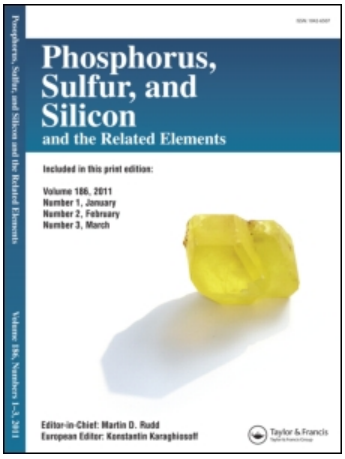

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UNEXPECTED INSERTION REACTION OF DIMETHOXYCARBENE WITH IMIDAZOLE-2(3*H*)-THIONES

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The reaction of in situ generated dimethoxycarbene with 1,4,5-trisubstituted imidazole-2(3H)-thiones yields 3-(dimethoxymethyl)imidazole-2(3H)-thiones in good yields via insertion into the N−H bond. The structure of the products was established by spectroscopic data and, in the case of 7b, by X-ray crystallography.

Keywords Amide acetals; dimethoxycarbene; imidazole-2(3*H*)-thiones; insertion reactions

INTRODUCTION

Oxygen-containing carbenes with the general formula **1** (R^1, R^2 = alkyl, aryl, allyl, acetyl), which belong to the class of the so-called "nucleophilic carbenes," have been studied extensively within the last two decades.[1–3] The main attention has been focused on dimethoxycarbene (**1a**, R^1, R^2 = Me), which was described for the first time simultaneously by Hoffmann and Häuser [4] and Lemal et al.[5] In both cases, thermal decomposition of 7,7-dimethoxybicyclo[2.2.1]hepta-2,5-diene derivatives led to **1a** via a cheletropic elimination.

Moss et al. described the thermolytic decomposition of 3,3-dimethoxy-3*H*-diazirine as a method for the generation of **1a** for spectroscopic studies.[6] The third and most suitable method based on the thermal cycloreversion of 2,2-dimethoxy-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazole (**2a**, R = Me) was developed by El-Saidi et al.[7] The same method was successfully applied for the generation of nucleophilic carbenes of type **3** (Scheme 1), in which X is an O- or S-atom.[8,9]

The easily available dimethoxycarbene (**1a**) found numerous applications for synthetic purposes in two- or three-component reactions. The nucleophilic properties of **1a** are reflected in reactions with electron-deficient alkenes,[10] carbonyl,[11a] and thiocarbonyl compounds[12] as well as some imines.[13] Zwitterionic species generated in situ from **1a**

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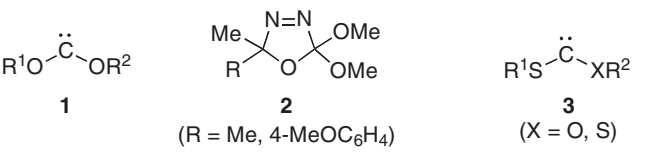
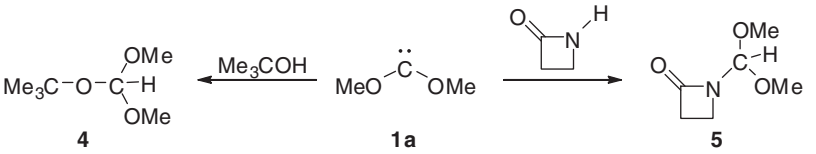


Scheme 1

and dimethyl acetylenedicarboxylate can be trapped with various dipolarophiles yielding five-membered hetero- or carbocyclic products.[14]

