9 H), 0.82 (d, J = 6.9 Hz, 3 H), 0.00 (s, 6 H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 172.1, 80.3, 66.1, 49.7, 41.9, 40.1, 28.1, 25.9, 18.2, 11.1, −5.5. Anal. Calcd for $C_{16}H_{35}SiNO_3$: C, 60.52; H, 11.11; N, 4.41. Found: C, 60.70; H, 11.42; N, 4.49.

The corresponding 1-naphthamide displayed in 8:1 mixture of diastereomers according to HPLC: Pirkle column,[23] 10% DME in hexanes, 3.0 mL/min, retention times 30.27 and 31.63 min, second peak predominant).

Acknowledgment. J.M.H. thanks the National Science Foundation (Presidential Young Investigator Award, CHE-8857453), the Camille and Henry Dreyfus Foundation (New Faculty Grant), the Shell Oil Company Foundation (Shell Faculty Fellowship), the Merck Sharp & Dohme Research Laboratories, the Xerox Corporation, the Monsanto Company, and Hoffmann-La Roche for financial support.

Registry No. (±)-1, 102518-95-6; (*S*)-1, 97551-09-2; **2a** (isomer 1), 138877-95-9; **2a** (isomer 2), 138922-40-4; **2b** (isomer 1), 138877-96-0; **2b** (isomer 2), 138922-41-5; **3a**, 79218-15-8; **3b**, 87947-76-0; **3c**, 87947-77-1; **3d**, 138877-97-1; **3e**, 87776-18-9; **3f**, 138877-98-2; **3g**, 138877-99-3; **4a** (isomer 1), 138878-00-9; **4a** (isomer 2), 138922-42-6; (±)-**4a** (isomer 1), 138922-43-7; (±)-**4a** (isomer 2), 138922-44-8; **4b** (isomer 1), 138878-01-0; **4b** (isomer 2), 138922-45-9; **4d** (isomer 1), 138878-02-1; **4d** (isomer 2), 138922-46-0; (±)-**4d** (isomer 1), 138922-47-1; (±)-**4d** (isomer 2), 138922-48-2; **4e** (isomer 1), 138878-03-2; **4e** (isomer 2), 138922-49-3; (±)-**4e** (isomer 1), 138922-50-6; (±)-**4e** (isomer 2), 138922-51-7; **4f** (isomer 1), 138878-04-3; **4f** (isomer 2), 138922-52-8; **4g** (isomer 1), 138878-05-4; **4g** (isomer 2), 138922-53-9; **4h** (isomer 1), 138922-54-0; **4h** (isomer 2), 138922-55-1; **5a** (*R*-MTPA amide), 138878-07-6; **5b** (1-napthamide), 138878-08-7; **5d** (1-naphthamide), 138878-09-8; **5e**, 138878-10-1; **5f**, 138878-11-2; **5g**, 138878-12-3; **5g** 1-naphthamide derivative, 138878-13-4; **5h**, 138878-14-5; **5h** 1-naphthamide derivative, 138878-15-6; octanal, 124-13-0; *tert*-butyl (triphenylphosphoranylidene)acetate, 35000-38-5; 3-(*tert*-butyldimethylsiloxy)-1-propanol, 73842-99-6; (*S*)-methyl 3-hydroxy-2-methylpropanoate, 80657-57-4; (*S*)-methyl 2-methyl-3-(*tert*-butyldimethylsiloxy)propanoate, 93454-85-4; (*R*)-3-(*tert*-butyldimethylsiloxy)-2-methyl-1-propanol, 112057-64-4; (*E*)-methyl 2-decenoate, 7367-85-3; (*E*)-isopropyl 2-decenoate, 138878-06-5; 1-naphthoyl chloride, 879-18-5; 1,3-propanediol, 504-63-2; *tert*-butyldimethylsilyl chloride, 18162-48-6.

Three-Component Cyclocondensations. An Efficient Synthesis of 4-Amino-2-(methylthio)imidazolium Salts via the Reaction of Methyl Chlorothioimidates with Benzaldimines and Isocyanides. Autoxidation of the Imidazole Derivatives

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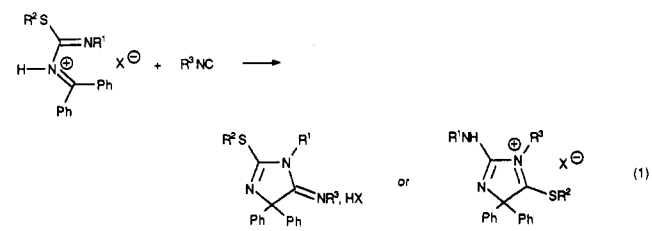
Treatment of imino chlorosulfides **1** with a mixture of benzaldimine and isocyanide provides 4-aminoimidazolium chlorides **5**. Presumably this reaction involves the *N*-imidoylbenzylideniminium chlorides **4** as transient intermediates. 1- and 3-*tert*-Butyl imidazolium salts **5** undergo fast isobutene elimination giving the corresponding imidazole and imidazoline hydrochlorides **10** and **13**. Compounds **13** autoxidize to afford 5-hydroxy derivatives **14** under atmospheric oxygen. The structural assignment of **14** has been confirmed by X-ray diffraction analysis. Under similar conditions, treatment of ketimines **17** with methyl chlorothioimidate **1** and isocyanide gives 2-thioxodiazolidines **19**.

The [1 + 4] cycloaddition of isocyanides to conjugated electron-deficient heterodienes is an effective means to a range of five-membered cyclic systems.[1,2] Also, it has been known for many years that isocyanides react readily with iminium salts.[3-5] To date, however, the use of isocyanides in a ring-closure reaction with N-unsaturated iminium salts has remained limited.[6] The acid-catalyzed conversions of arylidenanilines and *N*-acylimines to 3-aminoindoles[7] and 5-iminooxazolines[8] via [1 + 4] cycloadditions with *tert*-butyl isocyanide have been reported in the literature. Moreover, we have recently disclosed the successful protonation of 2-(alkylthio)- and 2-(arylthio)-1,3-diazabutadienes to give 5-iminoimidazolines or unstable imidazolium salts, upon the addition of isocyanides (eq 1).[9]



(1)

There are several literature reports concerning the participation of unsaturated iminium species as 4π components in hetero-Diels–Alder reactions.[10-13] For example,

(1) See, for instance: Foucaud, A.; Razorilalana-Rabearivony, C.; Loukakou, E.; Person, H. *J. Org. Chem.* **1983**, *48*, 3639. Morel, G.; Marchand, E.; Foucaud, A. *J. Org. Chem.* **1985**, *50*, 771; **1990**, *55*, 1721 and references cited therein.

(2) See also the related reaction of tri-*tert*-butylazete with isocyanides to yield 2- and 3-imino-substituted 2*H*- and 3*H*-pyrrole derivatives: Hees, U.; Schneider, J.; Wagner, O.; Regitz, M. *Synthesis* **1990**, 834.

(3) Gokel, G.; Lüdke, G.; Ugi, I. In *Isonitrile Chemistry*; Ugi, I., Ed.; Academic Press: New York, 1971; Chapter 8, p 145.

(4) Shono, T.; Matsumura, Y.; Tsubata, K. *Tetrahedron Lett.* **1981**, *22*, 2411.

(5) Al-Talib, M.; Jibril, I.; Jochims, J. C.; Huttner, G. *Tetrahedron* **1985**, *41*, 527.

(6) Moderhack, D. *Synthesis* **1985**, 1083.

(7) Deyrup, J. A.; Vestling, M. M.; Hagan, W. V.; Yun, H. Y. *Tetrahedron* **1969**, *25*, 1467.

(8) Deyrup, J. A.; Killion, K. K. *J. Heterocycl. Chem.* **1972**, *9*, 1045.

(9) Morel, G.; Marchand, E.; Foucaud, A.; Toupet, L. *J. Org. Chem.* **1989**, *54*, 1185.

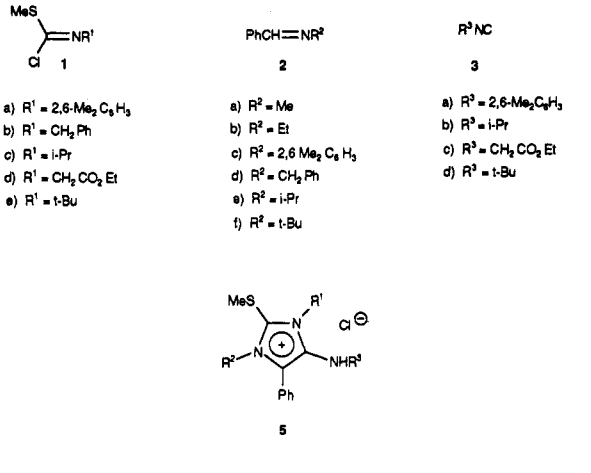
(10) Böhme, H.; Haake, M. Methyleniminium Salts. In *Iminium Salts in Organic Chemistry*; Böhme, H., Viehe, H. G., Eds.; John Wiley: New York, 1976; Part 1, p 107.

