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# 5-Aminothiazolium Salts as Potential Cyclic Azomethine Ylides: Base-Induced Cycloaddition Reactions with Aryl, Alkyl, and Benzoyl Isothiocyanates

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ABSTRACT: *Reactions of the in situ generated thiazoles* **2** *with aryl and alkyl isothiocyanates appear to be totally regioselective and give the unexpected 5-(phenylthio)imidazolium-4-thiolates* **3**. *Such rapid interconversion of mesoionic compounds is explained by a 1,3-dipolar addition to the C=N bond of the heterocumulene followed by tBuNCS elimination. Similar interactions with benzoyl isothiocyanate exclusively proceed on the C=S unsaturation of the heteroallene moiety and produce the 4-(phenylthio)thiazolium-5-amidines* **12**. *Structural assignment of isolated imidazoles and thiazoles is based on* $^{13}C$ *NMR data and chemically confirmed by the* $NaBH_4$ *reduction of the alkylated derivatives* **5** *and* **13**. *Efforts to isomerize the starting mesoionic thiazole* **2a** *without the use of tBuNCS are unsuccessful.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 10: 16–26, 2000

## *INTRODUCTION*

Mesoionic ring systems have been known for many years and used as substrates in numerous 1,3-dipolar cycloaddition reactions [1,2]. We previously reported [3] the preparation of the 5-(*tert*-butylamino)-2-(phenylthio)thiazolium chlorides **1**, which are precursors in basic media for the transient mesoionic thiazoles **2**. The compounds **2** were recognized as active 1,3-dipoles versus a range of electron-deficient alkenes and alkynes [4] or internal olefinic moieties [5]. The reactions involved the cycloaddition of the masked azomethine ylide across the considered π-bond, which yielded *N*-bridged adducts as the first step, and resulted in practical syntheses of functionalized monocyclic or ring-annulated polycyclic systems. Of special interest was the formation of 2-(phenylthio)thiazolium-5-thiolates through a highly regioselective addition of carbon disulfide and a subsequent extrusion of *tert*-butyl isothiocyanate [6]. Interconversion of mesoionic heterocycles by the use of heterocumulenes requires a very reactive substrate and has essentially been successful with a few münchnones and thiazolium-5-(thi)olates [1,2] or dithiolium-4-olates [7].

These results encouraged us to explore the behavior of the thiazolium chlorides **1** toward a series of isothiocyanates in the presence of triethylamine. It was anticipated that *tert*-butyl isothiocyanate would be extruded from the primary cycloadducts, giving new mesoionic systems. Such study is mechanistically interesting because isothiocyanates are ambident dipolarophiles that can react at the carbon–nitrogen or carbon–sulfur double bond. In principle, two regioisomers can arise from the unsym-

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metrically substituted salts **1**, whatever C=N or C=S site of heterocumulene the reaction may implicate.

1,3-Cycloaddition reactions between phenyl isothiocyanate and dipolar systems have several precedents in the literature including münchnones [8] and thiazoles [9] as cyclic azomethine ylides. The latter interconversion reactions occurred on the C=N unsaturation of the heteroallene and were achieved in the way to connect the C-2 atom of the starting mesoionic compound to the nitrogen atom of the dipolarophile. They were perhaps under a thermodynamic control [2].

We describe here our observations related to the site and orientation of the cycloaddition of thiazoles **2** with representative isothiocyanates and our attempts to isomerize the starting thiazolium-5-aminide **2a**, without *tert*-butyl isothiocyanate, under the action of ethoxide or thiophenoxide anion.

## *RESULTS AND DISCUSSION*

### *Cycloadditions with Aryl and Alkyl Isothiocyanates*

Our results are described in Table 1. The reactions were performed at room temperature in tetrahydrofuran (THF) solution containing the salt **1a,b** and a large excess of $R^2NCS$ and triethylamine. All these conversions were entirely regioselective and occured with elimination of *tert*-butyl isothiocyanate, which was easily detected in the crude product by $^1H$ NMR spectroscopy ($\delta$ 1.42 ppm). The generated compounds **3** can be isolated (entries 1–6 in Table 1), and alkylated by iodomethane in $CH_2Cl_2$ in a few minutes (Scheme 1). In other cases, the mesoionic imidazoles **3** were methylated in *situ* by a direct addition of $CH_3I$ to the reaction mixture (entries 7–9 in Table 1).

**TABLE 1** Reactions of 5-Aminothiazolium Salts **1** with $R^2NCS$/triethylamine[a]

| | *Educts* | | | | |
|---|---|---|---|---|---|
| *Entry* | *Salt* | *Isothiocyanate, $R^2$* | Other | Time[b] (hours) | Product (*yield, %*)[c] |
| 1 | **1a** | Ph | – | 1 | **3a** (70) |
| 2 | **1b** | Ph | – | 1 | **3b** (70) |
| 3 | **1a** | 4-$MeOC_6H_4$ | – | 1 | **3c** (82) |
| 4 | **1a** | $CH_2Ph$ | – | 3 | **3g** (45) |
| 5 | **1a** | Me | – | 3 | **3h** (53) |
| 6 | **1a** | *t*-Bu | – | 25 | **3i** (45) |
| 7 | **1a** | 4-$NO_2C_6H_4$ | MeI | 1.5 | **5d** (75) |
| 8 | **1b** | 4-$NO_2C_6H_4$ | MeI | 1.5 | **5e** (70) |
| 9 | **1a** | 4-$ClC_6H_4$ | MeI | 1.5 | **5f** (73) |
| 10 | **1a** | PhC(O) | – | 1 | **12a** (75) |
| 11 | **1b** | PhC(O) | – | 1 | **12b** (72) |

