino]-4,4-diphenylthiazole (4n): mp 168 °C (ether/petroleum ether); ^{1}H NMR δ 1.82 (s, 6 H), 6.92 (s, 3 H), 7.2–7.9 (m, 15 H). Anal. Calcd for $C_{30}H_{25}N_3OS$: C, 75.79; H, 5.26; N, 8.84; S, 6.73. Found: C, 76.08; H, 5.18; N, 8.70; S, 6.81.

2-(Benzoylamino)-5-(*tert*-butylimino)-4,5-dihydro-4,4-diphenylthiazole (4o): mp 156 °C (ether/petroleum ether); ^{1}H NMR δ 1.30 (s, 9 H), 7.2–7.97 (m, 15 H). Anal. Calcd for $C_{26}H_{25}N_3OS$: C, 73.06; H, 5.85; N, 9.83; S, 7.49. Found: C, 73.00; H, 5.82; N, 10.00; S, 7.48.

2-[*tert*-Butyl(2-nitrophenyl)amino]-4,5-dihydro-5-[(2,6-dimethylphenyl)imino]-4,4-diphenylthiazole (4p): mp 190 °C (MeCN); ^{1}H NMR δ 1.43 (s, 9 H), 1.60 (br, 3 H), 1.80 (br, 3 H), 6.77 (s, 3 H), 7.2–8.0 (m, 14 H); IR 1621, 1589, 1525 cm^{-1}. Anal. Calcd for $C_{33}H_{32}N_4O_2S$: C, 72.26; H, 5.84; N, 10.22; S, 5.84. Found: C, 72.06; H, 5.79; N, 10.23; S, 5.99.

2-[*tert*-Butyl(2-nitrophenyl)amino]-4,5-dihydro-4,4-diphenyl-5-(isopropylimino)thiazole (4q): mp 160 °C (MeOH); ^{1}H NMR δ 0.98, 1.05 (2 d, J = 7 Hz, 6 H), 1.45 (s, 9 H), 2.80 (m, 1 H), 7.15–7.87 (m, 14 H); MS calcd for $C_{24}H_{23}N_3O_2$, m/e 385.1790 (M$^+$ – iPrNCS), found 385.1801; m/e (rel intensiy) 385 (10), 328 (50), 315 (40), 298 (20), 208 (100); IR 1627, 1589, 1528 cm^{-1}. Anal. Calcd for $C_{28}H_{30}N_4O_2S$: C, 69.13; H, 6.17; N, 11.52; S, 6.58. Found: C, 69.35; H, 6.22; N, 11.55; S, 6.56.

4,5-Dihydro-2-(dimethylamino)-4,4-diphenyl-5-(isopropylimino)thiazole (4r): mp 124 °C (MeOH); ^{1}H NMR δ 1.10 (d, J = 7 Hz, 6 H), 2.92 (s, 6 H), 3.02 (m, 1 H), 7.02–7.47 (m, 10 H). Anal. Calcd for $C_{20}H_{23}N_3S$: C, 71.21; H, 6.82; N, 12.46; S, 9.49. Found: C, 71.44; H, 6.86; N, 12.68; S, 9.73.

The reactions of heterodienes **3a–c** with isocyanide **1a** and of **3c** and **3d** with isocyanide **1c** were also carried out in refluxing MeCN under similar conditions. They are faster than reactions in THF but the rearranged cycloadduct **5** or **6** was predominantly formed. For example, **1a** (0.81 g, 6.2 mmol) was added to a solution of **3b** (1.34 g, 5 mmol) in MeCN (15 mL). The reaction mixture was concentrated after refluxing for 64 h. The ^{1}H NMR analysis of the residue showed the presence of **4e** and **5e** in the ratio 15:85. Treatment was identical with that described above (**4e**, 0.1 g, 5% yield; **5e**, 1.6 g, 80% yield). When subjected to the same conditions for 43 h, **3a** gave a mixture of **4a** and **5a** in the ratio 26:74. Isocyanide **1c** (0.7 g, 10 mmol) and **3c** or **3d** (5 mmol) gave a mixture of **4** and **6** in the ratio 50:50 in refluxing MeCN for 19 h.

