

## First Examples of Reactions of Azole *N*-Oxides with Thioketones: A Novel Type of Sulfur-Transfer Reaction

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Dedicated to Professor *George A. Olah* on the occasion of his 70th birthday

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The reactions of 1,4,5-trisubstituted imidazole 3-oxides **1a–k** with cyclobutanethiones **5a,b** in CHCl<sub>3</sub> at room temperature give imidazole-2(3*H*)-thiones **9a–k** in high yield. The second product formed in this reaction is 2,2,4,4-tetramethylcyclobutane-1,3-dione (**6a**; *Scheme 2*). Similar reactions occur with **1** and adamantane-thione (**5c**) as thiocarbonyl compound, as well as with 1,2,4-triazole-4-oxide derivative **10** and **5a** (*Scheme 3*). A reaction mechanism by a two-step formation of the formal cycloadduct of type **7** via zwitterion **16** is proposed in *Scheme 5*. Spontaneous decomposition of **7** yields the products of this novel sulfur-transfer reaction. The starting imidazole 3-oxides are conveniently prepared by heating a mixture of 1,3,5-trisubstituted hexahydro-1,3,5-triazines **3** and  $\alpha$ -(hydroxyimino) ketones **2** in EtOH (*cf. Scheme 1*). As demonstrated in the case of **9d**, a 'one-pot' procedure allows the preparation of **9** without isolation of the imidazole 3-oxides **1**. The reaction of **1c** with thioketene **12** leads to a mixture of four products (*Scheme 4*). The minor products, **9c** and the ketene **15**, result from an analogous sulfur-transfer reaction (*Path a* in *Scheme 5*), whereas the parent imidazole **14** and thiiranone **13** are the products of an oxygen-transfer reaction (*Path b* in *Scheme 5*).

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**Introduction.** – Due to our current interest in cycloaddition chemistry involving thiocarbonyl compounds, we decided to examine whether imidazole 3-oxides of type **1** undergo reactions with thioketones which were recognized as excellent dipolarophiles<sup>2)</sup>. To the best of our knowledge, no reaction of an aza-aromatic *N*-oxide and a thioketone has been reported so far.

Studies on syntheses and chemical behavior of aromatic *N*-oxides are of considerable interest [4]. Several thermal and photochemical transformations gave rise to unexpected products *via* unusual mechanistic pathways [5–7]. Among intermolecular transformations with *N*-oxides, one of the most significant type involves reactions with dipolarophiles. In analogy to nitrones, aromatic *N*-oxides behave as 1,3-dipoles, and several examples of reactions with electron-deficient olefins and acetylenes as well as with isocyanates have been reported [4–8]. Imidazole *N*-oxides are well-known representatives of azole *N*-oxides, and reports on their synthesis go back to the beginning of this century (*cf.* [9]). However, 2-unsubstituted imidazole *N*-oxides **1**, being convenient starting materials for syntheses of imidazole derivatives, were reported only in the seventies by an English and a Polish group [10][11]. Until now, there is only a very limited use of these compounds with respect to syntheses of imidazole derivatives functionalized at C(2). Described reactions of some representatives of **1** concern substitution of the H-atom at C(2) by Cl, deoxygenation, the photochemical rearrangement to the

<sup>1)</sup> Part of the projected Ph.D. thesis of *T.G.*, University of Łódź

<sup>2)</sup> Thioketones have been shown to be the most reactive dipolarophiles towards thiocarbonyl ylides [1], Ph<sub>2</sub>CN<sub>2</sub> [2], and nitrones [3].

corresponding imidazol-2-ones, as well as 1,3-dipolar cycloadditions with phenyl isocyanate and dimethyl acetylenedicarboxylate [10–12]. Recently, a smooth introduction of a CN group using  $\text{Me}_3\text{SiCN}$  has also been elaborated [12b].

The only related reactions with S-containing dipolarophiles were described by *Takahashi* and *Kano* [13]: 1-methylbenzimidazole 3-oxide and  $\text{CS}_2$  react to give 1-methylbenzimidazole, and with phenyl isothiocyanate a similar reaction results in the formation of 1-methyl-2-(phenylamino)benzimidazole. One of the postulated mechanisms of these reactions involve a 1,3-dipolar cycloaddition with subsequent elimination of  $\text{COS}^3$ .

**Results and Discussion.** – To prepare imidazole 3-oxides **1**,  $\alpha$ -(hydroxyimino) ketones **2** and 1,3,5-trisubstituted hexahydro-1,3,5-triazines **3** were heated in EtOH (*cf.* [11], *Scheme 1*). The crystalline products were obtained in high yields (*Table 1*).

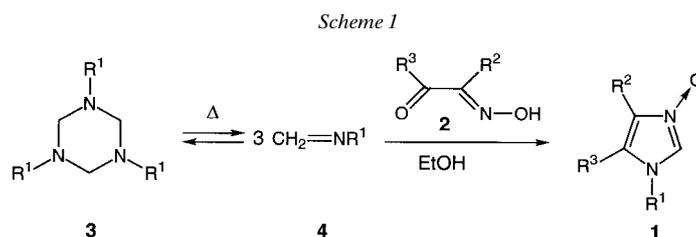


Table 1. Prepared 1,4,5-Trisubstituted Imidazole 3-Oxides **1**

<b>1</b>	<b>2</b>	<b>3/4</b>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield of <b>1</b> [%]	M.p. [°]
<b>a</b>	<b>a</b>	<b>a</b>	Me	Me	Me	77	164–166
<b>b</b>	<b>a</b>	<b>b</b>	Et	Me	Me	54	61–63
<b>c</b>	<b>a</b>	<b>c</b>	PhCH <sub>2</sub>	Me	Me	95	199–201
<b>d</b>	<b>a</b>	<b>d</b>	Cyclohexyl	Me	Me	58	198–200
<b>e</b>	<b>b</b>	<b>a</b>	Me	Ph	Ph	61	255–257
<b>f</b>	<b>b</b>	<b>b</b>	Et	Ph	Ph	75	182–184
<b>g</b>	<b>b</b>	<b>c</b>	PhCH <sub>2</sub>	Ph	Ph	92	174–176
<b>h</b>	<b>b</b>	<b>d</b>	Cyclohexyl	Ph	Ph	74	179–180
<b>i</b>	<b>b</b>	<b>e</b>	PhCH <sub>2</sub> CH <sub>2</sub>	Ph	Ph	88	185–187
<b>j</b>	<b>c</b>	<b>a</b>	Me	Ph	Me	89	201–203
<b>k</b>	<b>c</b>	<b>f</b>	Bu	Ph	Me	80	155–157

