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

The reactions of 1,4,5-trisubstituted imidazole 3-oxides **1a**–**k** with cyclobutanethiones **5a**,**b** in $CHCl_3$ 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 adamantanethione (**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 α-(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*).

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[2]). 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

[1]) Part of the projected Ph.D. thesis of *T.G.*, University of Łódź

[2]) Thioketones have been shown to be the most reactive dipolarophiles towards thiocarbonyl ylides [1], Ph_2CN_2 [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 Me_3SiCN 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 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 COS[3]).

Results and Discussion. – To prepare imidazole 3-oxides **1**, α-(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*).

Scheme 1

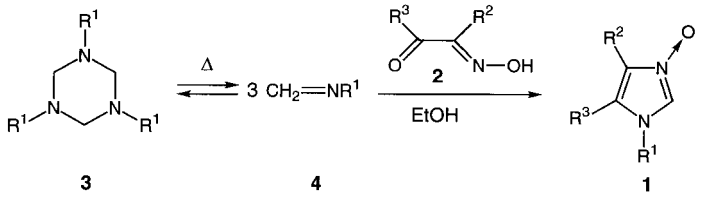


Table 1. *Prepared 1,4,5-Trisubstituted Imidazole 3-Oxides* **1**

1	**2**	**3/4**	R^1	R^2	R^3	Yield of **1** [%]	M.p. [°]
a	**a**	**a**	Me	Me	Me	77	164–166
b	**a**	**b**	Et	Me	Me	54	61–63
c	**a**	**c**	$PhCH_2$	Me	Me	95	199–201
d	**a**	**d**	Cyclohexyl	Me	Me	58	198–200
e	**b**	**a**	Me	Ph	Ph	61	255–257
f	**b**	**b**	Et	Ph	Ph	75	182–184
g	**b**	**c**	$PhCH_2$	Ph	Ph	92	174–176
h	**b**	**d**	Cyclohexyl	Ph	Ph	74	179–180
i	**b**	**e**	$PhCH_2CH_2$	Ph	Ph	88	185–187
j	**c**	**a**	Me	Ph	Me	89	201–203
k	**c**	**f**	Bu	Ph	Me	80	155–157

Solutions of *N*-oxides **1** in $CHCl_3$ 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 ^{1}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

[3]) 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^{-1}, and, in the ^{13}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

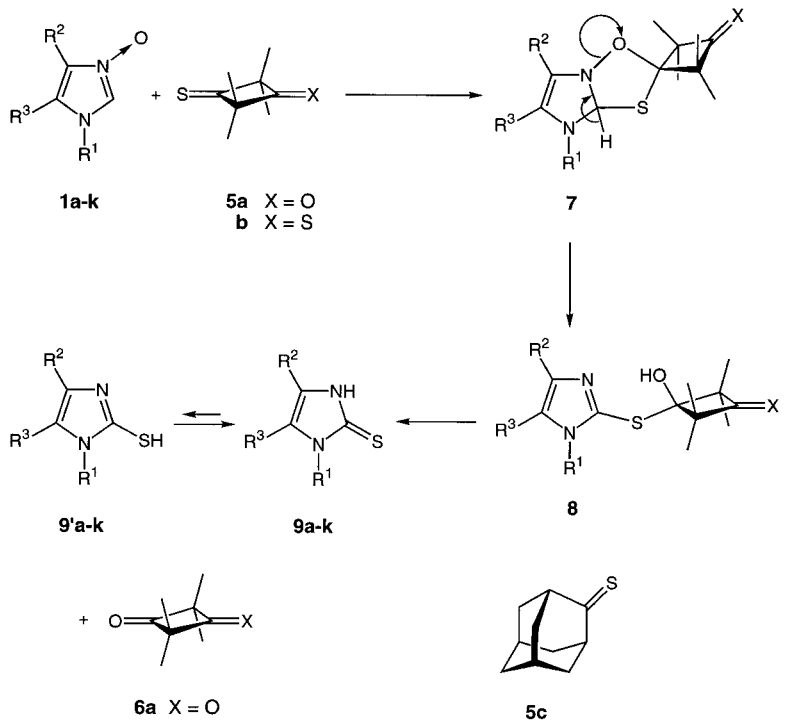


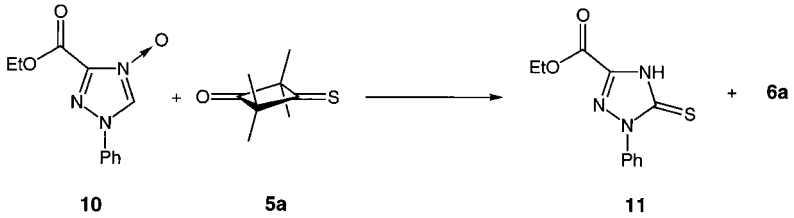
Table 2. *Prepared Imidazole-2(3*H*)-thiones* **9** *from* **1** *and* **5a**