DBN-Induced Rearrangement of Dihydrothiazoles 4. General Procedure. DBN was added to a solution of **4** (2.5 mmol) in MeCN (10 mL). Excess base and reflux time are indicated in Table II. After removal of the solvent, the residue was dissolved in Et_2O and washed with H_2O. The etheral solution was dried over Na_2SO_4 and concentrated to an oil, which was analyzed by ^{1}H NMR. This crude reaction product was treated with Et_2O to give crystalline imidazoline **5** or diazolidine **6**. When an equilibrium mixture was obtained, the rearranged compounds **5** and **6** and starting **4** were separated by fractional crystallization from petroleum ether (entries 4 and 10) or ether (entries 8, 13, and 15) (yields and ^{13}C NMR spectra, see Tables II and III; **5a**, **5c**, see previous paper[3]).

4,4-Diphenyl-1-(diphenylmethyl)-2-(methylamino)-2-imidazoline-5-thione (5b): mp 225 °C (MeCN); ^{1}H NMR δ 2.80 (d, J = 5 Hz, 3 H), 3.75 (br, NH), 7.2–7.55 (m, 20 H), 7.69 (s, 1 H); IR 3432, 1660 cm^{-1}. Anal. Calcd for $C_{29}H_{25}N_3S$: C, 77.85; H, 5.59; N, 9.39; S, 7.15. Found: C, 77.58; H, 5.68; N, 9.48; S, 7.00.

1-*tert*-Butyl-4,4-diphenyl-2-(methylamino)-2-imidazoline-5-thione (5d): mp 147 °C (MeOH); ^{1}H NMR δ 1.86 (s, 9 H), 2.99 (s, 3 H or d, J = 5 Hz, 3 H when DABCO was added to this solution), 3.95 (br, NH), 7.2–7.5 (m, 10 H). Anal. Calcd for $C_{20}H_{23}N_3S$: C, 71.21; H, 6.82; N, 12.46; S, 9.49. Found: C, 71.32; H, 6.84; N, 12.46; S, 9.51.

1-(2,6-Dimethylphenyl)-4,4-diphenyl-2-(ethylamino)-2-imidazoline-5-thione (5e): mp 148 °C (MeOH); ^{1}H NMR δ 1.15 (t, J = 7 Hz, 3 H), 2.05 (s, 6 H), 3.49 (m, br, 2 H), 3.72 (br, NH), 7.2–7.67 (m, 13 H). Anal. Calcd for $C_{25}H_{25}N_3S$: C, 75.18; H, 6.25; N, 10.52; S, 8.02. Found: C, 74.90; H, 6.26; N, 10.66; S, 8.41.

4,4-Diphenyl-2-(ethylamino)-1-isopropyl-2-imidazoline-5-thione (5f): mp 130 °C (CH_2Cl_2/petroleum ether); ^{1}H NMR δ 1.22 (t, J = 7 Hz, 3 H), 1.40 (d, J = 7 Hz, 6 H), 3.45 (m, br, 2 H), 4.10 (br, NH), 5.30 (m, 1 H), 7.2–7.5 (m, 10 H). Anal. Calcd for $C_{20}H_{23}N_3S$: C, 71.21; H, 6.82; N, 12.46; S, 9.49. Found: C, 70.95; H, 7.00; N, 12.50; S, 9.29.

1-(2,6-Dimethylphenyl)-4,4-diphenyl-2-(phenylamino)-2-imidazoline-5-thione (5g): mp 213 °C (MeCN) (in a mixture with **6g**, see Table II); ^{1}H NMR δ 2.07, 2.19 (2 s, br, 6 H), 5.49 5.70 (br, NH), 6.9–7.75 (m, 18 H); MS calcd for $C_{29}H_{25}N_3S$, m/e 447.1769 (M$^+$), found 447.1741; m/e (rel intensity) 447 (100), 415 (7), 370 (10), 355 (7), 338 (8), 329 (67), 284 (83), 283 (93). Anal. Calcd: C, 77.85; H, 5.59; N, 9.39; S, 7.15. Found: C, 78.03; H, 5.66; N, 9.24; S, 7.30.