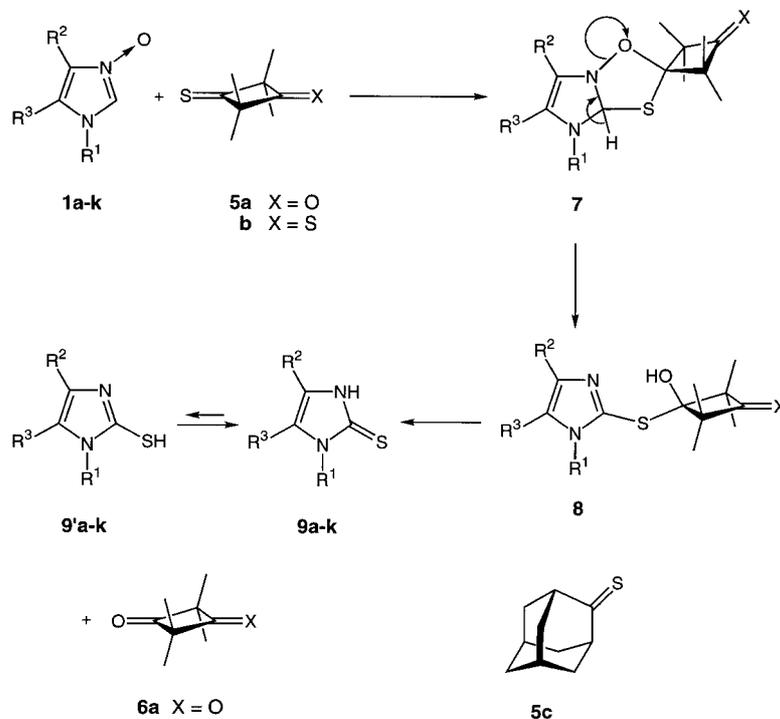
Solutions of *N*-oxides **1** in  $\text{CHCl}_3$  were treated with a slight excess of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**5a**) at room temperature. Immediately, an exothermic reaction started, and, within a few minutes, the characteristic red color of **5a** disappeared, and a colorless product precipitated. After removing the solvent, the crude mixture was analyzed by means of <sup>1</sup>H-NMR spectroscopy. In all cases, the characteristic Me absorption at 1.2 ppm of 2,2,4,4-tetramethylcyclobutane-1,3-dione (**6a**) appeared. Furthermore, the signal of H–C(2) of **1** at 8–8.5 ppm was no longer present. The colorless solids were washed with EtOH and recrystallized to give

<sup>3)</sup> For another proposal, see [14].

imidazole-2(3*H*)-thiones **9** in high yields (*cf.* Scheme 2 and Table 2). Some of the products have previously been described and were identified by the comparison of their melting points and spectral data. Typically, a medium intensive C=S absorption in the IR spectrum (KBr) was registered at 1220–1150 cm<sup>-1</sup>, and, in the <sup>13</sup>C-NMR spectrum, the C(2) signal appeared at 150–160 ppm.

An identical course of reaction was observed using dithione **5b** instead of **5a**. In this case, only 0.5 equiv. of **5b** was required for a complete conversion of **1** into **9**, *i.e.*, both C=S groups of **5b** were involved in the reaction, and again **6a** was formed.

Scheme 2

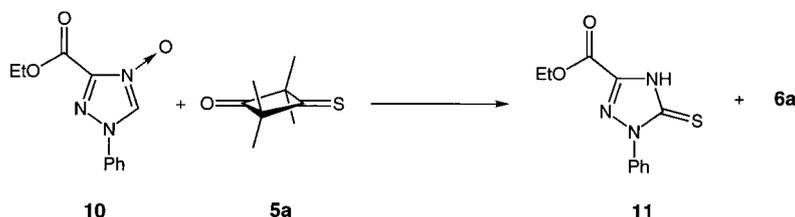
Table 2. Prepared Imidazole-2(3*H*)-thiones **9** from **1** and **5a**

<b>9</b>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield [%]	M.p. [°]
<b>a</b>	Me	Me	Me	83	212–214
<b>b</b>	Et	Me	Me	83	183–184
<b>c</b>	PhCH <sub>2</sub>	Me	Me	92	227–228
<b>d</b>	Cyclohexyl	Me	Me	95	221–223
<b>e</b>	Me	Ph	Ph	79	279–281
<b>f</b>	Et	Ph	Ph	96	292–294
<b>g</b>	PhCH <sub>2</sub>	Ph	Ph	95	268–270
<b>h</b>	Cyclohexyl	Ph	Ph	95	295–297
<b>i</b>	PhCH <sub>2</sub> CH <sub>2</sub>	Ph	Ph	88	261–263
<b>j</b>	Me	Ph	Me	94	254–256
<b>k</b>	Bu	Ph	Me	65	285–287

Adamantanethione (**5c**)<sup>4</sup> and **1** reacted as well in a very similar way, and, after a short reaction time, imidazole-2(3*H*)-thiones **9** were isolated in similar yields as from the reactions with **5a** (Table 2). To our surprise, the reaction of **1g** with thiobenzophenone was much more sluggish and was terminated only after *ca.* 30 h at room temperature. All attempted reactions with 9*H*-xanthene-9-thione or 9*H*-fluorene-9-thione failed completely. The influence of the steric hindrance of the substituent R<sup>1</sup> was examined in a competitive experiment in which a mixture of equal amounts of imidazole 3-oxides **1a** and **1d** was reacted with 0.5 equiv. of dithione **5b**. Product **9a** was found to be the major component in the crude mixture (<sup>1</sup>H-NMR; **9a/9d** 95:5). In a similar test with **1a** and **1c**, **9a** and **9c** were formed in almost equal amounts (ratio 45:55; <sup>1</sup>H-NMR). These results indicate that R<sup>1</sup> considerably influences the rate of the S transfer, probably at the ring-closure step of the zwitterionic intermediate **16** to give **7**.

The simple procedure of the reaction of **1** and **5** together with the high yields of synthetically useful imidazole-2(3*H*)-thiones **9**<sup>5</sup> prompted us to investigate whether similar conversions could be performed using other heterocyclic *N*-oxides. As an example, we tested the reaction of triazole derivative **10** with **5a** (Scheme 3). After a fast reaction, triazole-5(4*H*)-thione **11** was obtained in 84% yield.

Scheme 3



Unlike azole *N*-oxides, six-membered aromatic *N*-oxides did not undergo reactions neither with **5a** nor with **5c**. For example, solutions of substituted pyridine *N*-oxides and **5a** in CHCl<sub>3</sub> change the red color neither after 3 days at room temperature nor after refluxing for several hours. <sup>1</sup>H-NMR Analysis of the same reaction in CDCl<sub>3</sub> showed no change of starting materials. Several other experiments with pyrimidine-*N*-oxide derivatives<sup>6</sup>) were also unsuccessful. Based on these results, we conclude that the 'S-transfer reaction' resulting in the formation of heterocyclic thiones can be efficiently used in the series of azole *N*-oxides only.

