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Diisothiocyanates as Heterodienophiles or Dipolarophiles in the Presence of α-Thioxothioamides or Mesoionic Thiazoles

Georges Morel and Evelyne Marchand

Synthèse et Electrosynthèse Organiques, UMR 6510, Université de Rennes I, Campus de Beaulieu, Avenue du General Leclerc, 35042 Rennes Cedex, France

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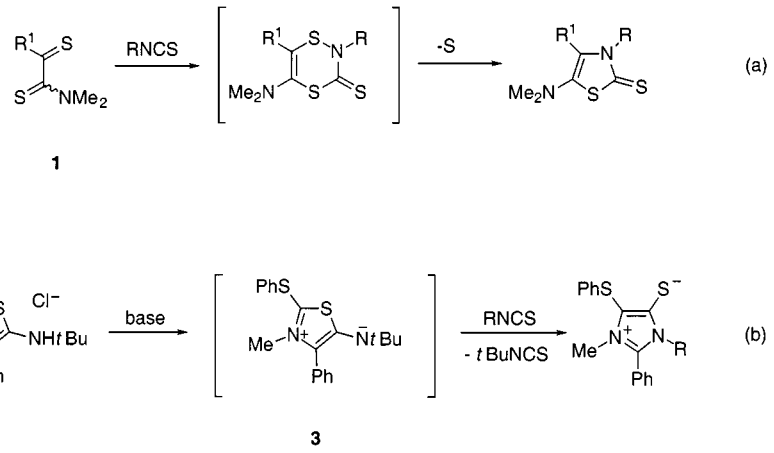
ABSTRACT: *Reactions of α-thioxothioamides (**1**) with diisothiocyanates were carried out in the hope of generating the N,N′-bis(1,3-thiazoline-2-thiones) (**A**). Although that purpose could not be achieved, we succeeded in preparing the monocycloadducts **7** from the phenylene-1,2-diisothiocyanate (**4**). The benzimidazole derivatives **8** and **9** were also characterized and a mechanism was assumed to account for this intramolecular process. On the other hand, the regioselective synthesis of the N,N′-biimidazole (**13**) containing the phenylene bridge was performed by the treatment of the 5-aminothiazolium chloride (**2**) with the diisothiocyanate (**4**) in a basic medium. The mesoionic derivative **13** probably arises from the monoimidazolium-4-thiolate (**12**) which was shown to react with the salt **2** under similar conditions to give the primary cycloadduct **14** as an intermediate towards the bis(imidazolium) (**13**).* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:617–624, 2001

INTRODUCTION

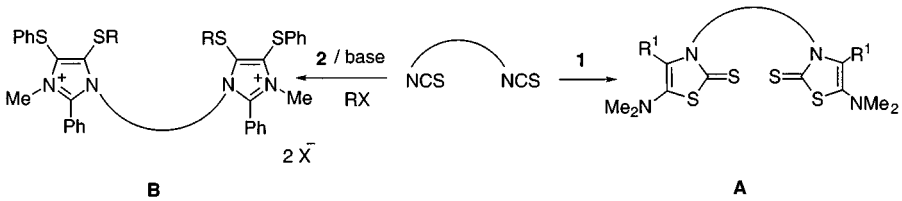
Isothiocyanates are important and versatile agents in organic chemistry which have been widely utilized for the synthesis of heterocyclic compounds [1]. In particular, we previously reported that treatment of α thioxothioamides (**1**) with aryl and methyl isothiocyanates afforded a range of 5-amino-2,3-dihydro-2-thioxothiazoles [2]. The process implied a regioselective [4 + 2] cycloaddition to the C=N bond of the heterocumulene, followed by S-1 extrusion in the transient 3-thioxo-1,4,2-dithiazines (path a, Scheme 1). More recently, aryl and alkyl isothiocyanates were demonstrated to react in a basic medium with the 2-(phenylthio)-5-aminothiazolium chloride (**2**). A rapid and regioselective interconversion of the mesoionic ring systems was observed, the starting azomethine yield **3** giving the corresponding 5-(phenylthio)imidazolium-4-thiolates under very mild conditions [3]. Such a result was explained by a 1,3-dipolar addition to the C=N unsaturation of the heteroallene, with subsequent *t* BuNCS elimination (path b, Scheme 1).