9	R^1	R^2	R^3	Yield [%]	M.p. [°]
a	Me	Me	Me	83	212–214
b	Et	Me	Me	83	183–184
c	$PhCH_2$	Me	Me	92	227–228
d	Cyclohexyl	Me	Me	95	221–223
e	Me	Ph	Ph	79	279–281
f	Et	Ph	Ph	96	292–294
g	$PhCH_2$	Ph	Ph	95	268–270
h	Cyclohexyl	Ph	Ph	95	295–297
i	$PhCH_2CH_2$	Ph	Ph	88	261–263
j	Me	Ph	Me	94	254–256
k	Bu	Ph	Me	65	285–287

Adamantanethione (**5c**)[4]) 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^1 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 (^{1}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; ^{1}H-NMR). These results indicate that R^1 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**[5]) 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



10 **5a** **11**

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 $CHCl_3$ change the red color neither after 3 days at room temperature nor after refluxing for several hours. ^{1}H-NMR Analysis of the same reaction in $CDCl_3$ showed no change of starting materials. Several other experiments with pyrimidine-*N*-oxide derivatives[6]) 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 nitrone, which unexpectedly led to thiiranone 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**[7]) in $CDCl_3$ at room temperature. After 2 h, deoxygenated imidazole **14** as well as imidazole-2(3*H*)-thione **9c** were formed in 84 and

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4) For convenience, the name adamantanethione is used for tricyclo[3.3.1.1^{3,7}]decane-2-thione.

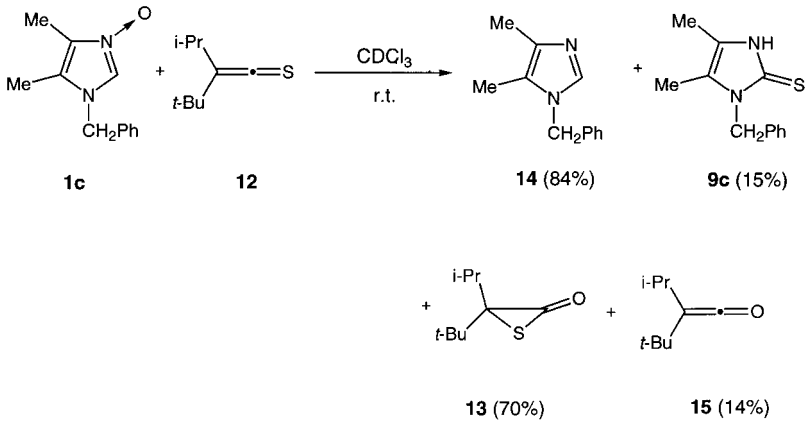
5) For the useability of imidazole-2(3*H*)-thiones, see [15][16] and refs. cit. therein.

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

Scheme 4



When thioketene **12** was treated with pyrimidine *N*-oxide under analogous conditions, the violet color of the solution disappeared after 7 days. ^{1}H-NMR Analysis of the mixture showed the presence of pyrimidine and thiiranone **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][9]). Furthermore, the

