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Addition of Isocyanides to α-(Methylthio)-benzylidenamidinium Iodides: A Surprising Access to 2-(Dialkylamino)imidazoles and 3,5-Diamino-2H-pyrrolium Salts

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ABSTRACT: *A number of 2-(dialkylamino)-5-(methylthio)imidazoles* **2** *are obtained by treating the formamidinium iodides* **1a,b** *with isocyanides* R^3 *NC under mild conditions. Reduction of these species can occur in the reaction medium to furnish the corresponding imidazoles* **3**. *In some cases, double cycloaddition across the imine bond of starting salts* **1** *also provides the (azetidin-1-yl-methylene)ammonium iodides* **4**. *Reactions with tert-butyl and isopropyl isocyanides in refluxing acetonitrile convert the acetamidinium iodide* **1c** *into the 3,5-diamino-2H-pyrrolium salts* **7**. *Mechanisms are suggested to account for these ring-closure processes.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:370–376, 2000

INTRODUCTION

Iminium salts are highly reactive species and useful synthetic intermediates in organic chemistry [1,2]. On the other hand, isocyanides are a class of compounds of great use due to their unique nucleophilic character [3,4]. Their interest has been widely demonstrated in heterocyclic synthesis [5,6]. We previously reported the protonation of 1,3-diazabutadienes to yield imidazole or triazine derivatives by addition of isocyanides. In these cyclizations, isocyanides behave as nucleophilic or basic partners, involving a formal [1 + 4] or [2 + 4] cycloaddition reaction [7]. Similarly, we described the preparation of 4-amino-2-(methylthio)imidazolium salts through the combined action of isocyanides and benzaldimines on methyl chlorothioimidates. Transient *N*-imidoylbenzylidenammonium chlorides were assumed to be trapped by isocyanides in such three-component condensations [8]. By the same reasoning, we have explored the treatment of chloroiminosulfides or phenyl chlorodithioformate with azines or aldimines in the presence of isocyanides as new routes to fused imidazolium [9] and 5-amino-2-(phenylthio)thiazolium salts [10].

Recently [11], the formation of 5-amino-2*H*-pyrrolium salts from 1-azabutadiene hydrochlorides and isocyanides was rationalized by a nucleophilic addition to the terminal C-4 (path a, Scheme 1). Reactions on the 2-position were also observed. For example, a 2,3-bis(imino)azetidine was obtained according to a [1 + 1 + 2] cycloaddition process across the iminium function (path b, Scheme 1).

The efficiency of conjugated iminium salts to promote incorporation of isocyanides encouraged us to investigate the behavior in similar conditions of the 2-aza-3-(methylthio)-3-phenyl-2-propene-1-iminium iodides **1** (Scheme 2). Such study is mechanis-

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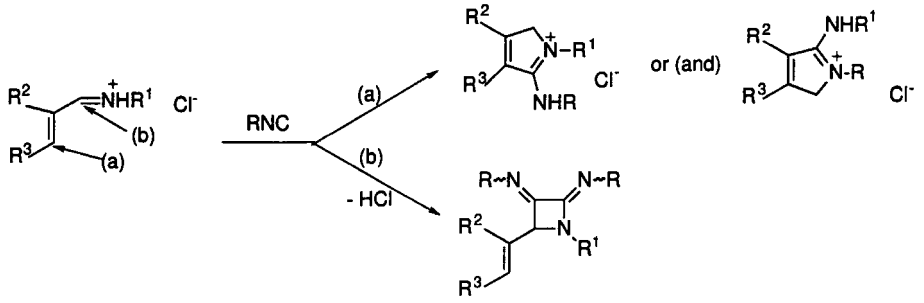
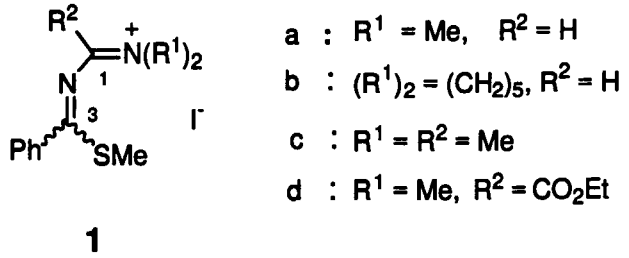


SCHEME 1



SCHEME 2

tically interesting because systems **1** are ambident electrophiles that can react at the carbon-1 or -3. Synthetic applications of this ambident property have already been mentioned in the presence of various monofunctional or bifunctional nucleophiles [12,13]. To date, however, the use of isocyanides was unprecedented.

