Calcd for $C_{19}H_{38}N_2O_2$: C, 69.89; H, 11.73; N, 8.58. Found: C, 70.00; H, 11.61; N, 8.35.

Acknowledgment. We are especially indebted to Dr. J. Dingwall for helpful discussions, and we gratefully acknowledge S. Helfer and S. Stutz for their skillful assistance in the laboratory.

Supplementary Material Available: Crystallographic data including tables of coordinates, anisotropic temperature factors, distances, and bond angles for **18** (6 pages). Ordering information is given on any current masthead page.

Reactions of Protonated 1,3-Diaza-4,4-diphenyl-2-(methylthio)butadienes with Isocyanides: Preparation of Imidazole and Triazine Derivatives

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Protonated 1,3-diazabutadienes **4** are prepared and treated with isocyanides. The reactions are much faster with salts **4** than with corresponding diazadienes **5**. The 5-iminoimidazolines **10** and **11**, which are the expected [1 + 4] cycloaddition products, are generally obtained. However, rearranged imidazoles **12** and **14** and 5-thioxoimidazolines **13** are predominantly formed in some cases. A mechanism is suggested to explain this rearrangement. A proton transfer from the more acidic salts **4** to isocyanides can also occur and the [2 + 4] cycloaddition reaction of resulting nitrilium salts with diazadienes **5** has been observed to give triazinium salts.

Cycloaddition reactions of heterodienes have been shown to be of great potential for synthesis in heterocyclic chemistry.[1-3] There are some literature reports concerning the participation of 1,3-diazabutadienes as 2π or 4π components in [2 + 2] or [2 + 4] cycloadditions.[2-5] However, examples of [1 + 4] cycloadditions of isocyanides with 1,3-diazabutadienes are rare and have not been exploited for the synthesis of heterocyclic compounds. Isocyanides easily react with 4,4-bis(trifluoromethyl)-1,3-diazabutadienes,[6,7] but these substances are not particularly representative for the parent system. Another reported reaction requires drastic conditions (only one example).[8]

Recently, we reported that the regioselective [1 + 4] cycloaddition of isocyanides with methyl 4,6-diaza-5-(methylthio)hepta-2,4,6-trienoates produces imidazoline derivatives in good yields.[9] We have now observed that the cycloaddition of isocyanides with 1,3-diaza-4,4-diphenyl-2-(methylthio)butadienes **5** proceeds more sluggishly. Therefore, we were attracted to the possibility that the rate of these reactions could be accelerated under acidic conditions.

It has been shown that Lewis acid catalysts can induce the [1 + 4] cycloaddition of isocyanides with α,β-unsaturated ketones[10,11] or *N*-acylimines.[12] Two examples of the protic acid catalyzed reaction of *tert*-butyl isocyanide with arylideneanilines have also been reported to give 3-amino-2-arylindoles.[13]

We have examined the reactivity of isocyanides **7–9** with protonated 1,3-diaza-2-(methylthio)(or *p*-tolylthio)butadienes **4** and found that most of these diazadiene salts **4** rapidly gave the [1 + 4] cycloaddition products. However, a proton transfer from **4** to isocyanides can also occur, and the [2 + 4] cycloaddition of resulting nitrilium salts with diazabutadienes **5** can be expected. The present paper describes the results of our investigations for elucidating the various reactions of protonated diazabutadienes **4** opposite to isocyanides.

Results and Discussion

Preparation of Diazabutadienes 5 and Their Salts 4. Two alternative procedures were used. The addition of diphenylmethylenamine (**1**) to isothiocyanates **2** yielded 3-aza-1-thiabutadienes **3**, which were alkylated with MeI to afford **4a–c**. In $CHCl_3$ solution containing an excess of triethylamine, **4a–c** led to diazadienes **5a–c**. Diazadienes **5e–h** were obtained by the reaction of **1** with imino chloro sulfides **6e–h**, in the presence of an excess of Et_3N. The treatment of a etheral solution of **5e–h** with dry HCl gave **4e–h** in good yields.

Reactions of Protonated Diazabutadienes 4 with Isocyanides 7–9. The reactions were carried out with an excess of isocyanide, in chloroform solution at room temperature (method A) or in refluxing acetonitrile (method B). Salts **4d,e** were also prepared and converted in situ by the treatment of corresponding diazadienes **5c,e** with pyridinium chloride and *tert*-butyl isocyanide in refluxing MeCN (method C).[14] The complexity of these reactions was revealed by considering the number of isolated products (Table I). On one hand, we observed some expected

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(14) In Table I, we have selected procedure A, B, or C in order to optimize the yields of resulting compounds. That choice did not induce any perturbation in the products distribution.

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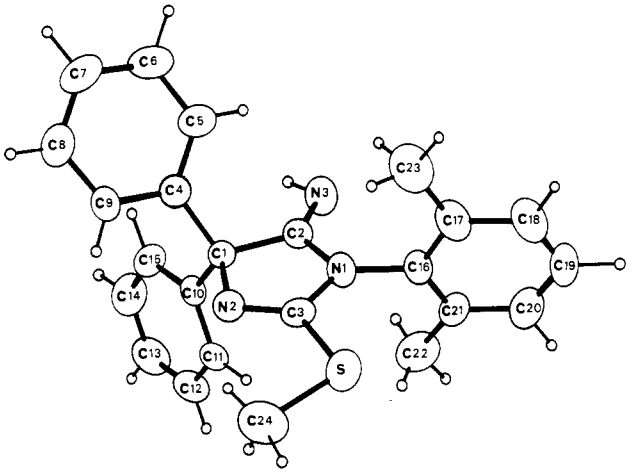


Figure 1. X-ray crystallographic structure of **11g**.