Very little is known about insertion reactions of carbenes of type **1**. In the case of **1a**, insertion reactions into C—C bonds led to ring enlargement of some cyclopropanone and butanone derivatives.[11,12b] The reaction of **1a** with 2,4-dinitrofluorobenzene occurred via the insertion into the C—F bond, leading, after hydrolysis, to 2,4-dinitrobenzoic acid.[15] Insertion of nucleophilic carbenes **1** into O-H bonds were reported as inter-[10a] and intramolecular processes.[16] Thermal decomposition of **2b** (R = 4-MeOC$_6$H$_4$) in benzene in the presence of *t*-BuOH gave the orthoester **4** in 73% yield (Scheme 2).[10a]



Scheme 2

An earlier described example of an N—H insertion with **1a** is the formation of product **5** (76%) from the parent azetidinone.[11a] In a very recent paper analogous products were reported to be formed from **1a** and both, lactones and thiolactones, with a variable ring size.[11b] It is worth mentioning that in all reported cases, relating to azetidine derivatives, no ring-enlargement, analogous to that one obtained with cyclobutanone, was observed. Other insertion reactions of nucleophilic carbenes **1a** and **3** (R^1 = Pr, R^2X = PrS) were described in reactions with 2-pyrrolidones incorporated in fused aromatic systems.[17] To the best of our knowledge, there are no reports published on the insertion of nucleophilic carbenes **1** or **3** into S—H bonds.*

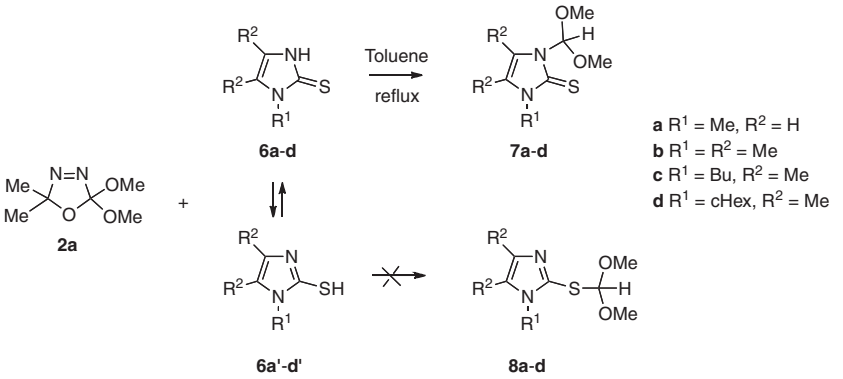
In some recent articles, we described a new method for the preparation of imidazole-2(3*H*)-thiones[20] as well as their reactions with some electrophilic reagents.[21] The results showed that, depending on the reagent, the reactions occurred selectively either at the S- (with dimethyl acetylenedicarboxylate) or N-atom (with phenylisocyanate). For the present study, selected imidazole-2(3*H*)-thiones of type **6** were used in reactions with **1a**.

RESULTS AND DISCUSSION

For preparation purposes, dimethoxycarbene has been generated, in general, by heating the precursor **2a** in hydrocarbon solutions, e.g., in toluene. Other solvents are less

*The reaction of the electrophilic dichlorocarbene with tautomerizable pyrimidine-2-thione derivatives yielded products of the insertion into the S—H bond.[18] The unsaturated carbene $Me_2C{=}C$: undergoes the insertion into the S—H bond of enethiols to give divinylsulfides.[19]

useful, as some undesired side reactions can occur. It is also known that imidazole-2(3*H*)-thiones **6** are crystalline compounds with limited solubility in nonpolar organic solvents. For this reason, four imidazole-2(3*H*)-thiones **6a–d** bearing aliphatic substituents were selected, which could be dissolved in toluene in reasonable concentration.** In all cases, a 20% excess of **2a** was used, and the reaction was complete after 8 h in boiling toluene. After evaporation of the solvent, the residue was analyzed by ^{1}H NMR spectroscopy. Thus, in the case of **6b**, the crude product was obtained in almost quantitative yield as a solid material. In the ^{1}H NMR spectrum, along with three signals of Me groups at 3.55, 2.20, and 2.08 ppm, two signals appeared at 6.87 and 3.42 ppm. The intensities of these two signals corresponded to one and six H-atoms, respectively, indicating that a 1:1-adduct of **6b** and dimethoxycarbene was formed. The presence of the signal at low field suggested the formation of a product containing a $(MeO)_2CH$ group as the result of an insertion reaction. However, the location of the signal is not decisive for the insertion into the N—H (in **6**) or S—H (in **6′**) bond (Scheme 3).