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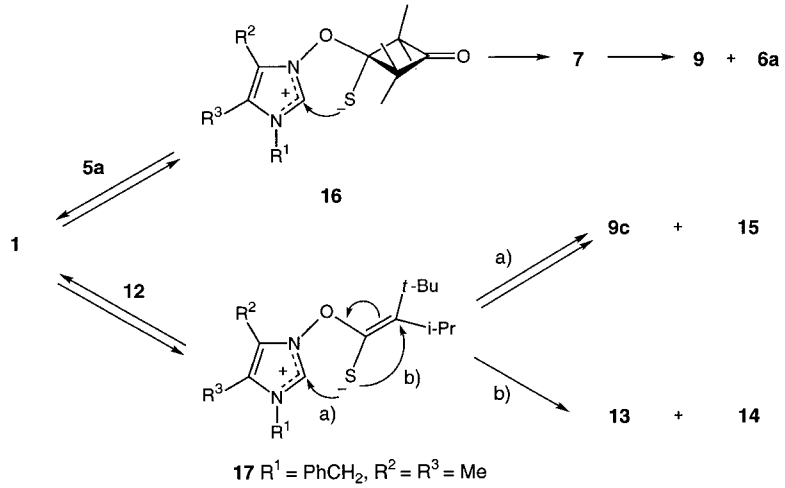
[8]) Determined in the reaction mixture by means of ^{1}H-NMR spectroscopy.

[9]) The reaction of thiobenzophenone methanide with thiobenzophenone was *ca.* 10^3 times faster than with **5a** [2a]. Reaction rates with Ph_2CN_2 showed a similar difference [2b].

Scheme 5



'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[10]).

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** → **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 cycloalkanethiones offers a simple and efficient route to azole-thiones. Taking into account that a

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[10]) 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**, α-(hydroxyimino) ketones **2**, and cyclobutane-1,3-dithione **5b** without isolation of the intermediate imidazole 3-oxide **1**.

We thank the analytical sections of our institutes for spectra and analyses and the *Polish National Committee for Scientific Research* (*KBN*), the *Swiss National Science Foundation*, and *F. Hoffmann-La Roche AG*, Basel, for financial support. *G.M.* thanks Mrs. *M. Celeda* for technical assistance in the preparation of imidazole 3-oxides.