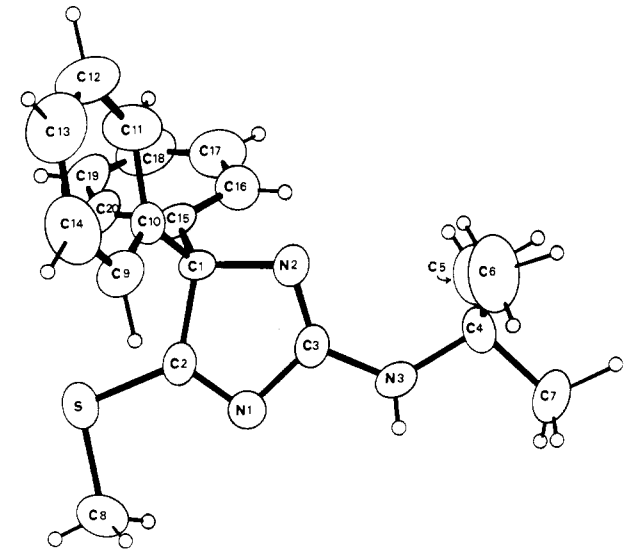


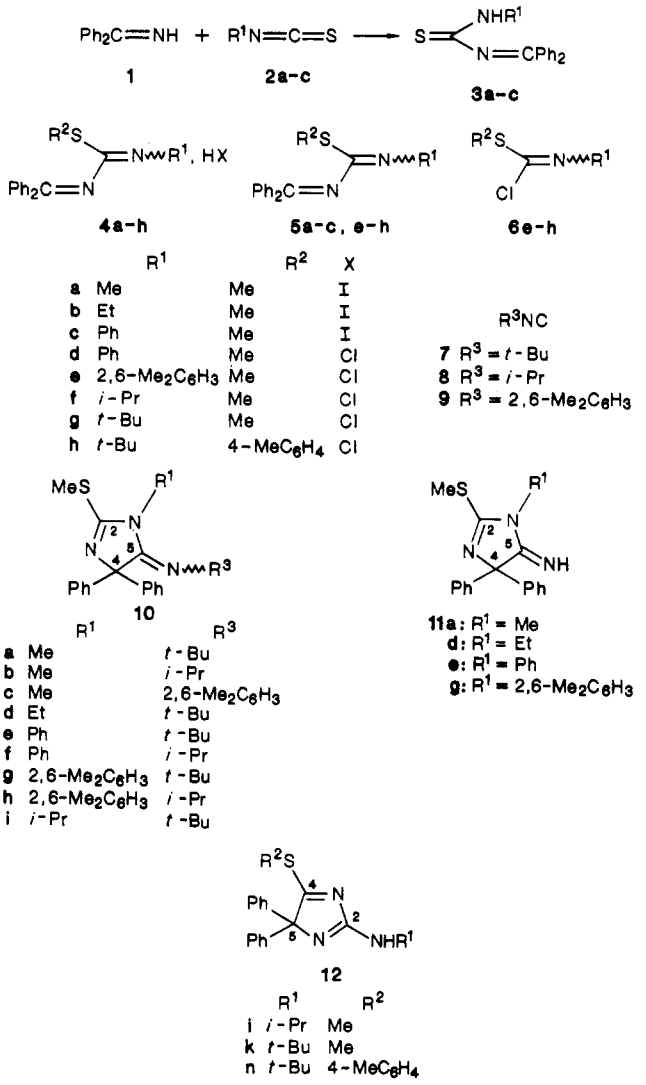
Figure 2. X-ray crystallographic structure of **12k**.

5-iminoimidazolines **10** and **11** and 2-(methylthio)dihydrotriazines **16** or triazinium halides **17**. On the other hand, several rearranged cycloadducts were formed: 2-aminoimidazoles **12** and **14**, thioxoimidazolines **13**, and thiazolines **15**. Compounds **10–16**, generally obtained as salts with HI or HCl, were easily isolated by treatment with triethylamine or aluminum oxide. Triazinium halides **17** were unstable in the presence of Et_3N, giving starting products **5**.

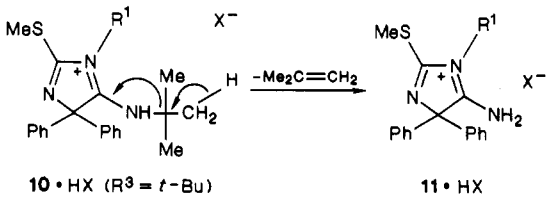
The reactions are much faster with salts **4** than with less electrophilic diazadienes **5**. For instance, a 50% yield of imidazoline **10g** and a 46% yield of imidazole **12k** were respectively obtained after treatment of **5e** and **5g** with **7**, in acetonitrile under reflux for 20 and 10 days. **5f** reacted poorly with *tert*-butyl isocyanide to give little **10i** (10%) in refluxing MeCN for 24 days. **5h** failed to react under similar conditions (compare with entries 10, 15, 13, and 18, Table I).

Structural assignments were based on NMR spectral data (Tables II and III). For imidazole **14l**, the carbon-13 chemical shifts of the three endocyclic atoms were attributed by heteronuclear decoupling experiments (irradiation of the aromatic H_2 and H_6 at δ 7.33 caused the C-4 signal to collapse to a broad singlet and the C-5 signal to turn into a doublet; irradiation of the isopropylic H atom at δ 4.08 caused the C-2 signal to collapse to a singlet and the C-5 signal to turn into a triplet). The slow autoxidation of **14l** into **18** using aerial oxygen was in good agreement with the structural assignment of **14**.

Chart I



Scheme I



Structures **11g** and **12k** were confirmed by a single-crystal X-ray analysis as shown in Figures 1 and 2. Mass spectrometry fragmentation showed the abundant $[R^1N{=}C{=}NR^3]^{+\bullet}$ for the 5-imino-2-imidazolines **10**[6] and the $[R^3N{=}C{=}S]^{\bullet+}$ for **13**. The ^{13}C NMR spectral data of **13** prove the presence of thione function (δ(C-5) = 212–213 ppm, Table II). The structure **15** was determined by comparison of the ^1H and ^{13}C NMR spectra of **15b** and **15c** with those of thiazolines obtained by the [1 + 4] cycloaddition of isocyanides **8** and **9** with **3a**.[15] We have not studied the *E*/*Z* configuration[6] of **5** and cycloadducts **10** nor the exact tautomeric forms of **4** and **12–15** in solution (Charts I and II).

Imidazolines **10**·HX were the results of the expected [1 + 4] cycloaddition of isocyanides with protonated hete-

(15) These results will be published separately.

Table I. Product Distributions in Reactions of Protonated Diazadienes 4 with Isocyanides 7-9

	educts		reaction conditions			products yields,[a] %		
entry	diazadiene, 4	isocyanide, R^3	$R^3NC/4$ ratio	method	time,[b] h	10, 11	12, 13, 14	16, 17
1	**4a**	t-Bu	2	A	72	71 **10a**		
2	**4a**	t-Bu	2	B	1.5	36 **10a** 38 **11a**		
3	**4a**	i-Pr	1.5	B	1	48 **10b**[c]	16 **13b**	
4	**4a**	2,6-$Me_2C_6H_3$	1.2	B	3	7 **10c**[d]	48 **13c**	
5	**4b**	t-Bu	2	A	66	84 **10d**		
6	**4b**	t-Bu	2	B	1.5	36 **10d** 34 **11d**		
7	**4c**	t-Bu	2	B	1			15 **16e**
8	**4c**	i-Pr	1.5	A	20	19 **10f**		41 **17f**
9	**4d**	t-Bu	2	C	1.5	39 **10e** 31 **11e**		*e*
10	**4e**	t-Bu	2	A	75	66 **10g**		5 **16g**
11	**4e**	t-Bu	1.7	C	5	73 **11g**		*e*
12	**4e**	i-Pr	2	A	24	9 **10h**		62 **17h**
13	**4f**	t-Bu	2	B	4	20 **10i**	52 **12i**	
14	**4f**	2,6-$Me_2C_6H_3$	1.2	B	5		50 **13j**	
15	**4g**	t-Bu	2.5	A	24		76 **12k**	
16	**4g**	i-Pr	2.4	B	1		30 **13l** 35 **14l**	
17	**4g**	2,6-$Me_2C_6H_3$	1.3	B	4		78 **13m**	
18	**4h**	t-Bu	2.1	A	24		80 **12n**	
19	**4h**	i-Pr	2.1	B	2		47 **14l**	
20	**4h**	2,6-$Me_2C_6H_3$	2.1	B	3		72 **14m**	

[a] Isolated products yields, eventually after treatment with NEt_3 or aluminum oxide. [b] Time required for the entire conversion of the starting diazadiene. [c] 9% of **15b** was also obtained. [d] 11% of **15c** was also obtained. [e] Small quantities of non isolated triazine **16** were also observed.

Table II. Selected ^{13}C NMR Shifts at 75.469 MHz for Some Imidazole Derivatives 10-14 and Thiazolines 15[a,b]

no.	C-2	C-4	C-5
10a	160.6	80.7	156.0
10b	161.9	80.7	161.4
10d	160.1	80.7	154.9
10e	162.9	80.0	152.7
10g	162.2	80.5	150.6
10h	161.5	81.1	159.1
10i	160.3	80.0	155.1
11a	162.1	81.1	174.7
11e	161.1	80.5	172.8
11g	161.4	81.0	171.7
12i	164.7	200.3	92.2
12k	163.5	198.8	92.9
12n	163.5	197.5	93.4
13b	154.9	86.6	213.0
13c	154.6	89.1	213.0
13j	152.8	89.0	213.0
13l	152.1	88.3	213.3
13m	151.2	89.3	212.1
14l	148.3	137.0	124.9
14m	148.2	136.8	124.2
15b	155.1	88.5	168.0
15c	154.9	88.9	177.0