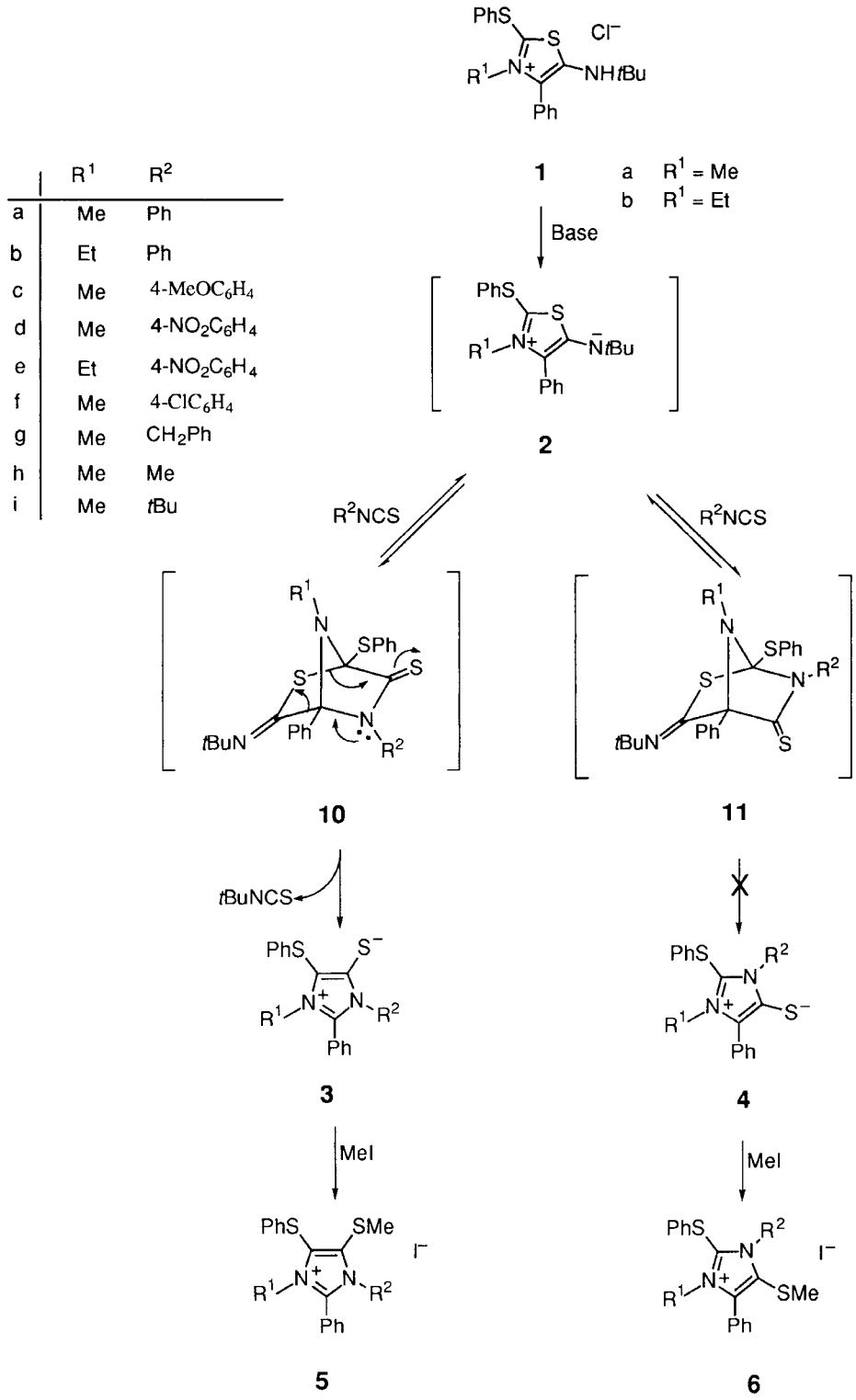
[a]The reactions were performed at room temp, starting from a suspension of **1** in THF (0.25 M), and then adding 3 equiv. of isothiocyanate (except for entries 5, 6 : 10 equiv.) and 3 equiv. of $NEt_3$. For entries 7–9, a 2-fold excess of MeI was poured into the reaction mixture about 1 hour after the $NEt_3$ addition.
[b]Time required for the full conversion of salt **1**.
[c]Purified product yield.

The rate of cycloaddition closely depends on the nature of the heterocumulene. The reaction worked well with phenyl isothiocyanate and analogs possessing either an electron-releasing or an electron-withdrawing substituent on the *para* position. Alkyl isothiocyanates were much less reactive than aryl isothiocyanates. In particular, *tert*-butyl and methyl isothiocyanates required higher concentration and longer reaction time to generate the corresponding adducts in only moderate yields (entries 5,6 in Table 1). Reactions with alkyl isothiocyanates also resulted in the decomposition or rearrangement of the starting thiazole **2a** and the formation of several minor compounds that are not isomeric cycloadducts.

Formation of imidazolium-4-thiolates **3** (or **4**) was shown by their ready conversion into salts **5** (or **6**) on treatment with iodomethane [9a]. The methiodides **5** were further characterized by their analytical and spectral data as well as the chemical evidence described subsequently. Selected $^{13}C$ NMR chemical shifts and multiplicities are given in Table 2. When $R^2$ is the benzyl or methyl group, the quadruplet attributed to the C-5 bearing the phenylthio proves unambiguously to be the regioisomer **3** or **5 g,h** and not the corresponding **4** or **6**. For example, the 2-(phenylthio)imidazolium iodides **6g,h** would exhibit multiplets for the three endocyclic carbons, because of long-range couplings with the protons of $R^1$and $R^2$. Assignments for **5g,h** were confirmed by selective decoupling experiments (cf. Table 2).

When $R^2$ is a *tert*-butyl or an aryl group, the structures of products were elucidated by the reduction of some imidazolium iodides **5**. Reactions of salts **5a,d,i** with sodium borohydride in an ethanol solution took place rapidly at room temperature to afford the 2,3-dihydroimidazoles **7** or oxidation derivatives **8** and **9** in satisfying yields (Scheme 2). Air-induced oxidation of dihydroimidazoles and fast isobutene elimination from *N-tert*-butyl imidazolium salts were already reported [10]. Structural assignments of compounds **7–9** were based upon $^1H$ and $^{13}C$ NMR and confirmed by high resolution mass spectra (cf. the Experimental section). A similar reduction of the 2-(phenylthio)imidazolium species **6** would probably induce the loss of thiophenol [6].

Formation of mesoionic imidazoles **3** rather than the anticipated regioisomers **4** may be rationalized assuming the tandem [3+2] cycloaddition/cy-


PhS
S
Cl⁻
R¹
N⁺
NHtBu
Ph
1
a R¹ = Me
b R¹ = Et
Base
PhS
S
R¹
N⁺
N̄tBu
Ph
2
R¹ R²
a Me Ph
b Et Ph
c Me 4-MeOC6H4
d Me 4-NO2C6H4
e Et 4-NO2C6H4
f Me 4-ClC6H4
g Me CH2Ph
h Me Me
i Me tBu
R²NCS
R²NCS
R¹
N
SPh
S
S
tBuN
Ph
N
R²
10
R¹
N
SPh
S
N
R²
tBuN
Ph
S
11
tBuNCS
PhS
S⁻
R¹
N⁺
N
R²
Ph
3
PhS
R²
N
R¹
N⁺
S⁻
Ph
4
MeI
MeI
PhS
SMe
I⁻
R¹
N⁺
N
R²
Ph
5
PhS
R²
N
I⁻
R¹
N⁺
SMe
Ph
6