(11) Zaugg, H. E. *Synthesis* **1984**, 181.

(12) Boger, D. L.; Weinreb, S. M. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: London, 1987; Chapter 9, p 278.

0022-3263/92/1957-2121$03.00/0

Chart I



	R¹	R²	R³		R¹	R²	R³
a)	2,6-Me_2 C_6 H_3	Me	t-Bu	i)	CH_2CO_2Et	Me	t-Bu
b)	CH_2 Ph	Me	t-Bu	j)	i-Pr	t-Bu	i-Pr
c)	i-Pr	Me	2,6-Me_2 C_6 H_3	k)	t-Bu	Me	t-Bu
d)	i-Pr	Me	i-Pr	l)	t-Bu	Et	t-Bu
e)	i-Pr	Me	CH_2CO_2 Et	m)	t-Bu	2,6-Me_2 C_6 H_3	t-Bu
f)	i-Pr	Me	t-Bu	n)	t-Bu	CH_2Ph	t-Bu
g)	i-Pr	Et	t-Bu	o)	t-Bu	i-Pr	t-Bu
h)	i-Pr	2,6-Me_2 C_6 H_3	i-Pr	p)	t-Bu	t-Bu	t-Bu

the *N*-acyliminium cation that is generated in situ by treatment of benzylidenemethylamine with methyl chloroformate has been shown to be a useful partner in a [2 + 4] cycloaddition reaction with the dienophile 1,3-cyclooctadiene.[14]

Therefore, we were intrigued by the possibility that the *N*-imidoylbenzylideniminium salts **4** could be produced via the addition of methyl chlorothioimidates **1** to benzaldimines **2** and then trapped by isocyanides **3**. The present paper describes the results of this investigation and is an extension of our earlier study on the cyclization of protonated diazabutadienes.[9]

Results and Discussion

A number of 4-amino-2-(methylthio)imidazolium chlorides **5**, which are not readily available by other methods, have been obtained from a mixture of compounds **1**, **2**, and **3**. Two series of products **5** are distinguished according to the nature of the R^1 and R^2 substituents (Chart I).

Preparation of Imidazolium Chlorides 5a–i (R^1 and $R^2 \neq t$-Bu). An equimolar mixture of compounds **1a–d** and **2a–c** was treated with 2 equiv of representative isocyanides **3a–d** to produce stable imidazolium salts **5a–i** in good to moderate yields (Table I). The reactions were carried out in 2M $CHCl_3$ solution at rt (method A) or else in a more dilute (0.4 M) refluxing ether solution (method B). Most of the crude salts **5** were isolated as yellowish viscous oils or amorphous semisolids which were purified with difficulty and showed indeterminate melting points (except **5c–e, h**).

The rate of the reaction sharply decreases when the nitrogen atom of the starting product **1** or **2** is hindered by a bulky 2,6-dimethylphenyl group (compare entries 1 and 10, respectively, with entries 2 and 5, Table I). These cyclocondensations were most effectively conducted in a concd medium by method A (for instance, compare entries 10 and 11, 2 and 3). Moreover, the reaction of **2a** and **3d** with imidoyl chloride **1d**, which possesses an electron-withdrawing ester moiety, was very difficult under similar conditions and gave imidazolium chloride **5i** in only poor yield (entry 12).

Structural assignment of the salts **5** was based on ^1H and ^{13}C NMR spectral data. The ^1H NMR spectra showed a broad N–H resonance at 3–6 ppm. Selected ^{13}C NMR chemical shifts and corresponding multiplicities are given in Table II. The atom C-2 bearing the methylthio function and the quaternary aromatic C of the 5-phenyl group appeared at high field (δ = 132–139 ppm and 125–127 ppm, respectively). In most cases, the multiplicity of the signal attributed to the amino-substituted C-4 (δ = 135–139 ppm) proved to be conclusive in establishing structure **5**. For example, this carbon exhibited a singlet for **5a**, a triplet for **5b**, and a doublet for **5f**, owing to the coupling with the proton on the N-3.

Salts **5** were further characterized by their mass spectra, as described in the experimental section. Thioxoimidazolines that derived from cleavage of the methylthio substituent were generally the parent radical ion (MeCl eliminates by nucleophilic attack of the chloride ion). In some cases, the mesoionic imidazoles produced by the loss of HCl were also apparent.

Table I. Reactions of Methyl Chlorothioimidates 1a–d with Imines 2a–c and 15a,b in the Presence of Isocyanides 3. Preparation of Imidazolium Salts 5a–i or 16a,b

entry	educts			reactn condns[a] method	reactn condns[a] time[b]	product yield,[c] (%)	
1	**1a**	**2a**	**3d**	A	5 d	58	**5a**
2	**1b**	**2a**	**3d**	A	24 h	73	**5b**
3	**1b**	**2a**	**3d**	B	49 h	47	**5b**
4	**1c**	**2a**	**3a**	B	57 h	43	**5c**
5	**1c**	**2a**	**3b**	A	17 h	70	**5d**
6	**1c**	**2a**	**3b**	B	28 h	56	**5d**
7	**1c**	**2a**	**3c**	A	65 h	50	**5e**
8	**1c**	**2a**	**3d**	B	54 h	61	**5f**
9	**1c**	**2b**	**3d**	B	54 h	45	**5g**
10	**1c**	**2c**	**3b**	A	60 h	76	**5h**
11	**1c**	**2c**	**3b**	B	5 d	55	**5h**
12	**1d**	**2a**	**3d**	A	26 d	25	**5i**
13	**1c**	**15a**	**3b**	A	7 d	66	**16a**
14	**1c**	**15b**	**3b**	A	15 h	62	**16b**

[a] The reactions were conducted with equimolar quantities of **1**, **2**, or **15** (method A: 2 M, $CHCl_3$, 20 °C; method B: 0.4 M, refluxing Et_2O) and a 2-fold excess of isocyanide **3**. [b] Time required for the entire conversion of starting compounds **1**, **2**, or **15**. [c] Isolated product yield.

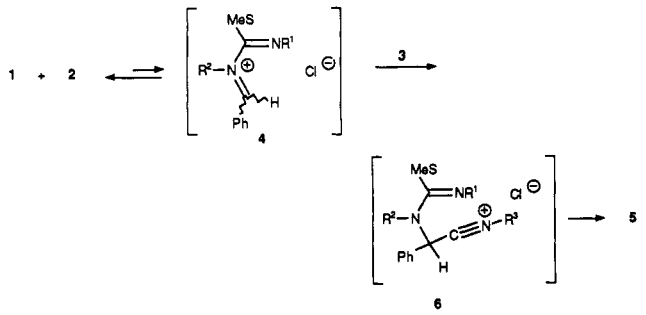
Table II. Selected ^{13}C NMR Chemical Shifts at 75.469 MHz for Some 4-Amino-2-(methylthio)imidazolium Chlorides 5 and 16[a] (mult) (*J*, Hz)

no.	C-2 (m)	C-4[b]	C-5 (m)	C_{arom}[c] (t)
5a	136.6	135.8 s	131.0	126.4
5b	136.3	135.9 t (3.7)	131.6	126.4
5c	138.8	136.7 d (3.2)	132.2	124.9
5d	133.1	137.3 d (3.5)[d]	126.5	126.1
5e	132.1	137.8 q (4.4)	121.5	125.7
5f	134.6	135.1 d (3.2)	132.6	126.9
5g	133.5	136.2 d (3.3)	131.8	127.0
5h	133.2	138.6 d (3.4)	131.9	125.6
5i	137.7	135.8 br	131.8	126.4
5k	136.5	137.3 s	133.7	127.1
16a	148.9	139.1 d (4)	133.5	133.7
16b	135.7	133.1 d (3.9)	128.6	

[a] δ in $CDCl_3$ solutions. [b] Listing multiplicities were the results of possible coupling with the protons of the R^1 groups ($^3J_{(CNCH)}$). The coupling with the H atoms of the R^3 group was not observed according to a very low coupling constant, except for **5e** ($^3J_{(CNCH)}$ = 4.4 Hz). [c] Quat arom C of the 5-phenyl group. [d] This multiplicity was confirmed by a heteronuclear decoupling experiment: irradiation of the isopropylic H atom at δ 5.40 (R^1) caused the C-4 signal to collapse to a singlet.

(13) Weinreb, S. M.; Scola, P. M. *Chem. Rev.* **1989**, *89*, 1525.
(14) Kahn, M.; Chen, B. *Tetrahedron Lett.* **1987**, *28*, 1623.