RESULTS AND DISCUSSION

Reactions of Isocyanides with Formamidinium Iodides **1a,b**

The reactions of isocyanides with formamidinium iodides **1a,b** were generally performed at room temperature in CH_2Cl_2 or CH_3CN solution containing a large excess of isocyanide (entries 1–10, Table 1). ^1H NMR analyses of crude mixtures after treatment with NEt_3 indicated the formation of two or three cycloadducts. Their relative proportions were found to be markedly dependent on the nature of the isocyanide and experimental conditions as summarized in the following paragraphs.

The reactions were clearly accelerated, and higher quantities of primary 5-(methylthio)imidazoles **2a,e** were obtained by increasing the concentration of *tert*-butyl isocyanide. By this way, reduction to imidazoles **3** occurred only with very poor yields. However, such conditions also promoted the formation of azetidines **4** that involve a 2:1 cycloaddition process (see entries 1, 2, and 8, 9, Table 1).

CH_3CN proved to be rather more effective as the solvent than CH_2Cl_2 without significant effect on the mixture distribution (compare entry 2 with entry 3, Table 1).

Benzyl isocyanide generated imidazoles **2** as the strongly dominant products. Satisfactory efficiencies were observed even upon treatment with a small excess of reactant (entries 6, 10, Table 1). In contrast, the cyclization worked sluggishly with 2,6-dimethylphenyl isocyanide, requiring forty hours in refluxing acetonitrile for completion (entry 7, Table 1). No azetidines **4** were formed in these two cases.

Structures of cycloadducts **2–4** were established by spectroscopic methods and analyses. In particular, selected ^{13}C NMR chemical shifts and multiplicities are given in Table 2. The NMR spectra of 2-(dialkylamino)-5-(methylthio)imidazoles **2** display resonances at approximately δ 154 ppm for the C-2 and 116 ppm for the C-5. These values compare favorably with shifts for carbon atoms C-2 of 2-(dimethylamino)imidazole derivatives [14] and C-5 of a 5-(phenylthio)imidazole derivative [15]. The proton on C-5 for reduced imidazoles **3** shows an NMR resonance at about δ 7 ppm. Structural assignment of compounds **3** was corroborated by their ^{13}C NMR spectra, which give a large doublet for the C-5 ($\delta \approx$ 110 ppm, ^1J = 186 Hz). Each 1:2 adduct **4** shows the nonequivalence of the two carbons on the iminium nitrogen atom. The four C-methyl groups in azetidine **4b** also exhibit different chemical shifts due to the asymmetry introduced by the substituents on the C-4 (cf. Experimental section). The ^{13}C spectrum of azetidine **4a** reveals a doublet at δ 166.5 ppm as a result of a long-range coupling constant with the formamidinium proton and a large doublet of multiplets at δ 162.5 ppm (^1J = 192 Hz). Such a low-field resonance is typical of iminium centers [16].

We believe that the first step of the reaction occurs via the formation of the transient nitrilium iodide **5**, corresponding to the exclusive addition of isocyanide on the electrophilic terminal C-3 (Scheme 3). This regioselective process is presumed

