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LETTERS

Iron(II)-mediated Nitrene Transfer from *t*-Butyloxycarbonyl Azide ($BocN_3$) to Sulfoxides, Sulfides, and Ketene Acetals

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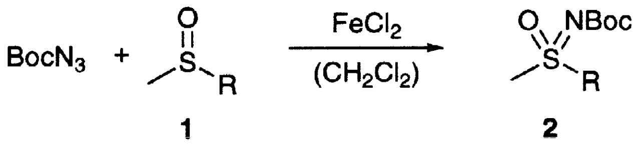
Abstract: The nitrene transfer from *t*-butyloxycarbonyl azide ($BocN_3$) to several nucleophiles is promoted by ferrous chloride ($FeCl_2$) and yields the corresponding *N*-Boc protected sulfoximides, sulfimides, or α-amino alkanoates. Whereas the sulfoximide formation occurs spontaneously in CH_2Cl_2 as solvent the $FeCl_2$-catalyzed nitrene transfer to sulfides and ketene acetals requires addition of a polar solvent. DMF was found to be best suited for this purpose.

Keywords: Sulfoximides; Sulfimides; Catalysis; Nitrenes.

The transfer of a nitrene fragment from an alkoxycarbonyl azide, e.g. from *t*-butyloxycarbonyl azide ($BocN_3$), to a nucleophile can be induced thermally or photochemically. By this means sulfoximides [1,2], sulfimides (iminosulfuranes, sulfilimines) [3], or α-amino alkanoates [4] are accessible from sulfoxides, sulfides, or ketene acetals. Due to the harsh reaction conditions the yields of these transformations have remained low, however, and side reactions occur. We have looked for alternative methods to induce a transfer of a Boc-protected nitrene fragment from $BocN_3$ and we would like to report our preliminary results in this area.

Upon treatment with certain Fe(II)-salts in organic solvents at ambient temperature $BocN_3$[1] [6] readily evolves nitrogen [7]. If the reaction was conducted with $FeCl_2$ in DMSO (**1c**) the major product obtained was the corresponding sulfoximide **2c** (scheme 1). For a complete reaction an excess of sulfoxide was neccessary. In general, 2-3 equivalents of the nucleophile sufficed to guarantee reasonable yields.



a	R = Bn	70%
b	R = Ph	45%
c	R = Me	64%
d	R= 4-MeOPh	52%

Scheme 1

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[1] CAUTION! Explosions have been reported to occur during attempted distillation of $BocN_3$ [5]. The substance is a potential explosive and is known to be health hazardous. Appropriate safety protection and utmost care is required while handling $BocN_3$.

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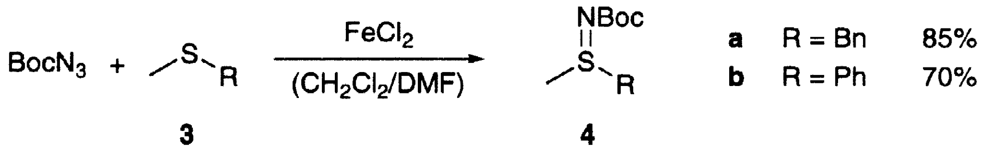
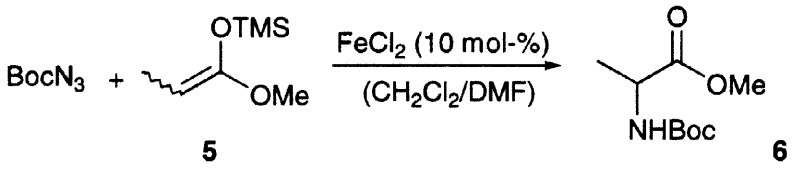
It was possible to initiate the nitrene transfer with substoichiometric amounts of $FeCl_2$ (0.25 equiv.) and the sulfoximide **2a**, for instance, was isolated in 56% yield.

The conditions employed for a successful nitrene transfer to sulfoxides could be applied to sulfides in CH_2Cl_2 if DMF was added to solubilize the iron salt. As an example, benzyl methyl sulfide (**3a**) was converted to the corresponding sulfimide (**4a**) in excellent yield (85%). It was gratifying to note that the very same reaction can equally well be conducted with catalytic quantities (0.1 equiv.) of $FeCl_2$ (68% yield).[2]



Scheme 2

Preliminary experiments have been performed with carbon nucleophiles. The electron rich ketene acetal **5** was selected to this end. With the $FeCl_2$/DMF/$BocN_3$ system a nitrene transfer [8] was observed (scheme 3).



Scheme 3

The reaction was unfortunately not as efficient as it is with sulfur nucleophiles and so far the alanine methyl ester (**6**) has only been isolated in low yields (10-20%). Further efforts are dedicated to improve this process.

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[2] Representative procedure: A mixture of 2 mmol $BocN_3$ (287 mg), 5 mmol benzyl methyl sulfide (**3a**) (720 mg) and 0.2 mmol $FeCl_2$ (32 mg) in 1.5 ml of dry CH_2Cl_2 were cooled to 0 °C. At this temperature 0.15 ml of dry DMF was slowly added (nitrogen evolution was observed). After stirring for 1 h at 0 °C the mixture was stirred over night at room temperature. It was subsequently poured into 10 ml of water and the aqueous layer was extracted with CH_2Cl_2 (5 x 5 ml). The combined organics were washed with water and were dried over $MgSO_4$. After filtration the solvent was removed and the residue was purified by column chromatography. 349 mg (68%) *N*-Boc protected benzyl methyl sulfimide (**4a**) were obtained as a colorless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): $\delta = 1.51$ (s, 9 H), 2.50 (s, 3 H), 4.02 (d, $^2J = 17.7$ Hz, 1 H), 4.44 (d, $^2J = 17.7$ Hz, 1 H), 7.32-7.44 (m, 5H).