The Preparation of *N*-*tert*-Butyloxycarbonyl-(Boc-)Protected Sulfoximines and Sulfimines by an Iron(II)-Mediated Nitrene Transfer from $BocN_3$ to Sulfoxides and Sulfides

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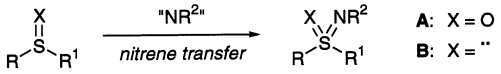
Keywords: Homogenous catalysis / Iron / Imidation / Sulfur / Synthetic methods

The imidation of sulfides and sulfoxides to the corresponding sulfimides and sulfoximides was carried out with *N*-*tert*-butyloxycarbonyl azide ($BocN_3$) in the presence of $FeCl_2$. Sulfoxides **1** reacted at room temperature in CH_2Cl_2 to give the corresponding sulfoximides **3** in 40–95% yield. The imidation of the sterically congested substrate *tert*-butyl methyl sulfoxide (**1f**) proceeded sluggishly (10% yield). The sterospecificity of the reaction was demonstrated with the enantiomerically enriched substrates (*R*)-(+)-**1b** and (*S*)-(–)-**1d** which yielded the sulfoximides (*R*)-(+)-**3b** and (*S*)-(–)-**3d** with retention of configuration. Mechanistically, an intermediate (nitrene)Fe^{IV} complex is postulated as the reactive nitrene transfer reagent which is formed from $FeCl_2$ and $BocN_3$. The more nucleophilic sulfides **2** reacted more readily in the imidation than sulfoxides. Their conversion to the corresponding sulfimides **4** was conducted with $BocN_3$ and a substoichiometric amount of $FeCl_2$ (0.25 equiv.). Yields ranged between 44 and 92%. In an alternative reaction mode, $BocN_3$ was utilized at 0°C in the presence of $FeCl_2$ and acetyl acetone. The sulfimidation, which did not otherwise occur at this temperature, was accelerated by the ligand (36–90% yield).

The transfer of a nitrene fragment to sulfur compounds leads to the corresponding *N*-substituted imides. Starting from sulfoxides sulfoximides[1] of the general structure **A** are accessible, whereas sulfides yield sulfimides[2] **B** (Scheme 1). Various reagents have been employed to achieve this transformation. Prominent examples include the transfer of "NTs" (Ts = *p*-toluenesulfonyl) from TsN_3,[3][4] chloramine T,[3e,5,6] or PhI=NTs,[7][8] of "NH" from HN_3,[3f,9] or *O*-mesitylsulfonyl hydroxylamine (MSH),[10][11] and of "*N*-alkyl" from a primary amine in the presence of an oxidant[12][13] to name some known methods.[14][15]

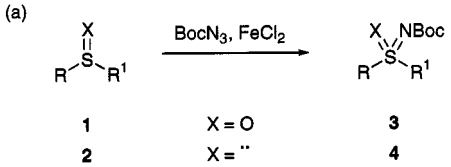


Scheme 1. General strategy for the imidation of sulfur compounds to sulfoximides **A** and sulfimides **B**

Sulfides and sulfoxides have comparably rarely been converted into their *N*-alkoxycarbonyl-substituted imide derivatives. Most procedures employed for this purpose utilize alkoxycarbonyl azides[16][17] from which the nitrene fragment is liberated thermally or photochemically.[4a,18] Transition-metal-mediated processes of this type are not known.[19][20] *N*-Chloro- and *N*-trifluormethanesulfonyloxy-substituted carbamates have been used for the imidation of sulfides.[21]