TABLE 1 Reactions of Isocyanides with *N*-Benzylidenamidinium Iodides **1**

	Reagents		*Reactions conditions*[a]			*Product ratio*[b]			
Entry	*Salt*	*Isocyanide, R^3*	*R^3NC mol. eq.*	*Solvent*	*Time (h), Temp.*	**2**	**3**	**4**	*Isolated products (yield, %)*
1	**1a**	*t*Bu	2	CH_2Cl_2	72, rt	30	50	20	**2a** (20); **3a** (42); **4a** (8)
2	**1a**	*t*Bu	5	CH_2Cl_2	18, rt	62	8	30	**2a** (55); **4a** (18)
3	**1a**	*t*Bu	5	MeCN	10, rt	60	5	35	**2a** (45); **4a** (25)
4	**1a**	*i*Pr	5	CH_2Cl_2	18, rt	50	—	50	**2b** (44); **4b** (30)
5	**1a**	*i*Pr	4	MeCN	14, rt	75	—	25	**2b** (58); **4b** (10)
6	**1a**	CH_2Ph	1.5	CH_2Cl_2	46, rt	92	8	—	**2c** (72)
7	**1a**	2,6-$Me_2C_6H_3$	2	MeCN	41, reflux	50	50	—	**2d** (20); **3d** (38)
8	**1b**	*t*Bu	2	CH_2Cl_2	48, rt	40	35	25	**2e** (28); **3e** (25); **4e** (16)
9	**1b**	*t*Bu	4	CH_2Cl_2	10, rt	65	—	35	**2e** (45); **4e** (25)
10	**1b**	CH_2Ph	1.5	CH_2Cl_2	30, rt	95	5	—	**2f** (70)
11	**1c**	*t*Bu	3	MeCN	75, reflux	—	—	—	**7a** (70)
12	**1c**	*i*Pr	3	MeCN	41, reflux	—	—	—	**7b** (55)

[a]Specified times are required for the full conversion of starting salts **1**.
[b]Distributions were estimated by integration of the pertinent peaks in the ^{1}H NMR spectra of crude mixtures, after treatment with NEt_3.

TABLE 2 NMR Chemical Shifts and Multiplicities for the Main Carbon Atoms of Isolated Heterocycles[a,b]

Compound	*C-2*	*C-3*	*C-4*	*C-5*	*$N(CH_3)_2$ or $N(CH_2)_2$*[c]
2a	155.4 (m)	—	144.6 (t)[d]	117.3 (q, ^3J = 4.6)	44.7 (qq)
2b	154.1 (m)	—	142.3 (t)[d]	115.6 (m)	40.0 (qq)
2c	154.8 (m)	—	142.3 (t)[d]	116.3 (m)	43.2 (qq)
2d	153.1 (m)	—	141.7 (t)[d]	115.7 (q, ^3J = 4.5)	40.8 (qq)
2e	155.3 (s)	—	144.7 (t)[d]	117.1 (q, ^3J = 4.7)	53.9 (tm)
2f	154.5 (s)	—	142.4 (t)[d]	116.2 (m)	52.3 (tm)
3a	154.0 (m)	—	136.9 (m)	110.2 (d, ^1J = 186)	45.2 (qq)
3e	153.7 (d, ^3J = 8.2)	—	136.8 (m)	110.1 (d, ^1J = 186)	53.8 (tm)
4a	166.5 (d, ^3J = 5.7)	150.4 (s)	93.6 (m)	162.5 (dm, ^1J = 192)	37.1 (qm); 44.6 (qm)
4b[e]	165.9	154.2	89.7	162.7	37.7; 44.6
4e[e]	166.9	150.4	93.4	160.2	45.9; 54.5
7a	79.1 (m)	164.4 (m)	82.2 (dt, ^1J = 180; ^3J = 5)	165.0 (m)	41.5 (qq); 42.9 (qq)
7b	77.7 (m)	164.7 (m)	81.5 (dt, ^1J = 179; ^3J = 4.5)	166.7 (m)	41.5 (qq); 42.4 (qq)