**SCHEME 1**

**TABLE 2** Selected $^{13}$C-NMR Chemical Shifts[a,b]

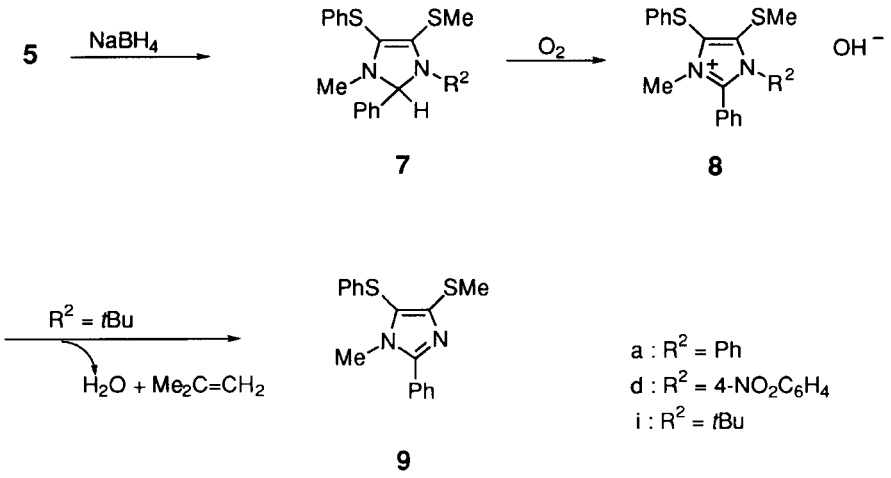
| *Compound* | *C-2* | *C-4* | *C-5* | *NCH$_3$* ($^1J$ = 144 Hz) | NCH$_2$ ($^1J$ = 142 Hz) | SCH$_3$ ($^1J$ = 143 Hz) | CO |
|---|---|---|---|---|---|---|---|
| **3a** | 141.6 (m) | 160.6 (s) | 117.7 (q, $^3J$ = 3) | 34.1 (q) | – | – | – |
| **3b**[c] | 141.2 (m) | 161.0 (s) | 116.6 (t, $^3J$ = 3.6) | – | 43.2 (tq, $^2J$ = 4.4) | – | – |
| **3c** | 142.1 (m) | 161.3 (s) | 117.9 (q, $^3J$ = 3) | 34.4 (q) | – | – | – |
| **3g** | 141.9 (m) | 159.3 (br) | 117.5 (q, $^3J$ = 3) | 33.4 (q) | 48.9 (tt, $^3J$ = 4.3) | – | – |
| **3h** | 141.3 (m) | 158.9 (q, $^3J$ = 3.3) | 117.5 (q, $^3J$ = 3.3) | 33.5 (q); 33.7 (q) | – | – | – |
| **3i** | 140.8 (m) | 159.5 (s) | 120.0 (q, $^3J$ = 2.9) | 33.6 (q) | – | – | – |
| **5a** | 148.3 (m) | 136.8 (q, $^3J$ = 5) | 131.4 (q, $^3J$ = 3.4) | 35.3 (q) | – | 19.7 (q) | – |
| **5d** | 148.4 (m) | 136.6 (q, $^3J$ = 5.1) | 132.2 (q, $^3J$ = 3.5) | 35.2 (q) | – | 20.0 (q) | – |
| **5g**[d] | 149.7 (m) | 137.1 (m) | 131.7 (q, $^3J$ = 3.6) | 35.5 (q) | 52.2 (t br) | 19.9 (q) | |
| **5h**[e] | 148.0 (m) | 136.2 (m) | 130.5 (q, $^3J$ = 3.4) | 34.7 (q); 35.5 (q) | – | 19.8 (q) | – |
| **5i** | 147.3 (m) | 135.9 (q, $^3J$ = 5.2) | 133.9 (q, $^3J$ = 3.1) | 35.0 (q) | – | 21.9 (q) | – |
| **8a**[f] | 149.2 (m) | 137.1 (q, $^3J$ = 5) | 130.7 (q, $^3J$ = 3) | 34.6 (q) | – | 19.4 (q) | – |
| **12a** | 153.7 (m) | 118.5 (q, $^3J$ = 3) | 158.5 (s) | 38.0 (q) | – | – | 173.4 (t, $^3J$ = 3.8) |
| **13a**[g] | 167.1 (m) | 132.3 (q, $^3J$ = 3) | 145.9 (q, $^3J$ = 3.4) | 40.6 (q); 42.1 (q) | – | – | 172.4 (m) |
| **13b** | 166.9 (m) | 131.7 (t, $^3J$ = 3.5) | 146.0 (q br) | 41.7 (q) | 48.8 (tq, $^2J$ = 4) | – | 172.4 (m) |
| **21** | 133.2 (dq, $^1J$ = 222, $^3J$ = 3) | 129.4 (d, $^3J$ = 5) | 136.0 (m) | 34.7 (qd, $^3J$ = 1.7) | – | – | – |
| **22** | 136.3 (dq, $^1J$ = 221, $^3J$ = 4) | 125.1 (m) | 141.3 (m) | 35.8 (qd, $^3J$ = 1.4) | – | 20.8 (q) | – |

[a]$\delta$(ppm), multiplicities and $J$ (Hz) for main carbon atoms of typical 5-(phenylthio)imidazolium **3**, **5**, **8**, 4-(phenylthio)thiazolium **12**, **13** and 5-phenylimidazolium derivatives **21**, **22**.
[b]At 75.5 MHz in $CDCl_3$ solutions (except for **5g**: $CD_3COCD_3$ and **21**: $CDCl_3$/EtOD).
[c]Decoupling experiments: selective irradiation on the $NCH_2$ at 4.08 ppm collapses the C-5 signal to a singlet and reduces the C-2 signal to a triplet ($^3J_{CCCH}$ = 3.2 Hz).
[d]Selective irradiation on the *N*-methyl group at 3.74 ppm collapses the C-5 signal to a singlet; the C-4 signal is reduced to a triplet ($^3J_{CNCH}$ = 4.2 Hz) by irradiation on the *S*-methyl group at 2.41 ppm and reduced to a quadruplet ($^3J_{CSCH}$ = 5.3 Hz) by irradiation on the $NCH_2$ at 5.64 ppm.
[e]Irradiation on the two *N*-methyl groups (about 3.75 ppm) causes the C-5 signal to turn into a singlet and the C-4 signal to turn into a quadruplet ($^3J_{CSCH}$ = 4.4 Hz); irradiation on the $SCH_3$ at 2.61 ppm reduces the C-4 signal to a quadruplet ($^3J_{CNCH}$ = 3.4 Hz).
[f]Irradiation on the $NCH_3$ at 3.78 ppm reduces the C-5 signal to a singlet and the C-2 signal to a triplet ($^3J_{CCCH}$ = 4.3 Hz); irradiation on the $SCH_3$ at 2.29 ppm collapses the C-4 signal to a singlet.
[g]Irradiation on the $NCH_3$ at 4.12 ppm reduces the C-4 signal to a singlet and the C-2 signal to a triplet ($^3J_{CCCH}$ = 4.3 Hz); irradiation on the $NCH_3$ at 3.73 ppm reduces the C-5 signal to a singlet and the carbonyl signal to a triplet ($^3J_{CCCH}$ = 3.6 Hz).

cloreversion sequence displayed in Scheme 1. The reaction is presumed to be under kinetic control, proceeding exclusively through the primary adduct **10** that undergoes spontaneous extrusion of *tert*-butyl isothiocyanate. However, the reversible formation of another bicyclic intermediate **11** cannot be excluded with certainty. The cycloadduct **11** would not participate in subsequent reaction to give **4**, and the observed regiochemistry would result from thermodynamic control [2].

### *Cycloadditions with Benzoyl Isothiocyanate*

Surprisingly, the reactions of salts **1a,b** with $C_6H_5CONCS$ occurred at the carbon–sulfur multiple bond, according to a similar, reverse mode of addition. Under usual conditions, the thiazolium-5-benzoylimides **12** were rapidly obtained in good yields as crystalline materials (entries 10,11, Table 1). Alkylation of mesoionic thiazoles **12** by iodomethane proved to be rather difficult, requiring several hours




**SCHEME 2**

in refluxing acetonitrile for completion. Starting from **12a**, the demethylation of the *in situ* generated thiazolium iodide **13a** became competitive, and the reaction afforded a mixture of the expected salt **13a** and thiazole **14** (Scheme 3). As precedented, the assigned structure of compounds **13** was substantiated by $^{13}C$ NMR (Table 2) and confirmed by the fast $NaBH_4$ reduction of one salt (**13a**) in aqueous ethanol. Spectral properties of the isolated product are clearly consistent with the 2,3-dihydro-4-(phenylthio)thiazole **15a**.

It has been previously observed that the C=S bond of an isothiocyanate in general displays low activity as a dipolarophile. Cycloadditions of this type were limited to aryl isothiocyanates and a few dipolar acyclic systems, such as nitrile imines or azomethine ylides, diazo compounds, and azides [11]. To the best of our knowledge, similar reactions with mesoionic heterocycles were unprecedented.