Considering the facility of these reactions, we wondered whether it might be possible, under suitable conditions, to involve some diisothiocyanates in similar procedures. If successful, double cycloadditions could provide useful and straightforward routes to new *N*,*N*′-bis(1,3-thiazoline-2-thiones) (**A**) and bis(imidazolium) salts (**B**) (Scheme 2). Compounds of class **A** are excellent precursors, by intramolecular coupling, for the formation of *N*,*N*′-bridged dithiadiazafulvalenes [4] which have been proved to be powerful electron π-donors in conducting charge transfer salts [5]. The 1,1′-polymethylene biimidazolium dications of class **B** have also received much attention in recent years [6]. Some of these salts exhibit interesting pharmacological

Correspondence to: Georges Morel; e-mail: Georges.Morel@univ-rennes1.fr



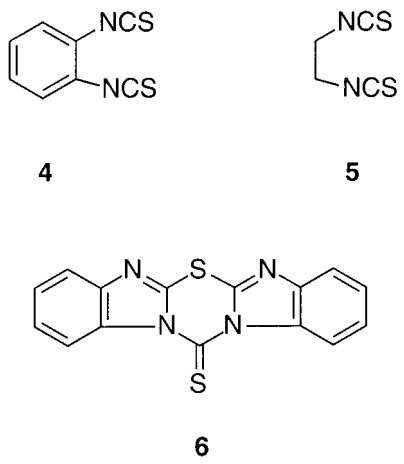
SCHEME 1



SCHEME 2

activities [7]. The *N,N′*-bridged diquaternary salts of 2,2′-biimidazole [8,9] and the *N,N′*-annulated 2,2′-unsubstituted bis(imidazolium) species [8] have generated considerable interest for their ability to provide highly air sensitive 2,2′-diimidazolinylidenes (tetraazafulvalenes).

To our knowledge, the use of diisothiocyanates for Diels Alder and dipolar cycloadditions was unprecedented in the literature. As representative models, we chose to investigate the behavior of the readily available phenylene-1,2-diisothiocyanate (**4**) [10] and ethylene diisothiocyanate (**5**) [11]. Compounds **4** and **5** (Scheme 3) are highly reactive heterocumulenes which undergo facile intramolecular reactions in the presence of nucleophiles [12,13]. For example, the thiadiazino bis(benzimidazole) (**6**) was rapidly obtained from the phenylene diisothiocyanate (**4**), according to a complex cyclodimerization/CS_2 elimination sequence [10,12]. The present article describes our trials to employ the reagents **4** and **5** in the procedures outlined in Scheme 2.



SCHEME 3

RESULTS AND DISCUSSION

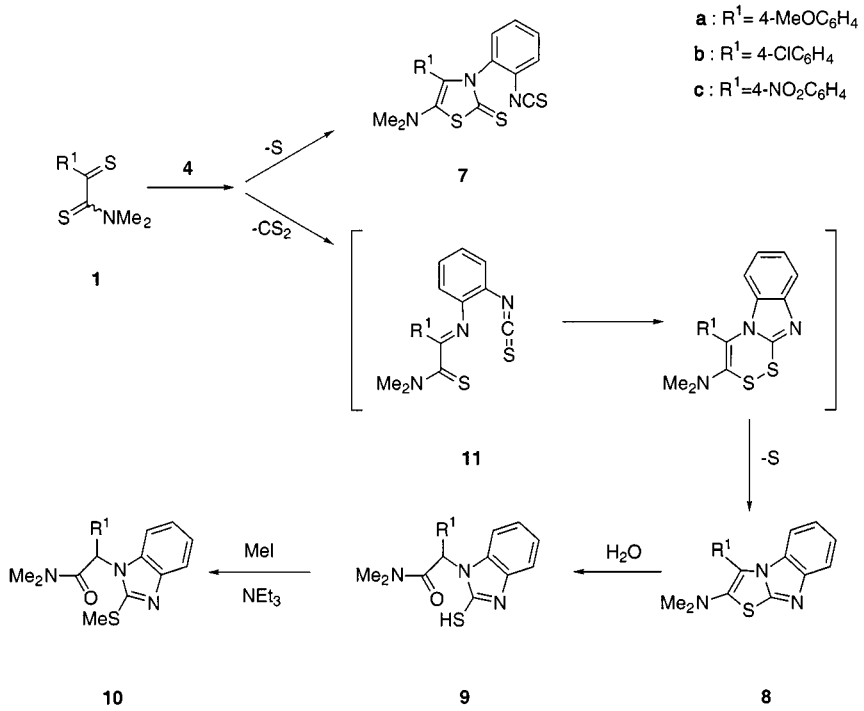
*Reactions of α-Thioxothioamides (**1**) with Diisothiocyanates*

^{1}H NMR analyses of crude mixtures obtained from substrates **1** and **4** indicated the formation of two cycloadducts **7** and **8** accompanied by smaller quantities of a hydrolyzed derivative **9** (Table 1, Scheme 4). Their relative proportions were found to be markedly dependent on the nature of the substituent R^1. Despite the use of a great excess of diisothiocyanate (**4**), large amounts of starting dithiocarbonyl compound **1** were recovered because **4** was rapidly converted into the pentacyclic derivative **6** which precipitated from the solution. Obtaining the adducts **7** and **8** in acceptable yields required either a second addition of **4** during the course of the reaction (entries 2, 5 and 7) or the use of an initial threefold

TABLE 1 Reactions of α-Thioxothioamides (**1**) with Phenylene-1,2-diisothiocyanate (**4**)