Scheme 3

The ^{13}C NMR data of the crystalline product solved the problem unambiguously as the absorption at 161.3 ppm corresponds well with the value reported for C(2) of imidazole-2(3*H*)-thiones[20a] but differs significantly from the value for C(2) found for imidazole-2-thiol derivatives.[21] In addition, the signals for $(MeO)_2CH$ appear at 105.3 and 54.2 ppm. Therefore, the structure of the product is **7b**, i.e., the product of the insertion into the N—H bond. Finally, the structure **7b** was established by X-ray crystallography (Figure 1).

The products obtained in the reactions of **2a** with **6a**, **6c**, and **6d** displayed similar spectroscopic properties as **7b**, which confirmed the structures of NH-insertion products of type **7**. In the case of **7b** and **7d**, pure compounds were obtained by crystallization. In the two other cases, the products were oily materials, and all attempts to crystallize them were unsuccessful. On the other hand, preparative TLC resulted in the conversion of the product **7** to the corresponding imidazole-2(3*H*)-thione **6**.

Taking into account the nucleophilic properties of dimethoxycarbene, the typical mechanism for insertion reactions of electrophilic carbenes into X—H (X = N, O, S) bonds, in which the carbene attacks the lone electron pair,[23] cannot be applied. It seems likely that

In the case of very low concentrations of **6, the dimerization of dimethoxycarbene leading to tetramethoxyethene was observed (for the formation of tetramethoxyethene, see ref. [7,11]).

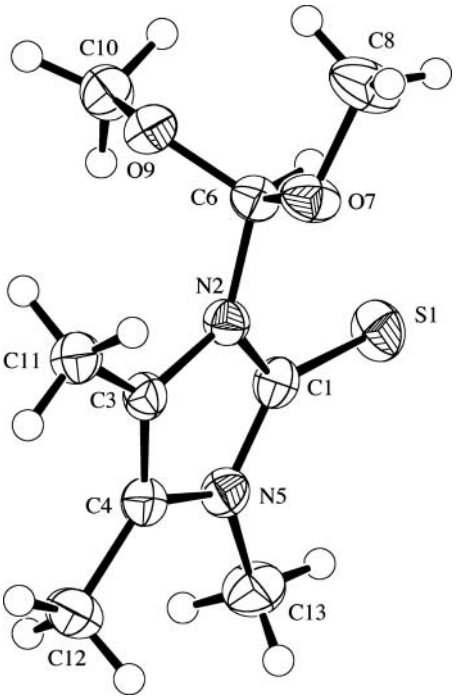


Figure 1 ORTEP plot[22] of the molecular structure of **7b** (50% probability ellipsoids, arbitrary numbering of the atoms).

the final product **7** is formed via an ion pair of type **A** (Figure 2), which results from the proton transfer between **6** and dimethoxycarbene.[1,24] The mechanism of the proton transfer is not clear, and transition states of type **B** and/or **C**, which could explain the selective formation of the N—C bond, may be proposed.

In an extension of the presented study, the exploration of the new "amide acetals" **7** for the synthesis of polycyclic sulfur compounds was examined. The strategy was based on the described reaction of thiourea with dimethylformamide dimethyl acetal, which yields bis(*N*,*N*-dimethylmethylidene)thiourea.[25] The latter is the key building block for a series of fused *S,N*-heterocycles. Unfortunately, the reaction of **7a** with thiourea carried out in boiling dichloromethane did not afford the product analogous to the already mentioned thiourea derivative. After 4 h heating, the unchanged **7a** was recovered. Apparently, the incorporation of the N-atom into the imidazole ring significantly reduced the reactivity of the "acetal" function of **7a**.