Scheme I



Scheme II

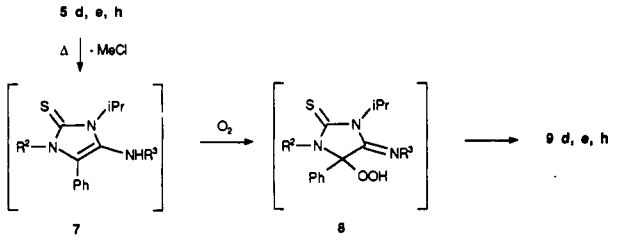
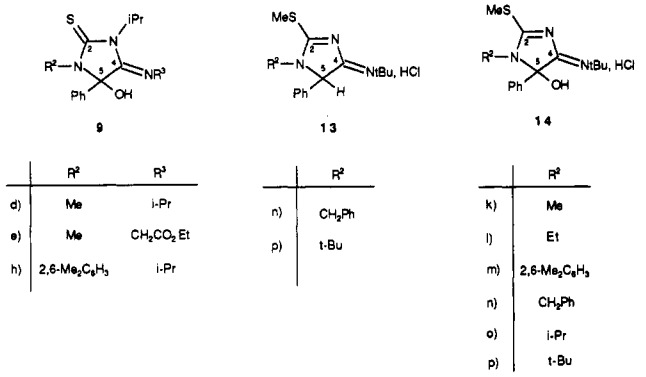


Chart II



The obtention of salts **5** could be explained by the formation of the *N*-imidoylbenzylideniminium chlorides **4** (Scheme I). The highly electrophilic, unstable cationic species **4** are trapped in situ by nucleophilic isocyanides.[15] The resulting nitrilium chlorides **6** produce **5** via the intramolecular attack of the imidoyl nitrogen atom and subsequent tautomerism. It is noteworthy that the sulfur atom does not take part in the cyclization process as has been observed in closely related cases.[9]

Imidazolium chlorides **5a–i** exhibited good stability at room temperature. Some were briefly thermolyzed in refluxing toluene to afford the corresponding 5-hydroxy-2-thioxo-1,3-diazolidines **9** (Chart II). Structure **9** was suggested by the presence of a strong O–H stretching band in the infrared spectra of the isolated compounds. This structure was confirmed by mass and NMR spectral data (see the experimental section and Table III). It probably resulted from a methyl chloride elimination followed by autoxidation of the thioxoimidazolines **7** by atmospheric O_2 (Scheme II). Although the details of this oxidation process are not known, the postulated formation of intermediate hydroperoxides **8** has some literature precedent in related cyclic[7,8,16,17] and acyclic[18] systems.

(15) Benzylideniminium salts **4** were extremely hygroscopic and could not be isolated. Without isocyanide, a mixture of compounds **1** and **2** gave benzaldehyde and the corresponding N,N'-disubstituted isothiourea hydrochloride.

(16) Schumann, D.; Naumann, A.; Wirtz, K. P. *Chem. Ber.* **1979**, *112*, 734.

(17) Burger, K.; Tremmel, S. *Chem. Ztg.* **1982**, *106*, 302.

Table III. Selected ^{13}C NMR Chemical Shifts at 75.469 MHz for the 4-Iminoimidazole Derivatives 9, 13, and 14[a] (mult) (*J*, Hz)

no.	C-2	C-4	C-5 (br)	C_{arom}[b]
9d	181.0 m	152.4 t (6.0)[c]	86.2	137.1
9e	181.2 m	159.1 q (6.7)[c]	86.7	136.0
9h	180.9 d (4.7)[c]	152.3 t (5.5)[c]	88.8	136.9
13n	183.5 m	177.6 d (4.4)[d]	72.4 d (^1J = 150)	132.6
13p	183.7 m	177.5 d (4.5)[d]	73.6 d (^1J = 153)	134.7
14k	183.7 m	179.8 s	97.5	134.9
14l	183.2 m	179.8 s	97.9	135.4
14m	184.5 q (4.5)[e]	180.2 s	100.4	136.4
14n	184.6 m	179.5 s	98.0	135.4
14o	182.2 m	179.3 s	98.7	135.4
14p	184.7 q (4.5)[e]	178.4 s	100.6	136.4

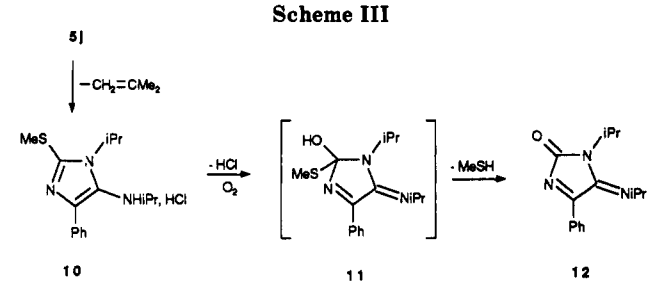
[a] δ in $CDCl_3$ solutions. [b] Quat arom C of the 5-phenyl group, multiplet owing to the coupling $^2J_{(CCH)}$ or $^3J_{(CCOH)}$, except for **14m**: triplet, $^3J_{(CCCH)}$ = 7.6 Hz. [c] $^3J_{(CNCH)}$. [d] $^2J_{(CCH)}$. [e] $^3J_{(CSCH)}$.

Table IV. Reactions of Imidoyl Chloride 1e with Benzaldimines 2a–f and *tert*-Butyl Isocyanide 3d. Preparation of Imidazolium Salts 5k–o or Imidazoline Hydrochlorides 13n,p and 14k–p

		reactn condns[a]		product yields,[b] (%)		
entry	R^2 (imine)	method	time (h)	**5**	**13**	**14**
1	Me (**2a**)	C	15	78 **5k**		
2	Me (**2a**)	C	28	54 **5k**		9 **14k**[c]
3	Et (**2b**)	C	18	20 **5l**		31 **14l**
4	Et (**2b**)	C	41			55 **14l**
5	2,6-$Me_2C_6H_3$ (**2c**)	A	31	*d*		45 **14m**
6	CH_2Ph (**2d**)	C	50	*d*	36 **13n**	18 **14n**
7	*i*-Pr (**2e**)	C	27	*d*		42 **14o**
8	*t*-Bu (**2f**)	C	120	*e*	66 **13p**	4 **14p**

[a] The reactions were conducted at rt with equimolar quantities of **1e**, **2** (method A: 2 M, $CHCl_3$; method C: 0.4 M, CCl_4) and a 2-fold excess of isocyanide **3d**. [b] Isolated product yields. [c] **14k** was only obtained (55% yield) when this mixture was refluxed in CCl_4 for 1 h under atm O_2. [d] The corresponding salt **5** was observed in the ^1H NMR spectra of the crude mixture by the use of limited reaction time. [e] Salt **5p** was never observed in the crude mixture using intermediate reaction times (24, 48 h). Starting products **1e** and **2f** were only accompanied with imidazoline hydrochloride **13p**.

Scheme III

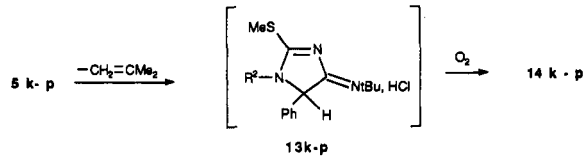


Preparation and Chemical Degradation of Imidazolium Chlorides 5j–p (R^1 or R^2 = *t*-Bu). The benzylidene-*tert*-butylamine **2f** has been added to methyl chlorothioimidate **1c** and isocyanide **3b** under the conditions of method A. After 20 h, the ^1H NMR spectrum of the crude product indicated the formation of salt **5j** in admixture with starting compounds and small amounts of the new imidazole derivative **10** (Scheme III). **5j** could not be isolated. By lengthening the reaction time (5d) **5j** was entirely decomposed to **10**, which was readily purified as the hydrochloride salt (72% yield).

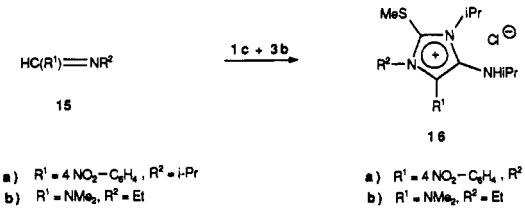
The obtention of HCl adduct **10** is explained by an isobutene elimination. A like pathway dominates the chemistry of the *N*-*tert*-butyltriazinium[9] and -nitrilium[5,19]

(18) Hawkins, E. G. E. *J. Chem. Soc. (C)* **1971**, 160.

Scheme IV



Scheme V



salts, owing to the stabilization of the tertiary carbenium ion. It is assumed that the heterolytic cleavage of the N–C bond is followed by a proton transfer to give isobutene and protonated product.[5]

Hydrochloride salt **10** did not show oxygen sensitivity. In contrast, after treatment with NEt_3, the corresponding imidazole was slowly transformed into the imidazolinone **12** on standing in air at rt. This autoxidation process presumably takes place via the thiohemiketal **11** (Scheme III).