4,4-Diphenyl-1-(diphenylmethyl)-2-(phenylamino)-2-imidazoline-5-thione (5h): mp 191 °C (MeCN) (in a mixture with **6h**, see Table II); IR 3380, 1654, 1590, 1532 cm^{-1}. Anal. Calcd for $C_{34}H_{27}N_3S$: C, 80.15; H, 5.30; N, 8.25; S, 6.28. Found: C, 79.88; H, 5.11; N, 8.28; S, 6.55.

5,5-Diphenyl-2-(phenylimino)-3-isopropyl-4-thioxo-1,3-diazolidine (6i): mp 175 °C (MeOH); ^{1}H NMR δ 1.73 (d, J = 7 Hz, 6 H), 5.27 (br, NH), 5.40 (m, 1 H), 6.95–7.4 (m, 15 H); MS calcd for $C_{24}H_{23}N_3S$, m/e 385.1613 (M$^+$), found 385.1614; calcd for $C_{20}H_{15}N_2$, m/e 283.1235 (M$^+$ – H – iPrNCS), found 283.1227; calcd for $C_{17}H_{17}NS$, m/e 267.1081 (M$^+$ – PhNHCN), found 267.1063; calcd for $C_{14}H_{10}S$, m/e 210.0503 ($Ph_2C{=}C{=}S^+$), found 210.0501; m/e (rel intensity) 385 (54), 343 (60), 311 (3), 308 (4), 284 (7), 283 (14), 267 (100), 210 (56), 193 (16).

3-*tert*-Butyl-5,5-diphenyl-2-(phenylimino)-4-thioxo-1,3-diazolidine (6j): mp 118 °C (EtOH); ^{1}H NMR δ 1.97 (s, 9 H), 5.10 (br, NH), 6.8–7.4 (m, 15 H). Anal. Calcd for $C_{25}H_{25}N_3S$: C, 75.18; H, 6.26; N, 10.52; S, 8.02. Found: C, 75.33; H, 6.34; N, 10.58; S, 8.37.

3-(2,6-Dimethylphenyl)-5,5-diphenyl-2-[(4-nitrophenyl)imino]-4-thioxo-1,3-diazolidine (6k): mp 245 °C (MeCN) (in a mixture with **5k**, see Table II); ^{1}H NMR δ 2.15 (s, 6 H), 7.15–8.05 (m, 17 H); IR 3385, 1691, 1578, 1500 cm^{-1}. Anal. Calcd for $C_{29}H_{24}N_4O_2S$: C, 70.73; H, 4.87; N, 11.38; S, 6.50. Found: C, 70.43; H, 4.88; N, 11.31; S, 6.58.

5,5-Diphenyl-2-[(4-nitrophenyl)imino]-3-isopropyl-4-thioxo-1,3-diazolidine (6l): mp 228 °C (MeCN); ^{1}H NMR δ 1.70 (d, J = 7 Hz, 6 H), 5.11 (m, 1 H), 7.22–8.17 (m, 14 H). Anal. Calcd for $C_{24}H_{22}N_4O_2S$: C, 66.97; H, 5.11; N, 13.02; S, 7.44. Found: C, 66.30; H, 5.06; N, 12.87; S, 7.41.

3-*tert*-Butyl-5,5-diphenyl-2-[(4-nitrophenyl)imino]-4-thioxo-1,3-diazolidine (6m): mp 210 °C (MeCN); ^{1}H NMR δ 1.97 (s, 9 H), 5.52 (br, NH), 6.9–8.07 (m, 14 H). Anal. Calcd for $C_{25}H_{24}N_4O_2S$: C, 67.56; H, 5.40; N, 12.61; S, 7.20. Found: C, 67.64; H, 5.27; N, 12.67; S, 7.04.