Some time ago, we wondered whether the transfer of an *N*-*tert*-butyloxycarbonyl-protected nitrene fragment from the readily available $BocN_3$[22] (Boc = *N*-*tert*-butyloxycarbonyl) (Caution!)[23] might be possible in the presence of a promoter, which would ideally be used in substoichiometric quantities. There were several reasons why this type of reaction appeared interesting to us. First of all, the nitrene transfer to sulfur nucleophiles is mechanistically related to the nitrene tranfer to alkenes (aziridination).[24] Conditions found for a successful imidation of sulfur compounds might hint at possible procedures for olefin aziridinations. The same notion holds good for mechanistic details and for intermediate (nitrene)metal complexes involved in these reactions. Secondly, the Boc group was assumed to be readily cleaved (vide infra),[25] so the free sulfoximines would be accessible by a mild method. If the imidation proceeded stereospecifically, enantiomerically pure *N*-Boc-protected sulfoximines and unprotected sulfoximines could be synthesized from enantiomerically pure sulfoxides. Thirdly, a new stereogenic center is established in the course of the sulfide imidation. If a suitable metal-based catalyst system for racemic sulfimide formation could be devised, an enantioselective variant would be conceivable by modifying the ligand or the counterion of the metal involved.[26]

Empirically, we have recently found that $FeCl_2$ is a useful promoter for the aforementioned nitrene transfer to sulfur compounds (Equation a).[27]



In the following account we report on the details of this method. It was demonstrated that the *N*-Boc imidation of sulfoxides proceeds stereospecifically under retention of configuration. Moreover, the ligand-accelerated imidation of sulfides to *N*-Boc-substituted sulfimines is described.

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Reaction with Sulfoxides

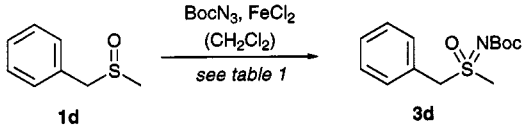
Preliminary experiments were carried out in order to identify possible transition metal compounds which induce the dediazotization of $BocN_3$. Upon treatment of $BocN_3$ (1 equiv.) with $FeCl_2$ (1 equiv.) in a polar solvent such as acetone or DMF at ambient temperature a gas evolution was observed. The color of the solution changed from yellow to a reddish brown and *O*-*tert*-butyl carbamate ($BocNH_2$) was isolated as the major reaction product after workup. Running the same reaction in DMSO as the solvent gave the sulfoximide **3a** in 58% yield. Lowering the amount of $FeCl_2$ to 25 mol-% (0.25 equiv.) led to a small deterioration in yield (55%).

R	Me	Ph	An	Bn	*i*Pr	*t*Bu	Bn	Bn
R^1	Me	Me	Me	Me	Me	Me	Et	Ph
	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**

This result is in contrast to the thermal reaction of alkoxycarbonyl azides in which a significant degree of nitrene transfer was observed only at elevated temperatures.[4a,16] In control experiments performed with DMSO and $BocN_3$ at room temperature there was no detectable formation of compound **3a**, indicating that the iron salt induces the nitrene transfer. A series of experiments in which other metal salts {$Mn(OAc)_2$, $MnBr_2$, $FeSO_4$, $FeCl_3$, $Fe_3(PO_4)_2$, $K_4[Fe(CN)_6]$, $RuCl_3$, $Co(OAc)_2$, $Rh_2(OAc)_4$, $RhCl_3$, $Ni(OAc)_2$, CuCl, CuI, $CuCl_2$, $Cu(OAc)_2$, AgOAc, $ZnCl_2$, $SnCl_4$} were tested revealed that $FeCl_2$ is particularly well suited for this purpose. The Lewis acidity appears to be a minor factor for the efficiency of the reaction, as compounds either more or less Lewis acidic (vide supra) than $FeCl_2$ did not induce a significant decomposition of $BocN_3$. $FeCl_3$ is unreactive, which clearly points to the importance of redox processes involved. For a more detailed study directed at an optimization of the reaction conditions the imidation of benzyl methyl sulfoxide (**1d**) was selected, which was run in degassed CH_2Cl_2 as the solvent (Equation b, Table 1). Pre-mixing of the starting materials at 0°C under argon and subsequent addition of $FeCl_2$ resulted in an evolution of nitrogen and the previously described color change. Upon warming to ambient temperature the reaction proceeded to completion and the product was isolated in analytically pure form after column chromatography. With a large excess of sulfoxide (5 equiv.) the yield was good (entry 1).