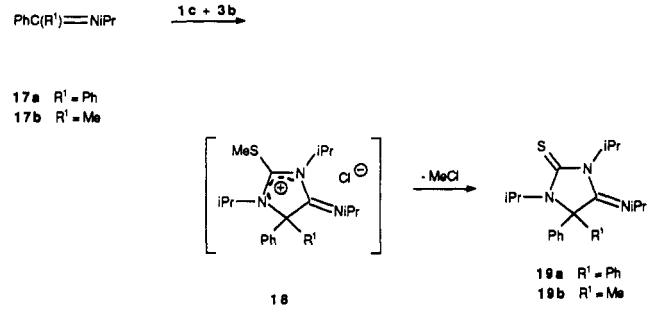
Similar reactions occurred when a 2-fold excess of isocyanide **3d** was added at rt to a mixture of the *N-tert*-butylimidoyl chloride **1e** and benzaldimine **2a–f** (Table IV). Salts **5k–o** were observed in ^1H NMR spectra of the crude products but, as before, a fast degradation precluded isolation of these initial adducts (except **5k** and **5l** which partially precipitated from the reaction medium). In solution, the *N-tert*-butylimidazolium salts **5k–p** rapidly gave the imidazole hydrochlorides **13** via an isobutene elimination. Compounds **13** were generally unstable toward autoxidation in the reaction medium and produced the 5-hydroxy derivatives **14** (Scheme IV). Only **13n,p** could be isolated and purified before their oxidation to the corresponding imidazoline hydrochlorides **14n,p** (Chart II). **5p** was never observed. In this case, a spontaneous loss of the 3-*t*-Bu group to afford **13p** was consistent with the subsequent conversion to **14p**. The alternative loss of the 1-*t*-Bu group would have furnished the 5-amino-4-phenylimidazole derivative which presumably would have autoxidized to the corresponding imidazolinone as previously reported for **10**. Furthermore, ^1H and ^{13}C NMR data for **13p** agreed with those observed for **13n** and were significantly different from those reported for **10**.

Structures **12**, **13**, and **14** have been established by the usual spectroscopic means. Some ^{13}C NMR chemical shifts are listed in Table III for the HCl adducts **13** and **14**. Mass spectra of **14** always showed the strong parent ion ($M^{\bullet+}$) after HCl elimination and $PhCO^+$ as the major ion. The structure **14k** was confirmed by a single-crystal X-ray analysis (supplementary material).

Preparation of Imidazolium Chlorides 16a,b and 2-Thioxodiazolidines 19a,b. In order to test the versatility of this three-component condensation, we have extended the procedure to some other aldimine, amidine, and ketimine derivatives, which were treated with a mixture of compounds **1c** and **3b**. The reactions were conducted in 2 M $CHCl_3$ solution at rt (method A).

Extension to imines **15a, b** that carry either an electron-withdrawing or an electron-donating R^1 substituent

Scheme VI



provided the imidazolium salts **16a,b** in satisfactory yields (Scheme V; Table I, entries 13 and 14). Attempts to use **17a,b** in a similar manner led exclusively to the 4-imino-2-thioxo-1,3-diazolidines **19a,b**. This result can be rationalized assuming the fast demethylation of the in situ generated imidazolinium chlorides **18** (Scheme VI).

In summary, a new methodology has been developed that brings together three components via the [1 + 4] cycloaddition of isocyanides with intermediate *N*-imidoyliminium chlorides **4**. Thus, 4-aminoimidazolium salts **5** and **16** could be obtained conveniently. Similar heterocycles and corresponding mesoionic 4-aminides–imidazolium have been rarely described in the literature.[20-22] The present method is a very useful and versatile entry to this ring system.

We have noted that salts **5** that did not bear the *tert*-butyl group on an endocyclic nitrogen atom exhibited good stability. In contrast, we have pointed out the fast degradation of the imidazolium chlorides **5j–p** (R^1 or R^2 = *t*-Bu) and the facile oxidation of the imidazole derivatives under atmospheric O_2.

This efficient three-component cyclocondensation suggests much potential for other useful reactions between iminochlorosulfides **1**, isocyanides **3** and various nucleophilic compounds. An analogous reaction that provides a new route to thiazolium salts is under investigation.

Experimental Section

Melting points are uncorrected. ^1H NMR (80 MHz) and ^{13}C NMR (75.5 MHz) spectra were taken in $CDCl_3$ solutions. HRMS were obtained from the Centre Régional de Mesures Physiques de l'Ouest. Infrared spectra were recorded as suspensions in Nujol. Elemental analyses were performed by the analytical laboratory Centre National de la Recherche Scientifique. X-ray crystallographic analysis was performed by L. Toupet, Groupe de Physique Cristalline, Université de Rennes I.

Imino chloro sulfides **1** were easily accessible as previously described[9,23] from the insertion reaction of isocyanides R^1NC into the S–Cl bond of methanesulfenyl chloride, in dry Et_2O, $CHCl_3$, or CCl_4 solution. Starting imines were prepared according to the following known procedures: condensation of primary amines R^2NH_2 with benzaldehyde or 4-nitrobenzaldehyde on Al_2O_3 without a solvent,[24] for **2** and **15a**; condensation of ethylamine with the dimethylformamide dimethyl acetal[25] in CH_2Cl_2 solution, for the formamidine **15b**; condensation of isopropylamine with

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(20) Newton, C. G.; Ramsden, C. A. *Tetrahedron* **1982**, *38*, 2965.

(21) Potts, K. T. Mesoionic Ring Systems. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; John Wiley: New York, 1984; Chapter 8, p 1.

(22) A few 4-aminoimidazolium halides have been prepared from the reaction of *N*-methyl(or *N*-phenyl)-*N*-(*N'*-phenylbenzimidoyl)aminoacetonitriles with acylating reagents or dry hydrogen chloride: Potts, K. T.; Husain, S. *J. Org. Chem.* **1971**, *36*, 3368. Chinone, A.; Sato, S.; Ohta, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 826.

(23) Morel, G.; Marchand, E.; Nguyen Thi, K. H.; Foucaud, A. *Tetrahedron* **1984**, *40*, 1075. Morel, G.; Marchand, E.; Haquin, C.; Foucaud, A. *J. Org. Chem.* **1986**, *51*, 4043.

(24) Texier-Boullet, F. *Synthesis* **1985**, 679.

(25) Abdulla, R. F.; Brinkmeyer, R. S. *Tetrahedron* **1979**, *35*, 1675.

benzophenone or acetophenone using $TiCl_4$ as catalyst in benzene solution,[26] for ketimines **17a,b**.

Preparation of Imidazolium Chlorides 5a–i and 16a,b. Isocyanide **3** (20 mmol) and appropriate benzaldimine or formamidine **2**, **15** (10 mmol) were dissolved in anhyd $CHCl_3$ (2 mL, procedure A) or Et_2O (10 mL, procedure B) then added to a solution of imidoyl chloride **1a–d** (10 mmol) in $CHCl_3$ (3 mL) or Et_2O (15 mL), according to A or B. The reaction mixture was stirred at 20 °C (method A) or refluxed (method B) under N_2 for the time indicated in Table I. Salts **5c,h** that slowly precipitated as yellowish solids from the etheral solution were filtered and washed with dry Et_2O (entries 4 and 11, Table I). The solvent was removed under reduced pressure. The brownish residual syrup was triturated with Et_2O, and the insoluble portion was dissolved in H_2O (40 mL). The aqueous solution was washed with Et_2O (2 × 10 mL) and saturated with NaCl and finally extracted with CH_2Cl_2 (3 × 10 mL). The CH_2Cl_2 extracts were dried over Na_2SO_4 and concd to a yellowish viscous oil. In some cases, trituration of the residue with THF gave crystalline material. Salts **5d,e,h** and **16a** were thus collected by filtration (entries 5–7, 10, 13) and then purified by recrystallization from CH_2Cl_2/Et_2O (1:1). Other salts **5** and **16b** were obtained as amorphous semisolids. ^1H NMR spectrometry confirmed that imidazolium chlorides **5a,b,f,g,i** and **16b** were greatly preponderant in this final product, along with some unidentified products (<5%). Neither bulb-to-bulb distillation nor silica gel column chromatography was effective to purify these crude salts which could be used for further reactions without additional purification (yields and ^{13}C NMR spectra, see Tables I and II).

4-(*tert*-Butylamino)-3-(2,6-dimethylphenyl)-1-methyl-2-(methylthio)-5-phenylimidazolium chloride (5a): ^1H NMR δ 0.67 (s, 9 H), 2.25 (s, 6 H), 2.53 (s, 3 H), 3.15 (br, NH), 4.00 (s, 3 H); MS calcd for $C_{22}H_{27}N_3S$, m/z 365.1926 (MeCl elim), found 365.1924; m/z (rel int) 365 (76), 309 (43), 277 (22), 276 (100), 145 (22), 118 (67).