2-(Benzoylimino)-3-(2,6-dimethylphenyl)-5,5-diphenyl-4-thioxo-1,3-diazolidine (6n): mp 228 °C (MeCN); ^{1}H NMR δ 2.10 (s, 6 H), 7.1–8.0 (m, 18 H). Anal. Calcd for $C_{30}H_{25}N_3OS$: C, 75.79; H, 5.26; N, 8.84; S, 6.73. Found: C, 75.66; H, 5.33; N, 8.49; S, 6.80.

2-(Benzoylimino)-3-*tert*-butyl-5,5-diphenyl-4-thioxo-1,3-diazolidine (6o): mp 164 °C (MeCN); ^{1}H NMR δ 2.02 (s, 9 H), 7.2–8.25 (m, 15 H), 10.95 (br, NH). Anal. Calcd for $C_{26}H_{25}N_3OS$: C, 73.06; H, 5.85; N, 9.83; S, 7.49. Found: C, 73.30; H, 5.85; N, 9.58; S, 7.19.

DABCO-Induced Rearrangement of Some Dihydrothiazoles 4. The rearrangement of **4c,f,n** was also performed in the presence of 1,4-diazabicyclo[2.2.2]octane as a basic compound, under conditions similar to that described above. But this compound was not as efficient as DBN and the reactions were incomplete after a reflux for a long time. For example, DABCO (0.37 g, 3.3 mmol) was added to a solution of **4c** (0.97 g, 3 mmol) in MeCN (10 mL). The solvent was evaporated after being refluxed for 20 h and the residue was washed with H_2O. The ^{1}H NMR analysis of the crude product showed the presence of **4c**

and **5c** in the ratio 75:25. Subjected to the same conditions for 4 h, **4f** and **4n** gave mixtures of **4** and **5** in the ratio 85:15 and 70:30, respectively. **4m** failed to react with DABCO in refluxing MeCN for 15 h (compare with entries 3, 6, 14, and 13, Table II).

Evidence for the Reversibility of the DBN-Induced Rearrangement of Dihydrothiazoles 4d and 4j. A mixture of DBN (0.3 g, 2.4 mmol) and **5d** or **6j** (2 mmol) in MeCN (10 mL) was refluxed for 2 h. The solvent was evaporated and the residue was treated according to the above-mentioned procedure. ^{1}H NMR analysis of the crude product showed the formation of **4d** (65%) or **4j** (35%).

N-Alkylation of 5c and 6i. General Procedure. A solution of **5c** or **6i** (4 mmol) in THF (35 mL) was treated with NaH (5 mmol) under dry N_2 to prepare the corresponding sodium salt. MeI (1.4 g, 10 mmol) was added and the reaction mixture was stirred for a further 3 h at ambient temperature. After concentration, the residue was dissolved in Et_2O and washed with 1 M HCl. The etheral solution was dried over Na_2SO_4 and then evaporated to give **5r** or a mixture of **5s** and **6s** as a oil. Crude product were precipitated by addition of Et_2O (**5r**, 1.11 g, 82% yield; **5s + 6s**, 1.28 g, 86% yield). **5s** and **6s** were separated by fractional crystallization from MeOH (pure **5s**, 0.19 g, 12% yield; pure **6s**, 0.86 g, 54% yield).

2-(Dimethylamino)-4,4-diphenyl-1-isopropyl-2-imidazoline-5-thione (5r): mp 123 °C (MeOH); ^{1}H NMR δ 1.64 (d, J = 7 Hz, 6 H), 2.82 (s, 6 H), 4.45 (m, 1 H), 7.2–7.48 (m, 10 H). Anal. Calcd for $C_{20}H_{23}N_3S$: C, 71.21; H, 6.82; N, 12.46; S, 9.49. Found: C, 71.24; H, 6.83; N, 12.40; S, 9.43.

4,4-Diphenyl-2-(methylphenylamino)-1-isopropyl-2-imidazoline-5-thione (5s): mp 130 °C (EtOH); ^{1}H NMR δ 1.25 (d, J = 7 Hz, 6 H), 3.37 (s, 3 H), 4.20 (m, 1 H), 6.95–7.58 (m, 15 H). Anal. Calcd for $C_{25}H_{25}N_3S$: C, 75.18; H, 6.26; N, 10.52; S, 8.02. Found: C, 75.21; H, 6.12; N, 10.43; S, 8.09.