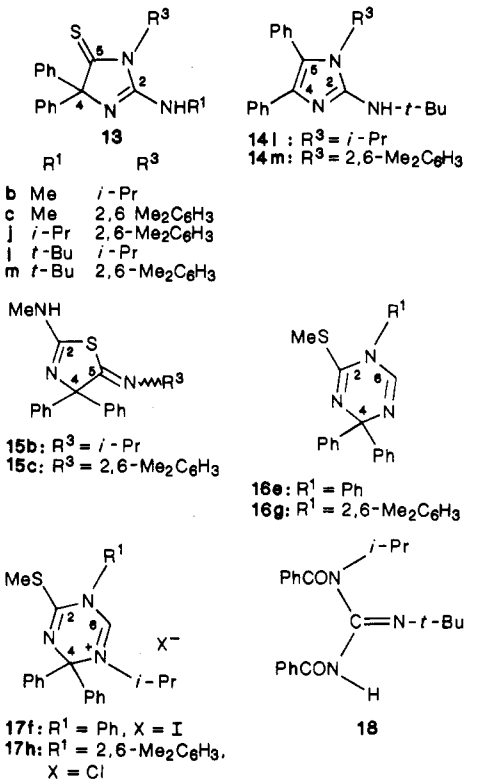
[a] Values are given in ppm referenced to Me_4Si and were obtained in $CDCl_3$ solutions, except for **14l,m** (CD_3CN). [b] Expected multiplicities for the assigned structures were observed, according to the typical examples: **10h**, C-2, q, $^3J_{CSCH}$ = 4.4 Hz; C-5, d, $^3J_{CNCH}$ = 6.4 Hz; **12k**, C-2, s; C-4, q, ^3J = 3.9 Hz; **13l**, C-2, d, ^3J = 5.5 Hz; C-5, d, ^3J = 3.3 Hz; **14l**, C-2, d, $^3J_{CNCH}$ = 5 Hz; C-4, t, $^3J_{CCCH}$ = 7 Hz; C-5, q, ^3J = 4 Hz; **15b**, C-2, q, ^3J = 3 Hz; C-5, d, ^3J = 10 Hz.

Table III. Selected Carbon-13 Chemical Shifts at 75.469 MHz for 16 and 17 in $CDCl_3$ Solutions. δ (ppm) from Internal TMS (mult)

no.	C-2 (qd)[a]	C-4 (m)	C-6
16e	150.7	78.4	142.6 (d)[b]
16g	151.2	78.3	143.1 (d)[b]
17f	153.0	85.3	151.3 (dd)[c]
17h	152.1	85.2	154.6 (dd)[c]

[a] $^3J_{CSCH} = {}^3J_{CNCH}$ = 4-5 Hz. [b] $^1J_{CH}$ = 204-205 Hz. [c] $^1J_{CH}$ = 205 Hz; $^3J_{CNCH}$ = 6-7 Hz.

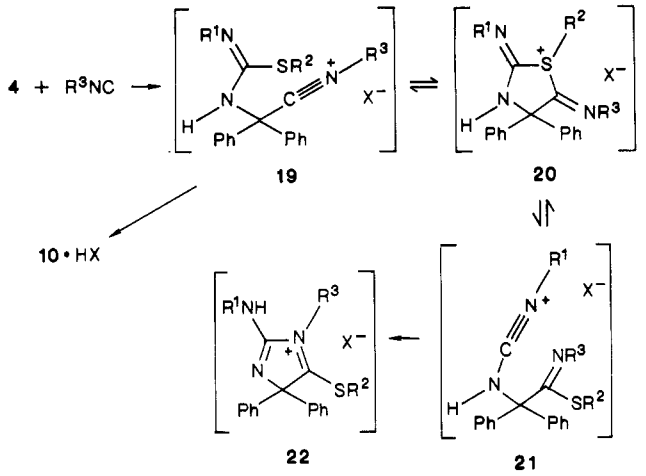
Chart II



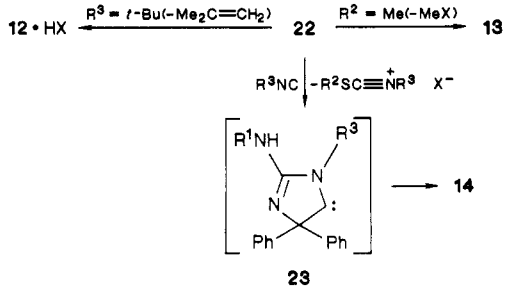
rodienes 4. Salts 11·HX were formed from 10·HX by a fast isobutene elimination when R^3 = t-Bu (Scheme I). Indeed, on heating a solution of **10g**·HCl in acetonitrile for 1 h, imidazoline **11g**·HCl was produced in 85% yield. The formation of compounds **12-17** could be explained by the following mechanisms.

Imidazole and Thiazole Derivatives 12-15. First, nucleophilic addition of isocyanide on **4** leads to the nitrilium salt **19** (Scheme II). The high electrophilicity of **4** allows this process to be fast. The cyclization of **19** can

Scheme II



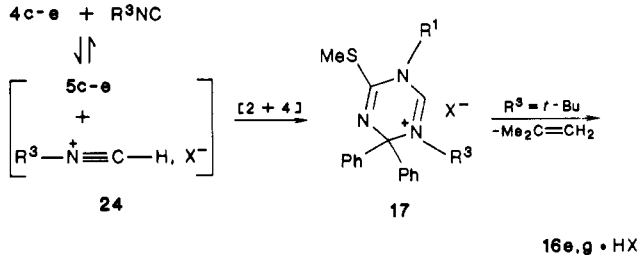
Scheme III



furnish the cycloadduct **10**·HX or the unstable intermediate **20**. The effectiveness of thio group in stabilizing carbocation is well known.[16] Indeed, it has been shown that the reaction of a carbocation with a neighboring alkylthio group gives a cyclic sulfonium ion.[17] The conversion of **20** into **21** by ring opening and then cyclization of **21** provide another intermediate **22**. This salt **22** is spontaneously transformed into stable compounds (Scheme III). Isobutene elimination from **22** explains the formation of aminoimidazole **12**·HX (R^3 = *t*-Bu).[18] Methyl halide elimination[19] from **22** affords thioxoimidazoline **13** ($R^3 \neq$ *t*-Bu, R^2 = Me). In some cases, excess of isocyanide can attack the sulfur atom of **22** to give the carbene **23**, which rearranges into imidazole **14** by the 1,2-migration of a phenyl group. This observation is consistent with the nucleophilic attack of isocyanide on a divalent sulfur atom.[9,20,21]

The nitrilium salts **19** and **21** would be in equilibrium through the thiazolium salt **20** (Scheme II). When the R^3 group has a greater electron-donating effect than the R^1 group (*t*-Bu, *i*-Pr > Me, Et, Ph, 2,6-$Me_2C_6H_3$), the intermediate **19** is more stabilized than **21** and imidazolines **10** and **11** are favored (entries 1–3, 5–12, Table I). In other cases, the R^1 group has a greater electron-donating effect (or practically the same effect) than the R^3 group. The intermediate **21** is more stabilized than **19**. Imidazole

Scheme IV



derivatives **12–14** resulting of **21** via **22** were predominantly formed.

The formation of thiazolines **15b,c** as minor products (Table I, entries 3 and 4) can be explained by two ways: MeI elimination from cycloadducts **20** or MeI elimination from starting product **4a** giving **3a**. 3-Aza-1-thiabutadienes **3** were converted into **15** by [1 + 4] cycloaddition reactions with isocyanides.[15]

Triazine Derivatives 16 and 17. Six-membered cycloadducts are formed with aromatic R^1 substituent (entries 7–12, Table I). The electron-withdrawing effect of these R^1 groups increases the acidity of salts **4c–e**. Then, their deprotonation by isocyanides becomes possible and gives nitrilium salts **24** (Scheme IV). Protonation of isocyanides is a not very studied process.[22] Diazadienes **5c–e** and **24** undergo [2 + 4] cycloaddition reactions to form triazinium salts **17**. When R^3 = *t*-Bu, isobutene elimination from **17** takes place to afford dihydrotriazines **16**·HX.