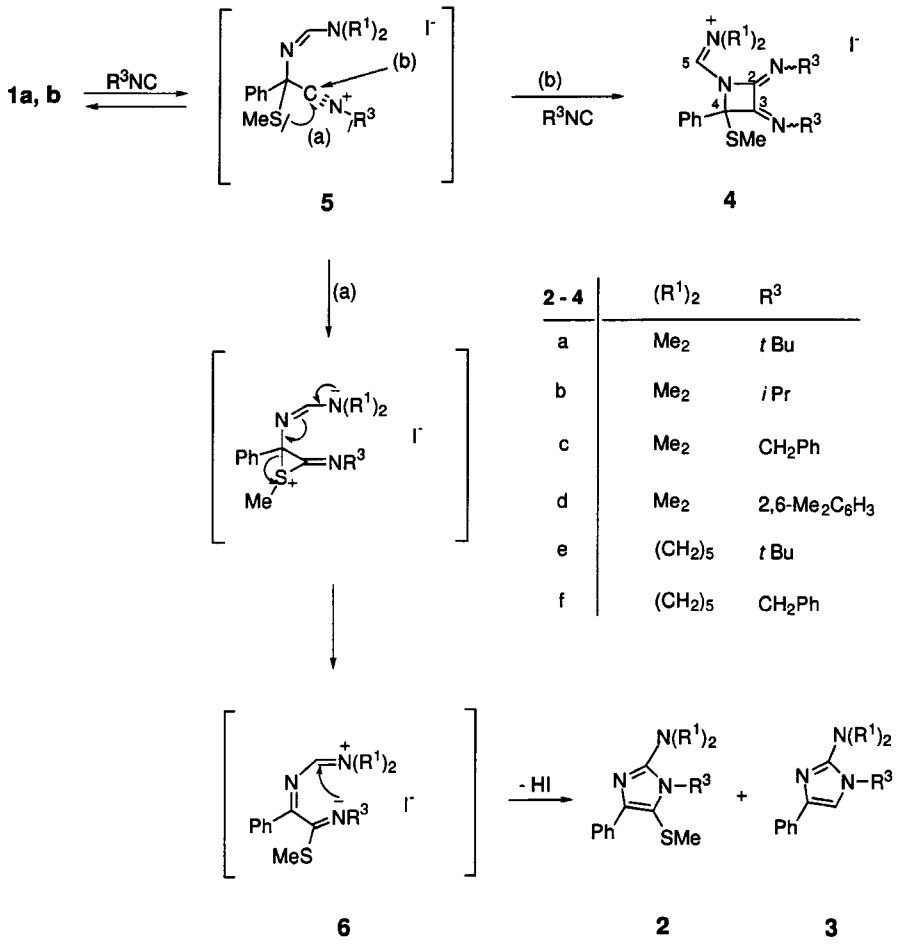
[a]δ (ppm) and J (Hz) in $CDCl_3$ solutions at 75.5 MHz.
[b]The ring atoms are numbered in such a way that the phenyl group is at C-2 in 2*H*-pyrrolium salts **7** and at C-4 in imidazoles **2, 3** and azetidines **4**.
[c]Nitrogen-connected atoms in the $N(R^1)_2$ substituent (**2, 3**: ^1J = 136 Hz, $^3J_{CNCH}$ = 4.5 Hz; **4, 7**: ^1J = 141 Hz, ^3J = 3 Hz).
[d]$^3J_{CCCH}$ = 3.9 Hz.
[e]The spectrum after protons decoupling was only recorded for this azetidine.

to be under a thermodynamic control [12b]. It was followed by the 1,2-migration of the methylthio group that appears to be a determining factor for the chemical pathway. We suggest that this rearrangement involves an episulfonium ion as illustrated in path (a) (Scheme 3). The resulting insertion product **6** readily undergoes the cyclization to the imidazolium salt **2,HI** through an intramolecular attack of the imino nitrogen atom on the iminium moiety.

Little information can be found in the literature concerning similar interconversions of isomeric carbenium ions (σ-complexes) via the generation and bridge opening of a thiiranium intermediate (π-complexe) [17].

Nucleophilic isocyanides are also able to induce the formation of 2,3-diimino azetidines **4** by the way of another addition to the nitrilium salt **5**. It is clear that the partition between the competitive paths (a) and (b) is dependent on the excess of isocyanide. The reaction (b) conforms to a [1 + 1 + 2] cycloaddition pattern across the C=N double bond of the starting salt **1**. Similar 1:2 cycloadditions giving rise to four-membered heterocyclic compounds have already been reported [5,11,18].

The protonated imidazole **2a,HI** precipitated from the reaction medium when the solvent was CH_3CN (entry 3, Table 1). It was isolated by filtration. Its decomposition was followed by ^{1}H NMR spec-



SCHEME 3

troscopy in $CDCl_3$ solution where we observed the slow formation of imidazole **3a** and dimethyldisulfide (δ 2.40 ppm). The mechanism of this reduction is rather doubtful and has not been elucidated.