### *Attempted Isomerization of Mesoionic Thiazole* 2a

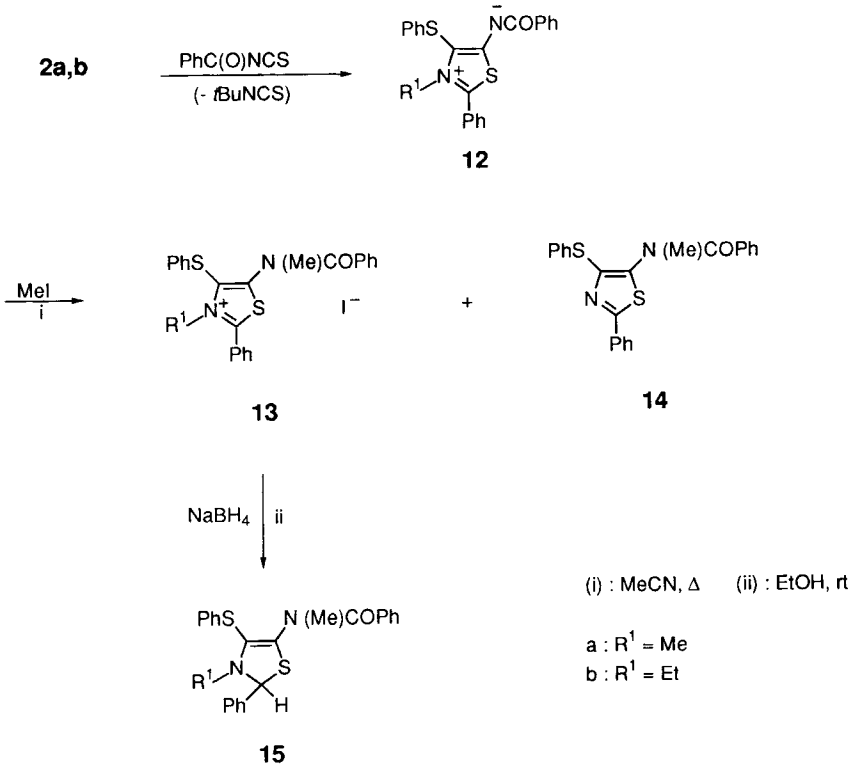
The mesoionic imidazoles **3i** and **4i** are isomeric forms of starting compound **2a**. At first sight, the hitherto nonobserved **4i** could result from **2a** via a Dimroth type rearrangement, and we have envisaged the possibility to perform such a rearrangement in the absence of *tert*-butyl isothiocyanate. Various methods and reagents have been used in the literature to promote the interconversion between mesoionic isomers. For example, Ollis and Ramsden have pointed out that the rearrangement of 1,3,4-thiadiazolium-2-anilides into 1,3,4-triazolium-2-thiolates can be achieved spontaneously at room temperature or by gentle heating in ethanol, besides the cycloaddition/extrusion process with $C_6H_5NCS$ [12]. The reaction was suggested to take place through the homolysis or heterolysis of the (C-5)-sulfur bond, whereas addition of ethanol involves a transient acyclic betaine. Similar interconversions between pairs of mesoionic heterocycles structurally related by exchange of exocyclic and endocyclic heteroatoms or groupings have led to assessments of their relative thermodynamic stability [1a,c].

The salt **1a** was first treated with triethylamine in THF solution at room temperature without any other reagent. The reaction provided a complex mixture of several products and failed to generate any detectable quantities of imidazole **4i**. The hydrolysis and oxidation derivatives **16–18** were isolated and identified as the major compounds of this mixture (Scheme 4). Their structural assignments were based on spectroscopic evidence and comparison with similar compounds [5].

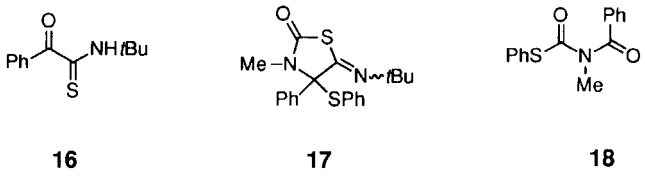
A like reaction performed with ethanolic sodium ethoxide readily produced the 4-(ethylthio)-2,3-dihydro-2-imidazolone **19**. A plausible explanation can be seen in the overall mechanism outlined in Scheme 5: formation and intramolecular *S*-alkylation of the betaine intermediate **20** then a ring-closure path via the nucleophilic attack of the amino nitrogen atom on the thiophenoxycarbonyl group.

In order to avoid this *S*-alkylation, the rearrangement of **1a** was induced by $C_6H_5SH/N(CH_2CH_3)_3$ in THF solution. Such treatment resulted in obtaining the imidazolium-4-thiolate **21**, which was easily converted into the salt **22** by iodomethane. The mesoionic derivative **21** presumably arises from the betaine **23** and the anticipated 2-(phenylthio)imidazole **4i**, which was reduced [5] *in situ* by thiophenol (Scheme 6). Large quantities of diphenyl disulfide were also isolated.

In conclusion, we have demonstrated the ability




**SCHEME 3**




**SCHEME 4**

of the 5-aminothiazolium chlorides **1** to undergo a base-catalyzed dipolar cycloaddition on the C = N or C = S bond of isothiocyanates. The regiochemistry of the reaction was provided by $^{13}C$ NMR data and chemical evidence. The additions occur in a reverse direction compared with earlier observations. Such interconversions afford new mesoionic imidazoles and thiazoles that cannot readily be obtained by other methods.

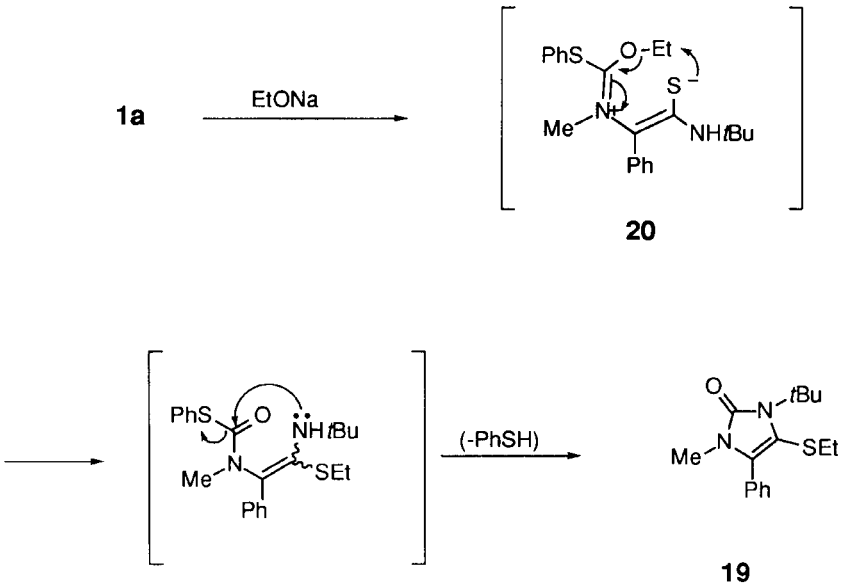
## *EXPERIMENTAL*

### *General*

- NMR spectra: Bruker AM 300 WB spectrometer (300 MHz for $^1H$ and 75.5 MHz for $^{13}C$) in $CDCl_3$ solution, unless otherwise indicated (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, except for compounds **3c**, **5c**, **12b**: MS/MS ZabSpec TOF Micromass spectrometer, in the ionization mode positive LSIMS with $CS^+$, matrix *m*NBA. With the exception of molecular-ion peaks, only mass-spectral fragments with relative intensities of 15% or more are reported.
- IR spectra: Perkin-Elmer 1420 spectrometer, suspensions in nujol.
- Elemental analyses: Analytical laboratory, CNRS.
- Crude products were separated and purified by fractional crystallization or Merck 60 silica gel column chromatography. $Na_2SO_4$ was used to dry organic layers after extractions.