Conclusion

We have shown that protonated 1,3-diazabutadienes **4** are greatly reactive toward nucleophilic isocyanides **7–9**. We have suggested several mechanisms to explain the formation of various imidazole derivatives **10–14**. Furthermore, when R^1 has a good electron-withdrawing effect, a proton transfer from **4** to isocyanides can also occur, giving nitrilium salts **24** as transitory dienophilic species. Thus, *tert*-butyl isocyanide **7** has been used as a synthetic equivalent for the highly unstable isocyanic acid[7,23] to yield **11** and for cyanic acid[11] to yield six-membered heterocyclic compounds **16**. We assume that these findings can offer much importance in organic synthesis. Similar reactions are under investigation.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded as suspensions in Nujol with a Perkin-Elmer 1420 spectrophotometer. NMR spectra (internal standard Me_4Si) were taken in $CDCl_3$, unless otherwise indicated, on Bruker WP 80 (^1H) and AM 300 WB (^{13}C) spectrometers. The mass spectra were obtained on a Varian MAT 311 spectrometer. 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. Diphenylmethylenamine (**1**) (5.4 g, 30 mmol) was added to a solution of isothiocyanate **2** (50 mmol) in Et_2O (30 mL). The precipitate that slowly formed at room temperature was filtered and washed with Et_2O.

3a: mp 197 °C (from MeOH) (93% yield, reaction time 3 days); ^1H NMR δ 2.89, 3.07 (2 d, J = 5 Hz, 3 H), 6.87 (br, 1 H), 7.4–7.6 (m, 10 H). Anal. Calcd for $C_{15}H_{14}N_2S$: C, 70.86; H, 5.51; N, 11.02; S, 12.59. Found: C, 70.85; H, 5.55; N, 11.03; S, 12.51.

3b: mp 175 °C (CH_2Cl_2/petroleum ether) (82% yield, 3 days); ^1H NMR δ 1.07, 1.15 (2 t, J = 7 Hz, 3 H), 3.55, 3.25 (2 m, 2 H),

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(18) Isobutene and salt **12k**·HCl were observed together by reacting **4g** with **7** in $CDCl_3$ solution analyzed by ^1H NMR.
(19) Cycloadducts **13–15** were predominantly obtained as salts with HI or HCl via a protonation by other salts of the mixture.
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6.67, 6.20 (2 br, 1 H), 7.3–7.6 (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, 71.51; H, 6.09; N, 10.25; S, 11.89.

3c: yellow prisms, mp 160 °C (MeCN) (92% yield, 24 h); ^{1}H NMR δ 7.2–7.4 (m, 15 H), 9.21 (br, 1 H). Anal. Calcd for $C_{20}H_{16}N_2S$: C, 75.95; H, 5.06; N, 8.86; S, 10.12. Found: C, 75.80; H, 4.81; N, 8.88; S, 10.20.

Conversion of 3 into 4,4-Diphenyl-2-(methylthio)-1,3-diazabuta-1,3-dienes 5a–c and Salts 4a–c. Methyl iodide (4.3 g, 30 mmol) was added to a solution of **3** (10 mmol) in THF (50 mL). The yellowish precipitate that formed at ambient temperature was filtered and washed with dry ether. The crude salts **4a–c** were used without further purification.

4a: mp 172–176 °C dec (86% yield, 27 h); ^{1}H NMR δ 2.57, 2.70 (2 s, 3 H), 3.0, 3.2 (2 s, 3 H), 7.5–7.8 (m, 10 H), 10.2 (br, 1 H).

4b: mp 194–198 °C dec (91% yield, 20 h); ^{1}H NMR δ 1.17, 1.40 (2 t, J = 7 Hz, 3 H), 2.57, 2.67 (2 s, 3 H), 3.65, 3.45 (2 q, J = 7 Hz, 2 H), 7.4–7.8 (m, 10 H).

4c: mp 182–186 °C dec (88% yield, 17 h); ^{1}H NMR δ 2.55, 2.57 (2 s, 3 H), 7.2–7.9 (m, 16 H).

A solution of salt **4** (10 mmol) and triethylamine (2 g, 20 mmol) in $CHCl_3$ (15 mL) was maintained at 20 °C for 20 min. The solvent was evaporated and the residue was triturated with Et_2O. The triethylammonium iodide was filtered off then the filtrate was concentrated to a oil. The crude diazadiene was purified by crystallization (**5a**, **5c**) or by bulb-to-bulb distillation under reduced pressure (**5b**). The yields were around 90–95%.

5a: mp 80 °C (petroleum ether); ^{1}H NMR δ 2.2, 2.3 (2 s, 3 H), 3.01, 2.99 (2 s, 3 H), 7.42–7.46 (m, 10 H); ^{13}C NMR δ 13.6, 14.0 (2 q, ^1J = 141 Hz, SCH_3), 37.7, 37.6 (2 q, ^1J = 135 Hz, NCH_3), 128.1, 128.2, 128.4, 128.5, 128.6, 128.9, 130.8, 136.5 (C_6H_5), 162.4, 161.3 (2 qq, C_2), 168.9, 169.3 (2 br, C_4). Anal. Calcd for $C_{16}H_{16}N_2S$: C, 71.64; H, 5.97; N, 10.44; S, 11.94. Found: C, 71.61; H, 5.99; N, 10.45; S, 12.30.

5b: pale yellow oil, bp 150 °C (0.01 Torr) (Buchi Kugelrohr apparatus); ^{1}H NMR δ 1.10, 1.0 (2 t, J = 7 Hz, 3 H), 2.21, 2.29 (2 s, 3 H), 3.22 (q, 2 H), 7.35–7.45 (m, 10 H).

5c: mp 92 °C (MeOH); ^{1}H NMR 2.38 (br, 3 H), 6.6–7.6 (m, 15 H). Anal. Calcd for $C_{21}H_{18}N_2S$: C, 76.36; H, 5.45; N, 8.48; S. 9.70. Found: C, 76.44; H, 5.47; N, 8.40; S, 9.59.

Synthesis of 1,3-Diazabuta-1,3-dienes 5e–h and Salts 4e–h. Imino chloro sulfides **6e–h** were easily prepared by the addition of sulfenyl chlorides R^2SCl to isocyanides R^1NC, in THF or CCl_4 solution.[9,20]

To a solution of the appropriate **6** (30 mmol) in THF (20 mL) was added dropwise a mixture of **1** (5.8 g, 32 mmol) and NEt_3 (3.5 g, 35 mmol) dissolved in THF (30 mL). After stirring at room temperature for 4 h, the triethylammonium chloride was filtered off. Evaporation of the filtrate and extraction of the residue with petroleum ether gave crystalline **5**.

1-(2,6-Dimethylphenyl)-4,4-diphenyl-2-(methylthio)-1,3-diazabuta-1,3-diene (5e): mp 101 °C (from MeOH) (55% yield); IR 1622, 1602, 1579 cm^{-1}; ^{1}H NMR δ 1.71 (s, 6 H), 2.34 (s, 3 H), 6.80 (br, 3 H), 7.35 (br, 10 H). Anal. Calcd for $C_{23}H_{22}N_2S$: C, 77.09; H, 6.14; N, 7.82; S, 8.93. Found: C, 76.99; H, 6.16; N, 7.83; S, 9.00.

4,4-Diphenyl-1-isopropyl-2-(methylthio)-1,3-diazabuta-1,3-diene (5f): mp 80 °C (petroleum ether) (80% yield); ^{1}H NMR δ 1.04 (d, J = 6 Hz, 6 H), 2.30, 2.36 (2 s, 3 H), 3.65 (m, 1 H), 7.35–7.55 (m, 10 H). Anal. Calcd for $C_{18}H_{20}N_2S$: C, 72.97; H, 6.75; N, 9.46; S, 10.81. Found: C, 72.70; H, 6.70; N, 9.55; S, 10.58.