3-Benzyl-4-(*tert*-butylamino)-1-methyl-2-(methylthio)-5-phenylimidazolium chloride (5b): ^1H NMR δ 0.80 (s, 9 H), 2.41 (s, 3 H), 3.85 (s, 3 H). 4.20 (br, NH), 5.67 (s, 2 H); MS calcd for $C_{21}H_{25}N_3S$, m/z 351.1769 (MeCl elim), found 351.1760; m/z (rel int) 351 (38), 295 (22), 209 (12), 204 (56), 145 (20), 118 (100).

4-[(2,6-Dimethylphenyl)amino]-1-methyl-2-(methylthio)-5-phenyl-3-isopropylimidazolium chloride (5c): mp 232 °C dec (CH_2Cl_2/Et_2O); ^1H NMR δ 1.77 (d, J = 7 Hz, 6 H), 2.02 (s, 6 H), 2.57 (s, 3 H), 3.56 (s, 3 H), 5.67 (m, 1 H), 6.55 (s, 3 H), 8.30 (br, NH); MS calcd for $C_{22}H_{27}N_3S$, m/z 365.1926 (HCl elim), found 365.1898; m/z (rel int) 365 (7), 351 (31), 309 (24), 276 (15), 235 (11), 221 (21), 220 (13), 130 (12), 120 (16), 119 (11), 118 (100); IR 3100, 1634, 1598 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_3SCl$: C, 65.75; H, 6.97; N, 10.46; S, 7.97; Cl, 8.84. Found: C, 65.41; H, 6.99; N, 10.44; S, 7.96; Cl, 9.08.

1-Methyl-2-(methylthio)-5-phenyl-3-isopropyl-4-(isopropylamino)imidazolium chloride (5d): mp 194 °C dec (CH_2Cl_2/Et_2O); ^1H NMR δ 0.91 (d, J = 7 Hz, 6 H), 1.74 (d, J = 7 Hz, 6 H), 2.67 (s, 3 H), 2.92 (m, 1 H), 3.80 (s, 3 H), 4.95 (d, br, J = 6 Hz, NH), 5.32 (m, 1 H); MS calcd for $C_{16}H_{23}N_3S$, m/z 289.1613 (MeCl elim), found 289.1626; m/z (rel int) 289 (16), 232 (9), 159 (11), 118 (40), 117 (10), 105 (32), 86 (28), 84 (45), 77 (18), 52 (30), 50 (100). Anal. Calcd for $C_{17}H_{26}N_3SCl$: C, 60.03; H, 7.65; N, 12.37, S, 9.42; Cl, 10.45. Found: C, 60.12; H, 7.78; N, 12.09; S, 9.39; Cl, 10.81.

4-[[(Ethoxycarbonyl)methyl]amino]-1-methyl-2-(methylthio)-5-phenyl-3-isopropylimidazolium chloride (5e): mp 150 °C dec (CH_2Cl_2/Et_2O); ^1H NMR δ 1.11 (t, J = 7.1 Hz, 3 H), 1.75 (d, J = 7 Hz, 6 H), 2.60 (s, 3 H), 3.52 (d, J = 5.6 Hz, 2 H), 3.71 (s, 3 H), 3.97 (q, J = 7.1 Hz, 2 H), 5.35 (m, 1 H), 5.77 (br, NH), 7.50 (s, 5 H); MS calcd for $C_{17}H_{23}N_3O_2S$, m/z 333.1511 (MeCl elim), found 333.1513; calcd for $C_{14}H_{17}N_3O_2S$, m/z 291.1041 [MeCl elim and $(M - MeCH{=}CH_2)^{\bullet+}$], found 291.1048; m/z (rel int) 333 (100), 291 (85), 260 (18), 246 (12), 218 (49), 203 (37), 190 (28), 118 (67).

4-(*tert*-Butylamino)-1-methyl-2-(methylthio)-5-phenyl-3-isopropylimidazolium chloride (5f): ^1H NMR δ 0.87 (s, 9 H), 1.72 (d, J = 7 Hz, 6 H), 2.75 (s, 3 H), 3.87 (s, 3 H), 4.37 (br, NH), 5.37 (m, 1 H); MS calcd for $C_{17}H_{25}N_3S$, m/z 303.1769 (MeCl elim), found 303.1785; m/z (rel int) 303 (58), 247 (41), 246 (49), 209 (24), 208 (18), 206 (11), 205 (84), 204 (18), 145 (34), 131 (12), 120 (15), 119 (12), 118 (100).

4-(*tert*-Butylamino)-1-ethyl-2-(methylthio)-5-phenyl-3-isopropylimidazolium chloride (5g): ^1H NMR δ 0.87 (s, 9 H), 1.17 (t, J = 7 Hz, 3 H), 1.76 (d, J = 7 Hz, 6 H), 2.74 (s, 3 H), 3.12 (br, NH), 4.40 (q, J = 7 Hz, 2 H), 5.40 (m, 1 H): MS calcd for $C_{18}H_{27}N_3S$, m/z 317.1926 (MeCl elim), found 317.1916; m/z (rel int) 317 (98), 261 (61), 260 (87), 220 (11), 219 (100).

1-(2,6-Dimethylphenyl)-2-(methylthio)-5-phenyl-3-isopropyl-4-(isopropylamino)imidazolium chloride (5h): mp 161 °C dec (CH_2Cl_2/Et_2O) (crystallized with H_2O); ^1H NMR δ 1.01 (d, J = 7 Hz, 6 H), 1.87 (d, 6 H), 2.00 (s, 6 H), 2.22 (s, 3 H), 3.02 (m, 1 H), 5.70 (m, 1 H), 6.35 (br, NH); IR 3120, 1610, 1584 cm^{-1}. Anal. Calcd for $C_{24}H_{34}N_3OSCl$: C, 64.35; H, 7.59; N, 9.38; S, 7.15; Cl, 7.93. Found: C, 64.48; H, 7.88; N. 9.56; S, 7.10; Cl, 7.98.

4-(*tert*-Butylamino)-3-[(ethoxycarbonyl)methyl]-1-methyl-2-(methylthio)-5-phenylimidazolium chloride (5i): ^1H NMR δ 0.85 (s, 9 H), 1.29 (t, J = 7 Hz, 3 H), 2.66 (s, 3 H), 3.88 (s, 3 H), 4.27 (q, J = 7 Hz, 2 H), 5.35 (s, 2 H); MS calcd for $C_{18}H_{25}N_3O_2S$, m/z 347.1667 (MeCl elim), found 347.1679; calcd for $C_{14}H_{17}N_3O_2S$, m/z 291.1041 [MeCl elim and $(M - Me_2C{=}CH_2)^{\bullet+}$], found 291.1026; m/z (rel int) 347 (49), 291 (100), 263 (16), 219 (13), 217 (12), 145 (19), 118 (61).

1,3-Diisopropyl-2-(methylthio)-5-(4-nitrophenyl)-4-(isopropylamino)imidazolium chloride (16a): mp 200 °C dec (CH_2Cl_2/Et_2O): ^1H NMR δ 0.92 (d, J = 7 Hz, 6 H), 1.55 (d, 6 H), 182 (d, 6 H), 2.70 (m, 1 H), 2.72 (s, 3 H), 4.96 (m, 1 H), 5.10 (d, br, NH), 5.35 (m, 1 H), 8.07 and 8.36 (AB syst, 4 H). Anal. Calcd for $C_{19}H_{29}N_4O_2SCl$: C, 55.27; H, 7.03; N, 13.58; S, 7.76; Cl, 8.61. Found: C, 55.21; H, 6.99; N, 12.84; S, 7.76; Cl, 9.11.

5-(Dimethylamino)-1-ethyl-2-(methylthio)-3-isopropyl-4-(isopropylamino)imidazolium chloride (16b): ^1H NMR δ 1.17 (d, J = 7 Hz, 6 H), 1.45 (t, J = 7 Hz, 3 H), 1.67 (d, 6 H), 2.61 (s, 3 H), 2.87 (s, 6 H), 3.40 (br, NH), 3.50 (m, 1 H), 4.25 (q, J = 7 Hz, 2 H), 5.26 (m, 1 H); MS calcd for $C_{11}H_{21}N_3S$, m/z 227.1456 [MeCl elim and $(M - MeN{=}CH_2)^{\bullet+}$], found 227.1446; m/z (rel int) 227 (14), 226 (12), 225 (55), 211 (12), 209 (32), 185 (15), 183 (17), 170 (12), 168 (12), 167 (17), 125 (15), 86 (11), 84 (16), 83 (46), 70 (57), 69 (18), 58 (13), 56 (20), 52 (33), 50 (100).

Thermolysis of Imidazolium Chlorides 5d,e,h. A solution of salt **5** (5 mmol) in toluene (15 mL) was refluxed for 1 h. The solvent was evaporated in vacuo. Trituration of the residue with petroleum ether gave a colorless solid material. Compounds **9** were isolated by filtration and then recrystallized from CH_2Cl_2/petroleum ether (^{13}C NMR spectra: Table III).