### *Reactions of Thiazolium Chlorides* **1** *with Isothiocyanates*

In a general procedure, $N(CH_2CH_3)_3$ (0.75 g) was added dropwise to a suspension of salt **1** (2.5 mmol) and isothiocyanate (7.5 mmol except for *tert*-butyl and methyl isothiocyanates: 25 mmol) in anhydrous




**SCHEME 5**

THF (10mL). A blood red color appeared immediately and the mixture was stirred at room temperature for the time indicated in Table 1. The solvent was removed in vacuo, and the brownish residue was poured into $H_2O$ and extracted with $CH_2Cl_2$ (2 × 10 mL). Concentration of the organic phase and trituration with diethyl ether gave the yellow crystalline imidazoles **3** and thiazoles **12,** which were collected by filtration, except for **3h,** which was purified by flash chromatography on silica gel using ether and then methanol as eluent. Compounds **3** were quantitatively alkylated by iodomethane in dry $CH_2Cl_2$ (room temperature, 10 min). In the cases of entries 7–9 in Table 1, the THF solution was treated with $CH_3I$ (0.7 g) during the course of the reaction, about 1 hour after the triethyl amine addition. The reactional mixture was worked up as described above to precipitate the yellowish imidazolium iodides **5.** All the following compounds were recrystallized from $CH_2Cl_2/(CH_3CH_2)_2O$ (yields and $^{13}C$ NMR data, see Tables 1 and 2).

*1-Methyl-2,3-diphenyl-5-(phenylthio)imidazolium-4-thiolate* (**3a**)

m.p. 232°C. $^1H$ NMR $\delta$ 3.65 (s, 3H), 7.17–7.50 (m, 15H). Anal. calcd for $C_{22}H_{18}N_2S_2$: C, 70.59; H, 4.81; N, 7.49; S, 17.11. Found: C, 70.30; H, 4.78; N, 7.74; S, 16.85.

*1-Ethyl-2,3-diphenyl-5-(phenylthio)imidazolium-4-thiolate* (**3b**)

Uncertain melting point. $^1H$ NMR $\delta$ 1.2 (t, 3H, $J$ = 7.2 Hz), 4.08 (q, 2H, $J$ = 7.2 Hz), 7.16–7.50 (m, 15H). MS calcd. for $C_{23}H_{20}N_2S_2$ *m/z* 388.1068 $[M]^+$, found 388.1085; *m/z* (rel. int.): 388 (100), 359 (18), 180 (24), 153 (45). Anal. calcd: C, 71.13; H, 5.15; N, 7.22; S, 16.50. Found: C, 71.41; H, 5.18; N, 6.84; S, 16.69.

*3-(4-Methoxyphenyl)-1-methyl-2-phenyl-5-(phenylthio)imidazolium-4-thiolate* (**3c**)

m.p. 226°C. $^1H$ NMR δ 3.62 (s, 3H), 3.7 (s, 3H), 6.8 (d, 2H, $J$ = 8.9 Hz), 7.14–7.47 (m, 12H). MS calcd for $C_{23}H_{21}N_2OS_2$ *m/z* 405.1095 $[M+H]^+$, found 405.110. Anal. calcd for $C_{23}H_{20}N_2OS_2$: C, 68.32; H, 4.95; N, 6.93; S, 15.84. Found: C, 67.95; H, 4.95; N, 6.63; S, 15.78.

*3-Benzyl-1-methyl-2-phenyl-5-(phenylthio)imidazolium-4-thiolate* (**3g**)

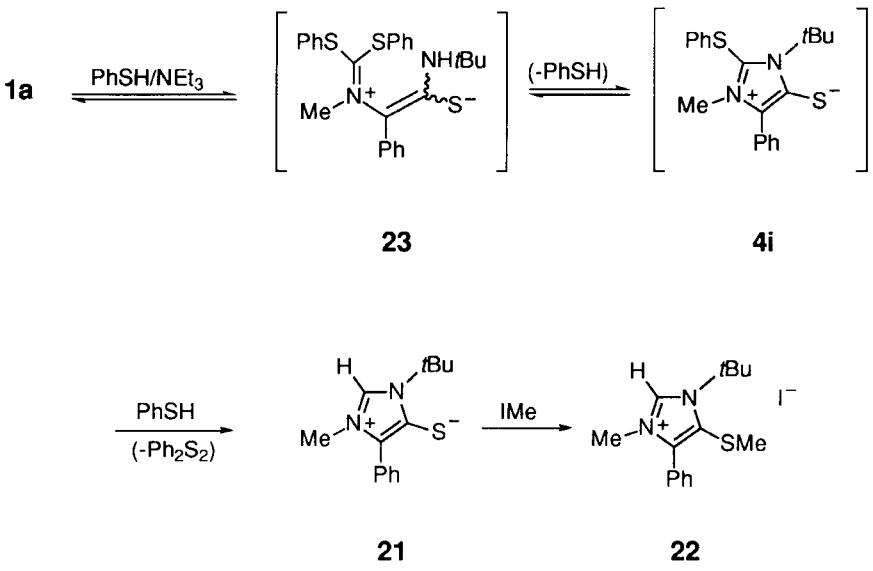
m.p. 178°C. $^1H$ NMR $\delta$ 3.48 (s, 3H), 5.54 (s, 2H), 7.05–7.57 (m, 15H). Anal. calcd for $C_{23}H_{20}N_2S_2$: C, 71.13; H, 5.15; N, 7.22. Found: C, 70.89; H, 5.24; N, 7.11.

*1,3-Dimethyl-2-phenyl-5-(phenylthio)imidazolium-4-thiolate* (**3h**)

m.p. 191°C. $^1H$ NMR δ 3.53 (s, 3H), 3.71 (s, 3H), 7.12–7.67 (m, 10H). MS calcd for $C_{17}H_{16}N_2S_2$ *m/z* 312.0755 $[M]^+$, found 312.0709; calcd for $C_{16}H_{13}N_2S_2$ *m/z* 297.0520 $[M\text{-}Me]^+$, found 297.0511.

*3-tert-Butyl-1-methyl-2-phenyl-5-(phenylthio)imidazolium-4-thiolate* (**3i**)

m.p. 208°C. $^1H$ NMR $\delta$ 1.84 (s, 9H), 3.23 (s, 3H), 7.1–7.63 (m, 10H). MS calcd for $C_{20}H_{22}N_2S_2$ *m/z* 354.1224




**SCHEME 6**

$[M]^+$, found 354.1158. Anal. calcd: C, 67.79; H, 6.21; N, 7.91; S, 18.08. Found: C, 67.52; H, 6.06; N, 7.85; S, 18.01.

*1-Methyl-4-(methylthio)-2,3-diphenyl-5-(phenylthio)imidazolium iodide* (**5a**)

m.p. 208°C. $^1$H NMR $\delta$ 2.34 (s, 3H), 3.77 (s, 3H), 7.26–7.48 (m, 9H), 7.65 (m, 2H), 7.83 (m, 2H), 7.95 (m, 2H). Anal. calcd for $C_{23}H_{21}IN_2S_2$ : C, 53.49; H, 4.07; I, 24.61; N, 5.43; S, 12.40. Found: C, 53.37; H, 4.07; I, 24.18; N, 5.27; S, 12.31.

*1-Ethyl-4-(methylthio)-2,3-diphenyl-5-(phenylthio)imidazolium iodide* (**5b**)

m.p. 222°C. $^1$H NMR $\delta$ 1.24 (t, 3H, $J$ = 7.3 Hz), 2.31 (s, 3H), 4.28 (q, 2H, $J$ = 7.3 Hz), 7.3–7.48 (m, 9H), 7.67 (m, 2H), 7.91 (m, 2H), 8.04 (m, 2H). Anal. calcd for $C_{24}H_{23}IN_2S_2$: C, 54.34; H, 4.34; N, 5.28; S, 12.08. Found: C, 54.44; H, 4.39; N, 5.24; S, 11.93.