Entry	Thioamide	Reactions Conditions[a] **4** mol. eq. (time, h)	Compounds' Ratio[b] **1**	**7**	**8**	**9**	Isolated Products (yield, %)[c]
1	**1a**	1.5 (18)	58	5	29	8	–
2	**1a**	1.5 (18) then 0.5 (24)	50	6	30	14	**7a** (4); **8a** (20); **9a** (8)
3	**1a**	3 (17)	45	7	46	2	**7a** (4); **8a** (38)
4	**1b**	2 (6)	58	21	21	–	–
5	**1b**	2 (6) then 3 (24)	35	28	34	3	**7b** (23); **8b** (25); **9b** (5)
6	**1c**	2 (6)	40	47	11	2	–
7	**1c**	2 (6) then 2 (16)	17	67	6	10	**7c** (62); **9c** (7)
8	**1c**	3 (17)	18	70	5	7	**7c** (63); **9c** (5)

[a]The reactions were performed in refluxing acetonitrile, starting from a 0.5 M solution of thioamide and a large excess of diisothiocyanate. For entries 2, 5, and 7, an additional quantity of compound **4** was poured into the reaction mixture, according to the specified conditions.
[b]Distributions were estimated on the basis on the ^{1}H NMR spectra of crude mixtures.
[c]Yields represent purified products after flash chromatography and/or crystallization.



SCHEME 4

excess of **4** (entries 3 and 8). Attempts to prepare related cycloadducts by treatment of thioamide **1c** with ethylene diisothiocyanate (**5**) were unsuccessful, the heterodiene **1c** being essentially recovered, even after a prolonged heating in acetonitrile.

Structure assignments were based on elemental analyses and standard spectroscopic methods (see the Experimental section for ^{1}H and ^{13}C NMR data and mass fragmention patterns). Significantly, the presence of an NCS function in the 2-thioxothiazoles (**7**) was indicated in both their ^{13}C NMR (141 ppm, singlet) and IR spectra (2000 cm^{-1}, broad). The ^{13}C NMR spectra of the 2-(dimethylamino)-thiazolo[3,2-*a*]benzimidazoles (**8**) display resonances at δ 141 ppm for C-2, 124 ppm for C-3, and 152 ppm for C-9a. The last two values compare favorably with shifts for carbon atoms C-3 and C-7a of imidazo[2,1-*b*]thiazole derivatives [14]. Hydrolysis was shown by appearance of a typical IR band in the C=O region (1635 cm^{-1}) while a singlet at approximately δ 7.60 ppm was observed in the ^{1}H NMR spectra. The aromatic structure **9** seems to exist only as the single tautomeric form owing to the lack of an NH absorption peak and the lack of a low-field resonance

thioxo carbon. Additional evidence for structure **9a** is found in the easy methylation to afford the 2-(methylthio)benzimidazole (**10a**).

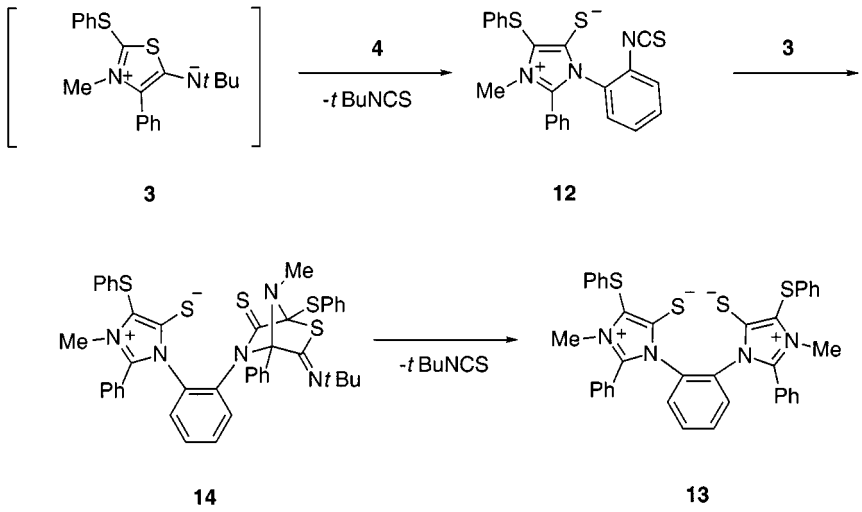
The overall sequence of reactions is summarized in Scheme 4. Formation of cycloadduct **7** appears to be totally regioselective and takes place according to the aforementioned ring contraction path a (Scheme 1). The isothiocyanate **7** is surprisingly unreactive towards the conjugated heterodiene **1**, no compound of class **A** being detected in the crude medium in spite of the continued presence of **1** (cf. Table 1). Further treatment of **7** in refluxing MeCN failed also to furnish the fused benzimidazole **8** and gave back starting material. This fact suggests the participation of the α-iminothioamide intermediate **11** in the generation of **8**, via elimination of CS_2 from the corresponding 2-thioxo-1,3-thiazetidine as previously described [2]. Intramolecular [4 + 2] cycloaddition of the compound **11** to the C=S bond of the heterocumulene moiety is followed by a sulfur extrusion to afford **8**. Separation of products by column chromatography on silica gel induces a partial hydrolysis to form the 2-mercaptobenzimidazole (**9**).