Experimental Part

1. *General.* See [20]. M.p.: in capillary, *Melt-Temp. II* (*Aldrich*) apparatus; uncorrected. IR Spectra: *Specord-71* IR spectrometer; in KBr. ^{1}H- and ^{13}C-NMR-Spectra: *Varian-Gemini-BB* spectrometer (200 MHz (^{1}H) and 50.4 MHz (^{13}C)); $CDCl_3$ soln.; TMS as an internal standard (δ(TMS) = 0). EI-MS: *Variant-MAT-112S* spectrometer; at 70 eV; CI-MS with NH_3. 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 $NH_2OH \cdot HCl$ 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_4S_{10} [28], adamantanethione (**5c**) was synthesized analogously from commercially available adamantanone according to [29], and *(*tert*-butyl)(isopropyl)-thioketene* (**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_2O_2 as oxidizing agent according to [30]. *3-(Ethoxycarbonyl)-1-phenyl-1,2,4(1*H*)-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_2O 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_2Cl_2/Et_2O). IR: 1660*m*, 1630*s*, 1450*s*, 1400*s*, 1350*s*, 1170*m*, 1080*m*. ^{1}H-NMR: 8.10 (*s*, H–C(2)); 3.60 (*s*, MeN); 2.18, 2.16 (2*s*, 2 Me). ^{13}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, $[M+1]^+$), 126 (12, $M^{+\cdot}$), 111 (100), 97 (12). Anal. calc. for $C_6H_{10}N_2O \cdot 0.75\ H_2O$ (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_2Cl_2/Et_2O). IR: 1660*s*, 1630*s*, 1470*m*, 1410*s*, 1395*s*, 1350*s*, 1160*s*. ^{1}H-NMR: 8.10 (*s*, H–C(2)); 3.94 (*q*, J = 7.2, MeCH_2); 2.19, 2.17 (2*s*, 2 Me); 1.39 (*t*, J = 7.2, *Me*CH_2). ^{13}C-NMR: 126.1, 120.6 (2*s*, C(4), C(5)); 123.8 (*d*, C(2)); 40.6 (*t*, CH_2); 15.8, 8.5, 7.2 (3*q*, 3 Me). Anal. calc. for $C_7H_{12}N_2O \cdot 2\ H_2O$ (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_2Cl_2/Et_2O). IR: 1620*s*, 1450*s*, 1410*s*, 1380*s*, 1360*s*, 1330v*s*, 1190*s*, 840*s*, 710*s*. ^{1}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). ^{13}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_2); 8.8, 7.2 (2*q*, 2 Me). CI-MS: 195 (6, $[M+1]^+$), 180 (11), 179 (100), 117 (6). Anal. calc. for $C_{11}H_{18}N_2O \cdot 0.5\ H_2O$ (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: 1485*s*, 1440*s*, 1370*s*, 1345*s*, 1200*m*, 1055*s*, 870*m*, 825*s*, 770v*s*, 710v*s*, 670*s*. ^{1}H-NMR: 8.11 (*s*, H–C(2)); 7.55–7.25 (*m*, 10 arom. H); 3.55 (*s*, MeN). ^{13}C-NMR: 130.6, 129.6, 129.5, 126.6 (4*s*, C(4), C(5), 2 arom. C); 129.1, 128.2, 128.1 (3*d*, 10 arom. CH, C(2)); 33.2 (*q*, MeN). CI-MS: 251 (12, $[M+1]^+$), 236(17), 235(100). Anal. calc. for $C_{16}H_{14}N_2O \cdot 0.3\ H_2O$ (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° ($CHCl_3$/benzene). IR: 1600*m*, 1480*s*, 1445*s*, 1380*s*, 1345v*s*, 1250*s*, 1210*s*, 1080*s*, 1050*s*, 1030*s*, 850*s*, 760v*s*, 705v*s*, 675*s*. ^{1}H-NMR: 8.20 (*s*, H–C(2)); 7.55–7.25 (*m*, 10 arom. H); 3.87 (*q*, $J = 7.2$, MeCH_2); 1.31 (*t*, $J = 7.2$, *Me*CH_2). ^{13}C-NMR: 130.6, 127.6, 127.0 (3*s*, C(4), C(5), 1 arom. C); 129.5, 129.1, 128.0, 125.5 (4*d*, C(2), 10 arom. CH); 41.3 (*t*, CH_2); 16.0 (*q*, Me). CI-MS: 265 (15, $[M+1]^+$), 250(18), 249 (100, $[M-16]^+$), 173(31). Anal. calc. for $C_{17}H_{16}N_2O \cdot H_2O$ (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_2O) ([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_2Cl_2/Et_2O). IR: 2860*s*, 1640*s*, 1510*s*, 1480*m*, 1440*s*, 1360*m*, 1320*s*, 1300*s*, 1210*s*, 1040v*s*, 1020v*s*, 880v*s*, 770v*s*, 720v*s*, 700v*s*. ^{1}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). ^{13}C-NMR: 132.6, 129.1, 127.4, 124.8 (4*s*, 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 (9*d*, C(2), 10 arom. CH); 55.8 (*d*, CH); 34.0, 25.3, 24.5 (3*t*, 5 CH_2). CI-MS: 319 (5, $[M+1]^+$), 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° ($CHCl_3$/petroleum ether). IR: 3040*s*, 1605*m*, 1440*s*, 1380*s*, 1350*s*, 1250*s*, 1205*m*, 1030*m*, 770v*s*, 720*s*, 705*s*. ^{1}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 (2*s*, 2 Me). ^{13}C-NMR: 129.6, 128.4, 128.3 (3*d*, C(2), 5 arom. CH); 127.3, 125.5, 122.7 (3*s*, C(4), C(5), 1 arom. C); 32.4 (*q*, MeN); 9.4 (*q*, Me). CI-MS: 189 (14, $[M+1]^+$), 188 (11, $M^{+\bullet}$), 174(12), 173(100), 159 (17). Anal. calc. for $C_{11}H_{12}N_2O \cdot H_2O$ (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(3*H*)-thiones* **9**. *General Procedure.* A cooled soln. (H_2O/ice bath) of **5a** (156 mg, 1 mmol)[11]) in $CHCl_3$ (1 ml) was stirred magnetically, and a soln. of the corresponding *N*-oxide **1** (1 mmol) in $CHCl_3$ (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(3*H*)-thione isolated after recrystallization.