*3-(4-Methoxyphenyl)-1-methyl-4-(methylthio)-2-phenyl-5-(phenylthio)imidazolium iodide* (**5c**)

m.p. 178°C. $^1$H NMR $\delta$ 2.39 (s, 3H), 3.79 (s, 6H), 6.86 (d, 2H, $J$ = 8.8 Hz), 7.3–7.51 (m, 6H), 7.67 (m, 2H), 7.78 (d, 2H, $J$ = 8.8 Hz), 7.99 (m, 2H). MS calcd for $C_{24}H_{23}N_2OS_2$ *m/z* 419.1252 $[M\text{-}I]^+$, found 419.125. Anal. calcd for $C_{24}H_{23}IN_2OS_2$: C, 52.74; H, 4.21; N, 5.13; S, 11.72. found: C, 52.40; H, 4.22; N, 4.96; S, 11.19.

*1-Methyl-4-(methylthio)-3-(4-nitrophenyl)-2-phenyl-5-(phenylthio)imidazolium iodide* (**5d**)

m.p. 220°C. $^1$H NMR $\delta$ 2.41 (s, 3H), 3.75 (s, 3H), 7.24–7.52 (m, 6H), 7.7, 8.05, 8.19, 8.31 (4d, 8H, $J$ = 8.8 Hz). Anal. calcd for $C_{23}H_{20}IN_3O_2S_2$: C, 49.20; H, 3.57; I, 22.64; N, 7.49; S, 11.41. Found: C, 49.33; H, 3.59; I, 22.69; N, 7.15; S, 11.60.

*1-Ethyl-4-(methylthio)-3-(4-nitrophenyl)-2-phenyl-5-(phenylthio)imidazolium iodide* (**5e**)

m.p. 252°C. $^1$H NMR $\delta$ 1.29 (t, 3H, $J$ = 7.2 Hz), 2.39 (s, 3H), 4.26 (q, 2H, $J$ = 7.2 Hz), 7.25–7.55 (m, 6H), 7.73 (d, 2H, $J$ = 8.6 Hz), 8.16 (m, 4H), 8.42 (m, 2H). Anal. calcd for $C_{24}H_{22}IN_3O_2S_2$: C, 50.09; H, 3.83; N, 7.30; S, 11.13. Found: C, 50.02; H, 3.87; N, 7.32; S, 11.68.

*3-(4-Chlorophenyl)-1-methyl-4-(methylthio)-2-phenyl-5-(phenylthio)imidazolium iodide* (**5f**)

m.p. 214°C. $^1$H NMR $\delta$ 2.37 (s, 3H), 3.77 (s, 3H), 7.26–7.47 (m, 8H), 7.67 (m, 2H), 7.92 (d, 2H, $J$ = 8.7 Hz), 8.01 (m, 2H). MS calcd for $C_{22}H_{17}ClN_2S_2$ *m/z* 408.0521 $[M\text{-}MeI]^+$, found 408.0518; *m/z* (rel. int.) : 408 (100), 392 (22), 153 (45), 142 (27).

*3-Benzyl-1-methyl-4-(methylthio)-2-phenyl-5-(phenylthio)imidazolium iodide* (**5g**)

Uncertain melting point. $^1$H NMR ($CD_3COCD_3$) $\delta$ 2.41 (s, 3H), 3.74 (s, 3H), 5.64 (s, 2H), 7.27 (m, 2H), 7.38–7.70 (m, 11H), 8.23 (m, 2H).

*1,3-Dimethyl-4-(methylthio)-2-phenyl-5-(phenylthio)imidazolium iodide* (**5h**)

Uncertain melting point. $^1$H NMR $\delta$ 2.61 (s, 3H), 3.63 (s, 3H), 3.91 (s, 3H), 7.24–7.68 (m, 8H), 8.09 (m, 2H). MS calcd for $C_{17}H_{16}N_2S_2$ *m/z* 312.0755 $[M\text{-}MeI]^+$, found 312.0761.

*3-tert-Butyl-1-methyl-4-(methylthio)-2-phenyl-5-(phenylthio)imidazolium iodide* (**5i**)

m.p. 163°C. $^1$H NMR $\delta$ 1.79 (s, 9H), 2.72 (s, 3H), 3.37 (s, 3H), 7.27–7.65 (m, 8H), 8.12 (m, 2H). MS calcd for $C_{17}H_{16}N_2S_2$ *m/z* 312.0755 $[M\text{-}C_4H_9I]^+$, found 312.0767. Anal. calcd. for $C_{21}H_{25}IN_2S_2$: C, 50.80; H, 5.04; N, 5.64. Found: C, 50.84; H, 5.00; N, 5.70.

*3-Methyl-2-phenyl-4-(phenylthio)thiazolium-5-(benzoylaminide)* (**12a**)

m.p. 200°C. IR 1570, 1527 cm$^{-1}$. $^1$H NMR $\delta$ 3.91 (s, 3H), 7.25–7.51 (m, 13H), 8.35 (m, 2H). MS calcd for $C_{23}H_{18}N_2OS_2$ *m/z* 402.0861 $[M]^+$, found 402.0868; *m/z* (rel. int.): 402 (23), 121 (92), 118 (24), 105 (100). Anal. calcd: C, 68.65; H, 4.48; N, 6.97; S, 15.92. Found: C, 68.81; H, 4.55; N, 6.87; S, 15.93.

*3-Ethyl-2-phenyl-4-(phenylthio)thiazolium-5-(benzoylaminide)* (**12b**)

m.p. 223°C. IR 1569, 1520 cm$^{-1}$. $^1$H NMR $\delta$ 1.35 (t, 3H, $J$ = 7.2 Hz), 4.47 (q, 2H, $J$ = 7.2 Hz), 7.22–7.58 (m, 13H), 8.33 (m, 2H). MS calcd for $C_{24}H_{21}N_2OS_2$ *m/z* 417.1095 $[M+H]^+$, found 417.109. Anal. calcd for $C_{24}H_{20}N_2OS_2$: C, 69.23; H, 4.80; N, 6.73; S, 15.38. Found: C, 69.16; H, 4.89; N, 6.51; S, 15.25.

*Alkylation of Mesoionic Thiazoles* **12**

$CH_3I$ (2.1 g) was added to a suspension of **12** (5 mmoles) in anhydrous $CH_3CN$ (20 mL) and the mixture was refluxed for 16 h. The solvent was removed under reduced pressure. The residual syrup was worked up with $(CH_3CH_2)_2O/CH_2Cl_2$ to give a yellowish crystalline material, which was filtered off and washed with $(CH_3CH_2)_2O$ (**13a,b**). The filtrate was concentrated to dryness. The thiazole **14** precipitated as colorless solid by trituration with ether/petoleum ether.

*5-[N-Benzoyl(methylamino)]-3-methyl-2-phenyl-4-(phenylthio)thiazolium iodide* (**13a**)

m.p. 154°C (41% yield). IR 1632 cm$^{-1}$. $^1$H NMR $\delta$ 3.73 (s, 3H), 4.12 (s, 3H), 7.3–7.70 (m, 13H), 7.95 (m, 2H). $^{13}$C NMR, see Table 2. MS calcd for $C_{23}H_{18}N_2OS_2$ *m/z* 402.0861 $[M\text{-}MeI]^+$, found 402.0868.