5,5-Diphenyl-1-methyl-2-(phenylimino)-3-isopropyl-4-thioxo-1,3-diazolidine (6s): mp 159 °C (MeOH); ^{1}H NMR δ 1.62 (d, J = 7 Hz, 6 H), 2.20 (s, 3 H), 5.40 (m, 1 H), 6.8–7.35 (m, 15 H). Anal. Calcd for $C_{25}H_{25}N_3S$: C, 75.18; H, 6.26; N, 10.52; S, 8.02. Found: C, 74.95; H, 6.34; N, 10.53; S, 7.72.

X-ray Analysis of 5t. Crystal data: orthorhombic P_{bca}, a = 9.799 (3), b = 17.107 (2), and c = 24.303 (4) Å, V = 4074.1 (6) Å^3, Z = 8, D_x = 1.19 g cm^{-3}, μ = 1.6 cm^{-1}; 1933 reflections with $I \geq \sigma(I)$ collected with a Enraf-Nonius CAD-4 diffractometer (Mo Kα radiations). The structure was solved by direct methods[17] and the hydrogen atoms were found between 0.43 and 0.22 e Å^{-3}. The best full-matrix refinement gave R = 0.045, R_w = 0.045.

X-ray Analysis of 6i. Crystal data: monoclinic $P2_1/c$; a = 14.958 (4), b = 9.698 (4), and c = 13.891 (5) Å, V = 2010.2 (5) Å^3, Z = 4, D_x = 1.27 g cm^{-3}, μ = 1.7 cm^{-1}; 2100 independent (R_{INT} = 0.011) reflections with $I \geq 3\sigma(I)$. The structure was solved by direct methods[17] and the hydrogen atoms were found between 0.44 and 0.31 e Å^{-3}. The best full-matrix refinement gave R = 0.044, R_w = 0.036.

All calculations were performed on a PDP 11/60 digital computer with the SDP package.[18]

Registry No. **1a**, 2769-71-3; **1b**, 3128-85-6; **1c**, 598-45-8; **1d**, 7188-38-7; **2a**, 124512-06-7; **2b**, 118514-79-7; **3a**, 34979-85-6; **3b**, 118514-70-8; **3c**, 23490-81-5; **3d**, 124512-04-5; **3e**, 124512-10-3; **3f**, 124512-07-8; **3g**, 124512-09-0; **4a**, 118515-10-9; **4b**, 124535-44-0; **4c**, 118515-09-6; **4d**, 124535-45-1; **4e**, 124512-11-4; **4f**, 124512-12-5; **4g**, 124512-13-6; **4h**, 124512-14-7; **4i**, 124512-15-8; **4j**, 124512-16-9; **4k**, 124535-46-2; **4l**, 124512-17-0; **4m**, 124512-18-1; **4n**, 124512-19-2; **4o**, 124512-20-5; **4p**, 124512-21-6; **4q**, 124512-22-7; **4r**, 124512-23-8; **5a**, 118515-03-0; **5b**, 124512-26-1; **5c**, 118515-02-9; **5d**, 124512-27-2; **5e**, 124512-24-9; **5f**, 124512-25-0; **5g**, 124512-28-3; **5h**, 124512-30-7; **5k**, 124512-34-1; **5r**, 124512-40-9; **5s**, 124512-41-0; **5t**, 118515-05-2; **6g**, 124512-29-4; **6h**, 124512-31-8; **6i**, 124512-32-9; **6j**, 124512-33-0; **6k**, 124512-35-2; **6l**, 124512-36-3; **6m**, 124512-37-4; **6n**, 124512-38-5; **6o**, 124512-39-6; **6s**, 124512-42-1; **7**, 124512-05-6; **8**, 124512-08-9; DABCO, 280-57-9; DBN, 3001-72-7; diphenylmethylenamine, 552-82-9; 4-nitrophenyl isothiocyanate, 2131-61-5.

Supplementary Material Available: Final coordinates and bond geometry tables for **5t** and **6i** (6 pages). Ordering information is given on any current masthead page.

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