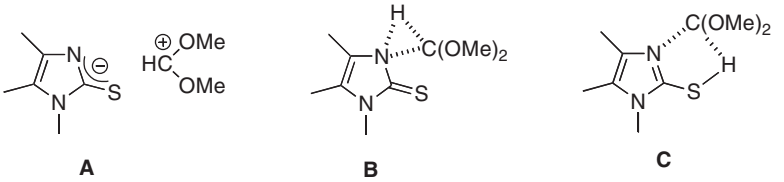


Figure 2 Possible intermediate ion pair **A** and transition states **B** and **C**.

CONCLUSIONS

A series of experiments with imidazole-2(3*H*)-thiones **6** and in situ generated nucleophilic dimethoxycarbene evidenced that products of the carbene insertion into the N—H bond of type **7** are formed exclusively and in good yields. This chemoselectivity corresponds with that observed in the reactions of **6** with phenylisocyanate.[21] Neither products of the nucleophilic attack onto the C=S group nor products of the insertion into the S—H bond could be detected. To the best of our knowledge, these are the first reactions of dimethoxycarbene with thiourea-type reagents, and only the third case of an insertion into an N—H bond (see Schemes 2 and 3).

EXPERIMENTAL

Melting points were determined in capillary using a Meltemp 2 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were registered with a Tesla BS 687 (80 and 20 MHz, respectively) or a Bruker 300 (300 and 75 MHz, respectively) spectrometer using TMS ($\delta_{TMS} = 0$) as an internal standard. The multiplicity of the signals was elucidated based on DEPT experiments. IR spectra were registered with a Nexus spectrophotometer. MS (EI, 70 eV) were recorded using a Finnigan-Mat-95 spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Institute of Organic Chemistry, University of Zürich.

Starting Materials

Imidazole-2(3*H*)-thiones **6a**–**d** used in the present study were prepared from the corresponding imidazole *N*-oxides using the sulfur transfer method described in earlier articles of our group.[20] 2,2-Dimethoxy-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazole (**2a**) used as the precursor of dimethoxycarbene (DMC) (**1**) was synthesized following Warkentin's protocol.[7]

Reactions of Imidazole-2(3*H*)-thiones 6a-d with Dimethoxycarbene (1): General Procedure

A solution of the corresponding imidazole-2(3*H*)-thione **6** (1 mmol) and the DMC precursor **2a** (192 mg, 1.2 mmol) in 2 mL abs. toluene was heated under reflux for 8 h with no special precautions. After this time, **2a** was completely decomposed. Toluene was evaporated, and the crude products, after preliminary inspection in the ^{1}H NMR spectrum, were purified either by microdistillation in vacuum (oil bath 130–135°C/0.08 hPa) or by crystallization.

1-Dimethoxymethyl-3-methylimidazole-2(3*H*)-thione (7a). Yield: 128 mg (68%). Colorless oil, purified by microdistillation. IR (neat): 3170*m*, 3138*m*, 3103*m*, 2941*s*, 2839*m*, 1573*m*, 1455*s*, 1403*s*, 1370*s*, 1321*m*, 1287*s*, 1212*s*, 1142*m*, 1112*s*, 1073*s*, 979*m*, 912*m*, 824*s*, 794*m*, 722*s*, 674*s*. ^{1}H-NMR ($CDCl_3$): 3.44 (*s*, 2 MeO), 3.60 (*s*, MeN), 6.48 (*s*, $(MeO)_2CH$), 6.68, 6.89 (2*d*, $J_{H,H} = 2.5$ Hz, 2 CH, imidazole). ^{13}C-NMR ($CDCl_3$): 33.9 (MeN), 54.2 (2 MeO), 103.8 ($(MeO)_2CH$), 112.6, 118.2 (2 CH, imidazole), 162.3 (C=S). EI-MS: 188 (19, $M^{+\cdot}$), 157 (22), 129 (10), 128 (100), 127 (21), 114 (57), 113 (23), 95 (53), 83 (18), 82 (20), 81 (20), 75 (57). HR-EI-MS: Calcd. $C_7H_{12}N_2O_2S$: 188.0619; found:

188.0617. Anal. Calcd. for $C_7H_{12}N_2O_2S$ (188.25): C 44.66, H 6.43. Found: C 44.55, H 6.49.

1-Dimethoxymethyl-3,4,5-trimethylimidazole-2(3*H*)-thione (7b). Yield: 188 mg (87%). Colorless plates, mp 70–71°C (petroleum ether/CH_2Cl_2). IR (KBr): 3009*w*, 2943*m*, 2928*m*, 2837*m*, 1666*w*, 1459*m*, 1437*m*, 1395*vs*, 1376*s*, 1367*s*, 1330*vs*, 1224*s*, 1200*m*, 1112*vs*, 1094*vs*, 1075*vs*, 1021*m*, 996*s*, 978*m*, 871*m*. ^{1}H-NMR ($CDCl_3$): 2.08, 2.20 (2*s*, 2 Me), 3.42 (*s*, 2 MeO), 3.55 (*s*, MeN), 6.87 (*s*, $(MeO)_2CH$). ^{13}C-NMR ($CDCl_3$): 8.0, 8.2 (2 Me), 30.8 (MeN), 54.2 (2 MeO), 105.3 ($(MeO)_2CH$), 119.5, 121.5 (2 C_q, imidazole), 161.3 (C=S). EI-MS: 216 42, $M^{+\cdot}$), 185 (33), 157 (12), 156 (93), 155 (10), 143 (7), 142 (62), 141 (32), 123 (44), 109 (11), 75 (100). HR-EI-MS: Calcd. for $C_9H_{16}N_2O_2S$: 216.0932; found: 216.0933. Anal. Calcd. for $C_9H_{16}N_2O_2S$ (216.30): C 49.97, H 7.46. Found: C 50.10, H 7.31.

1-Dimethoxymethyl-3-butyl-4,5-dimethylimidazole-2(3*H*)-thione (7c). Yield: 190 mg (74%). Colorless oil, purified by microdistillation. IR (neat): 2957*s*, 2935*s*, 2872*m*, 1657*m*, 1443*s*, 1410*s*, 1389*s*, 1329*s*, 1220*s*, 1194*s*, 1105*s*, 1070*s*, 992*m*, 869*m*. ^{1}H-NMR ($CDCl_3$): 0.95 (t, $J_{H,H}$ = 7.3 Hz, *Me*CH_2), 1.15–1.95 (*m*, -CH_2-CH_2-), 2.09, 2.30 (2*s*, 2 Me), 3.43 (*s*, 2 MeO), 4.02 (*t*, $J_{H,H}$ = 7.2 Hz, CH_2N), 6.89 (*s*, $(MeO)_2CH$). ^{13}C-NMR ($CDCl_3$): 8.3, 8.7, 13.4 (3 Me), 19.7, 30.3 (2 CH_2), 44.4 (CH_2N), 54.7 (2 MeO), 105.7 ($(MeO)_2CH$), 120.3, 121.5 (2 C_q, imidazole), 161.5 (C=S). EI-MS: 258 (8, $M^{+\cdot}$), 227 (8), 198 (36), 184 (10), 183 (11), 169 (15), 151 (23), 142 (11), 141 (8), 128 (9), 127 (10), 123 (8), 116 (17), 109 (17), 101 (8), 75 (100). HR-EI-MS: Calcd. for $C_{12}H_{22}N_2O_2S$: 258.1402; found: 258.1398. Anal. Calcd. for $C_{12}H_{22}N_2O_2S$ (258.38): C 55.78, H 8.58. Found: C 55.90, H 8.32.