Several years ago, *Schaumann* and *Behrens* reported on the reaction of thioketenes of type **12** with 1-pyrroline *N*-oxide, a cyclic nitron, which unexpectedly led to thiirane derivatives of type **13** and 2,3-dihydropyrrole [17]. Thus, no S but only O transfer occurred converting **12** into **13**. With respect to these results, we performed the reaction of **1c** with thioketene **12**<sup>7</sup>) in CDCl<sub>3</sub> at room temperature. After 2 h, deoxygenated imidazole **14** as well as imidazole-2(3*H*)-thione **9c** were formed in 84 and

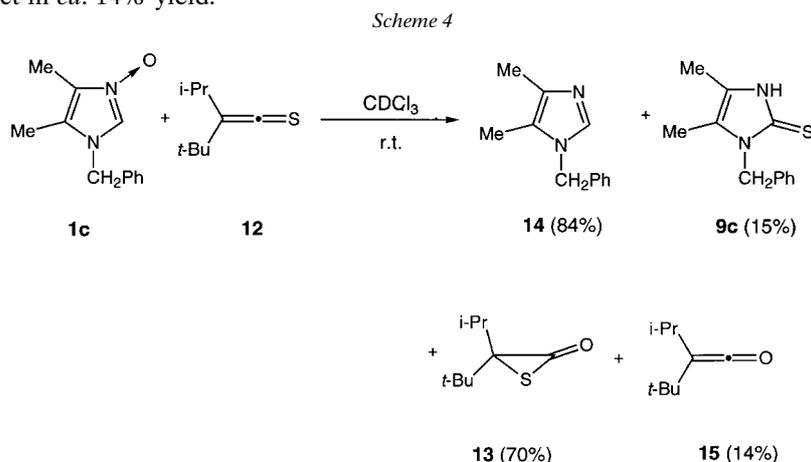
4) For convenience, the name adamantanethione is used for tricyclo[3.3.1.1<sup>3,7</sup>]decane-2-thione.

5) For the useability of imidazole-2(3*H*)-thiones, see [15][16] and refs. cit. therein.

6) We thank Dr. S. *Ostrowski*, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, for his generous gift of pyrimidine *N*-oxides.

7) We thank Prof. Dr. E. *Schaumann*, Technical University of Clausthal, for providing us with the ketene.

15% yield<sup>8</sup>), respectively (*Scheme 4*). Furthermore, **12** has been transformed into thiranone **13** in *ca.* 70% yield, and the corresponding ketene **15** was found as a minor product in *ca.* 14% yield.



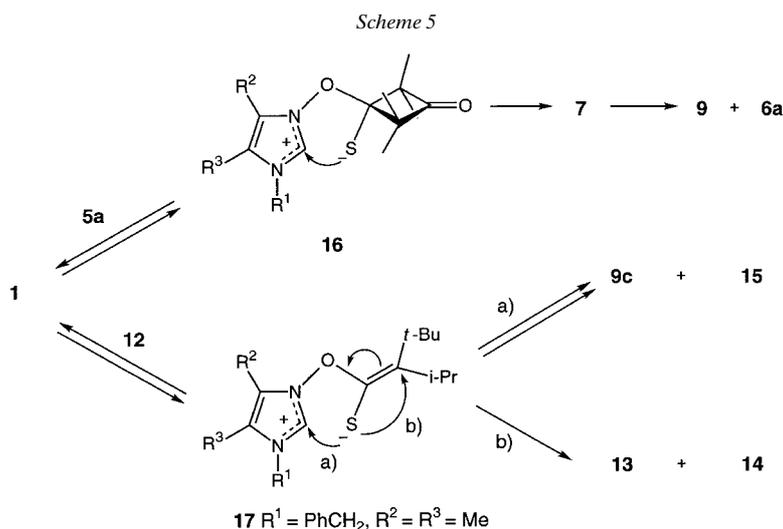
When thioketene **12** was treated with pyrimidine *N*-oxide under analogous conditions, the violet color of the solution disappeared after 7 days.  $^1\text{H-NMR}$  Analysis of the mixture showed the presence of pyrimidine and thiranone **13**, formed in quantitative yields. The latter was isolated after chromatographic workup and characterized by the comparison of the spectral data with those reported [17].

Our results, supported by some observations described earlier, enable us to formulate a mechanistically convincing pathway for the reactions of *N*-oxides with thiocarbonyl compounds. The first step of the reaction of azole *N*-oxides with thioketones is a nucleophilic attack of the O-atom of the *N*-oxide onto the C=S group to give the dipolar intermediate **16** (*Scheme 5*). Ring closure between the S-atom and C(2) of the imidazolium ion leads to the formal [2 + 3] cycloadduct **7**. This intermediate has never been observed in our NMR experiments but decomposed, probably *via* O,S-hemiacetal **8** (*Scheme 2*), in a fast and irreversible reaction to yield the final products **8** and **6a**.

Stable 1,4,2-oxathiazolidines of type **7** have been described by *Black and Watson* who carried out reactions of **5a–c** with both acyclic and cyclic nitrones (*e.g.*, pyrroline *N*-oxides) [18]. Some of these oxathiazolidines, upon irradiation with UV light, dissociated to give pyrrolidine-2-thiones and the ketone corresponding to **5**. For this process, a thiaziridine was postulated as an intermediate. Formation of the stable oxathiazolidines was explained as the result of a 1,3-dipolar cycloaddition. In contrast to this proposal, it is likely that the reaction between **1** and **5a–c** to **7** occurs stepwise *via* the initial formation of **16**. An additional result supporting this mechanism is the much slower reaction of **1** with thiobenzophenone, which has been shown in several experiments to be a more reactive dipolarophile than **5a–c** [1][2]<sup>9</sup>). Furthermore, the

<sup>8</sup>) Determined in the reaction mixture by means of  $^1\text{H-NMR}$  spectroscopy.

<sup>9</sup>) The reaction of thiobenzophenone methanide with thiobenzophenone was *ca.*  $10^3$  times faster than with **5a** [2a]. Reaction rates with  $\text{Ph}_2\text{CN}_2$  showed a similar difference [2b].



'superdipolarophile' thiofluorenone resisted to react with **1**, and this observation is rationalized in terms of an ionic process. The polarization of the C=S bond in thiofluorenone is considerably increased in comparison with other aromatic thioketones, as the negative charge is partially delocalized within the aromatic skeleton. Therefore, the electrophilicity of the C=S C-atom is reduced, and the nucleophilic attack of the O-atom to give **16**, initiating the formation of **7**, does not occur.

The low stability of the 'cycloadduct' **7** in comparison with 1,4,2-oxathiazolidines described by *Black* and *Watson* can be understood by the fact that the dissociation of **7** into **9** and **6a** occurs by re-aromatization of the azole ring<sup>10</sup>).

The stepwise mechanism may also explain the lack of reaction of pyridine and pyrimidine *N*-oxides with thioketones. The key step of the conversion  $1 + 5a \rightarrow 9 + 6a$  is the formation of zwitterion **16** which, in the case of six-membered aromatic *N*-oxides, is much less favored due to the lack of stabilization of the positive charge by the lone pair of the second N-atom.

A further evidence of the stepwise mechanism of the reaction of azole *N*-oxides with thioketones is provided by the reaction of **1c** with thioketene **12** (Scheme 4). In analogy to **16**, zwitterion **17** is proposed as the key intermediate (Scheme 5). Cyclization *via Path a* initiate a cascade of reactions which result in formation of imidazole-2(3*H*)-thione **9c** and the corresponding ketene **15**. However, the main product is formed *via Path b* involving formation of a thiirane ring and simultaneous cleavage of the N–O bond, yielding thiiranone **13** and deoxygenated imidazole **14**. In the slow reaction of pyrimidine *N*-oxide and **12**, apparently *Path b* is followed exclusively leading to the parent heterocycle and **13**.