*1,4,5-Trimethylimidazole-2(3*H*)-thione* (**9a**): 118 mg (85%). Colorless crystals. M.p. 212–214° (EtOH). IR: 3020v*s*, 2960v*s*, 1660*s*, 1500*s*, 1440*s*, 1395*s*, 1260*s*, 1150*m*, 1110*m*, 795*m*. ^{1}H-NMR: 11.80 (br. *s*, NH); 3.50, 2.09, 2.06 (3*s*, 3 Me). ^{13}C-NMR: 157.8 (*s*, C=S); 121.6, 119.9 (2*s*, C(4), C(5)); 31.1 (*q*, MeN); 9.0, 8.9 (2*q*, 2 Me). EI-MS: 143 (25, $[M+1]^+$), 142 (100, $M^{+\bullet}$), 141 (65, $[M-1]^+$), 127 (35, $[M-Me]^+$), 109 (44, $[M-SH]^+$), 100(8), 82(12), 71(18), 68(29). Anal. calc. for $C_6H_{10}N_2S$ (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(3*H*)-thione* (**9b**): 130 mg (83%). Colorless crystals. M.p. 183–184° ($CHCl_3$). IR: 3000v*s*, 2880*s*, 2690*m*, 1660*m*, 1500*s*, 1470*s*, 1410*s*, 1390*s*, 1320*s*, 1255*s*, 1205*m*, 1140*m*, 1120*m*, 795*s*. ^{1}H-NMR: 10.5 (br. *s*, NH); 4.05 (*q*, $J = 7.2$, MeCH_2); 2.08 (*s*, 2 Me); 1.30 (*t*, $J = 7.2$, *Me*CH_2). ^{13}C-NMR: 157.5 (*s*, C=S); 120.9, 119.9 (2*s*, C(4), C(5)); 39.4 (*t*, CH_2); 14.0, 9.0, 8.8 (3*q*, 3 Me). Anal. calc. for $C_7H_{12}N_2S$ (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(3*H*)-thione* (**9c**): 201 mg (92%). Colorless crystals. M.p. 227–228° ($CHCl_3$). IR: 3020*s*, 1660*s*, 1500*s*, 1450*s*, 1405*m*, 1380*m*, 1370*m*, 1250*m*, 1240*m*, 1195*m*, 790*m*. ^{1}H-NMR: 10.75 (br. *s*, NH); 7.28 (br. *s*, 5 arom. H); 5.34 (*s*, CH_2); 2.11, 1.97 (2*s*, 2 Me). ^{13}C-NMR: 160.1 (br. *s*, C=S); 135.8