Imidazothiazoles have been mentioned over many years in the literature on account of their numerous biological activities [14,15]. However, the 2-(dimethylamino)-thiazolo[3,2-*a*]benzimidazoles (**8**) are new compounds. Similar fused heteropentalenes having a phenylazo substituent at the 2-position have generally been prepared by the addition of 2-mercaptobenzimidazole to hydrazonoyl halides [16].

Cycloaddition of the Mesoionic Compound **3** *with Diisothiocyanates*

The thiazolium chloride **2** underwent a fast reaction with the phenylene-1,2-diisothiocyanate (**4**) at room temperature in the presence of triethylamine. In addition to the side-compound **6**, two mesoionic species could be isolated in yields which were highly dependent upon the amount of the reagent **4** that was employed. The use of diisothiocyanate **4** in a threefold excess resulted in the formation of **12** in excellent yield (isolated 68%) and **13** in only trace amount. Formation of the bis(imidazolium) adduct **13** as the major product required a smaller excess of the substrate **4** (1.2 mol. eq.). Cycloadducts **12** and **13** were thereby obtained in 26% and 28% yields, respectively. We have verified that the monoimidazole (**12**) readily reacts with the salt **2** under similar conditions to provide the *N*,*N*′-biimidazole (**13**) in good yield (66%). This result is rationalized through the tandem [3 + 2] cycloaddition/cycloreversion sequence displayed in Scheme 5. The primary adduct **14** occurs as an unstable intermediate which could only be observed by ^{1}H NMR spectroscopy of the crude mixture, before extrusion of *tert*-butyl isothiocyanate (cf. Experimental section).

The mesoionic heterocycles **12** and **13** were characterized by their NMR spectral data and mass spectra. Assignment of the regiochemistry of their formation is based upon analogy to closely related imidazolium-4-thiolates (path b, Scheme 1) with particular regard to the chemical shifts for the three endocyclic carbons [3]. As anticipated, alkylation of **12**



SCHEME 5

and **13** works very well with iodomethane at room temperature to afford the stable mono and *N*,*N*′-biimidazolium salts **15** and **16** (Scheme 6).

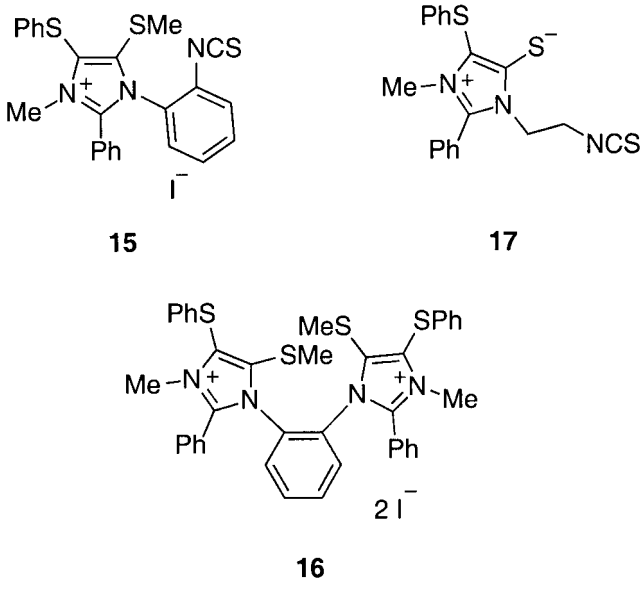
Treatment of salt **2** with triethylamine and ethylene diisothiocyanate (**5**) (1.6 mol. eq.) in THF solution at room temperature gave only one isolable product whose mass spectral data and elemental analysis indicated a molecular formula $C_{19}H_{17}N_3S_3$. This adduct was deduced to be mesoionic monoimidazole (**17**) in full accord with the NMR and IR spectroscopic studies. The reaction failed to generate any detectable quantities of the bis(imidazolium) compound.

In conclusion, we have demonstrated for the first time the ability of phenylene-1,2-diisothiocyanate (**4**) to undergo hetero Diels Alder and 1,3-dipolar cycloaddition reactions in the context of a reaction with a suitable heterodiene and dipole. The two heterocumulene moities successively react with mesoionic thiazole (**3**) to give the expected *N*,*N*′-biimidazolium species **13** under satisfactory conditions. Unfortunately, only one isothiocyanate function behaves as an active dienophile towards α-thioxothioamides (**1**) and attempts to construct bis(thiazolinethiones) of type **A** were unsuccessful. However, our results provide a new contribution for the synthesis of thiazolo[3,2-*a*]benzimidazoles.