1-*tert*-Butyl-4,4-diphenyl-2-(methylthio)-1,3-diazabuta-1,3-diene (5g): mp 95 °C ($CHCl_3/Et_2O$) (85% yield); IR 1607, 1596, 1566 cm^{-1}; ^{1}H NMR δ 1.16, 1.28 (2 br, 9 H), 2.30, 2.13 (2 br, 3 H), 7.25–7.65 (m, 10 H). Anal. Calcd for $C_{19}H_{22}N_2S$: C, 73.54; H, 7.09; N, 9.03; S, 10.32. Found: C, 73.63; H, 7.09; N, 9.22; S, 10.16.

1-*tert*-Butyl-4,4-diphenyl-2-[(4-methylphenyl)thio]-1,3-diazabuta-1,3-diene (5h): mp 90 °C (petroleum ether) (78% yield); IR 1604, 1572, 1487 cm^{-1}; ^{1}H NMR δ 1.42 (s, 9 H), 2.29 (s, 3 H), 6.9–7.5 (m, 14 H). Anal. Calcd for $C_{25}H_{26}N_2S$: C, 77.72; H, 6.73; N, 7.25; S. 8.29. Found: C, 77.55; H, 6.81; N, 7.20; S, 8.20.

A solution of **5** (10 mmol) in anhydrous Et_2O (50 mL) was saturated with dry HCl. A white solid separated immediately. It was collected, washed with ether, and dried in vacuo. These crude salts **4** melted with decomposition on the Kofler apparatus (undetermined melting points). The yields varied between 80% and 90%. They were used without further purification.

4e: ^{1}H NMR δ 2.07 (br, 6 H), 2.52 (br, 3 H), 7.02 (m, 3 H), 7.45–7.85 (m, 10 H).

4f: ^{1}H NMR δ 1.38, 1.50 (2 d, J = 7 Hz, 6 H), 2.67, 2.66 (2 s, 3 H), 3.87 (m, 1 H), 7.5–7.85 (m, 10 H).

4g: ^{1}H NMR δ 1.46, 1.58 (2 s, 9 H), 2.63, 2.26 (2 s, 3 H), 7.42–7.8 (m, 10 H), 12.8 (br, 1 H).

4h: ^{1}H NMR δ 1.54, 1.61 (2 s, 9 H), 2.19, 2.29 (2 s, 3 H), 6.25 (s, 4 H), 7.2–7.7 (m, 10 H), 13.03 (br, 1 H).

An alternative route was to prepare **4** from **1** and **6**, without NEt_3, by the following procedure: **1** (2 g, 11 mmol) was added to a solution of **6g** (10 mmol) in dry ether (30 mL) at room temperature. Stirring was continued for 1 h and the mixture was filtered to give **4g** as white solid (2.55 g, 73% yield).

Reactions of Protonated Diazabutadienes 4 with Isocyanides. Method A. General Procedure. Isocyanide was added to a solution of **4** (5 mmol) in $CHCl_3$ (10 mL). The mixture was maintained at room temperature in a stoppered flask. Excess of isocyanide and reaction time are indicated in Table I. The solvent was distilled under reduced pressure. The residue was triturated with THF/ether (1:1) and the insoluble material was collected by filtration (**10a,d**·HI, **10g**·HCl, or **12k,n**·HCl) (entries 1, 5, 10, 15, and 18). The filtrate was concentrated to a syrup. **16g**·HCl was precipitated by addition of Et_2O (entry 10). Crude products of entries 8 and 12 were fractionated by crystallization from Et_2O/MeCN (1:1) to afford **17f,h** and then from MeOH to afford **10f,h**. The protonated imidazolines **10**·HX, imidazoles **12**·HCl, and triazine **16g**·HCl were treated with $NEt_3/CHCl_3$ to give **10**, **12**, and **16** after elimination of the ammonium halide, according to the above-mentioned procedure (yields, see Table I; ^{13}C NMR spectra, see Tables II and III).

5-(*tert*-Butylimino)-4,4-diphenyl-1-methyl-2-(methylthio)-2-imidazoline (10a): mp 126 °C (petroleum ether); ^{1}H NMR δ 0.87 (s, 9 H), 2.45 (s, 3 H), 3.12 (s, 3 H), 7.25–7.4 (m, 10 H). Anal. Calcd for $C_{21}H_{25}N_3S$: C, 71.79; H, 7.12; N, 11.96; S, 9.11. Found: C, 71.90; H, 7.19; N, 11.95; S, 9.20.

5-(*tert*-Butylimino)-4,4-diphenyl-1-ethyl-2-(methylthio)-2-imidazoline (10d): mp 116 °C (MeOH); ^{1}H NMR δ 0.85 (s, 9 H), 1.21 (t, J = 7 Hz, 3 H), 2.40 (s, 3 H), 3.61 (q, J = 7 Hz, 2 H), 7.2–7.4 (m, 10 H). Anal. Calcd for $C_{22}H_{27}N_3S$: C, 72.32; H, 7.39; N, 11.50; S, 8.76. Found: C, 72.55; H, 7.23; N, 11.69; S, 8.78.

2-(Methylthio)-5-(isopropylimino)-1,4,4-triphenyl-2-imidazoline (10f): mp 195 °C (MeOH); ^{1}H NMR δ 0.53 (d, J = 6 Hz, 6 H), 2.37 (s, 3 H), 3.6 (m, 1 H), 7.25–7.5 (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, 75.23; H, 6.29; N, 10.61; S, 8.04.

5-(*tert*-Butylimino)-1-(2,6-dimethylphenyl)-4,4-diphenyl-2-(methylthio)-2-imidazoline (10g): mp 162 °C (MeCN); ^{1}H NMR δ 0.80 (s, 9 H), 2.12 (s, 6 H), 2.40 (s, 3 H), 7.0–7.6 (m, 13 H); MS calcd for $C_{28}H_{31}N_3S$, m/e 441.2239 (M^+), found 441.2243; m/e (relative intensity) 441 (9), 311 (20), 239 (72), 224 (100). Anal. Calcd: C, 76.19; H, 7.03; N, 9.52; S, 7.25. Found: C, 75.51; H, 7.07; N, 9.23; S, 7.20.

1-(2,6-Dimethylphenyl)-4,4-diphenyl-2-(methylthio)-5-(isopropylimino)-2-imidazoline (10h): mp 132 °C (petroleum ether); IR 1670, 1560 cm^{-1}; ^{1}H NMR δ 0.52 (d, J = 6 Hz, 6 H), 2.25 (s, 6 H), 2.42 (s, 3 H), 3.65 (m, 1 H), 7.15–7.4 (m, 13 H); MS calcd for $C_{27}H_{29}N_3S$, m/e 427.2082 (M^+), found 427.2091; m/e (relative intensity) 427 (26), 311 (18), 239 (41), 224 (100). Anal. Calcd: C, 75.87; H, 6.79; N, 9.83; S, 7.49. Found: C, 75.61; H, 6.87; N, 9.85; S, 7.60.

2-(*tert*-Butylamino)-5,5-diphenyl-4-(methylthio)-5-isoimidazole (12k): mp 180 °C (MeOH); IR 3320, 1623 cm^{-1}; ^{1}H NMR δ 1.41 (s, 9 H), 2.47 (s, 3 H), 4.86 (br, 1 H), 7.2–7.4 (m, 10 H); MS calcd for $C_{20}H_{23}N_3S$, m/e 337.1613 (M^+), found 337.1615; m/e (relative intensity) 337 (100), 322 (25), 281 (70), 266 (30), 248 (30), 235 (25), 208 (35), 207 (90). Anal. Calcd: C, 71.21; H, 6.82; N, 12.46; S, 9.49. Found: C, 71.49; H, 6.94; N, 12.51; S, 9.59.

2-(*tert*-Butylamino)-5,5-diphenyl-4-[(4-methylphenyl)thio]-5-isoimidazole (12n): mp 123 °C (petroleum ether); ^{1}H NMR δ 1.35 (s, 9 H), 2.30 (s, 3 H), 4.75 (br, 1 H), 7.2–7.4 (m, 14 H); MS calcd for $C_{26}H_{27}N_3S$, m/e 413.1926 (M^+), found 413.1931; m/e (relative intensity) 413 (50), 357 (14), 356 (23), 264 (16), 234

(12), 235 (34), 208 (36), 207 (100), 165 (34). Anal. Calcd: C, 75.54; H, 6.53; N, 10.17; S, 7.74. Found: C, 75.27; H, 6.54; N, 10.04; S, 7.95.