1-Dimethoxymethyl-3-cyclohexyl-4,5-dimethylimidazole-2(3*H*)-thione (7d). Yield: 187 mg (66%). Colorless plates, mp 84–86°C (petroleum ether/CH_2Cl_2). IR (KBr): 2954*s*, 2851*w*, 1649*w*, 1447*w*, 1405*s*, 1377*vs*, 1362*s*, 1335*s*, 1219*m*, 1189*m*, 1200*m*, 1108*vs*, 1067*vs*, 993*s*, 859*m*. ^{1}H-NMR ($CDCl_3$): 2.18 (*br. s*, 2 Me), 1.00–2.30 (*m*, 10H, 5 CH_2), 3.43 (*s*, 2 MeO), 5.15 (*m*, CH), 6.98 (*s*, $(MeO)_2CH$). ^{13}C-NMR ($CDCl_3$): 8.5, 10.3 (2 Me), 25.1, 25.8, 30.3 (5 CH_2), 54.7 (2 MeO), 57.0 (CHN), 106.0 ($(MeO)_2CH$), 120.9, 121.5 (2 C_q, imidazole), 161.5 (C=S). EI-MS: 284 (26, $M^{+\cdot}$), 253 (17), 225 (9), 224 (57), 210 (13), 209 (10), 171 (7), 143 (10), 142 (91), 141 (9), 128 (36), 127 (16), 109 (61), 75 (100). HR-EI-MS: Calcd. for $C_{14}H_{24}N_2O_2S$: 284.1558; found: 284.1553. Anal. Calcd. for $C_{14}H_{24}N_2O_2S$ (284.42): C 59.12, H 8.51. Found: C 59.27, H 8.77.

X-Ray Crystal-Structure Determination of 7b

All measurements were performed on a Nonius KappaCCD area-diffractometer[26] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. The data collection and refinement parameters are given below,[27] and a view of the molecule is shown in Figure 1. Data reduction was performed with HKL Denzo and Scalepack.[28] The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method[29] was applied. Equivalent reflections were merged. The structure was solved by direct methods using SIR92,[30] which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent C-atom (1.5U_{eq} for the methyl groups). The

refinement of the structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. Neutral atom scattering factors for non-H-atoms were taken from ref.[31], and the scattering factors for H-atoms were taken from ref.[32] Anomalous dispersion effects were included in F_c;[33] the values for f' and f'' were those of ref.[34] The values of the mass attenuation coefficients are those of ref.[35] All calculations were performed using the *SHELXL97*[36] program.

Crystal data for **7b**: $C_9H_{16}N_2O_2S$, $M = 216.30$, colorless, plate, crystal dimensions $0.08 \times 0.15 \times 0.30$ mm, monoclinic, space group $P2_1/c$, Z = 4, reflections for cell determination 64835, $a = 9.9728(2)$ Å, $b = 15.8607(4)$ Å, $c = 7.5623(2)$ Å, $\beta = 108.752(2^\circ)$, $V = 1132.68(5)$ Å^3, T = 160(1) K, $D_x = 1.268$ g·cm^{-3}, $\mu(\text{Mo}K_\alpha) = 0.265$ mm^{-1}, scan type ϕ and ω, $2\theta_{(\max)} = 60^\circ$, transmission factors (min; max) 0.915; 0.981, total reflections measured 33116, symmetry independent reflections 3303, reflections with $I > 2\sigma(I)$ 2224, reflections used in refinement 3303, parameters refined 132, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0488, $wR(F^2)$ [all data] = 0.1238 ($w = [\sigma^2(F_o^2) + (0.0507P)^2 + 0.6043P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.019, final $\Delta_{\max}/\sigma$ 0.001, $\Delta\rho$ (max; min) = 0.27; −0.29 e Å^{-3}.

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