5-Hydroxy-1-methyl-5-phenyl-3-isopropyl-4-(isopropylimino)-2-thioxo-1,3-diazolidine (9d): mp 152 °C (70% yield); ^1H NMR δ 0.49 (d, J = 6.5 Hz, 3 H), 1.08 (d, 3 H), 1.54 (d, 6 H), 2.84 (s, 3 H), 3.90 (m, 1 H), 4.42 (br, OH), 5.23 (m, 1 H), 7.35 (s, 5 H); MS calcd for $C_{16}H_{23}N_3OS$, m/z 305.1562 ($M^{\bullet+}$), found 305.1563; m/z (rel int) 305 (33), 288 (12), 263 (34), 189 (9), 158 (12), 133 (15), 131 (61), 118 (58), 105 (100); IR 3230, 1670 cm^{-1}. Anal. Calcd for $C_{16}H_{23}N_3OS$: C, 62.95; H, 7.54; N, 13.77; S, 10.49. Found: C, 62.79; H, 7.44; N, 13.88; S, 10.56.

4-[[(Ethoxycarbonyl)methyl]imino]-5-hydroxy-1-methyl-5-phenyl-3-isopropyl-2-thioxo-1,3-diazolidine (9e): mp 162 °C (65% yield); ^1H NMR δ 1.22 (t, J = 7 Hz, 3 H), 1.52 (d, J = 7 Hz, 3 H), 1.55 (d, 3 H), 2.87 (s, 3 H), 3.90, 4.31 (AB syst, J = 17 Hz, 2 H), 4.10 (q, 2 H), 5.28 (m, 1 H), 5.38 (br, OH), 7.38 (s, 5 H); IR 3320, 1720, 1670 cm^{-1}. Anal. Calcd for $C_{17}H_{23}N_3O_3S$: C, 58.45; H, 6.59; N, 12.03; S, 9.17. Found: C, 58.90; H, 6.50; N, 11.98; S, 9.07.

1-(2,6-Dimethylphenyl)-5-hydroxy-5-phenyl-3-isopropyl-4-(isopropylimino)-2-thioxo-1,3-diazolidine (9h): mp 191 °C (73% yield); ^1H NMR δ 0.88 (d, J = 6.5 Hz, 3 H), 1.06 (s, 3 H), 1.14 (d, 3 H), 1.60 (d, 3 H), 1.70 (d, 3 H), 2.37 (s, 3 H), 3.24 (br, OH), 3.64 (m, 1 H), 5.37 (m, 1 H); MS calcd for $C_{22}H_{29}N_3OS$, m/z 395.2031 ($M^{\bullet+}$), found 395.2042; m/z (rel int) 395 (13), 221 (13), 208 (11), 189 (12), 105 (100); IR 3290, 1680 cm^{-1}.

Preparation and Degradation of Imidazolium Chloride 5j. Oxidation to Imidazolinone 12. Isopropyl isocyanide **3b** (2.1 g, 30 mmol) was added dropwise to methanesulfenyl chloride (10 mmol) in $CHCl_3$ (5 mL). Benzylidene-*tert*-butylamine (**2f**)

(26) Weingarten, H.; Chupp, J. P.; White, W. A. *J. Org. Chem.* **1967**, *32*, 3246. Moretti, I.; Torre, G. *Synthesis* **1970**, 141.

(1.6 g, 10 mmol) was added to this solution which was maintained at rt for 20 h. A small portion of the resulting brownish solution was concd under reduced pressure. The ^1H NMR analysis of the residue showed a mixture of compounds **1c**, **2f** and cycloadducts **5j**, **10**. [**5j**: ^1H NMR δ 1.29 (d, 6 H), 1.52 (s, 9 H), 1.70 (d, 6 H), 1.97 (s, 3 H), 3.62 (m, 1 H), 5.34 (m, 1 H).] The entire conversion of starting **1** and **2** required a longer reaction time (5 days) in the same conditions. However, the complete degradation of the unstable salt **5j** was also observed. This degradation was proved by successive ^1H NMR analysis of the crude mixture as above-mentioned in this procedure. Evaporation of the solvent and trituration of the residue with Et_2O gave crystalline product **10** as the HCl salt (2.3 g, 72% yield).

2-(Methylthio)-4-phenyl-1-isopropyl-5-(isopropylamino)-imidazole hydrochloride (10): mp 182 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 1.31 (d, J = 7 Hz, 6 H), 1.59 (d, 6 H), 2.13 (s, 3 H), 4.70 (m, 1 H), 5.10 (m, 1 H), 6.82 (br, NH); ^{13}C NMR δ 20.7 (q, ^1J = 141 Hz, SCH_3), 21.0, 22.9 (2 qm, ^1J = 127 Hz, other methyl groups, 47.5, 48.6 (2 dm, ^1J = 130 Hz, $CHMe_2$), 116.4 (t, ^3J = 5 Hz, C-4), 126.6 (t, ^3J = 7 Hz, quat arom C), 128.0, 129.0, 128.9 (2 dt and dd, ^1J = 161 Hz, other arom C), 133.1 (t, ^3J = 3 Hz, C-5), 145.5 (m, C-2); MS calcd for $C_{16}H_{23}N_3S$, m/z 289.1613 (HCl elim), found 289.1626; m/z (rel int) 289 (100), 274 (96), 246 (42), 232 (52), 204 (42), 190 (43), 148 (53), 104 (38). Anal. Calcd for $C_{16}H_{24}N_3SCl$: C, 58.98; H, 7.37; N, 12.90; S, 9.83; Cl, 10.90. Found: C, 58.69; H, 7.43; N, 12.60; S, 9.61; Cl, 11.19.

Oxidation of this imidazole derivative was only observed after treatment with NEt_3. A solution of **10** (1.7 g, 5 mmol) and NEt_3 (1 g, 10 mmol) in dry THF (15 mL) was prepared. The precipitate ($HNEt_3Cl$) that rapidly formed at ambient temperature was filtered, and the filtrate was concd to afford an oil. The unprotonated imidazole could be bulb-to-bulb distilled in vacuo [bp 175 °C (0.02 torr); ^1H NMR δ 1.19 (d, J = 6.5 Hz, 6 H), 1.40 (d, 6 H), 2.06 (s, 3 H), 3.32 (d, br, NH), 4.05 (m, 1 H), 4.77 (m, 1 H), 7.10–8.06 (m, 5 H)] but was contaminated by small amounts of imidazolinone **12**. The oil was maintained at 20 °C under atmospheric O_2 for 7 d to afford a crystalline material that was suspended in petroleum ether and filtered. Recrystallization of this white powder afforded a pure sample of oxidized product **12**.

4-Phenyl-1-isopropyl-5-(isopropylimino)-3-imidazolin-2-one (12): mp 105 °C (ether/petroleum ether) (0.65 g, 50% yield); ^1H NMR δ 1.27 (d, J = 6.5 Hz, 6 H), 1.48 (d, 6 H), 4.58 (m, 1 H), 4.78 (m, 1 H); ^{13}C NMR δ 19.8, 24.7 (2 qm, ^1J = 127 Hz, CH_3), 44.5, 50.0 (2 dm, ^1J = 138 Hz, $CHMe_2$), 129.6 (t, ^3J = 7.8 Hz, quat arom C), 128.7, 130.1, 133.3 (dd and 2 dt, ^1J = 162 Hz, other arom C), 152.6, (dd, ^3J = 4.6 Hz, C-5), 164.9 (d, ^3J = 3.8 Hz, C-2), 165.0 (t, ^3J = 4 Hz, C-4); MS calcd for $C_{15}H_{19}N_3O$, m/z 257.1528 ($M^{\cdot+}$), found 257.1530; m/z (rel int) 257 (95), 242 (23), 215 (28), 214 (13), 200 (15), 126 (13), 112 (31), 111 (12), 104 (35), 103 (15), 84 (48), 83 (37), 69 (100); IR 1735, 1695, 1675 cm^{-1}. Anal. Calcd for $C_{15}H_{19}N_3O$: C, 70.03; H, 7.39; N, 16.34. Found: C, 70.18; H, 7.19; N, 16.04.