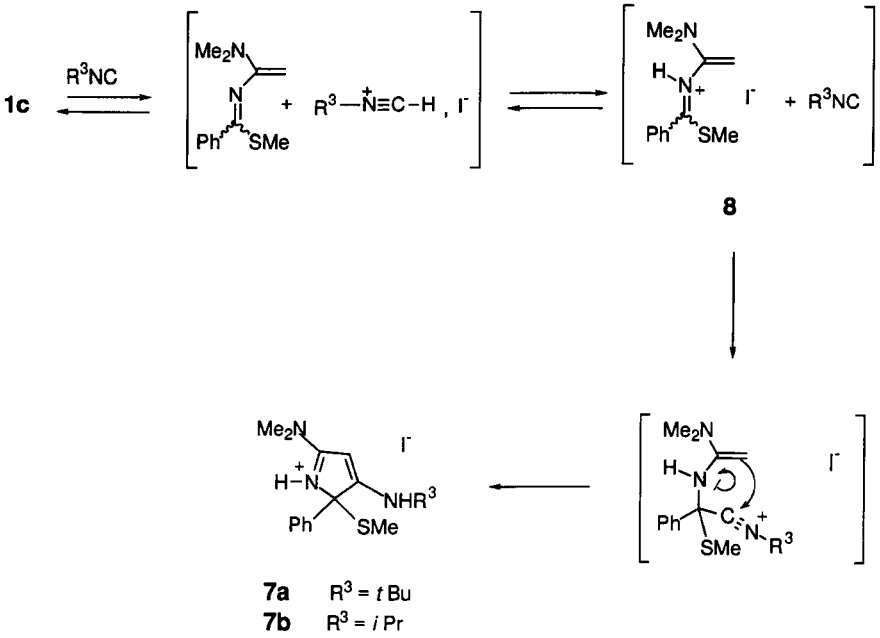
Reactions of Isocyanides with Amidinium Iodides **1c,d**

The acetamidinium salt **1c** exhibits a particular reactivity due to the acidity of the methyl group on the 1-position. Addition of isocyanides proved to be rather difficult. Prolonged reflux times in acetonitrile were required to give the 2*H*-pyrrolium iodides **7a,b** as the single products in the cases of *tert*-butyl and isopropyl isocyanides (entries 11, 12 in Table 1). Benzyl and 2,6-dimethylphenyl isocyanides are too poor basic species to react with salt **1c** even in refluxing CH_3CN. No conversion was evident and starting compounds were essentially recovered. Under the same conditions, the use of amidinium halide **1d** generated only intractable mixtures of several products.

The stable pyrrolium iodides **7a,b** were identified by their spectral properties. The presence of the NH functions was indicated in both their IR and ^1H NMR spectra. Additionally, the salt **7a** shows two intense absorption peaks about 1660 and 1610 cm^{-1} which may be assigned to conjugated five-membered ring iminium and C=C groups, respectively. The structure **7** was also supported by the ^{13}C NMR data reported in Table 2, in satisfying agreement with values in the literature for related 2*H*-pyrrolium salts [11].

The pyrrolium halides **7** could simply arise from the deprotonation of the starting salt **1c** [19] by isocyanides. The formation of the *N*-protonated 2-azabutadiene **8**, which is an intermediate in the process of Scheme 4, thus proceeds through the generation of a transient nitrilium iodide and a C to N proton transfer [20]. Addition of isocyanide and ring-closure processes are consistent with the previously reported reactivity of *N*-aryliminium species [18].

In conclusion, the reactivity of the amidinium iodides **1** toward isocyanides strongly differs with



SCHEME 4

the nature of the starting compounds. Functionalized imidazoles, azetidines, or 2*H*-pyrrolium salts were obtained according to the substitution pattern and experimental conditions. All these results improve the synthetic convenience of isocyanides in heterocyclic chemistry.

EXPERIMENTAL

General

NMR spectra. Bruker ARX 200 spectrometer (200 MHz for ^1H) and Bruker AM 300 WB spectrometer (75.5 MHz for ^{13}C) in $CDCl_3$ solution (internal standard Me_4Si).

HRMS. Centre Régional de Mesures Physiques de l'Ouest; Varian MAT 311 instrument, electron impact mode using a potential of 70 eV. With the exception of molecular-ion peaks, only mass-spectral fragments with relative intensities of 10% or more are reported.

IR spectra. Perkin-Elmer 1420 spectrophotometer, suspensions in nujol.

Elemental analyses. Analytical laboratory, CNRS.

Dichloromethane and acetonitrile were freshly distilled from P_2O_5. Na_2SO_4 was used to dry organic layers after extractions. Starting salts **1** were readily available from the methylation of corresponding *N*-thiobenzoylamidines [21], as previously described [12a].