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[11]) 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 (3*d*, 5 arom. CH); 123.4, 109.5 (2*s*, C(4), C(5)); 48.1 (*t*, CH_2); 9.2, 9.1 (2*q*, 2 Me). EI-MS: 218 (100, $M^{+\cdot}$), 185 (43, $[M-SH]^+$), 127 (30, $[M-C_7H_7]^+$), 91 (79, $C_7H_7^+$). Anal. calc. for $C_{12}H_{14}N_2S$ (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(3*H*)-thione* (**9d**): 200 mg (95%). Colorless crystals. M.p. 221–223° (EtOH). IR: 3040v*s*, 2920v*s*, 2820v*s*, 2660*s*, 1660*s*, 1510*s*, 1455*s*, 1420*s*, 1400*s*, 1380*s*, 1280*s*, 1250*s*, 1120*m*, 1020*m*, 1000*m*, 800*s*. ^{1}H-NMR: 11.94 (br. *s*, NH); 4.86 (*m*, 1 H); 2.18, 2.06 (2*s*, 2 Me); 1.9–1.5 (br. *m*, 10 H). ^{13}C-NMR: 157.2 (*s*, C=S); 121.1, 120.8 (2*s*, C(4), C(5)); 57.1 (*d*, CH); 30.6, 26.1, 25.4 (3*t*, 5 CH_2); 10.6, 8.9 (2*q*, 2 Me). EI-MS: 210 (54, $M^{+\cdot}$), 128 (100), 95 (7). Anal. calc. for $C_{11}H_{18}N_2S$ (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(3*H*)-thione* (**9e**): 210 mg (79%). Colorless crystals. M.p. 279–281° (EtOH). IR: 2980*s*, 2880*s*, 1600*m*, 1495*s*, 1450*s*, 1430*s*, 1400*s*, 1385*s*, 1280*m*, 1145*m*, 800*s*. ^{1}H-NMR: 11.46 (br. *s*, NH); 7.5–7.25 (*m*, 10 arom. H); 3.49 (*s*, Me). ^{13}C-NMR: 159.2 (*s*, C=S); 129.6, 128.5, 127.9 (3*s*, C(4), C(5), 2 arom. C); 130.7, 129.3, 128.8, 128.6, 126.6 (5*d*, 10 arom. CH); 32.6 (*q*, Me). EI-MS: 266 (100, $M^{+\cdot}$), 265 (100, $[M-1]^+$), 233 (8, $[M-SH]^+$), 232 (13), 207 (20), 206 (12), 193 (15), 165 (18), 133 (18), 118 (13), 104 (10), 77 (19). Anal. calc. for $C_{16}H_{14}N_2S$ (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(3*H*)-thione* (**9f**): 269 mg (96%). Colorless crystals. M.p. 292–294° (EtOH). IR: 3000*s*, 2880*s*, 1600*m*, 1510*s*, 1490v*s*, 1460*s*, 1405*s*, 1380*m*, 1260*s*, 1140*m*, 780*s*. ^{1}H-NMR: 11.05 (br. *s*, NH); 7.5–7.2 (*m*, 10 arom. H); 4.04 (*q*, MeCH_2); 1.21 (*t*, *Me*CH_2). ^{13}C-NMR: 159.9 (*s*, C=S); 130.9, 128.0, 126.4 (3*s*, C(4), C(5), 1 arom. C); 129.7, 129.3, 128.8 (3*d*, 10 arom. CH); 40.3 (*t*, CH_2); 14.3 (*q*, Me). EI-MS: 280 (100, $M^{+\cdot}$), 279 (33, $[M-1]^+$), 252 (35), 240 (12), 193 (31), 165 (16), 104 (13), 103 (12), 77 (14). Anal. calc. for $C_{17}H_{16}N_2S$ (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(3*H*)-thione* (**9g**): 325 mg (95%). Colorless crystals. M.p. 268–270° ($CHCl_3$). IR: 3020*s*, 2900*s*, 1600*m*, 1490*s*, 1480*s*, 1460*s*, 1405*s*, 1240*s*, 1205*s*, 1195*s*, 1090*m*, 790*s*, 780*s*. ^{1}H-NMR: 11.78 (br. *s*, NH); 7.45–7.0 (*m*, 15 arom. H); 5.26 (*s*, CH_2). ^{13}C-NMR: 160.5 (br. *s*, C=S); 131.1, 128.5, 127.8 (3*s*, C(4), C(5), 3 arom. C); 129.5, 128.9, 128.7, 128.4, 128.0, 127.5, 127.4, 126.5 (8*d*, 15 arom. CH); 48.4 (*t*, CH_2). EI-MS: 343 (18, $[M+1]^+$), 342 (75, $M^{+\cdot}$), 309 (24, $[M-SH]^+$), 193 (100), 178 (50), 165 (12), 91 (49), 77 (14). Anal. calc. for $C_{22}H_{18}N_2S$ (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(3*H*)-thione* (**9h**): 318 mg (95%). Colorless crystals. M.p. 295–297° (EtOH; [32]: 316–317°). ^{1}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(3*H*)-thione* (**9i**): 314 mg (88%). Colorless crystals. M.p. 261–263° (acetone). IR: 3000v*s*, 2890*s*, 1600*m*, 1500v*s*, 1460*s*, 1410*s*, 1370*s*, 1270*s*, 1180*s*, 790*s*, 780*s*. ^{1}H-NMR: 10.10 (br. *s*, NH); 7.5–7.4, 7.25–7.15, 7.0–6.95 (3*m*, 15 arom. H); 4.16, 3.00 (2*t*, 2 CH_2). ^{13}C-NMR: 154.0 (*s*, C=S); 131.0, 126.6, 126.3 (3*s*, C(4), C(5), 3 arom. C); 129.7, 129.2, 128.9, 128.8, 128.6, 128.1 (6*d*, 15 arom. CH); 46.6, 34.6 (2*t*, 2 CH_2). EI-MS: 356 (49, $M^{+\cdot}$), 252 (100, $[M-PhCH_2CH_2]^+$), 193 (9), 165 (9), 104 (12, $PhCH_2CH_2^+$), 77 (8). Anal. calc. for $C_{23}H_{20}N_2S$ (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(3*H*)-thione* (**9j**): 192 mg (94%). Colorless crystals. M.p. 254–256° (acetone; [33]: 247–249°). ^{1}H-NMR: 11.43 (br. *s*, NH); 7.45–7.25 (*m*, 5 arom. H); 3.60, 2.30 (2*s*, 2 Me).