Preparation and Degradation of Imidazolium Chlorides 5k–p. *tert*-Butyl isocyanide **3d** (2.5 g, 30 mmol) was treated with methanesulfenyl chloride (10 mmol) in $CHCl_3$ (3 mL) or CCl_4 (15 mL), according to procedure A or C. After a few min, a solution of benzaldimine **2a–f** (10 mmol) in the same solvent (2 or 10 mL) was added. The mixture was stirred at rt for the time indicated in Table IV. Salt **5k** precipitated as yellowish solid and was filtered before its entire redissolving in the reaction medium (compare entries 1 and 2, Table IV). Hydrochloride **13p** also slowly precipitated from the reaction mixture and was filtered off (entry 8). Evaporation of filtrate and subsequent trituration of the residue with THF/Et_2O under atmospheric O_2 gave **14k,p** in low yield (entries 2, 8). These cycloadducts were easily purified as the HCl salt by recrystallization from CH_2Cl_2/Et_2O (1:1). In other cases, the reaction mixture was concd to an oil which was washed with dry ether. Crude products of entry 3 (**5l**, **14l**) and entry 6 (**13n**, **14n**) were separated by addition of THF/Et_2O and progressive precipitation. Imidazoline hydrochlorides **14l,m,o** (entries 4, 5, 7) were isolated by filtration after addition of Et_2O and then purified by recrystallization (yields and ^{13}C NMR spectra, see Tables III and IV). The entire oxidation of pure compounds **13n,p** was observed in MeOH solution, over 3 d under atmospheric O_2, without any effort to maximize the surface area exposure (neither air bubbling nor solution agitation).

Cycloadducts **5m–p** could not be isolated. However, **5m–o** were identified in the reaction mixtures using shorter reaction times (about 10 h) than the times described in Table IV. After evaporation of the solvent, the crude syrups were complex mixtures of compounds **1**, **2**, and **5** accompanied with some unidentified products, according to ^1H NMR analyis [**5m**: δ 0.82 (s, 9 H), 1.94 (br, 6 H), 2.14 (s, 9 H), 2.80 (s, 3 H), 4.87 (br, N H). **5n**: δ 0.85 (s, 9 H), 2.07 (s, 9 H), 2.65 (s, 3 H), 4.50 (br, NH), 5.67 (br, 2 H). **5o**: δ 0.77 (s, 9 H), 1.55 (d, J = 7 Hz, 6 H), 2.05 (s, 9 H), 2.72 (s, 3 H), 3.70 (br, NH), 4.94 (m, 1 H)]. Continuation of the reaction for 2 or 3 d predominantly afforded **14** (entries 5, 7) or **13** (entry 6, Table IV). Salts **5** were not detected and side compounds were found in moderate quantities (<15%).

Crude imidazolium chlorides **5k,l** were washed with dry ether, but they could not be recrystallized. Indeed, these salts rapidly decomposed with evolution of isobutene by standing in solution at rt. An experiment with **5k** (0.37 g, 1 mmol) in $CDCl_3$ (1 mL) under atmospheric O_2 was studied by ^1H NMR for 3 d. Some intermediates were detected but the total conversion of **5k** into **14k** and isobutene[9] was finally observed. Hydrochloride **14k** was isolated as described above (0.26 g, 80% yield).

3-*tert*-Butyl-4-(*tert*-butylamino)-1-methyl-2-(methylthio)-5-phenylimidazolium chloride (5k): mp 130 °C dec (crude); ^1H NMR δ 0.82 (s, 9 H), 2.05 (s, 9 H), 2.75 (s, 3 H), 3.90 (s, 3 H), 5.60 (br, NH); ^{13}C NMR, see Table II; MS calcd for $C_{15}H_{21}N_3S$, m/z 275.1456 [HCl elim and ($M - Me_2C{=}CH_2)^{\cdot+}$], found 275.1448; m/z (rel int) 275 (93), 260 (50), 245 (10), 219 (50), 204 (43), 186 (15), 145 (23), 118 (100); IR 3170, 1620, 1590 cm^{-1}.

3-*tert*-Butyl-4-(*tert*-butylamino)-1-ethyl-2-(methylthio)-5-phenylimidazolium chloride (5l): mp 192 °C dec (crude); ^1H NMR δ 0.81 (s, 9 H), 1.15 (t, J = 7 Hz, 3 H), 2.06 (s, 9 H), 2.75 (s, 3 H), 4.16 (br, NH), 4.42 (q, 2 H); MS calcd for $C_{16}H_{23}N_3S$, m/z 289.1613 [HCl elim and ($M - Me_2C{=}CH_2)^{\cdot+}$], found 289.1624; m/z (rel int) 289 (38), 274 (26), 233 (22), 218 (12), 132 (14), 104 (17), 77 (10), 57 (15), 56 (61), 55 (24), 41 (100); IR 3175, 1635, 1532 cm^{-1}.

1-Benzyl-4-(*tert*-butylimino)-2-(methylthio)-5-phenyl-2-imidazoline hydrochloride (13n): mp 148 °C dec (CH_2Cl_2/petroleum ether); ^1H NMR δ 1.45 (s, 9 H), 2.87 (s, 3 H), 4.07, 4.69 (AB syst, J = 16 Hz, 2 H), 6.15 (s, 1 H). Anal. Calcd for $C_{21}H_{26}N_3SCl$: C, 65.03; H, 6.71; N, 10.83; S, 8.25. Found: C, 65.00; H, 6.83; N, 10.67; S, 7.72.

1-*tert*-Butyl-4-(*tert*-butylimino)-2-(methylthio)-5-phenyl-2-imidazoline hydrochloride (13p): mp 180 °C dec (CH_2Cl_2/Et_2O); ^1H NMR δ 1.42 (s, 9 H), 1.45 (s, 9 H), 2.90 (s, 3 H), 6.75 (s, 1 H), 10.67 (br, NH); MS calcd for $C_{18}H_{27}N_3S$, m/z 317.1926 (HCl elim), found 317.1934; calcd for $C_{14}H_{19}N_3S$, m/z 261.1299 ($M - Me_2C{=}CH_2)^{\cdot+}$, found 261.1277; m/z (rel int) 317 (13), 261 (63), 246 (39), 205 (100), 190 (22), 172 (15), 132 (25), 131 (32), 104 (43).

4-(*tert*-Butylimino)-5-hydroxy-1-methyl-2-(methylthio)-5-phenyl-2-imidazoline hydrochloride (14k): mp 235 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 1.52 (s, 9 H), 2.85 (s, 3 H), 2.87 (s, 3 H), 7.42 (s, 5 H), 8.91 (br, 1 H), 10.50 (br, 1 H); MS calcd for $C_{15}H_{21}N_3OS$, m/z 291.1405 (HCl elim), 291.1410; calcd for $C_{14}H_{18}N_3OS$, m/z 276.1170 ($M - CH_3)^+$, found 276.1172; calcd for $C_{15}H_{21}N_3S$, m/z 275.1456 ($M - O)^{\cdot+}$, found 275.1466; calcd for $C_{14}H_{18}N_3S$, m/z 260.1221 ($M - OCH_3)^+$, found 260.1226; m/z (rel int) 291 (10), 276 (19), 275 (9), 260 (6), 220 (12), 219 (19), 216 (31), 188 (31), 187 (10), 160 (31), 118 (26), 105 (100); IR 2900, 1630, 1530 cm^{-1}. Anal. Calcd for $C_{15}H_{22}N_3OSCl$: C, 54.96; H, 6.72; N, 12.82; Cl, 10.84. Found: C, 54.85; H, 6.93; N, 12.64; Cl, 10.74.

4-(*tert*-Butylimino)-1-ethyl-5-hydroxy-2-(methylthio)-5-phenyl-2-imidazoline hydrochloride (14l): mp 196 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 0.97 (t, J = 7 Hz, 3 H), 1.54 (s, 9 H), 2.87 (s, 3 H), 3.35 (m, 2 H), 7.42 (s, 5 H), 8.80 (br, 1 H), 10.46 (br, 1 H); MS calcd for $C_{16}H_{23}N_3OS$, m/z 305.1562 (HCl elim), found 305.1544; calcd for $C_{15}H_{20}N_3OS$, m/z 290.1327 ($M - Me)^+$, found 290.1348; calcd for $C_{16}H_{23}N_3S$, m/z 289.1613 ($M - O)^{\cdot+}$, found 289.1612; m/z (rel int) 305 (13), 290 (13), 289 (9), 234 (10), 233 (11), 230 (24), 202 (21), 160 (10), 132 (17), 105 (100); IR 2900, 1636, 1530 cm^{-1}. Anal. Calcd for $C_{16}H_{24}N_3OSCl$: C, 56.22; H, 7.03; N, 12.30; S, 9.37; Cl, 10.40. Found: C, 55.88; H, 7.17; N, 12.19; S, 9.11; Cl, 10.79.

4-(*tert*-Butylimino)-1-(2,6-dimethylphenyl)-5-hydroxy-2-(methylthio)-5-phenyl-2-imidazoline hydrochloride (14m):

mp 238 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 0.98 (s, 3 H), 1.67 (s, 9 H), 2.40 (s, 3 H), 2.72 (s, 3 H); MS calcd for $C_{22}H_{27}N_3OS$, m/z 381.1875 (HCl elim), found 381.1894; m/z (rel int) 381 (7), 335 (16), 334 (28), 278 (30), 220 (10), 172 (14), 147 (29), 146 (32), 131 (12), 130 (22), 106 (10), 105 (100); IR 2900, 1640, 1535 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_3OSCl$: C, 63.23; H, 6.71; N, 10.06; S, 7.66. Found: C, 62.84; H, 6.83; N, 9.77; S, 7.31.

