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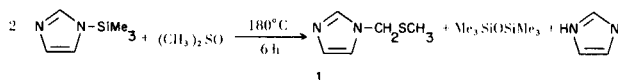
N-[(Methylthio)methyl]imidazole may be prepared from dimethylsulfoxide and *N*-(trimethylsilyl)imidazole or *N*-(*t*-butyldimethylsilyl)imidazole at elevated temperatures via a Pummerer rearrangement. The product was characterized by elemental analysis, mass spectrometry and proton and carbon nmr. Preliminary experiments show that corresponding derivatives of 2-methylimidazole, pyrazole, triazole and benzimidazole may also be prepared in an analogous manner.

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Sir:

The Pummerer rearrangement involves the conversion of a sulfoxide to a sulfide with an oxygen containing substituent in the α -position (1). A similar rearrangement with various halides introduces a halogen substituent into the α -position (2).

We find that dimethylsulfoxide (DMSO) and several *N*-trialkylsilyl heterocycles also rearrange in an analogous manner to give sulfides with imidazolyl, 2-methylimidazolyl, pyrazolyl, triazolyl and benzimidazolyl substituents in the α -position. Thus DMSO and *N*-(trimethylsilyl)imidazole (0.25 mole) in a 1:2 ratio at 180° for 6 hours gave *N*-[(methylthio)methyl]imidazole **1** in 60% yield. Compound **1** was purified by column chromatography (alumina, eluted with benzene) or by extraction with carbon tetrachloride followed by vacuum distillation at 95° (0.01 mm) and identified by



mass spectrometry (M^+ , $M-\text{CH}_3^+$, $M-\text{SCH}_3^+$), proton nmr: δ 2.04 (CH₃), δ 4.98 (CH₂), δ 7.12-7.17 (H₄,H₅), δ 7.67 (H₂), and carbon nmr: δ 13.4 (CH₃), δ 48.7 (CH₂), δ 118.1 (C₅), δ 129.0 (C₄), δ 136.3 (C₂). The nmr data confirm the structure of **1** since the chemical shifts of the ring carbons are very similar to those of *N*-(trimethylsilyl)imidazole (**3**) while the CH₂SCH₃ group in **1** is similar to FCH₂SCH₃ (**4**) and ClCH₂SCH₃ (**5**).

Anal. Calcd. for C₅H₈N₂S: C, 46.85; H, 6.29; N, 21.85. Found: C, 46.89; H, 6.19; N, 22.20.

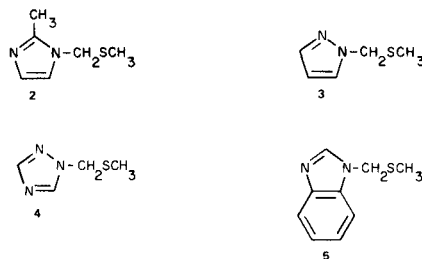
Reaction of DMSO with the sterically crowded *N*-(*t*-butyldimethylsilyl)imidazole in a 1:2 ratio at 150° for 3 hours gave **1** in 40% yield.

In separate experiments it was shown that DMSO did not react at 180° with silicon-nitrogen compounds such

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as hexamethyldisilazane or diethylaminotrimethylsilane, therefore, the synthesis of **1** was accomplished by simply heating a mixture of DMSO, imidazole and hexamethyldisilazane at 180° for 6 hours. In this case, *N*-(trimethylsilyl)imidazole was formed *in situ* from imidazole and hexamethyldisilazane (**6**), followed by reaction with DMSO to give **1** in 70% yield.

Preliminary experiments have shown that related heterocyclic derivatives **2-5**, identified by mass spectrometry and proton nmr, may also be prepared by reaction of DMSO with trimethylsilyl- or *t*-butyldimethylsilyl-heterocycles at elevated temperatures, 140-180°.



REFERENCES AND NOTES

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