EXPERIMENTAL

General

- *NMR spectra*: Bruker ARX 200 spectrometer (200 MHz for ^1H and 50.3 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 **12, 13, 15** and **16**: MS/MS ZabSpec TOF Micromass spectrometer, ionization mode positive LSIMS with Cs^+, matrix *m*NBA.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.
- Acetonitrile and tetrahydrofuran (THF) were freshly distilled from P_2O_5 and NaH, respectively. Na_2SO_4 was used to dry organic layers after extractions.



SCHEME 6

Starting Materials

We previously described the procedures for preparing the α-thioxothioamides (**1**) [17] and salt (**2**) [18]. Hull has reported on the formation of the phenylene-1,2-diisothiocyanate (**4**) by the fission of benzimidazole under the action of thiophosgene and base [10]. The yellow crystalline thiadiazino bis(benzimidazole) (**6**) was clearly identified on the basis of elemental analysis and NMR evidences [10]. The ethylene diisothiocyanate (**5**) was synthesized using a slight modification to a literature method [11], i.e., on the decomposition, at room temperature, of the carbethoxy ethylene bis(dithiocarbamate) on alumina-dispersed potassium fluoride as solid support in CH_2Cl_2. Although the solution of **5** might be stored (refrigerator) for long periods without alteration, evaporation under reduced pressure gave an oil which rapidly polymerized on standing under usual conditions.

*Reactions of α-Thioxothioamides (**1**) with the Phenylene Diisothiocyanate (**4**)*

An excess of diisothiocyanate (see Table 1) was added to a solution of thioamide (5 mmol) in CH_3CN (10 ml), and the mixture was maintained at reflux temperature for the time indicated in this Table. The side-product **6** precipitated in large quantities from the reaction medium and was filtered off. The solvent was removed in vacuo, and the residual substance was analyzed by ^1H NMR spectroscopy in order to monitor the progress and distribution of the reaction. Trituration with diethyl ether gave the crystalline 2-thioxothiazoles (**7a–c**) which were

collected by filtration. The filtrate was purified by a flash chromatography on Merck 60 silica gel. The column was first eluted with CH_2Cl_2/CCl_4 (2:1) to recover the starting heterodiene **1** and remaining parts of **7**. Other products of Table 1 were isolated with diethyl ether as eluent and recrystallized from CH_2Cl_2/petroleum ether (compounds **8**) or diethyl ether/petroleum ether (compounds **9**, unprecise melting points).

The 2-mercaptobenzimidazole (**9a**) (0.68 g, 2 mmol) was alkylated by iodomethane (0.43 g, 3 mmol) in dry CH_2Cl_2 (20 ml) containing triethylamine (0.4 g, 4 mmol). The mixture was stirred at room temperature for 10 min, washed with H_2O and concentrated to yield the 2-(methylthio) derivative (**10a**) as a viscous product (0.65 g, 1.8 mmol).

*2,3-Dihydro-5-(dimethylamino)-3-(2-isothiocyanatophenyl)-4-(4-methoxyphenyl)-2-thioxothiazole (***7a***).* m.p. 185°C (CH_2Cl_2/petroleum ether). IR 2000 cm^{-1}. ^1H NMR δ 2.60 (s, 6H), 3.72 (s, 3H), 6.74 (d, 2H, $J = 8.9$ Hz), 7.09 (d, 2H, $J = 8.9$ Hz), 7.00–7.30 (m, 4H). ^{13}C NMR δ 45.5 (NCH_3), 55.1 (OCH_3), 113.7, 121.4, 125.5, 127.5, 130.3, 130.6, 130.8, 131.5, 135.8, 159.7 (arom. C), 131.9 (t, $^3J = 3.4$ Hz, C-4), 140.9 (s, NCS), 141.8 (m, C-5), 184.8 (s, C-2). Anal. calcd. for $C_{19}H_{17}N_3OS_3$: C, 57.14; H, 4.26; N, 10.53. Found: C, 56.81; H, 4.12; N, 10.39.

*4-(4-Chlorophenyl)-2,3-dihydro-5-(dimethylamino)-3-(2-isothiocyanatophenyl)-2-thioxothiazole (***7b***).* m.p. 189°C (CH_2Cl_2/petroleum ether). ^1H NMR δ 2.61 (s, 6H), 7.11 (d, 2H, $J = 8.5$Hz), 7.21 (d, 2H, $J = 8.5$ Hz), 7.30 (m, 4H). ^{13}C NMR δ 45.4 (NCH_3), 125.7, 127.6, 127.7, 128.7, 130.5, 130.6, 130.8, 131.4, 135.0, 135.4 (arom. C), 130.5 (screened, C-4), 141.0 (s, NCS), 142.5 (m, C-5), 185.1 (s, C-2). Anal. calcd. for $C_{18}H_{14}ClN_3S_3$: C, 53.53; H, 3.47; Cl, 8.79; N, 10.40; S, 23.79. Found: C, 53.15; H, 3.37; Cl, 8.81; N, 10.30; S, 23.88.