*1-Butyl-5-methyl-4-phenylimidazole-2(3*H*)-thione* (**9k**): 160 mg (65%). Colorless crystals. M.p. 285–287° ($CHCl_3$). IR: 3000v*s*, 2880v*s*, 1635*m*, 1600*m*, 1500v*s*, 1450*s*, 1410*s*, 1400*s*, 1370*s*, 1280*s*, 1250*m*, 1230*m*, 1190*m*, 1130*s*, 940*m*, 920*m*, 790*s*, 780*s*. ^{1}H-NMR: 11.53 (br. *s*, NH); 7.45–7.25 (*m*, 5 arom. H); 2.33 (*s*, Me); 4.07 (*t*, CH_2); 1.76, 1.44 (2*m*, 2 CH_2); 0.98 (*t*, *Me*CH_2). ^{13}C-NMR ((D_6)DMSO): 159.7 (*s*, C=S); 138.6, 122.4, 121.2 (3*s*, C(4), C(5), 1 arom. C); 127.7, 125.8 (2*d*, 5 arom. CH); 42.4, 29.3, 18.5 (3*t*, 3 CH_2); 12.7, 8.8 (2*q*, 2 Me). EI-MS: 246 (99, $M^{+\cdot}$), 213 (100, $[M-SH]^+$), 204 (32), 190 (66), 130 (14), 115 (10), 103 (13), 77 (9). Anal. calc. for $C_{14}H_{18}N_2S$ (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-[1*H*]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: 2880*s*, 1740v*s* (C=O), 1600*w*, 1505*m*, 1470*s*, 1420*m*, 1390*s*, 1285*s*, 1240*m*, 1200*s*, 1105*m*, 1030*m*, 1020*m*, 805*m*, 790*m*, 700*m*. ^{1}H-NMR ((D_6)DMSO): 8.0–7.9, 7.55–7.4 (2*m*, 5 arom. H); 4.50 (*q*, MeCH_2); 1.44 (*t*, *Me*CH_2). ^{13}C-NMR ((D_6)DMSO): 167.4 (*s*, C=S); 155.5, 137.3 (2*s*, C(3), 1 arom. C); 128.7, 128.4, 124.4 (3*d*, 5 arom. CH); 62.3 (*t*, CH_2); 13.8 (*q*, Me). EI-MS: 249 (100, $M^{+\cdot}$), 220 (14, $[M-Et]^+$), 202 (20), 175 (34), 91 (42), 77 (23). Anal. calc. for $C_{11}H_{11}N_3O_2S$ (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(3*H*)-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_2O. After 1 h in the refrigerator, the crude product was filtered and recrystallized from CH_2Cl_2/Et_2O yielding 130 mg (61%) of **9d**. Colorless crystals. M.p. 220–222°.

5. *Reactions of (*tert*-Butyl)(isopropyl)thioketene* (**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 $CDCl_3$ (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 ^{1}H-NMR spectrum showed well separated signals of *1-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 $CDCl_3$ (1 ml) was placed in an NMR tube and stored at r.t. The initially red-violet color disappeared after 7 d. The ^{1}H-NMR spectrum of the crude mixture revealed the presence of **13** and pyrimidine in a ratio of 1:1. Chromatography on SiO_2-coated plates (hexane/$CHCl_3$ 6:4) yielded 140 mg (44%) of **13** as a colorless oil which showed identical IR absorptions as those described in [17]. ^{1}H-NMR: 2.66 (*sept.*, $J = 6.0$, Me_2CH); 1.08 (*s*, Me_3C); 1.08, 0.83 (2*d*, $J = 6.0$, Me_2CH). ^{13}C-NMR: 190.1 (*s*, C=O); 59.2, 37.7 (2*s*, C(2), Me_3C); 28.4 (*d*, Me_2CH); 27.6 (*q*, Me_3C); 21.8, 19.9 (2*q*, Me_2CH). 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 $CDCl_3$ (0.5 ml) in an NMR tube, a soln. of **5b** (10.3 mg, 0.06 mmol) in $CDCl_3$ (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 ^{1}H-NMR spectroscopy, and the yields of **9a** and **9d** were determined to 95 and 5%, respectively, in relation to CCl_4 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.

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