Reactions of Formamidinium Iodides with Isocyanides

General Procedure. We prepared a solution of salt **1a,b** (5 mmol) in CH_2Cl_2 or CH_3CN (20 mL), and we added an excess of isocyanide. The conditions of the reaction are indicated in Table 1. The solvent was evaporated in vacuo. The dark-red residue was dissolved into tetrahydrofuran (THF) (20 mL) and treated with $N(CH_2CH_3)_3$ (10 mmol) to precipitate the triethylammonium iodide that was filtered off. The volatile materials were removed under reduced pressure. The residual substance was analyzed by ^1H NMR spectroscopy in order to monitor the progress and distribution of the reaction. It was dissolved in a mixture of diethyl ether (20 mL) and H_2O (80 mL).

After decantation, the aqueous solution was washed with diethyl ether (2 × 10 mL), saturated with NaCl and extracted with dichloromethane (2 × 15 mL). The CH_2Cl_2 extracts were concentrated to a reddish viscous oil. Trituration with petroleum ether gave the iminium salts **4a,b** as crystalline materials. The salt **4b** was obtained as an amorphous hemisolid.

The ethereal solutions were combined and evaporated to dryness. The imidazoles **2a,e** and **3a,e** were separated by a bulb-to-bulb distillation (170°/0.02 Torr) and purified by crystallization from petroleum ether. Other imidazoles **2** and **3** were purified by column chromatography on Merck 60 silica gel using diethyl ether/CH_2Cl_2 (9:1) as eluent.—Selected ^{13}C NMR data: see Table 2.

1-tert-Butyl-2-(dimethylamino)-5-(methylthio)-4-phenylimidazole **2a**. m.p. 77°C (petroleum ether). ^{1}H NMR δ 1.79 (s, 9H), 2.04 (s, 3H), 2.66 (s, 6H), 7.15–8.10 (m, 5H). MS calcd for $C_{16}H_{23}N_3S$ *m/z* 289.1613 $[M]^{\cdot+}$; found 289.1600; *m/z* (rel. int.): 289 (2), 243 (13), 233 (30), 232 (100), 218 (20), 187 (50), 186 (51), 172 (14). Anal. calcd.: C, 66.39; H, 8.01; N, 14.52; S, 11.08. Found: C, 66.22; H, 8.13; N, 14.41; S, 11.10.

2-(Dimethylamino)-1-isopropyl-5-(methylthio)-4-phenylimidazole **2b**. m.p. 90°C (petroleum ether). ^{1}H NMR δ 1.61 (d,J = 7 Hz, 6H), 2.16 (s, 3H), 2.87 (s, 6H), 4.77 (m, 1H), 7.20–8.20 (m, 5H). MS calcd for $C_{15}H_{21}N_3S$ *m/z* 275.1456 $[M]^{\cdot+}$, found 275.1450; *m/z* (rel. int.): 275 (39), 233 (14), 232 (100), 218 (14), 186 (11), 148 (16). Anal. calcd.: C, 65.45; H, 7.64; N, 15.27; S, 11.64. Found: C, 65.58; H, 7.82; N, 15.15; S, 11.44.

1-Benzyl-2-(dimethylamino)-5-(methylthio)-4-phenylimidazole **2c**. Oily product. ^{1}H NMR δ 1.92 (s, 3H), 2.76 (s, 6H), 5.22 (s, 2H), 7.00–8.25 (m, 10H). MS calcd for $C_{19}H_{21}N_3S$ *m/z* 323.1456 $[M]^{\cdot+}$, found 323.1460; *m/z* (rel. int.): 323 (9), 233 (14), 232 (100). Anal. calcd.: C, 70.59; H, 6.50; N, 13.00; S, 9.91. Found: C, 70.33; H, 6.84; N, 12.61; S, 10.04.

2-(Dimethylamino)-1-(2,6-dimethylphenyl)-5-(methylthio)-4-phenylimidazole **2d**. m.p. 114°C (diethyl ether/petroleum ether). IR 1595, 1540, 1525 cm^{-1}. ^{1}H NMR δ 1.85 (s, 3H), 2.05 (s, 6H), 2.65 (s, 6H), 7.00–8.30 (m, 8H). MS calcd for $C_{20}H_{23}N_3S$ *m/z* 337.1613 $[M]^{\cdot+}$, found 337.1610; *m/z* (rel. int.): 338 (17), 337 (70), 323 (22), 322 (100). Anal. calcd.: C, 71.22; H, 6.82; N, 12.46; S, 9.50. Found: C, 71.41; H, 6.72; N, 12.29; S, 9.69.