1,4-Dihydro-1-(2,6-dimethylphenyl)-4,4-diphenyl-2-(methylthio)-1,3,5-triazine (16g): mp 185 °C (MeOH); IR 1665, 1590 cm^{-1}; ^1H NMR δ 2.15 (s, 6 H), 2.50 (s, 3 H), 7.1–7.75 (m, 14 H); MS calcd for $C_{24}H_{23}N_3S$, *m/e* 385.1613 (M^+), found 385.1611; *m/e* (relative intensity) 385 (9), 338 (14), 311 (31), 308 (100).

1,4-Dihydro-2-(methylthio)-5-isopropyl-1,4,4-triphenyl-1,3,5-triazinium iodide (17f): mp 208 °C ($MeOH/Et_2O$); ^1H NMR δ 1.48 (d, J = 7 Hz, 6 H), 2.35 (s, 3 H), 3.86 (m, 1 H), 7.5 (br, 15 H), 9.72 (s, 1 H); MS, *m/e* (relative intensity) 330 (M^+ – HI – iPrNC, 7), 283 (33), 224 (16), 180 (65), 165 (36), 135 (55), 77 (100). Anal. Calcd for $C_{25}H_{26}N_3SI$: N, 7.97; S, 6.07; I, 24.09. Found: N, 7.73; S, 6.08; I, 23.81.

1,4-Dihydro-1-(2,6-dimethylphenyl)-4,4-diphenyl-2-(methylthio)-5-isopropyl-1,3,5-triazinium chloride (17h): mp 240 °C ($MeCN/Et_2O$); IR 3400, 1695, 1605 cm^{-1}; ^1H NMR δ 1.53 (d, J = 7 Hz, 6 H), 2.21 (s, 6 H), 2.32 (s, 3 H), 3.62 (m, 1 H), 7.27 (s, 3 H), 7.48 (s, 10 H), 11.04 (s, 1 H); MS calcd for $C_{27}H_{30}N_3SCl$, *m/e* 427.2082 (M^+ – HCl), found 427.2091; *m/e* (relative intensity) 427 (2), 358 (11), 312 (30), 311 (100), 308 (12), 224 (21).

The reaction of *tert*-butyl isocyanide **7** (21 mg, 0.25 mmol) with salt **4g** (35 mg, 0.1 mmol) was also performed in $CDCl_3$ (0.4 mL) at room temperature. The solution was analyzed by ^1H NMR. Conversion of starting **4g** to **12k**·HCl and isobutene [δ 1.78 (t, J = 1 Hz, 6 H), 4.65 (m, 2 H)] was complete after 22 h.

Method B. General Procedure. A solution of MeCN (15 mL) containing **4** (5 mmol) and isocyanide was refluxed for the time indicated in Table I. The mixture was cooled to 20 °C and the products that precipitated in some cases were filtered (**12i**·HCl, **14l,m**·HCl) (entries 13, 16, 19, and 20). The filtrate was concentrated in vacuo. Ether was added to the residue to give crystalline triazine **16e** as a salt with HCl (entry 7). These salts were treated with $NEt_3/CHCl_3$ according to the usual procedure. Removal of ether gave a brown oil, which was fractionated by an aluminum oxide column chromatography (petroleum ether and then ether as eluents). This treatment directly gave the unprotonated imidazolines **10**, **11**, and **13** (entries 2–4, 6, 13, 14, 16, 17) or the dihydrothiazoles **15** (entries 3 and 4). All compounds were purified by recrystallization from the solvents given below (yields, see Table I; ^{13}C NMR spectra, see Tables II and III).

4,4-Diphenyl-1-methyl-2-(methylthio)-5-(isopropylimino)-2-imidazoline (10b): mp 97 °C (petroleum ether); ^1H NMR δ 0.62 (d, J = 6 Hz, 6 H), 2.47 (s, 3 H), 3.12 (s, 3 H), 3.62 (m, 1 H), 7.3 (s, 10 H); MS calcd for $C_{20}H_{23}N_3S$, *m/e* 337.1613 (M^+), found 337.1615; *m/e* (relative intensity) 337 (11), 322 (2), 294 (3), 239 (32), 224 (100), 192 (6), 165 (45).

5-[(2,6-Dimethylphenyl)imino]-4,4-diphenyl-1-methyl-2-(methylthio)-2-imidazoline (10c): mp 131 °C (ether/petroleum ether); ^1H NMR δ 1.84 (s, 6 H), 2.56 (s, 3 H), 2.61 (s, 3 H), 6.82 (m, 3 H), 7.2–7.8 (m, 10 H); MS calcd for $C_{25}H_{25}N_3S$, *m/e* 399.1769 (M^+), found 399.1760; *m/e* (relative intensity) 399 (46), 239 (24), 224 (100), 192 (3), 165 (24).

5-(*tert*-Butylimino)-4,4-diphenyl-2-(methylthio)-1-isopropyl-2-imidazoline (10i): mp 100 °C (EtOH); ^1H NMR δ 0.80 (s, 9 H), 1.50 (d, J = 7 Hz, 6 H), 2.33 (s, 3 H), 4.22 (m, 1 H), 7.25–7.4 (m, 10 H); MS calcd for $C_{23}H_{29}N_3S$, *m/e* 379.2082 (M^+), found 379.2089; *m/e* (relative intensity) 379 (3), 364 (6), 239 (58), 224 (100), 165 (23). Anal. Calcd: C, 72.82; H, 7.65; N, 11.08; S, 8.44. Found: C, 72.78; H, 7.67; N, 11.21; S, 8.27.

4,4-Diphenyl-5-imino-1-methyl-2-(methylthio)-2-imidazoline (11a): mp 145 °C (EtOH); ^1H NMR δ 2.57 (s, 3 H), 3.10 (s, 3 H), 6.3 (br, 1 H), 7.3 (s, 10 H). Anal. Calcd for $C_{17}H_{17}N_3S$: C, 69.15; H, 5.76; N, 14.23; S, 10.84. Found: C, 69.23; H, 5.86; N, 14.14; S, 11.07.

4,4-Diphenyl-1-ethyl-5-imino-2-(methylthio)-2-imidazoline (11d): mp 94 °C (petroleum ether); ^1H NMR δ 1.22 (t, J = 7 Hz, 3 H), 2.57 (s, 3 H), 3.6 (q, 2 H), 6.37 (br, 1 H), 7.3 (s, 10 H). Anal. Calcd for $C_{18}H_{19}N_3S$: C, 69.90; H, 6.14; N, 13.59; S, 10.35. Found: C, 70.08; H, 6.13; N, 13.60; S, 10.40.

5,5-Diphenyl-4-(methylthio)-2-(isopropylamino)-5-isoimidazole (12i): mp 130 °C (petroleum ether); IR 1700, 1630 cm^{-1}; ^1H NMR δ 1.26 (d, J = 7 Hz, 6 H), 2.55 (s, 3 H), 4.18 (m, 1 H), 7.28 (s, 10 H); MS calcd for $C_{19}H_{21}N_3S$, *m/e* 323.1456 (M^+), found 323.1430; *m/e* (relative intensity) 323 (100), 308 (30), 290 (12), 280 (13), 277 (22), 207 (40). Anal. Calcd: C, 70.58; H, 6.50; N, 13.00; S, 9.90. Found: C, 70.65; H, 6.58; N, 12.96; S, 10.02.