*5-[N-Benzoyl(methylamino)]-3-ethyl-2-phenyl-4-(phenylthio)thiazolium iodide* (**13b**)

Uncertain melting point (70% yield). IR 1640 cm$^1$. $^1$H NMR $\delta$ 1.40 (t, 3H, $J$ = 7.2 Hz), 3.69 (s, 3H), 4.6 (q, 2H, $J$ = 7.2 Hz), 7.2–7.80 (m, 13H), 7.99 (m, 2H). $^{13}$C NMR, see Table 2. MS calcd for $C_{23}H_{18}N_2OS_2$ *m/z* 402.0861 $[M\text{-}EtI]^+$, found 402.0868; *m/z* (rel. int.) 402 (29), 297 (33), 293 (20), 121 (100), 105 (77).

*5-[N-Benzoyl(methylamino)]-2-phenyl-4-(phenylthio)thiazole* (**14**)

m.p. 95°C (ether/petroleum ether) (35% yield). IR 1634 cm$^{-1}$. $^1$H NMR $\delta$ 3.36 (s, 3H), 7.15–7.45 (m, 13H), 7.78 (m, 2H). $^{13}$C NMR $\delta$ 39.1 (q, $^1J$ = 142 Hz), 126.3, 127, 128.1, 128.2, 129, 129.1, 129.7, 130.5, 130.9, 132.9, 134, 134.8 (12 arom. C), 142.8 (s, C-4), 142.9 (q, $^3J$ = 3.2 Hz, C-5), 165 ,5 (t, $^3J$ = 4.5 Hz, C-2), 171.4 (m, CO). Anal. calcd for $C_{23}H_{18}N_2OS_2$: C, 68.65; H, 4.48; N, 6.97; S, 15.92. Found: C, 68.56; H, 4.52; N, 6.78; S, 15.90.

*$NaBH_4$ Reductions*

Sodium borohydride (150 mg) was added portionwise to a solution of the thiazolium salt **13a** or imidazolium salt **5a,d,i** (2 mmol) in ethanol (20 mL). After 10 minutes at room temperature, the mixture was poured into $H_2O$ then extracted with diethyl ether (2 × 20 mL). The combined organic layers were washed with $H_2O$ and concentrated to a yellowish oily material. The $^1$H NMR analysis of this crude product showed the formation of the expected dihydrothiazole **15a** or dihydroimidazole **7** [**7i**: *S* 1.32(s, 9H), 2.19 (s, 3H), 2.66 (s, 3H), 5.31 (s, 1H)]. Compounds **7a,i** were transformed into the imidazolium hydroxide **8a** or imidazole **9** on standing under atmospheric $O_2$ at room temperature. The crystalline **9** was suspended in methanol/petroleum ether and filtered off.

*2,3-Dihydro-1-methyl-4-(methylthio)-2,3-diphenyl-5-(phenylthio)imidazole* (**7a**)

Crude oily product (68% yield). $^1$H NMR δ 2.09 (s, 3H), 2.59 (s, 3H), 5.34 (s, 1H), 7–7.60 (m, 15H). $^{13}$C NMR $\delta$ 17.6 (q, $^1J$ = 141 Hz), 39.2 (qd, $^1J$ = 136 Hz, $^3J$ = 5.4 Hz), 91.4 (dm, $^1J$ = 145 Hz, C-2), 123.2, 124.2, 125.7, 127.3, 127.4, 127.8, 128.3, 128.6, 128.7, 128.9, 136.2, 146.4 (12 arom. C), 129.8 (screened, C-

5), 141.5 (m, C-4). Heteronuclear decoupling experiments : irradiation on the $NCH_3$ at 2.59 ppm causes the C-2 signal to turn into a dt ($^3J_{CCCH}$ = 4 Hz), and irradiation on the CH at 5.34 ppm reduces the $NCH_3$ signal (39.2 ppm) to a quadruplet. MS calcd for $C_{23}H_{22}N_2S_2$ *m/z* 390.1224 $[M]^+$, found 390.1242; *m/z* (rel. int. ): 390 (33), 375 (43), 313 (81), 251 (25), 150 (34), 105 (62), 104 (23), 77 (100).

### *2,3-Dihydro-1-methyl-4-(methylthio)-3-(4-nitrophenyl)-2-phenyl-5-(phenylthio)imidazole* (**7d**)

Crude oily product (80% yield). $^1$H NMR $\delta$ 2.18 (s, 3H), 2.67 (s, 3H), 5.71 (s, 1H), 7.11 (s, 5H), 7.30 (d, 2H, $J$ = 9.2 Hz), 7.41 (m, 5H), 8.08 (d, 2H, $J$ = 9.2 Hz). $^{13}$C NMR δ 18.7 (q, $^1J$ = 141 Hz), 38.6 (qd, $^1J$ = 137 Hz, $^3J$ = 4.5 Hz), 87.5 (dm, $^1J$ = 148 Hz, C-2), 117.4, 124, 125. 2, 126.4, 128.1, 128.8, 129, 129.2, 134.5, 139.9, 150.8 (arom. C), 134.1 (qd, $^3J$ = 3.6 Hz, C-5), 141.1 (m, C-4). Decoupling experiment: irradiation on the $NCH_3$ at 2.67 ppm reduces the C-5 signal to a doublet ($^3J$ = 2.8 Hz). MS calcd for $C_{23}H_{21}N_3O_2S_2$ m/z 435.1075 $[M]^+$, found 435.1059; m/z (rel. int.) : 435 (92), 420 (74), 358 (100), 312 (20), 199 (30), 153 (25), 150 (75).

### *1-Methyl-4-(methylthio)-2,3-diphenyl-5-(phenylthio)imidazolium hydroxide* (**8a**)

Amorphous hemisolid. $^1$H NMR $\delta$ 2.29 (s, 3H), 3.78 (s, 3H), 7.3–7.90 (m, 15H). $^{13}$C NMR, see Table 2. MS calcd for $C_{22}H_{18}N_2S_2$ *m/z* 374.0911 $[M\text{-}MeOH]^+$, found 374.0919; *m/z* (rel. int.): 374 (15), 266 (42), 180 (17), 135 (17), 119 (52), 118 (64), 105 (80), 77 (100).

### *1-Methyl-4-(methylthio)-2-phenyl-5-(phenylthio)imidazole* (**9**)

m.p. 101°C (methanol/petroleum ether) (90% yield). $^1$H NMR $\delta$ 2.56 (s, 3H), 3.6 (s, 3H), 7.1–7.70 (m, 10 H). $^{13}$C NMR $\delta$ 16.5 (q, $^1J$ = 141 Hz), 32.8 (q, $^1J$ = 141 Hz), 119 (q, $^3J$ = 3 Hz, C-5), 126.2, 126.5, 128.7, 128.8, 129.3, 130.3, 136.3 (arom. C), 144.8 (q, $^3J$ = 4.4 Hz, C-4), 150.7 (m, C-2). MS calcd for $C_{17}H_{16}N_2S_2$ *m/z* 312.0755 $[M]^+$, found 312.0753; *m/z* (rel. int.): 312 (100), 266 (16), 203 (69). Anal. calcd : C, 65.38; H, 5.13; N, 8.97; S, 20.51. Found : C, 65.15; H, 5.14; N, 8.73; S, 20.57.