In conclusion, the reaction of azole *N*-oxides with easily available cycloalkane-thiones offers a simple and efficient route to azole-thiones. Taking into account that a

<sup>10)</sup> Imidazole-2(3*H*)-thiones like other azole-thiones are in a tautomeric equilibrium with the corresponding azole-thiole structures (*cf.* [15][19]).

series of differently substituted imidazole 3-oxides are easily prepared, the described reaction sequence constitutes a very useful synthesis of imidazole-2(3*H*)-thiones. It is especially worth mentioning that a ‘one-pot’ reaction has been elaborated which allows to prepare imidazole-2(3*H*)-thiones **9** from perhydro-1,3,5-triazines **3**,  $\alpha$ -(hydroxyimino) ketones **2**, and cyclobutane-1,3-dithione **5b** without isolation of the intermediate imidazole 3-oxide **1**.

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### Experimental Part

1. *General.* See [20]. M.p.: in capillary, *Melt-Temp. II (Aldrich)* apparatus; uncorrected. IR Spectra: *Specord-71* IR spectrometer; in KBr. <sup>1</sup>H- and <sup>13</sup>C-NMR-Spectra: *Varian-Gemini-BB* spectrometer (200 MHz (<sup>1</sup>H) and 50.4 MHz (<sup>13</sup>C)); CDCl<sub>3</sub> soln.; TMS as an internal standard ( $\delta(\text{TMS}) = 0$ ). EI-MS: *Variat-MAT-112S* spectrometer; at 70 eV; CI-MS with NH<sub>3</sub>. Elemental analyses were performed in the microanalytical laboratories of the Polish Academy of Sciences in Łódź and the Institute of Organic Chemistry of the University of Zürich.

2. *Starting Materials.* The perhydro-1,3,5-triazines **3a–f** were prepared from the corresponding primary amines and HCHO according to known protocols: *1,3,5-trimethylperhydro-1,3,5-triazine (3a)*, *1,3,5-triethylperhydro-1,3,5-triazine (3b)*, and *1,3,5-tributylperhydro-1,3,5-triazine (3f)* [21], *1,3,5-tribenzylperhydro-1,3,5-triazine (3c)* [22], *1,3,5-tris(2-phenylethyl)perhydro-1,3,5-triazine (3e)* [23], and *1,3,5-tri(cyclohexyl)perhydro-1,3,5-triazine (3d)* [24]. For preparation of diketone monoximes **2**, described methods have been applied to: *3-(hydroxyimino)butan-2-one (2a)* by nitrosation of butan-2-one using amyl nitrite [25], *2-(hydroxyimino)-1,2-diphenylethanone* (benzil monoxime; **2b**) from benzil and NH<sub>2</sub>OH·HCl hydrochloride [26], and *3-(hydroxyimino)-3-phenylpropan-2-one (2c)* by nitrosation of 1-phenylpropan-2-one [27]. The *2,2,4,4-tetramethyl-3-thioxocyclobutanone (5a)* and *2,2,4,4-tetramethylcyclobutane-1,3-dithione (5b)* were prepared by thionation of 2,2,4,4-tetramethylcyclobutane-1,3-dione using P<sub>4</sub>S<sub>10</sub> [28], adamantanethione (**5c**) was synthesized analogously from commercially available adamantanone according to [29], and *(tert-butyl)(isopropyl)thioiketene (11)* was provided by Prof. Dr. *E. Schaumann*, Technical University of Clausthal, Germany. Pyridine and pyrimidine *N*-oxides were obtained from pyridine and pyrimidine, respectively, using H<sub>2</sub>O<sub>2</sub> as oxidizing agent according to [30]. *3-(Ethoxycarbonyl)-1-phenyl-1,2,4(1H)-triazole 4-oxide (10)* was obtained following the procedure described in [31].

Some imidazole 3-oxides **1** have not been described in the literature so far. Typically, they were prepared by heating 1.7 mmol of the corresponding perhydro-1,3,5-triazine **3** with 5 mmol of the corresponding diketone monoxime in boiling EtOH for 1–10 h; required reaction times are given. Generally, compounds **1** tend to form hydrates with variable amount of H<sub>2</sub>O which could not be removed by boiling with benzene using a *Dean-Stark* column.

*1,4,5-Trimethylimidazole 3-Oxide (1a)*: 3 h; yield 486 mg (77%). Colorless crystals. M.p. 164–166° (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O). IR: 1660*m*, 1630*s*, 1450*s*, 1400*s*, 1350*s*, 1170*m*, 1080*m*. <sup>1</sup>H-NMR: 8.10 (*s*, H–C(2)); 3.60 (*s*, MeN); 2.18, 2.16 (2*s*, 2 Me). <sup>13</sup>C-NMR: 124.9 (*d*, C(2)); 126.0, 121.4 (2*s*, C(4), C(5)); 32.2 (*q*, MeN); 8.5, 7.2 (2*q*, 2 Me). CI-MS: 127 (89, [M + 1]<sup>+</sup>), 126 (12, M<sup>++</sup>), 111 (100), 97 (12). Anal. calc. for C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>O · 0.75 H<sub>2</sub>O (139.61): C 51.63, H 8.32, N 20.06; found: C 51.38, H 9.00, N 19.88.

*1-Ethyl-4,5-dimethylimidazole 3-Oxide (1b)*: 3 h; yield 377 mg (54%). Colorless crystals. M.p. 61–63° (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O). IR: 1660*s*, 1630*s*, 1470*m*, 1410*s*, 1395*s*, 1350*s*, 1160*s*. <sup>1</sup>H-NMR: 8.10 (*s*, H–C(2)); 3.94 (*q*, *J* = 7.2, MeCH<sub>2</sub>); 2.19, 2.17 (2*s*, 2 Me); 1.39 (*t*, *J* = 7.2, MeCH<sub>2</sub>). <sup>13</sup>C-NMR: 126.1, 120.6 (2*s*, C(4), C(5)); 123.8 (*d*, C(2)); 40.6 (*t*, CH<sub>2</sub>); 15.8, 8.5, 7.2 (3*q*, 3 Me). Anal. calc. for C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>O · 2 H<sub>2</sub>O (176.22): C 47.71, H 9.15, N 15.90; found: C 47.53, H 9.03, N 15.76.

*1-Benzyl-4,5-dimethylimidazole 3-Oxide (1c)*: yield 860 mg (85%). Colorless crystals. M.p. 197–199° ([11]; 199–201°).

*1-Cyclohexyl-4,5-dimethylimidazole 3-Oxide (1d)*: 5 h; yield 2.63 g (90%). Colorless crystals. M.p. 198–200° (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O). IR: 1620*s*, 1450*s*, 1410*s*, 1380*s*, 1360*s*, 1330*vs*, 1190*s*, 840*s*, 710*s*. <sup>1</sup>H-NMR: 7.84 (*s*, H–C(2)); 3.78 (*m*, CH); 2.18, 2.17 (2*s*, 2 Me); 2.05–1.2 (*m*, 10 H). <sup>13</sup>C-NMR: 126.1, 120.2 (2*s*, C(4), C(5)); 121.8 (*d*, C(2)); 55.4 (*d*, CH); 33.8, 25.5, 24.9 (3*t*, 5 CH<sub>2</sub>); 8.8, 7.2 (2*q*, 2 Me). CI-MS: 195 (6, [M + 1]<sup>+</sup>), 180 (11), 179 (100), 117 (6). Anal. calc. for C<sub>11</sub>H<sub>18</sub>N<sub>2</sub>O · 0.5 H<sub>2</sub>O (203.28): C 64.99, H 9.42, N 13.79; found: C 65.09, H 9.49, N 13.95.