4,4-Diphenyl-2-(methylamino)-1-isopropyl-2-imidazoline-5-thione (13b): mp 115 °C (ether/petroleum ether); ^1H NMR δ 1.44 (d, J = 7 Hz, 6 H), 3.02 (s, 3 H), 3.92 (br, 1 H), 5.30 (m, 1 H), 7.2–7.5 (m, 10 H); MS calcd for $C_{19}H_{21}N_3S$, *m/e* 323.1456 (M^+), found 323.1462; *m/e* (relative intensity) 323 (82), 291 (3), 281 (63), 267 (74), 222 (100), 210 (70), 207 (41). Anal. Calcd: C, 70.58; H, 6.50; N, 13.00; S, 9.90. Found: C, 70.47; H, 6.73; N, 12.94; S, 10.08.

1-(2,6-Dimethylphenyl)-4,4-diphenyl-2-(methylamino)-2-imidazoline-5-thione (13c): mp 176 °C (ether/petroleum ether); ^1H NMR δ 2.07 (s, 6 H), 3.02 (s, 3 H), 3.62 (br, 1 H), 7.2–7.7 (m, 13 H); MS calcd for $C_{24}H_{23}N_3S$, *m/e* 385.1613 (M^+), found 385.1611; *m/e* (relative intensity) 385 (100), 308 (9), 222 (93), 207 (77), 165 (62). Anal. Calcd: C, 74.80; H, 5.97; N, 10.91; S, 8.31. Found: C, 74.72; H, 5.96; N, 10.80; S, 8.40.

1-(2,6-Dimethylphenyl)-4,4-diphenyl-2-(isopropylamino)-2-imidazoline-5-thione (13j): mp 184 °C (MeCN); ^1H NMR δ 1.21 (d, J = 7 Hz, 6 H), 2.07 (s, 6 H), 3.52 (d, br, 1 H), 4.20 (m, 1 H), 7.2–7.7 (m, 10 H); MS calcd for $C_{26}H_{27}N_3S$, *m/e* 413.1926 (M^+), found 413.1931; *m/e* (relative intensity) 413 (100), 381 (7), 250 (31), 208 (41), 207 (70), 161 (21), 104 (63). Anal. Calcd: C, 75.54; H, 6.53; N, 10.16; S, 7.75. Found: C, 75.27; H, 6.58; N, 10.09; S, 7.79.

2-(*tert*-Butylamino)-4,4-diphenyl-1-isopropyl-2-imidazoline-5-thione (13l): mp 124 °C (EtOH); IR 3470, 1665 cm^{-1}; ^1H NMR δ 1.41 (d, J = 7 Hz, 6 H), 1.52 (s, 9 H), 4.12 (br, 1 H), 5.40 (m, 1 H), 7.2–7.6 (m, 10 H); MS calcd for $C_{22}H_{27}N_3S$, *m/e* 365.1926 (M^+), found 365.1926; *m/e* (relative intensity) 365 (36), 267 (28), 264 (34), 208 (65), 207 (100), 165 (19), 104 (58). Anal. Calcd: C, 72.32; H, 7.39; N, 11.50; S, 8.76. Found: C, 72.26; H, 7.43; N, 11.53; S, 8.84.

2-(*tert*-Butylamino)-1-(2,6-dimethylphenyl)-4,4-diphenyl-2-imidazoline-5-thione (13m): mp 155 °C (MeOH); ^1H NMR δ 1.42 (s, 9 H), 2.03 (s, 6 H), 3.55 (br, 1 H), 7.2–7.7 (m, 13 H); MS calcd for $C_{27}H_{29}N_3S$, *m/e* 427.2082 (M^+), found 427.2088; *m/e* (relative intensity) 427 (34), 395 (12), 371 (12), 339 (17), 264 (16), 208 (47), 207 (100), 165 (16), 104 (50). Anal. Calcd: C, 75.87; H, 6.79; N, 9.83; S, 7.49. Found: C, 75.47; H, 7.07; N, 10.00; S, 7.36.

2-(*tert*-Butylamino)-4,5-diphenyl-1-isopropylimidazole (14l): mp 130 °C (petroleum ether); IR 1600, 1555 cm^{-1}; ^1H NMR δ 1.31 (d, J = 6 Hz, 6 H), 1.50 (s, 9 H), 3.30 (br, 1 H), 4.10 (m, 1 H), 7.0–7.5 (m, 10 H); MS calcd for $C_{22}H_{27}N_3$, *m/e* 333.2205 (M^+), found 333.2192; *m/e* (relative intensity) 333 (80), 318 (5), 227 (60), 276 (30), 235 (100), 234 (100), 193 (60).

2-(*tert*-Butylamino)-1-(2,6-dimethylphenyl)-4,5-diphenylimidazole (14m): mp 169 °C (petroleum ether); ^1H NMR δ 1.45 (s, 9 H), 2.05 (s, 6 H), 3.19 (br, 1 H), 7.05–7.7 (m, 13 H); MS calcd for $C_{27}H_{29}N_3$, *m/e* 395.2361 (M^+), found 395.2356; *m/e* (relative intensity) 395 (95), 380 (4), 339 (100), 338 (18), 324 (8), 323 (20), 297 (6), 296 (9).

4,5-Dihydro-4,4-diphenyl-2-(methylamino)-5-(isopropylimino)thiazole (15b): mp 155 °C (MeOH); ^1H NMR δ 1.18 (d, J = 6 Hz, 6 H), 2.84 (s, 3 H), 3.04 (m, 1 H), 4.9 (br, 1 H), 7.2–7.55 (m, 10 H). Anal. Calcd for $C_{19}H_{21}N_3S$: C, 70.58; H, 6.50; N, 13.00; S, 9.90. Found: C, 70.83; H, 6.65; N, 13.10; S, 9.88.

4,5-Dihydro-5-[(2,6-dimethylphenyl)imino]-4,4-diphenyl-2-(methylamino)thiazole (15c): mp 210 °C (MeOH); ^1H NMR δ 1.85 (s, 6 H), 2.87 (s, 3 H), 4.12 (br, 1 H), 6.92 (s, 3 H), 7.2–7.75 (m, 10 H); MS calcd for $C_{24}H_{23}N_3S$, *m/e* 385.1613 (M^+), found 385.1611; *m/e* (relative intensity) 385 (1), 254 (16), 223 (16), 222 (100), 221 (22), 207 (31), 180 (12), 165 (59). Anal. Calcd: C, 74.80; H, 5.97; N, 10.91; S, 8.31. Found: C, 74.58; H, 6.06; N, 11.07; S, 8.50.

1,4-Dihydro-2-(methylthio)-1,4,4-triphenyl-1,3,5-triazine (16e): mp 142 °C (petroleum ether); ^1H NMR δ 2.45 (s, 3 H), 7.1–7.7 (m, 16 H); MS calcd for $C_{22}H_{19}N_3S$, *m/e* 357.1300 (M^+), found 357.1304; *m/e* (relative intensity) 357 (6), 310 (8), 284 (6), 283 (20), 280 (100), 180 (16). Anal. Calcd: C, 73.94; H, 5.32; N, 11.76; S, 8.96. Found: C, 73.71; H, 5.29; N, 11.66; S, 9.07.

Method C. Pyridinium chloride (1 g, 10 mmol) and diazadiene **5c,e** (5 mmol) were dissolved in MeCN (15 mL). An excess of **7** was added and the mixture was refluxed for the time indicated in Table I. After cooling to room temperature, **11g**·HCl was

collected (entry 11) or the solvent was evaporated in vacuo. Crude products of entry 9 were fractionated by extraction with ether (40 mL). Concentration of the etheral solution and subsequent crystallization of the residue from petroleum ether gave the imidazoline **10e**. The pyridinium chloride and the cycloadduct **11e**, insoluble in ether, were separated by the above-mentioned aluminum oxide column chromatography (petroleum ether and then ether as eluents).

5-(*tert*-Butylimino)-2-(methylthio)-1,4,4-triphenyl-2-imidazoline (10e): mp 93 °C (EtOH); ^{1}H NMR δ 0.85 (s, 9 H), 2.42 (s, 3 H), 7.2–7.7 (m, 15 H). Anal. Calcd for $C_{26}H_{27}N_3S$: C, 75.54; H, 6.53; N, 10.17; S, 7.75. Found: C, 75.61; H, 6.54; N, 10.29; S, 8.03.