1-tert-Butyl-5-(methylthio)-4-phenyl-2-piperidinoimidazole **2e**. m.p. 108°C (petroleum ether). ^{1}H NMR δ 1.63 (br, 6H), 1.83 (s, 9H), 2.06 (s, 3H), 3.00 (br, 4H), 7.15–8.10 (m, 5H). MS calcd for $C_{19}H_{27}N_3S$ *m/z* 329.1926 $[M]^+$, found 329.1920; *m/z* (rel. int.): 329 (3), 273 (28), 272 (100), 258 (17), 252 (11). Anal. calcd.: C, 69.25; H, 8.26; N, 12.75. Found: C, 69.50; H, 8.16; N, 13.10.

1-Benzyl-5-(methylthio)-4-phenyl-2-piperidinoimidazole **2f**. m.p. 119°C (diethyl ether/petroleum ether). ^{1}H NMR δ 1.51 (br, 6H), 1.87 (s, 3H), 3.00 (br, 4H), 5.17 (s, 2H), 7.00–8.50 (m, 10H). MS calcd for $C_{22}H_{25}N_3S$ *m/z* 363.1769 $[M]^{\cdot+}$, found 363.1770; *m/z* (rel. int.): 363 (11), 273 (12), 272 (100).

1-tert-Butyl-2-(dimethylamino)-4-phenylimidazole **3a**. m.p. 108°C (petroleum ether). IR 1597 cm^{-1}. ^{1}H NMR δ 1.57 (s, 9H), 2.68 (s, 6H), 7.00 (s, 1H), 7.05–7.80 (m, 5H). MS calcd for $C_{15}H_{21}N_3$ *m/z* 243.1735 $[M]^{\cdot+}$, found 243.1730; *m/z* (rel. int.): 243 (18), 187 (100), 186 (60), 172 (20), 158 (26). Anal. calcd.: C, 74,03; H, 8,70; N, 17,27. Found: C, 73.80; H, 8.90; N, 17.33.

2-(Dimethylamino)-1-(2,6-dimethylphenyl)-4-phenylimidazole **3d**. m.p. 98°C (diethyl ether/petroleum ether). IR 1540, 1525 cm^{-1}. ^{1}H NMR δ 2.10 (s, 6H), 2.67 (s, 6H), 6.81 (s, 1H), 7.10–7.85 (m, 8H). MS calcd for $C_{19}H_{21}N_3$ *m/z* 291.1735 $[M]^{\cdot+}$, found 291.1760; *m/z* (rel. int.): 292 (21), 291 (100), 276 (24), 247 (30). Anal. calcd.: C, 78.35; H, 7.22; N, 14.43. Found: C, 77.92; H, 7.14; N, 14.46.

1-tert-Butyl-4-phenyl-2-piperidinoimidazole **3e**. m.p. 130°C (diethyl ether/petroleum ether). ^{1}H NMR δ 1.61 (s, 9H), 1.61 (br, 6H), 3.00 (br, 4H), 7.01 (s, 1H), 7.10–7.80 (m, 5H). MS calcd for $C_{18}H_{25}N_3$ *m/z* 283.2048 $[M]^{\cdot+}$, found 283.2050; *m/z* (rel. int.): 283 (29), 228 (12), 227 (72), 226(100), 198 (39).

[2,3-bis(tert-Butylimino)-4-(methylthio)-4-phenylazetidin-1-yl-methylene]dimethylammonium Iodide **4a**. m.p. 210°C (CH_2Cl_2/diethyl ether). IR 1700, 1592 cm^{-1}. ^{1}H NMR δ 1.06 (s, 9H), 1.43 (s, 9H), 2.33 (s, 3H), 3.40 (s, 3H), 3.60 (s, 3H), 7.35–7.65 (m, 5H), 9.50 (s, 1H). MS calcd. for $C_{21}H_{33}N_4S$ *m/z* 373.2426 $[M\text{-}I]^+$, found 373.2420; *m/z* (rel. int.): 373 (3), 269 (13), 214 (10), 213 (64), 212 (56), 197 (24), 183 (23), 128 (32), 41 (100). Anal. calcd. for $C_{21}H_{33}IN_4S$: C, 50.40; H, 6.60; I, 25.40; N, 11.20. Found: C, 50.23; H, 6.65; I, 25.68; N, 11.24.