*1-Methyl-4,5-diphenylimidazole 3-Oxide (1e)*: 6 h; yield 763 mg (61%). Colorless crystals. M.p. 255–257°. IR: 1485s, 1440s, 1370s, 1345s, 1200m, 1055s, 870m, 825s, 770vs, 710vs, 670s. <sup>1</sup>H-NMR: 8.11 (s, H–C(2)); 7.55–7.25 (m, 10 arom. H); 3.55 (s, MeN). <sup>13</sup>C-NMR: 130.6, 129.6, 129.5, 126.6 (4s, C(4), C(5), 2 arom. C); 129.1, 128.2, 128.1 (3d, 10 arom. CH, C(2)); 33.2 (q, MeN). CI-MS: 251 (12, [M + 1]<sup>+</sup>), 236 (17), 235 (100). Anal. calc. for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O · 0.3 H<sub>2</sub>O (255.70): C 75.16, H 5.76, N 10.95; found: C 75.34, H 5.58, N 10.94.

*1-Ethyl-4,5-diphenylimidazole 3-Oxide (1f)*: 3 h; yield 990 mg (75%). Colorless crystals. M.p. 182–184° (CHCl<sub>3</sub>/benzene). IR: 1600m, 1480s, 1445s, 1380s, 1345vs, 1250s, 1210s, 1080s, 1050s, 1030s, 850s, 760vs, 705vs, 675s. <sup>1</sup>H-NMR: 8.20 (s, H–C(2)); 7.55–7.25 (m, 10 arom. H); 3.87 (q, J = 7.2, MeCH<sub>2</sub>); 1.31 (t, J = 7.2, MeCH<sub>2</sub>). <sup>13</sup>C-NMR: 130.6, 127.6, 127.0 (3s, C(4), C(5), 1 arom. C); 129.5, 129.1, 128.0, 125.5 (4d, C(2), 10 arom. CH); 41.3 (t, CH<sub>2</sub>); 16.0 (q, Me). CI-MS: 265 (15, [M + 1]<sup>+</sup>), 250 (18), 249 (100, [M – 16]<sup>+</sup>), 173 (31). Anal. calc. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O · H<sub>2</sub>O (282.33): C 72.25, H 6.37, N 9.91; found: C 72.18, H 6.19, N 10.38.

*1-Benzyl-4,5-diphenylimidazole 3-Oxide (1g)*: 2 h; yield 1.30 g (80%). Colorless crystals. M.p. 174–176° (pentane/Et<sub>2</sub>O) ([11]: 176–178°).

*1-Cyclohexyl-4,5-diphenylimidazole 3-Oxide (1h)*: 6 h; yield 1.19 g (75%). Colorless crystals. M.p. 179–180° (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O). IR: 2860s, 1640s, 1510s, 1480m, 1440s, 1360m, 1320s, 1300s, 1210s, 1040vs, 1020vs, 880vs, 770vs, 720vs, 700vs. <sup>1</sup>H-NMR: 8.18 (s, H–C(2)); 7.65–7.2 (m, 10 arom. H); 3.67 (m, CH); 1.85–1.05 (m, 10 H). <sup>13</sup>C-NMR: 132.6, 129.1, 127.4, 124.8 (4s, C(4), C(5), 2 arom. C); 130.8, 130.7, 129.7, 129.6, 129.2, 128.1, 128.0, 127.9, 126.4 (9d, C(2), 10 arom. CH); 55.8 (d, CH); 34.0, 25.3, 24.5 (3t, 5 CH<sub>2</sub>). CI-MS: 319 (5, [M + 1]<sup>+</sup>), 303 (54), 302 (100).

*4,5-Diphenyl-1-(2-phenylethyl)imidazole 3-Oxide (1i)*: 2 h; yield 1.26 g (74%). Colorless crystals. M.p. 185–187° (benzene/petroleum ether; [11]: 188–190°).

*1,5-Dimethyl-4-phenylimidazole 3-Oxide (1j)*: 3 h; yield 837 mg (89%). Colorless crystals. M.p. 201–202° (CHCl<sub>3</sub>/petroleum ether). IR: 3040s, 1605m, 1440s, 1380s, 1350s, 1250s, 1205m, 1030m, 770vs, 720s, 705s. <sup>1</sup>H-NMR: 7.96 (s, H–C(2)); 7.65–7.6 (m, 3 arom. H); 7.5–7.25 (m, 2 arom. H); 3.60, 2.28 (2s, 2 Me). <sup>13</sup>C-NMR: 129.6, 128.4, 128.3 (3d, C(2), 5 arom. CH); 127.3, 125.5, 122.7 (3s, C(4), C(5), 1 arom. C); 32.4 (q, MeN); 9.4 (q, Me). CI-MS: 189 (14, [M + 1]<sup>+</sup>), 188 (11, M<sup>++</sup>), 174 (12), 173 (100), 159 (17). Anal. calc. for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O · H<sub>2</sub>O (206.24): C 64.06, H 7.09, N 13.58; found: C 63.91, H 6.70, N 13.55.

*1-Butyl-5-methyl-4-phenylimidazole 3-Oxide (1k)*: 1 h; yield 875 mg (76%). Colorless crystals. M.p. 155–157° (benzene/petroleum ether; [11]: 157–158°).

3. *Conversions of Imidazole 3-Oxides 1 to Imidazole-2(3H)-thiones 9. General Procedure.* A cooled soln. (H<sub>2</sub>O/ice bath) of **5a** (156 mg, 1 mmol)<sup>11</sup> in CHCl<sub>3</sub> (1 ml) was stirred magnetically, and a soln. of the corresponding *N*-oxide **1** (1 mmol) in CHCl<sub>3</sub> (1 ml) was added dropwise. Then, the cooling bath was removed and stirring continued for 1 h at r.t. The decolorized soln. with partially precipitated products were evaporated *in vacuo*, and solid residues were triturated with pentane (5 ml) to remove 2,2,4,4-tetramethylcyclobutane-1,3-dione (**6a**) formed as a by-product. The crude products were fairly pure and could be used for further reactions without purification. Anal. samples were prepared by subsequent recrystallization. Reported yields refer to imidazole-2(3H)-thione isolated after recrystallization.

*1,4,5-Trimethylimidazole-2(3H)-thione (9a)*: 118 mg (85%). Colorless crystals. M.p. 212–214° (EtOH). IR: 3020vs, 2960vs, 1660s, 1500s, 1440s, 1395s, 1260s, 1150m, 1110m, 795m. <sup>1</sup>H-NMR: 11.80 (br. s, NH); 3.50, 2.09, 2.06 (3s, 3 Me). <sup>13</sup>C-NMR: 157.8 (s, C=S); 121.6, 119.9 (2s, C(4), C(5)); 31.1 (q, MeN); 9.0, 8.9 (2q, 2 Me). EI-MS: 143 (25, [M + 1]<sup>+</sup>), 142 (100, M<sup>++</sup>), 141 (65, [M – 1]<sup>+</sup>), 127 (35, [M – Me]<sup>+</sup>), 109 (44, [M – SH]<sup>+</sup>), 100 (8), 82 (12), 71 (18), 68 (29). Anal. calc. for C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>S (142.22): C 50.67, H 7.09, N 19.70, S 19.88; found: C 50.46, H 7.38, N 19.46, S 19.70.