5-Imino-2-(methylthio)-1,4,4-triphenyl-2-imidazoline (11e): mp 138 °C (EtOH); ^{1}H NMR δ 2.54 (s, 3 H), 6.50 (br, 1 H), 7.2–7.6 (m, 15 H). Anal. Calcd for $C_{22}H_{19}N_3S$: C, 73.95; H, 5.32; N, 11.76; S, 8.96. Found: C, 73.77; H, 5.31; N, 11.68; S, 9.04.

1-(2,6-Dimethylphenyl)-4,4-diphenyl-5-imino-2-(methylthio)-2-imidazoline (11g): mp 114 °C (MeOH); IR 1655, 1570 cm^{-1}; ^{1}H NMR δ 2.16 (s, 6 H), 2.57 (s, 3 H), 7.1–7.6 (m, 14 H); MS calcd for $C_{24}H_{23}N_3S$, *m/e* 385.1613 (M$^+$), found 385.1611; *m/e* (relative intensity) 385 (57), 370 (6), 338 (29), 311 (15), 308 (12), 239 (12), 224 (100), 193 (14). Anal. Calcd: C, 74.80; H, 5.97; N, 10.90; S, 8.31. Found: C, 75.00; H, 6.13; N, 10.89; S, 8.48.

Reactions of Diazabutadienes 5 with Isocyanides. General Procedure. A solution of **5e–g** (5 mmol) and *tert*-butyl isocyanide **7** (1 g, 12 mmol) in MeCN (15 mL) was refluxed for several days. Removal of the solvent under reduced pressure gave a brown oil as residue, which was analyzed by ^{1}H NMR. The imidazoline **10g,i** or imidazole **12k** was separated from substantial quantities of unidentified side products by silica gel column chromatography and then fractional crystallization from MeOH. Reactions of **5h** with **7** and **5g,h** with **8** were carried out in the same manner but the resulting solution only afforded a viscous blackish oil whose ^{1}H NMR spectrum showed that starting diazadiene was the main compound.

Isobutene Elimination from 10g. A solution of **10g** (0.44 g, 1 mmol) in Et_2O (30 mL) was treated with dry HCl for 1 min. The precipitated **10g**·HCl was isolated in 94% yield (0.45 g) as a white solid, which was poured into MeCN (15 mL). After being refluxed for 1 h, the suspension was cooled to 20 °C. **11g**·HCl was collected by filtration and dried (0.36 g, 85% yield).

Oxidation of 14l. A solution of **14l** (0.33 g) in $CHCl_3$ (20 mL) was maintained at room temperature for 7 days under aerial oxygen. The reaction mixture was concentrated to a solid material, which was suspended in Et_2O (10 mL) and filtered. Sublimation of this white powder afforded a pure sample of **18**: mp 187 °C; IR 3310, 1635, 1570, 1525 cm^{-1}; ^{1}H NMR δ 1.23 (s, 9 H), 1.36 (d, J = 6 Hz, 6 H), 4.52 (m, 1 H), 5.17 (br, 1 H), 7.2–8.0 (m, 10 H); MS calcd for $C_{22}H_{27}N_3O_2$, *m/e* 365.2103 (M$^+$), found 365.2099; *m/e* (relative intensity) 308 (2), 260 (26), 204 (11), 105 (100). Anal. Calcd: C, 72.32; H, 7.40; N, 11.50. Found: C, 71.71; H, 7.52; N, 12.25.

X-ray Analysis of 11g. Crystal data: orthorhombic $Pna2_1$, a = 15.541 (5), b = 8.908 (2), and c = 15.194 (4) Å, V = 2103.6 (6) Å^3, Z = 4, D_x = 1.22 g cm^{-3}, μ = 1.67 cm^{-1}; 1595 reflections with $I \geq \sigma(I)$ collected with a Enraf-Nonius CAD-4 diffractometer (Mo Kα radiations). The structure was solved by direct methods[24] and the hydrogen atoms were found between 0.37 and 0.16 e Å^{-3}. The best full-matrix refinement gave R = 0.033, R_w = 0.031, S_w = 1.37 (321 variables and 1595 reflections).

X-ray Analysis of 12k. Crystal data: orthorhombic P_{ccn}, a = 11.343 (5), b = 25.390 (5), and c = 13.211 (8) Å, V = 3807 (2) Å^3, Z = 8, D_x = 1.34 g cm^{-3}, μ = 1.69 cm^{-1}, 1374 reflections with $I \geq \sigma(I)$. The structure was solved by direct methods[24] and the hydrogen atoms were found between 0.30 and 0.15 e Å^{-3}. The best full-matrix least-square refinement gave R = 0.056, R_w = 0.056, S_w = 1.29 (261 variables and 1374 reflections). All calculations were performed on a PDP 11/60 Digital computer with the SDP package.[25]

Registry No. 1, 1013-88-3; **2a**, 556-61-6; **2b**, 542-85-8; **2c**, 103-72-0; **3a**, 34979-85-6; **3b**, 118514-70-8; **3c**, 23490-81-5; **4a**, 118514-71-9; **4b**, 118514-72-0; **4c**, 118514-73-1; **4d**, 118514-74-2; **4e**, 118514-75-3; **4f**, 118514-76-4; **4g**, 118514-77-5; **4h**, 118514-78-6; **5a**, 118514-79-7; **5b**, 118514-80-0; **5c**, 118514-81-1; **5e**, 118514-82-2; **5f**, 118514-83-3; **5g**, 118514-84-4; **5h**, 118514-85-5; **6e**, 94518-64-6; **6f**, 94518-60-2; **6g**, 90496-26-7; **6h**, 118514-86-6; **7**, 7188-38-7; **8**, 598-45-8; **9**, 2769-71-3; **10a**, 118514-87-7; **10b**, 118514-88-8; **10c**, 118514-89-9; **10d**, 118514-90-2; **10e**, 118514-91-3; **10f**, 118514-92-4; **10g**, 118514-93-5; **10g**·HCl, 118515-16-5; **10h**, 118514-94-6; **10i**, 118514-95-7; **11a**, 118514-96-8; **11d**, 118514-97-9; **11e**, 52461-01-5; **11g**, 118514-98-0; **11g**·HCl, 118515-17-6; **12i**, 118514-99-1; **12k**, 118515-00-7; **12n**, 118515-01-8; **13b**, 118515-02-9; **13c**, 118515-03-0; **13j**, 118515-04-1; **13l**, 118515-05-2; **13m**, 118515-06-3; **14l**, 118515-07-4; **14m**, 118515-08-5; **12b**, 118515-09-6; **15c**, 118515-10-9; **16e**, 118515-11-0; **16g**, 118515-12-1; **17f**, 118515-13-2; **17h**, 118515-14-3; **18**, 118515-15-4; MeSCl, 5813-48-9.

Supplementary Material Available: Final coordinates and bond geometry tables for **11g** and **12k** (5 pages). Ordering information is given on any current masthead page.

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Preparation of Polymer-Supported (*R*)- and (*S*)-Styrene Oxide

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Polymer-supported (*R*)- and (*S*)-styrene oxide have been prepared via reduction of chloroacetylated styrene–1% divinylbenzene with (–)- and (+)-*B*-chlorodiisopinocampheylborane, respectively, and subsequent base treatment. The ee values for the reductions were estimated to be 85–91% by ^{19}F NMR analyses of diastereomeric MTPA ((*S*)-(–)-α-methoxy-α-(trifluoromethyl)phenylacetic acid) esters of the intermediate chloro alcohols.

Introduction

Polymers containing chiral chelating ligands are receiving increasing attention for use in asymmetric synthesis. Examples include chiral polymer-supported amino alcohols complexed to $LiAlH_4$[1] and to BH_3[2] in asymmetric reductions of ketones, and to Et_2Zn[3] in enantioselective additions to benzaldehyde as well as polymer-bound chiral

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