*2,3-Dihydro-5-(dimethylamino)-3-(2-isothiocyanatophenyl)-4-(4-nitrophenyl)-2-thioxothiazole (***7c***).* m.p. 183°C (CH_2Cl_2/diethyl ether). IR 2005 cm^{-1}. ^1H NMR δ 2.64 (s, 6H), 7.10–7.45 (m, 6H), 8.09 (d, 2H, $J = 8.9$ Hz). ^{13}C NMR δ 45.4 (NCH_3), 123.5, 126.0, 127.9, 130.5, 130.8, 135.0, 135.6, 147.3 (arom. C), 128.7 (t, $^3J = 3.7$ Hz, C-4), 141.2 (s, NCS), 144.0 (m, C-5), 185.2 (s, C-2). MS calcd. for $C_{18}H_{14}N_4O_2S_3$ *m/z* 414.0279 $[M]^+$, found 414.0267; *m/z* (rel. int.): 414 (100), 356 (70), 310 (10), 282 (12). Anal. calcd.: C, 52.17; H, 3.38; N, 13.52; S, 23.18. Found: C, 52.18; H, 3.22; N, 13.42; S, 23.24.

*2-(Dimethylamino)-3-(4-methoxyphenyl)-thiazolo[3,2-a]benzimidazole (***8a***).* m.p. 126°C. ^1H NMR δ 2.65 (s, 6H), 3.89 (s, 3H), 6.80–7.20 (m, 3H), 7.06 (d, 2H, $J = 8.8$ Hz), 7.47 (d, 2H, $J = 8.8$ Hz), 7.70 (d, 1H, $J = 8$ Hz). ^{13}C NMR δ 46.4 (NCH_3), 55.3 (OCH_3), 111.5, 114.2, 118.7, 120.1, 120.6, 122.7, 130.4, 131.4, 147.2, 160.5 (arom. C), 124.2 (t, $^3J = 3$ Hz, C-3), 140.5 (m, C-2), 152.3 (s, C-9a). MS calcd. for $C_{18}H_{17}N_3OS$ *m/z* 323.1092 $[M]^+$, found 323.1086; *m/z* (rel. int.): 323 (100), 267 (70), 224 (10). Anal. calcd.: C, 66.87; H, 5.26; N, 13.00; S, 9.90. Found: C, 66.94; H, 5.20; N, 13.11; S, 10.13.

*3-(4-Chlorophenyl)-2-(dimethylamino)-thiazolo[3,2-a]benzimidazole (***8b***).* m.p. 130°C dec. ^1H NMR δ 2.65 (s, 6H), 6.85–7.30 (m, 3H), 7.51 (s, 4H), 7.79 (d, 1H, $J = 8$ Hz). ^{13}C NMR δ 46.3 (NCH_3), 111.3, 118.9, 120.4, 122.9, 127.0, 129.1, 130.2, 131.3, 135.6, 147.1 (arom. C), 123.1 (br, C-3), 141.6 (m, C-2), 152.3 (s, C-9a). Anal. calcd. for $C_{17}H_{14}ClN_3S$: C, 62.29; H, 4.27; N, 12.82; S, 9.77. Found: C, 62.08; H, 4.18; N, 12.65; S, 10.11.

*N-[(Dimethylcarbamoyl) (4-methoxyphenyl)methyl]-2-mercaptobenzimidazole (***9a***).* m.p. 120°C dec. IR 1635 cm^{-1}. ^1H NMR δ 3.13 (s, 3H), 3.14 (s, 3H), 3.77 (s, 3H), 6.90 (m, 6H), 7.30 (d, 2H, $J = 8.7$ Hz), 7.60 (s, 1H), 11.60 (br, 1H). ^{13}C NMR δ 35.3, 36.5 (NCH_3), 54.3 (OCH_3), 58.6 (dt, $^1J = 137$ Hz, $^3J = 4.3$ Hz, CH), 108.9, 111.9, 113.4, 121.5, 121.8, 124.2, 128.7, 129.5, 131.4, 158.8 (arom. C), 167.4 (m, CO), 167.4 (screened, C-2). MS calcd. for $C_{18}H_{19}N_3O_2S$ *m/z* 341.1198 $[M]^+$, found 341.1179; *m/z* (rel. int.): 341 (20), 296 (100), 273 (10), 167 (90). Anal. calcd.: C, 63.34; H, 5.57; N, 12.32; S, 9.38. Found: C, 63.21; H, 5.52; N, 12.25; S, 9.56.

*N-[(4-Chlorophenyl) (dimethylcarbamoyl) methyl]-2-mercaptobenzimidazole (***9b***).* m.p. 125°C dec. IR 1630 cm^{-1}. ^1H NMR δ 3.13 (s, 3H), 3.14 (s, 3H), 6.97 (m, 4H), 7.31 (m, 4H), 7.61 (s, 1H), 11.70 (br, 1H). ^{13}C NMR δ 36.4, 37.6 (NCH_3), 59.1 (d, $^1J = 137$ Hz, CH), 110.1, 112.7, 122.8, 123.1, 129.2, 129.7, 130.5, 132.0, 134.7 (arom. C), 167.8 (m, CO), 168.5 (t, $J = 4.6$ Hz, C-2). MS calcd. for $C_{17}H_{16}ClN_3O$ *m/z* 345.0703 $[M]^+$, found 345.0705; *m/z* (rel. int.): 345 (20), 300 (100), 273 (20), 271 (15), 168 (35).