1-Benzyl-4-(*tert*-butylimino)-5-hydroxy-2-(methylthio)-5-phenyl-2-imidazoline hydrochloride (14n): mp 169 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 1.51 (s, 9 H), 2.72 (s, 3 H), 4.27, 4.40 (AB syst, J = 16 Hz, 2 H), 9.12 (br, 1 H), 10.57 (br, 1 H); MS calcd for $C_{21}H_{25}N_3OS$, m/z 367.1718 (HCl elim), found 367.1704; m/z (rel int) 367 (2), 292 (18), 276 (10), 220 (27), 105 (82), 104 (12), 91 (100). Anal. Calcd for $C_{21}H_{26}N_3OSCl$: C, 62.45; H, 6.44; N, 10.40; S, 7.93; Cl, 8.79. Found: C, 61.93; H, 6.48; N, 10.33; S, 7.76; Cl, 8.97.

4-(*tert*-Butylimino)-5-hydroxy-2-(methylthio)-5-phenyl-1-isopropyl-2-imidazoline hydrochloride (14o): mp 220 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 1.05 (d, J = 7 Hz, 3 H), 1.27 (d, 3 H), 1.51 (s, 9 H), 2.88 (s, 3 H), 3.87 (m, 1 H), 7.44 (s, 5 H), 8.87 (br, 1 H), 10.10 (br, 1 H); MS calcd for $C_{17}H_{25}N_3S$, m/z 303.1769 [HCl elim and $(M - O)^{\cdot+}$], found 303.1770; m/z (rel int) 303 (4), 272 (12), 174 (18), 166 (11), 158 (17), 146 (9), 110 (53), 105 (100); IR 2900, 1640, 1541 cm^{-1}. Anal. Calcd for $C_{17}H_{26}N_3OSCl$: C, 57.38; H, 7.31; N, 11.81; S, 9.00; Cl, 9.99. Found: C, 57.25; H, 7.49; N, 11.61; S, 8.76; Cl, 10.46.

1-*tert*-Butyl-4-(*tert*-butylimino)-5-hydroxy-2-(methylthio)-5-phenyl-2-imidazoline hydrochloride (14p): mp 218 °C (CH_2Cl_2/Et_2O); ^1H NMR δ 1.45 (s, 18 H), 2.90 (s, 3 H), 7.45 (br, 5 H), 8.97 (br, 1 H), 9.22 (s, 1 H). Anal. Calcd for $C_{18}H_{28}N_3OSCl$: C, 58.45; H, 7.57; N, 11.36; S, 8.66; Cl, 9.60. Found: C, 58.66; H, 7.61; N, 11.14; S, 8.78; Cl, 9.68.

Preparation of 2-Thioxodiazolidines 19a,b. By a similar procedure, an equimolar mixture of imidoyl chloride **1c** (10 mmol) and ketimine **17a** (2.2 g) or **17b** (1.6 g) was treated with 2 equiv of isopropyl isocyanide **3b** (1.4 g) in $CHCl_3$ (5 mL) at rt for 3 or 5 d (method A). Workup of the brownish solution in the usual way gave a crystalline compound which was triturated with MeOH and collected by filtration. MeCl elimination was observed when the reaction was carried out in $CDCl_3$ and analyzed by ^1H NMR.

1,3-Diisopropyl-5,5-diphenyl-4-(isopropylimino)-2-thioxo-1,3-diazolidine (19a): mp 189 °C (from MeOH) (56% yield); ^1H NMR δ 0.46 (d, J = 7 Hz, 6 H), 1.15 (d, 6 H), 1.51 (d, 6 H), 3.35 (m, 1 H), 3.65 (m, 1 H), 5.42 (m, 1 H); ^{13}C NMR δ 18.4, 19.6, 22.9 (3 qm, ^1J = 127 Hz, CH_3), 47.3, 48.9, 49.1 (3 dm, ^1J = 137 Hz, $CHMe_2$), 74.6 (m, C-5), 135.2 (t, ^3J = 7 Hz, 2 quat arom C), 128.6, 129.1, 128.7 (2 dt and dd, ^1J = 160 Hz, other arom C), 152.8 (t, ^3J = 6 Hz, C-4), 178.5 (dd, ^3J = 5 Hz, C-2); MS calcd for $C_{24}H_{31}N_3S$, m/z 393.2239 ($M^{\cdot+}$), found 393.2264; m/z (rel int) 393 (14), 236 (11), 235 (63), 224 (21), 194 (18), 193 (100), 165 (28); IR 1673 cm^{-1}. Anal. Calcd for $C_{24}H_{31}N_3S$: C, 73.28; H, 7.89; N, 10.69; S, 8.14. Found: C, 73.38; H, 8.03; N, 11.13; S, 7.70.

1,3-Diisopropyl-5-methyl-5-phenyl-4-(isopropylimino)-2-thioxo-1,3-diazolidine (19b): mp 129 °C (MeOH) (54% yield); ^1H NMR δ 0.45 (d, J = 7 Hz, 3 H), 0.97 (d, 3 H), 1.17 (d, 3 H), 1.50 (d, 3 H), 1.47 (d, 6 H), 1.82 (s, 3 H), 3.30 (m, 1 H), 3.51 (m, 1 H), 5.36 (m, 1 H), 7.30 (s, 5 H); IR 1665 cm^{-1}. Anal. Calcd for $C_{19}H_{29}N_3S$: C, 68.88; H, 8.76; N, 12.69; S, 9.67. Found: C, 68.59; H, 8.91; N, 12.41; S, 9.49.

Registry No. **1a**, 94518-64-6; **1b**, 94518-63-5; **1c**, 94518-60-2; **1d**, 138877-64-2; **1e**, 90496-26-7; **2a**, 622-29-7; **2b**, 6852-54-6; **2c**, 3096-95-5; **2d**, 780-25-6; **2e**, 6852-56-8; **2f**, 6852-58-0; **3a**, 2769-71-3; **3b**, 598-45-8; **3c**, 2999-46-4; **3d**, 7188-38-7; **5a**, 138877-65-3; **5b**, 138877-66-4; **5c**, 138877-67-5; **5d**, 138877-68-6; **5e**, 138877-69-7; **5f**, 138877-70-0; **5g**, 138877-71-1; **5h**, 138877-72-2; **5i**, 138877-73-3; **5j**, 138877-74-4; **5k**, 138877-75-5; **5l**, 138877-76-6; **5m**, 138877-77-7; **5n**, 138898-83-6; **5o**, 138898-84-7; **9d**, 138877-78-8; **9e**, 138877-79-9; **9h**, 138877-80-2; **10**, 138877-81-3; **12**, 138877-82-4; **13n**, 138877-83-5; **13p**, 138877-84-6; **14k**, 138877-85-7; **14l**, 138877-86-8; **14m**, 138877-87-9; **14n**, 138877-88-0; **14o**, 138877-89-1; **14p**, 138877-90-4; **15a**, 25105-60-6; **15b**, 74119-36-1; **16a**, 138877-91-5; **16b**, 138877-92-6; **17a**, 27126-12-1; **17b**, 6907-73-9; **19a**, 138877-93-7; **19b**, 138877-94-8.

Supplementary Material Available: X-ray data for **14k** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Azide Ring-Opening–Ring-Closure Reactions and Tele-substitutions in Vicinal Azidopyrazole-, Pyrrole- and Indolecarboxaldehydes

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5-Chloro-1-methylpyrazole-4-carboxaldehydes **1** react with excess sodium azide in dimethyl sulfoxide to produce a mixture of 1-azidomethyl-4-cyanopyrazoles **2** and 4-cyano-5-hydroxy-1-methylpyrazoles **3**. Application of this reaction to the corresponding 5-chloro-1-phenylpyrazole-4-carboxaldehydes **5** gave 4-cyano-5-hydroxy-1-phenyl-pyrazoles **7** as the sole products in high yields. Likewise, 2-aryl-5-chloro-1-methylpyrrole-3,4-dicarboxaldehydes **9** rearranged to 2-aryl-4-cyano-5-hydroxy-1-methylpyrrole-3-carboxaldehydes **10** in high yields. In the indole series, treatment of 1-aryl-2-chloroindole-3-carboxaldehydes **11** with NaN_3 yielded a mixture of 1-aryl-3-cyano-2(3*H*)-indolones **13** and 1-aryl-5-azido-3-cyanoindoles **12**, both products resulting from a ring-opening–ring-closure reaction with concomitant nucleophilic tele-substitution at the 5-position of the indole ring.

We have previously[1,2] demonstrated that many vicinal chloro heteroaryl carboxaldehydes react with azide anion to yield the corresponding vicinal heteroarylcarboxaldehydes in fair yields if the reaction is carried out below 60 °C. At slightly higher temperatures, however, many heterocyclic azides are labile and undergo ring opening with concomitant rearrangement.[3] In two recent com-

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