[2,3-bis(Isopropylimino)-4-(methylthio)-4-phenylazetidin-1-yl-methylene]dimethylammonium Iodide **4b**. Dark-red viscous oil. ^{1}H NMR δ 0.85, 1.22, 1.36, 1.45 (4d, $J \sim 7$ Hz, 12H), 2.26 (s, 3H), 3.32 (m, 1H), 3.43 (s, 3H), 3.56 (s, 3H), 3.88 (m, 1H), 7.30–7.70 (m, 5H), 9.27 (s, 1H).

1-[2,3-bis(tert-Butylimino)4-(methylthio)-4-phenylazetidin-1-yl-methylene]piperidinium Iodide **4e**. m.p. 228°C (CH_2Cl_2/diethyl ether). ^{1}H NMR δ 1.09 (s, 9H), 1.44 (s, 9H), 1.86 (br, 6H), 2.36 (s, 3H), 3.97 (br, 4H), 7.25–7.75 (m, 5H), 9.52 (s, 1H). MS calcd. for $C_{23}H_{33}N_4$ *m/z* 365.2705 $[M\text{-HI-}SCH_3]^+$, found 365.2700; *m/z* (rel. int.): 365 (10), 310 (10), 309 (27), 272 (10), 254 (21), 253 (100), 252 (64), 251 (11), 223 (25). Anal. calcd. for $C_{24}H_{37}IN_4S$: C, 53.33; H, 6.85; N, 10.37; S, 5.93. Found: C, 53.18; H, 6.90; N, 10.45; S, 6.27.

Reactions of the Acetaminium Iodide **1c** *with Isocyanides*. A solution of salt **1c** (1.74 g, 5 mmol)

and isocyanide (15 mmol) in dry CH_3CN (20 mL) was maintained at reflux temperature until no more of the starting material **1c** could be detected (^{1}H NMR, entries 11,12 of Table 1). The reaction mixture was concentrated under reduced pressure. Trituration of the residue with diethyl ether gave the pyrrolium iodides **7a,b,** which were recrystallized from $(CH_3CH_2)_2O/CH_2Cl_2$ (9:1). For ^{13}C NMR data, see Table 2.

3-(tert-Butylamino)-5-(dimethylamino)-2-(methylthio)-2-phenyl-2H-pyrrolium Iodide **7a**. m.p. 212°C. IR 3333, 3150, 3095, 1665, 1610, 1510 cm^{-1}. ^{1}H NMR δ 1.37 (s, 9H), 1.95 (s, 3H), 3.27 (s, 3H), 3.41 (s, 3H), 5.20 (br, NH), 5.27 (d, br, 1H), 7.20–7.70 (m, 5H), 8.90 (br, NH). MS calcd. for $C_{17}H_{25}N_3S$ *m/z* 303.1769 $[M\text{-}HI]^{\cdot+}$, found 303.1760; *m/z* (rel. int.): 303 (0.2), 257 (44), 256 (32), 255 (52), 242 (12), 240 (44), 201 (18), 200 (37), 199 (20), 128 (60), 96 (100). Anal. calcd. for $C_{17}H_{26}IN_3S$: C, 47.33; H, 6.03; I, 29.47; N, 9.74. Found: C, 47.14; H, 6.12; I, 29.64; N, 9.79.

5-(Dimethylamino)-3-(isopropylamino)-2-(methylthio)-2-phenyl-2H-pyrrolium Iodide **7b**. m.p. 168°C. ^{1}H NMR δ 1.23 (d, J = 7 Hz, 3H), 1.27 (d, J = 7 Hz, 3H), 1.97 (s, 3H), 3.26 (s, 3H), 3.40 (s, 3H), 3.81 (m, 1H), 5.15 (d, br, J = 7.2 Hz, NH), 5.37 (d, br, 1H), 7.25–7.75 (m, 5H), 8.97 (br, NH). MS calcd. for $C_{16}H_{23}N_3S$ *m/z* 289.1613

$[M\text{-}HI]^{\cdot+}$, found 289.1630; *m/z* (rel. int.): 289 (0.7), 243 (19), 241 (27), 226 (13), 128 (11), 18 (100).

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