*N-[(Dimethylcarbamoyl) (4-nitrophenyl) methyl]-2-mercaptobenzimidazole (***9c***).* m.p. 180°C dec. ^1H NMR δ 3.13 (s, 3H), 3.15 (s, 3H), 7.04 (m, 4H), 7.49 (d, 2H, $J = 8.6$ Hz), 7.67 (s, 1H), 8.19 (d, 2H, $J = 8.6$ Hz), 11.70 (br, 1H). ^{13}C NMR δ 36.7, 37.7 (NCH_3), 59.0 (dt, $^1J = 136$ Hz, $^3J = 3.6$ Hz, CH), 110.3, 112.2,

123.2, 123.6, 124.0, 129.2, 130.5, 131.6, 141.2, 147.8 (arom. C), 167.2 (m, CO), 168.8 (t, $J = 5.4$ Hz, C-2). MS calcd. for $C_{17}H_{16}N_4O_3S$ *m/z* 356.0943 $[M]^+$, found 356.0935.

*N-[(Dimethylcarbamoyl) (4-methoxyphenyl) methyl]-2-(methylthio)benzimidazole (***10a***).* Crude oily product. IR 1650 cm^{-1}. ^1H NMR δ 2.69 (s, 3H), 2.80 (s, 3H), 2.94 (s, 3H), 3.65 (s, 3H), 6.32 (s, 1H), 6.75–7.10 (m, 6H), 7.54 (d, 1H, $J = 7.9$ Hz). ^{13}C NMR δ 14.2 (SCH_3), 35.1, 36.0 (NCH_3), 54.2 (OCH_3), 58.6 (dt, $^1J = 134$ Hz, $^3J = 3.9$ Hz, CH), 110.7, 113.3, 117.0, 120.7, 121.0, 124.4, 128.5, 135.0, 142.7, 158.8 (arom. C), 151.4 (qd, $^3J = 4.2$ Hz, C-2), 166.3 (m, CO). MS calcd. for $C_{19}H_{21}N_3O_2S$ *m/z* 355.1354 $[M]^+$, found 355.1354; *m/z* (rel. int.): 355 (40), 283 (90), 235 (20), 192 (30), 164 (100).

Reactions of the Thiazolium Chloride **2** *with Diisothiocyanates*

In a general procedure, triethylamine (1.5 g, 15 mmol) was added dropwise to a suspension of salt **2** (1.95 g, 5 mmol) and diisothiocyanate in dry THF (25 ml). Quantities of the dipolarophile were the following: 2.88 g, 15 mmol or 1.15 g, 6 mmol for phenylene-1,2-diisothiocyanate (**4**); 1.15 g, 8 mmol for ethylene diisothiocyanate (**5**) (see the discussion before). A blood red color appeared immediately but disappeared very rapidly. The reaction medium was stirred at room temperature for 2 h in the case of **4** and for 6 h in that of **5**. A mixture of triethylammonium chloride and imidazolium-4-thiolate (**12**) or (**17**) was collected by filtration and successively washed with H_2O and diethyl ether to give the crude monocycloadduct as the insoluble part (**12**: 1.45 g, 3.4 mmol or 0.56 g, 1.3 mmol according to the excess of **4**; **17**: 0.46 g, 1.2 mmol). Diethyl ether (10 mL) was poured into the filtrate in order to precipitate the remaining adduct **12** in admixture with the side-product **6**. Concentration of the last filtrate and trituration with diethyl ether gave the yellow crystalline biimidazole **13** (0.47 g, 0.7 mmol).

The reaction of the monoimidazole **12** (1.3 g, 3 mmol) with the salt **2** (1.56 g, 4 mmol) and triethylamine (1 g, 10 mmol) was also performed in THF (30 mL) at room temperature for 12 h. As previously described, the workup procedure consists of filtration, washing with H_2O, then diethyl ether, to afford a yellowish solid material. The ^1H NMR analysis of this crude product showed the primary cycloadduct **14** as the strongly dominant compound [δ 1.08 (s, 9H), 2.35 (s, 3H), 3.62 (s, 3H), 6.95–7.70 (m, 24H)] and only small amounts of biimidazole **13**. The cycloadduct **14** was decomposed into the biimidazole **13** and *tert*-butyl isothiocyanate (δ 1.42 s) by standing in $CDCl_3$ solution at room temperature. After complete degradation, the bis(mesoinic imidazole) **13** was isolated in the usual way (1.34 g, 2 mmol).

Compounds **12** and **13** were quantitatively alkylated by iodomethane in dry CH_2Cl_2 during 10 min. The solvent was removed under reduced pressure and the residual syrup was triturated with diethyl ether to give a yellowish insoluble material. The methiodides **15** and **16** are stable amorphous hemisolids (undefined melting points).