*1-Ethyl-4,5-dimethylimidazole-2(3H)-thione (9b)*: 130 mg (83%). Colorless crystals. M.p. 183–184° (CHCl<sub>3</sub>). IR: 3000vs, 2880s, 2690m, 1660m, 1500s, 1470s, 1410s, 1390s, 1320s, 1255s, 1205m, 1140m, 1120m, 795s. <sup>1</sup>H-NMR: 10.5 (br. s, NH); 4.05 (q, J = 7.2, MeCH<sub>2</sub>); 2.08 (s, 2 Me); 1.30 (t, J = 7.2, MeCH<sub>2</sub>). <sup>13</sup>C-NMR: 157.5 (s, C=S); 120.9, 119.9 (2s, C(4), C(5)); 39.4 (t, CH<sub>2</sub>); 14.0, 9.0, 8.8 (3q, 3 Me). Anal. calc. for C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>S (156.25): C 53.81, H 7.74, N 17.93, S 20.52; found: C 53.86, H 8.07, N 17.81, S 20.86.

*1-Benzyl-4,5-dimethylimidazole-2(3H)-thione (9c)*: 201 mg (92%). Colorless crystals. M.p. 227–228° (CHCl<sub>3</sub>). IR: 3020s, 1660s, 1500s, 1450s, 1405m, 1380m, 1370m, 1250m, 1240m, 1195m, 790m. <sup>1</sup>H-NMR: 10.75 (br. s, NH); 7.28 (br. s, 5 arom. H); 5.34 (s, CH<sub>2</sub>); 2.11, 1.97 (2s, 2 Me). <sup>13</sup>C-NMR: 160.1 (br. s, C=S); 135.8

<sup>11</sup>) Identical reactions were observed using 154 mg (1 mmol) of adamantanethione (**5c**) or 86 mg (0.5 mmol) of 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**5b**). Thiobenzophenone reacted significantly slower and decolorization of the soln. at r.t. was completed only after 30 h.

(s, 1 arom. C); 128.8, 127.7, 127.0 (3d, 5 arom. CH); 123.4, 109.5 (2s, C(4), C(5)); 48.1 (t, CH<sub>2</sub>); 9.2, 9.1 (2q, 2 Me). EI-MS: 218 (100, M<sup>+</sup>), 185 (43, [M – SH]<sup>+</sup>), 127 (30, [M – C<sub>7</sub>H<sub>7</sub>]<sup>+</sup>), 91 (79, C<sub>7</sub>H<sub>7</sub><sup>+</sup>). Anal. calc. for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>S (218.32): C 66.02, H 6.46, N 12.83, S 14.69; found: C 65.91, H 6.83, N 13.07, S 14.80.

**1-Cyclohexyl-4,5-dimethylimidazole-2(3H)-thione (9d)**: 200 mg (95%). Colorless crystals. M.p. 221–223° (EtOH). IR: 3040vs, 2920vs, 2820vs, 2660s, 1660s, 1510s, 1455s, 1420s, 1400s, 1380s, 1280s, 1250s, 1120m, 1020m, 1000m, 800s. <sup>1</sup>H-NMR: 11.94 (br. s, NH); 4.86 (m, 1 H); 2.18, 2.06 (2s, 2 Me); 1.9–1.5 (br. m, 10 H). <sup>13</sup>C-NMR: 157.2 (s, C=S); 121.1, 120.8 (2s, C(4), C(5)); 57.1 (d, CH); 30.6, 26.1, 25.4 (3t, 5 CH<sub>2</sub>); 10.6, 8.9 (2q, 2 Me). EI-MS: 210 (54, M<sup>+</sup>), 128(100), 95(7). Anal. calc. for C<sub>11</sub>H<sub>18</sub>N<sub>2</sub>S (210.34): C 68.81, H 8.63, N 13.32, S 15.24; found: C 68.67, H 8.75, N 13.35, S 15.35.

**1-Methyl-4,5-diphenylimidazole-2(3H)-thione (9e)**: 210 mg (79%). Colorless crystals. M.p. 279–281° (EtOH). IR: 2980s, 2880s, 1600m, 1495s, 1450s, 1430s, 1400s, 1385s, 1280m, 1145m, 800s. <sup>1</sup>H-NMR: 11.46 (br. s, NH); 7.5–7.25 (m, 10 arom. H); 3.49 (s, Me). <sup>13</sup>C-NMR: 159.2 (s, C=S); 129.6, 128.5, 127.9 (3s, C(4), C(5), 2 arom. C); 130.7, 129.3, 128.8, 128.6, 126.6 (5d, 10 arom. CH); 32.6 (q, Me). EI-MS: 266 (100, M<sup>+</sup>), 265 (100, [M – 1]<sup>+</sup>), 233 (8, [M – SH]<sup>+</sup>), 232(13), 207(20), 206(12), 193(15), 165(18), 133(18), 118(13), 104(10), 77(19). Anal. calc. for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>S (266.36): C 72.16, H 5.30, N 10.53, S 12.02; found: C 72.19, H 5.42, N 10.54, S 11.93.

**1-Ethyl-4,5-diphenylimidazole-2(3H)-thione (9f)**: 269 mg (96%). Colorless crystals. M.p. 292–294° (EtOH). IR: 3000s, 2880s, 1600m, 1510s, 1490vs, 1460s, 1405s, 1380m, 1260s, 1140m, 780s. <sup>1</sup>H-NMR: 11.05 (br. s, NH); 7.5–7.2 (m, 10 arom. H); 4.04 (q, MeCH<sub>2</sub>); 1.21 (t, MeCH<sub>2</sub>). <sup>13</sup>C-NMR: 159.9 (s, C=S); 130.9, 128.0, 126.4 (3s, C(4), C(5), 1 arom. C); 129.7, 129.3, 128.8 (3d, 10 arom. CH); 40.3 (t, CH<sub>2</sub>); 14.3 (q, Me). EI-MS: 280 (100, M<sup>+</sup>), 279 (33, [M – 1]<sup>+</sup>), 252(35), 240(12), 193(31), 165(16), 104(13), 103(12), 77(14). Anal. calc. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>S (280.39): C 72.82, H 5.75, N 9.99, S 11.43; found: C 72.54, H 6.05, N 10.05, S 11.28.

**1-Benzyl-4,5-diphenylimidazole-2(3H)-thione (9g)**: 325 mg (95%). Colorless crystals. M.p. 268–270° (CHCl<sub>3</sub>). IR: 3020s, 2900s, 1600m, 1490s, 1480s, 1460s, 1405s, 1240s, 1205s, 1195s, 1090m, 790s, 780s. <sup>1</sup>H-NMR: 11.78 (br. s, NH); 7.45–7.0 (m, 15 arom. H); 5.26 (s, CH<sub>2</sub>). <sup>13</sup>C-NMR: 160.5 (br. s, C=S); 131.1, 128.5, 127.8 (3s, C(4), C(5), 3 arom. C); 129.5, 128.9, 128.7, 128.4, 128.0, 127.5, 127.4, 126.5 (8d, 15 arom. CH); 48.4 (t, CH<sub>2</sub>). EI-MS: 343 (18, [M + 1]<sup>+</sup>), 342 (75, M<sup>+</sup>), 309 (24, [M – SH]<sup>+</sup>), 193(100), 178(50), 165(12), 91(49), 77(14). Anal. calc. for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>S (342.46): C 77.16, H 5.30, N 8.18, S 9.36; found: C 77.00, H 4.99, N 8.16, S 9.16.