### *5-[N-Benzoyl(methylamino)]-2,3-dihydro-3-methyl-2-phenyl-4-(phenylthio)thiazole* (**15a**)

Crude oily product (95% yield). IR 1640 cm$^{-1}$. $^1$H NMR (at 57°C) $\delta$ 2.36 (s, 3H), 3.22 (s, 3H), 5.72 (s, 1H), 7.05–7.75 (m, 15H). $^{13}$C NMR (57°C) $\delta$ 36.5 (q, $^1J$ = 137 Hz), 36.5 (qd, $^1J$ = 137 Hz, $^3J$ = 4.6 Hz), 74.7 (dm, $^1J$ = 147 Hz, C-2), 126.6, 127.3, 127.6, 127.9, 128.5, 128.7, 129, 130.1, 134, 135.8, 140.4 (arom. C), 128.3, 129.8 (br, C-4 and C-5), 171.6 (m, CO). Decoupling experiments: irradiation on the $NCH_3$ at 2.36 ppm reduces the C-2 signal to a dt ($^3J$ = 4.5 Hz); irradiation on the $NCH_3$ at 3.22 ppm causes the CO signal to turn into a triplet ($^3J$ = 3.9 Hz). MS calcd for $C_{24}H_{22}N_2OS_2$ *m/z* 418.1173 $[M]^+$, found 418.1158; *m/z* (rel. int.): 418 (13), 313 (25), 150 (100).

### *Attempted Isomerization of Mesoionic Thiazole* **2a**

The thiazolium chloride **1a** was treated with triethylamine at room temperature for 3 hours, as precedentially described in the general procedure, without an isothiocyanate. The reactional medium was worked up in the same way to afford a complex mixture of compounds **16**, **17** and **18,** and several unidentified side products. Major compounds **17** and **18** were isolated by column chromatography on silica gel using ether/petroleum ether (3:2) as eluent, then recrystallized from methanol. We already reported the $\alpha$-oxothioamide **16** [5].

### *5-(tert-Butylimino)-3-methyl-4-phenyl-4-(phenylthio)-2-thiazolidinone* (**17**)

m.p. 98°C. IR 1681, 1635 cm$^{-1}$. $^1$H NMR $\delta$ 1.09 (s, 9H), 3.15 (s, 3H), 7.3–7.54 (m, 10H). $^{13}$C NMR $\delta$ 28.1 (qm $^1J$ = 128 Hz), 29.7 (q, $^1J$ = 140 Hz), 57.3 (m), 87.9 (m, C-4), 126.8, 128.5, 128.6, 129, 130, 136.9, 138.3 (arom. C), 153 (s, C-5), 166.4 (q, $^3J$ = 3.5 Hz, C-2). MS calcd for $C_{14}H_{17}N_2OS$ *m/z* 261.1062 $[M\text{-}PhS]^+$, found 261.1074; *m/z* (rel. int.): 261 (37), 145 (100), 118 (97). Anal. calcd for $C_{20}H_{22}N_2OS_2$: C, 64.86; H, 5.94; N, 7.56; S, 17.29. Found : C, 64.74, H, 5.94; N, 7.65; S, 17.33.

### *Phenyl N-benzoyl-N-methyl-thiooxocarbamate* (**18**)

m.p. 82°C. IR 1640 cm$^{-1}$. $^1$H NMR $\delta$ 3.34 (s, 3H), 7.38–7.62 (m, 10H). $^{13}$C NMR $\delta$ 34.4 (q, $^1J$ = 142 Hz), 126.9, 127.4, 127.5, 128.1, 128.7, 130.9, 133.8, 134.3 (8 arom. C), 170.1 (q, $^3J$ = 3 Hz), 171.9 (m). MS calcd for $C_{15}H_{13}NO_2S$ *m/z* 271.0667 $[M]^+$, found 271.0668; *m/z* (rel. int.): 271 (1), 105 (100), 77 (15). Anal. calcd.: C, 66.42; H, 4.79; N, 5.16; S, 11.80. Found: C, 66.49; H, 4.64; N, 5.22; S, 11.78.

An ethanolic solution of sodium ethoxide (1.25

M, 20 mL) was slowly added to the thiazolium salt **1a** (1.95 g). The mixture was maintained at room temperature for 18 hours and concentrated in vacuo. The residue was poured into $H_2O$ and extracted with diethyl ether. The oily imidazolone **19** was purified by a $SiO_2$ column chromatography using ether/petoleum ether (1:1) as eluent.

### *3-tert-Butyl–4-(ethylthio)-2,3-dihydro-1-methyl-5-phenyl-2-imidazolone* (**19**)

(62% yield). IR 1670 $cm^{-1}$. $^1H$ NMR $\delta$ 0.85 (t, 3H, $J$ = 7.4 Hz), 1.72 (s, 9H), 2.33 (q, 2H, $J$ = 7.4 Hz), 3.01 (s, 3H), 7.26–7.36 (m, 5H). $^{13}C$ NMR $\delta$ 13.6 (qt, $^1J$ = 128 Hz, $^2J$ = 3.3 Hz), 29 (q, $^1J$ = 140 Hz), 30.5 (qm, $^1J$ = 127 Hz), 32.5 (tq, $^1J$ = 141 Hz, $^2J$ = 4.4 Hz), 59 (m), 110.3 (t, $^3J$ = 3.7 Hz, C-4), 128.3, 128.5, 129.5, 130.5 (arom. C), 133.2 (m, C-5), 153.6 (q, $^3J$ = 2.8 Hz, C-2). MS calcd for $C_{16}H_{22}N_2OS$ *m/z* 290.1453 $[M]^+$, found 290.1448; *m/z* (rel. int.): 290 (22), 234 (99), 205 (100), 201 (39), 148 (32), 118 (47).

A similar reaction was conducted under the following conditions: salt **1a** (1.95 g), $C_6H_5SH$ (2.2 g), $N(CH_2CH_3)_3$ (2 g), THF (20 mL), at room temperature for 18 hours. After concentration, the crude product was poured into $H_2O$ and extracted with $CH_2Cl_2$ . The organic layer was evaporated to dryness. Trituration of the residue with diethyl ether gave the mesoionic imidazole **21** which was readily alkylated by iodomethane to give the salt **22** ($CH_2Cl_2$, room temperature, 10 minutes).

### *3-tert-Butyl-1-methyl-5-phenylimidazolium-4-thiolate* (**21**)

m.p. 290–300°C (THF/ethanol) (45% yield). $^1H$ NMR ($CDCl_3/CF_3CO_2H$) $\delta$ 1.82 (s, 9H), 3.70 (s, 3H), 7.3–7.60 (m, 5H), 9.28 (s, 1H). $^{13}C$ NMR see Table 2. MS calcd for $C_{14}H_{18}N_2S$ *m/z* 246.1191 $[M]^+$, found 246.1192; *m/z* (rel. int.): 246 (36), 190 (70), 189 (100). Anal. calcd : C, 68.29; H, 7.32; N, 11.38; S, 13.01. Found: C, 67.82; H, 7.41; N, 11.36; S, 13.15.

### *3-tert-Butyl-1-methyl-4-(methylthio)-5-phenylimidazolium iodide* (**22**)

m.p. 220°C (diethyl ether/$CH_2Cl_2$). $^1H$ NMR $\delta$ 1.96 (s, 9H), 2.15 (s, 3H), 3.93 (s, 3H), 7.58 (s, 5H), 9.88 (s, 1H). $^{13}C$ NMR see Table 2. MS calcd for $C_{11}H_{12}N_2S$ *m/z* 204.0721 $[M\text{-}HI\text{-}C_4H_8]^+$, found 204.0722; *m/z* (rel. int.) : 204 (100), 189 (16), 171 (92), 144 (29). Anal. calcd for $C_{15}H_{21}IN_2S$: C, 46.39; H, 5.41; N, 7.22; S, 8.25. Found: C, 46.61; H, 5.42; N, 7.18; S, 7.76.

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