*3-(2-Isothiocyanatophenyl)-1-methyl-2-phenyl-5-(phenylthio)imidazolium-4-thiolate (***12***).* m.p. 160–165°C (CH_2Cl_2/diethyl ether). IR 2040 cm^{-1}. ^1H NMR δ 3.69 (s, 3H), 7.15–7.60 (m, 14H). ^{13}C NMR δ 34.2 (NCH_3), 122.9, 126.3, 126.5, 127.7, 127.8, 129.3, 129.5, 129.7, 130.9, 131.3, 131.8, 132.6, 135.5 (arom. C), 118.2 (q, $^3J = 3.1$ Hz, C-5), 139.4 (s, NCS), 141.4 (m, C-2), 161.4 (s, C-4). MS calcd. for $C_{23}H_{18}N_3S_3$ *m/z* 432.0663 $[M + H]^+$, found 432.0662.

*1,2-Bis[1-methyl-2-phenyl-5-(phenylthio)-4-thiolate-imidazolium-3-yl]phenyl (***13***).* m.p. 240–245°C (CH_2Cl_2/diethyl ether). ^1H NMR δ 3.55 (s, 6H), 6.75–7.90 (m, 24H). ^{13}C NMR δ 34.5 (NCH_3), 124.9, 125.5, 126.4, 128.5, 129.3, 130.8, 131.0, 131.7, 133.2, 136.4 (arom. C), 116.1 (q, $^3J = 3$ Hz, C-5), 143.5 (m, C-2), 158.3 (s, C-4). MS calcd. for $C_{38}H_{30}N_4S_4$ *m/z* 670.1353 $[M]^+$, found 670.1369; *m/z* (rel. int.): 670 (100), 593 (14), 444 (10), 373 (57), 307 (39).

*3-(2-Isothiocyanatophenyl)-1-methyl-4-(methylthio)-2-phenyl-5-(phenylthio)imidazolium iodide (***15***).* ^1H NMR δ 2.48 (s, 3H), 3.77 (s, 3H), 7.28–7.88 (m, 13H), 8.56 (dd, $^1J = 7.8$ and 1.4 Hz, 1H). ^{13}C NMR δ 20.0 (SCH_3), 35.5 (NCH_3), 121.2, 125.7, 128.3, 128.5, 129.4, 129.7, 129.9, 130.1, 130.2, 131.1, 131.2, 131.6, 132.4, 132.8 (arom. C), 133.0 (q, $^3J = 3.3$ Hz, C-5), 137.2 (q, $^3J = 4.4$ Hz, C-4), 141.0 (s, NCS), 148.9 (m, C-2). MS calcd. for $C_{24}H_{20}N_3S_3$ *m/z* 446.0819 $[M\text{-}I]^+$, Found 446.0815.

*1,2-Bis[1-methyl-4-(methylthio)-2-phenyl-5-(phenylthio)imidazolium-3-yl]phenyl diiodide (***16***).* ^1H NMR ($CDCl_3$+CF_3CO_2H) δ 2.08 (s, 6H), 3.85 (s, 6H), 7.20–8.10 (m, 24H). ^{13}C NMR ($CDCl_3$ + CF_3CO_2H) δ 20.0 (SCH_3), 37.2 (NCH_3), 120.1, 128.6, 129.6, 130.2, 130.3, 130.7, 132.3, 133.2, 133.6 (arom. C), 133.2 (q, $^3J = 3$ Hz, C-5), 138.7 (q, $^3J = 5$ Hz, C-4), 147.6 (m, C-2). MS calcd. for $C_{40}H_{36}N_4S_4I$ *m/z* 827.0868 $[M\text{-}I]^+$, Found 827.0868.

3-(2-Isothiocyanatoethyl)-1-methyl-2-phenyl-5-(phenylthio)imidazolium-4-thiolate (**17**). m.p. 186°C (CH_2Cl_2/petroleum ether). IR 2050 cm^{-1}. ^1H NMR δ 3.52 (s, 3H), 4.36 (m, 4H), 7.15–7.70 (m, 10H). ^{13}C NMR δ 34.0 (NCH_3), 43.4, 45.4 (NCH_2), 123.5, 126.9, 127.7, 129.8, 130.4, 130.5, 132.7, 135.9 (arom. C), 118.5 (q, $J = 3.1$ Hz, C-5), 133.4 (br, NCS), 142.7 (m, C-2), 157.9 (t, $^3J = 3.7$ Hz, C-4). MS calcd. for $C_{19}H_{17}N_3S_3$ *m/z* 383.0585 $[M]^+$, found 383.0586; *m/z* (rel. int.): 383 (15), 324 (10), 309 (100), 102 (80). Anal. calcd.: C, 59.53; H, 4.44; N, 10.97; S, 25.06. Found: C, 59.41; H, 4.38; N, 10.75; S, 25.19.

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