**1-Cyclohexyl-4,5-diphenylimidazole-2(3H)-thione (9h)**: 318 mg (95%). Colorless crystals. M.p. 295–297° (EtOH; [32]: 316–317°). <sup>1</sup>H-NMR: 10.36 (br. s, NH); 7.5–7.15 (m, 10 arom. H); 4.20 (m, 1 H); 1.8–1.2 (m, 10 H).

**4,5-Diphenyl-1-(2-phenylethyl)imidazole-2(3H)-thione (9i)**: 314 mg (88%). Colorless crystals. M.p. 261–263° (acetone). IR: 3000vs, 2890s, 1600m, 1500vs, 1460s, 1410s, 1370s, 1270s, 1180s, 790s, 780s. <sup>1</sup>H-NMR: 10.10 (br. s, NH); 7.5–7.4, 7.25–7.15, 7.0–6.95 (3m, 15 arom. H); 4.16, 3.00 (2t, 2 CH<sub>2</sub>). <sup>13</sup>C-NMR: 154.0 (s, C=S); 131.0, 126.6, 126.3 (3s, C(4), C(5), 3 arom. C); 129.7, 129.2, 128.9, 128.8, 128.6, 128.1 (6d, 15 arom. CH); 46.6, 34.6 (2t, 2 CH<sub>2</sub>). EI-MS: 356 (49, M<sup>+</sup>), 252 (100, [M – PhCH<sub>2</sub>CH<sub>2</sub>]<sup>+</sup>), 193(9), 165(9), 104(12, PhCH<sub>2</sub>CH<sub>2</sub><sup>+</sup>), 77(8). Anal. calc. for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>S (356.49): C 77.49, H 5.65, N 7.86, S 8.99; found: C 77.77, H 5.95, N 7.86, S 9.00.

**1,5-Dimethyl-4-phenylimidazole-2(3H)-thione (9j)**: 192 mg (94%). Colorless crystals. M.p. 254–256° (acetone; [33]: 247–249°). <sup>1</sup>H-NMR: 11.43 (br. s, NH); 7.45–7.25 (m, 5 arom. H); 3.60, 2.30 (2s, 2 Me).

**1-Butyl-5-methyl-4-phenylimidazole-2(3H)-thione (9k)**: 160 mg (65%). Colorless crystals. M.p. 285–287° (CHCl<sub>3</sub>). IR: 3000vs, 2880vs, 1635m, 1600m, 1500vs, 1450s, 1410s, 1400s, 1370s, 1280s, 1250m, 1230m, 1190m, 1130s, 940m, 920m, 790s, 780s. <sup>1</sup>H-NMR: 11.53 (br. s, NH); 7.45–7.25 (m, 5 arom. H); 2.33 (s, Me); 4.07 (t, CH<sub>2</sub>); 1.76, 1.44 (2m, 2 CH<sub>2</sub>); 0.98 (t, MeCH<sub>2</sub>). <sup>13</sup>C-NMR ((D<sub>6</sub>)DMSO): 159.7 (s, C=S); 138.6, 122.4, 121.2 (3s, C(4), C(5), 1 arom. C); 127.7, 125.8 (2d, 5 arom. CH); 42.4, 29.3, 18.5 (3t, 3 CH<sub>2</sub>); 12.7, 8.8 (2q, 2 Me). EI-MS: 246 (99, M<sup>+</sup>), 213 (100, [M – SH]<sup>+</sup>), 204(32), 190(66), 130(14), 115(10), 103(13), 77(9). Anal. calc. for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>S (246.37): C 68.25, H 7.36, N 11.37, S 13.01; found: C 68.30, H 7.56, N 11.40, S 12.67.

**Ethyl 4,5-Dihydro-1-phenyl-5-thioxo-1,2,4-[1H]triazole-3-carboxylate (11)**: Prepared according to the General Procedure described for imidazole 3-oxides **1** using triazole N-oxide **10** and **5a**. Yield: 209 mg (84%). Colorless crystals. M.p. 196–198° (EtOH). IR: 2880s, 1740vs (C=O), 1600w, 1505m, 1470s, 1420m, 1390s, 1285s, 1240m, 1200s, 1105m, 1030m, 1020m, 805m, 790m, 700m. <sup>1</sup>H-NMR ((D<sub>6</sub>)DMSO): 8.0–7.9, 7.55–7.4 (2m, 5 arom. H); 4.50 (q, MeCH<sub>2</sub>); 1.44 (t, MeCH<sub>2</sub>). <sup>13</sup>C-NMR ((D<sub>6</sub>)DMSO): 167.4 (s, C=S); 155.5, 137.3 (2s, C(3), 1 arom. C); 128.7, 128.4, 124.4 (3d, 5 arom. CH); 62.3 (t, CH<sub>2</sub>); 13.8 (q, Me). EI-MS: 249 (100, M<sup>+</sup>), 220 (14, [M – Et]<sup>+</sup>), 202(20), 175(34), 91(42), 77(23). Anal. calc. for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>S (249.29): C 53.00, H 4.45, N 16.86, S 12.86; found: C 52.91, H 4.56, N 16.85, S 12.71.

**4. 'One-Pot' Procedure for the Synthesis of Imidazole-2(3H)-thione 9d**. A soln. of **3d** (220 mg, 0.65 mmol), **2a** (200 mg, 2 mmol), and **5b** (170 mg, 1 mmol) in abs. EtOH (5 ml) was heated under reflux. After 6 h, the

initially red mixture turned colorless, the solvent was evaporated, and the solid residue triturated with a small amount of Et<sub>2</sub>O. After 1 h in the refrigerator, the crude product was filtered and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O yielding 130 mg (61%) of **9d**. Colorless crystals. M.p. 220–222°.

5. *Reactions of (tert-Butyl)(isopropyl)thio ketene (12) with Heterocyclic N-Oxides*. 5.1. *Reaction with 1c*. To a soln. of **1c** (100 mg, 0.5 mmol) and **12** (78 mg, 0.5 mmol) in CDCl<sub>3</sub> (0.5 ml) in an NMR tube, 1,1,2,2-tetrachloroethane (136 mg, 0.81 mmol) was added as an internal standard. The tube was closed and stored at r.t. The initially red-blue soln. decolorized after 1 h. The <sup>1</sup>H-NMR spectrum showed well separated signals of *l*-benzyl-4,5-dimethylimidazole (**14**; *s* at 7.51 ppm, 1 H), 3-(*tert*-butyl)-3-isopropylthiiran-2-one **13** (*s* at 1.08 ppm, 9 H), and **9c** (*s* at 5.28 ppm, 2 H), which allowed to establish the ratio of **14/13/9c/15** as 84:70:15:14.

5.2. *Reaction with Pyrimidine N-Oxide*. A soln. of pyrimidine *N*-oxide (96 mg, 1 mmol) and **12** (156 mg, 1 mmol) in CDCl<sub>3</sub> (1 ml) was placed in an NMR tube and stored at r.t. The initially red-violet color disappeared after 7 d. The <sup>1</sup>H-NMR spectrum of the crude mixture revealed the presence of **13** and pyrimidine in a ratio of 1:1. Chromatography on SiO<sub>2</sub>-coated plates (hexane/CHCl<sub>3</sub> 6:4) yielded 140 mg (44%) of **13** as a colorless oil which showed identical IR absorptions as those described in [17]. <sup>1</sup>H-NMR: 2.66 (*sept.*, *J* = 6.0, Me<sub>2</sub>CH); 1.08 (*s*, Me<sub>3</sub>C); 1.08, 0.83 (*2d*, *J* = 6.0, Me<sub>2</sub>CH). <sup>13</sup>C-NMR: 190.1 (*s*, C=O); 59.2, 37.7 (*2s*, C(2), Me<sub>3</sub>C); 28.4 (*d*, Me<sub>2</sub>CH); 27.6 (*q*, Me<sub>3</sub>C); 21.8, 19.9 (*2q*, Me<sub>2</sub>CH). The polar fraction afforded 40 mg (50%) of pyrimidine.

6. *Competitive Experiments of Imidazole 3-Oxides 1 and 5b*. To a soln. of **1a** (15.1 mg, 0.12 mmol), **1d** (23.3 mg, 0.12 mmol), and 1,1,2,2-tetrachloroethane (26.2 mg, 0.16 mmol) in CDCl<sub>3</sub> (0.5 ml) in an NMR tube, a soln. of **5b** (10.3 mg, 0.06 mmol) in CDCl<sub>3</sub> (0.3 ml) was added at r.t. by means of a syringe. The initially red mixture turned colorless after few s. After *ca.* 1 h, the mixture was analyzed by <sup>1</sup>H-NMR spectroscopy, and the yields of **9a** and **9d** were determined to 95 and 5%, respectively, in relation to CCl<sub>4</sub> as an internal standard.

In an analogous experiment with **1a**, **1c**, and **5b**, the yields of **9a** and **9c** were determined to 45 and 55%, respectively.

## REFERENCES

- [1] L. Fišera, R. Huisgen, I. Kalwinski, E. Langhals, X. Li, G. Mlostoń, K. Polborn, J. Rapp, W. Sicking, R. Sustmann, *Pure Appl. Chem.* **1996**, *68*, 789.
- [2] a) R. Huisgen, X. Li, *Tetrahedron Lett.* **1983**, *24*, 4185; b) R. Huisgen, E. Langhals, *ibid.* **1989**, *30*, 5369.
- [3] H. Giera, R. Huisgen, *Liebigs Ann./Recl.* **1997**, 1685.
- [4] A. R. Katritzky, J. M. Lagowski, 'Chemistry of the Heterocyclic *N*-Oxides', Academic Press, London, 1971.
- [5] P. DeShong, S. W. Lander, Jr., J. M. Leginus, C. M. Dicken, in 'Advances in Cycloaddition', Ed. D. P. Curre, JAI Press, London, 1988, Vol. 1, p. 87.
- [6] A. Padwa, A. M. Schoffstall, in 'Advances in Cycloaddition', Ed. D. P. Curren, JAI Press, London, 1990, Vol. 2, p. 1.
- [7] Y. Kurasawa, A. Takada, H. S. Kim, *J. Heterocycl. Chem.* **1995**, *32*, 1085.
- [8] A. W. Ryzhakov, L. L. Rodina, *Khim. Geterotsykl. Soedin.* **1992**, 579.
- [9] H. Lettau, *Z. Chem.* **1970**, *10*, 211.
- [10] I. J. Ferguson, K. Schofield, *J. Chem. Soc., Perkin Trans. 1* **1975**, 275.
- [11] R. Bartnik, W. Hahn, G. Mlostoń, *Roczniki Chem.* **1977**, *51*, 49 (*CA*: **1977**, *87*, 53155).
- [12] a) R. Bartnik, G. Mlostoń, *Roczniki Chem.* **1977**, *51*, 1747 (*CA*: **1978**, *88*, 62332); b) G. Mlostoń, unpublished results, USC Los Angeles, 1997.
- [13] S. Takahashi, H. Kano, *Tetrahedron Lett.* **1993**, 1687; *Chem. Pharm. Bull.* **1964**, *12*, 1290.
- [14] M. Hamana, B. Umezawa, S. Nakashima, *Chem. Pharm. Bull.* **1962**, *10*, 969.
- [15] B. V. Trzhtsinskaya, N. D. Abramova, *Sulfur Reports* **1991**, *10*, 389.
- [16] N. V. Harris, C. Smith, M. J. Ashton, A. W. Bridge, R. C. Bush, E. C. J. Coffee, D. I. Dron, M. F. Harper, D. J. Lythgoe, C. G. Newton, D. Riddell, *J. Med. Chem.* **1992**, *35*, 4384.
- [17] E. Schaumann, U. Behrens, *Angew. Chem.* **1977**, *89*, 750.
- [18] D. St. C. Black, K. G. Watson, *Aust. J. Chem.* **1973**, *26*, 2491.
- [19] J. Elguero, C. Marzin, A. R. Katritzky, P. Linda, 'The Tautomerism of Heterocycles', Academic Press, New York, 1976, p. 396ff.
- [20] G. Mlostoń, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1991**, *74*, 1386.
- [21] L. Kahovec, *Z. Phys. Chem., B* **1939**, *43*, 364.
- [22] J. Graymore, *J. Chem. Soc.* **1932**, 1353.
- [23] J. Graymore, *J. Chem. Soc.* **1935**, 865.

- [24] L. Stefaniak, T. Urbanski, M. Witanowski, H. Januszewski, *Roczniki Chem.* **1969**, 59, 1687 (*CA*: **1970**, 72, 210726).
- [25] W. L. Semon, V. R. Damerell, *Org. Synth.* **1943**, 2, 205.
- [26] T. Watson, J. Taylor, M. S. Marks, *J. Chem. Soc.* **1930**, 2302.
- [27] W. F. Beech, *J. Chem. Soc.* **1955**, 3095.
- [28] E. V. Elam, H. W. Davis, *J. Org. Chem.* **1967**, 32, 1562.
- [29] J. W. Greidanus, *Can. J. Chem.* **1970**, 48, 3530.
- [30] H. Bredereck, R. Gompper, H. Herlinger, *Chem. Ber.* **1958**, 91, 2832.
- [31] R. Huisgen, R. Grashey, E. Aufderhaar, R. Kuntz, *Chem. Ber.* **1965**, 98, 642.
- [32] V. B. Kaltscheva, L. J. Tsvetanska, *Khim. Geterotsikl. Soedin.* **1981**, 1028.
- [33] T. Kobayashi, H. Fujieda, Y. Murakami, T. Nakamura, K. Ono, S. Yamamoto, H. Kato, *Bull. Chem. Soc. Jpn.* **1994**, 67, 3082.

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