Lowering the amount of sulfoxide used led to a decrease in product formation (entry 2). A decrease in the catalyst concentration proved to have a minor influence, and the yield remained approximately constant if more than 0.25 equiv. $FeCl_2$ relative to $BocN_3$ were used (entries 3 and 4). Further lowering either the ratio of sulfoxide/$BocN_3$ or the amount of $FeCl_2$ relative to $BocN_3$ led to a decline of the reaction rate. Similarly, the increase of the initial temperature (entry 5) had a negative influence on the yield. Lower yields were recorded if the reaction was run under aerobic

(b)



1d **3d**

Table 1. The Fe^{II}-catalyzed imidation of sulfoxide **1d** with *tert*-butyloxycarbonyl azide according to Equation b

Entry	**1d** (equiv.)	$FeCl_2$ (equiv.)	Conditions	Yield (%)[a]
1	5	1	0°C → r.t.	70
2	2.5	1	0°C → r.t.	58
3	2.5	0.5	0°C → r.t.	65
4	2.5	0.25	0°C → r.t.	56
5	2.5	1	r.t.	29
6	2.5	1	0°C → r.t.[b]	26
7	2.5	1	0°C → r.t.[c]	28
8	2.5	0.5	0°C → r.t.[d]	28

[a] Yield of isolated product. – [b] Reaction conducted under aerobic conditions. – [c] Terminal addition of $BocN_3$. – [d] Terminal addition of the sulfoxide.

conditions (entry 6), or if the the mode of reagent addition was changed (entries 7 and 8).

The behavior of other sulfoxides with regard to a variation of reaction conditions was similar to what had been observed with sulfoxide **1d** but it was not studied systematically. Table 2 provides an overview about the reactions we have conducted with an array of substrates. Yields were in general moderate to good except for *tert*-butyl methyl sulfoxide (**1f**, entry 6), in which case the steric hindrance of the *tert*-butyl group apparently prohibits an approach of the nitrogen electrophile to the nucleophilic sulfur atom.

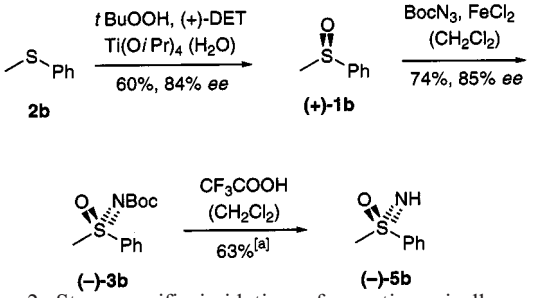
Table 2. The Fe^{II}-mediated imidation of various sulfoxides **1** with *tert*-butyloxycarbonyl azide according to Equation a in CH_2Cl_2 as the solvent

Entry	Sulfoxide	R	R^1	Product	Yield (%)[a]
1	**1a**	Me	Me	**3a**	58
2	**1b**	Ph	Me	**3b**	74
3	**1c**	An[b]	Me	**3c**	84
4	**1d**	Bn	Me	**3d**	70
5	**1e**	*i*Pr	Me	**3e**	54
6	**1f**	*t*Bu	Me	**3f**	10
7	**1g**	Bn	Et	**3g**	95
8	**1h**	Bn	Ph	**3h**	40

[a] Yield of isolated product. – [b] An = Anisyl.

The removal of the Boc group proceeded uneventfully[25] as was already alluded to in the introduction. By this means free sulfoximines are readily available. An example for a successful deprotection is depicted in Scheme 2. In order to investigate the stereochemical outcome of the sulfoxide imidation we prepared the sulfoxide (*R*)-(+)-**1b** in enantiomerically enriched form (84% *ee*) by the Ti-based oxidation of sulfide **2b**.[28] After the nitrogen transfer had been carried out in the usual manner, sulfoximide (*R*)-(−)-**3b** was analyzed by chiral HPLC (Daicel Chiracel OD). Both enantiomers were identified by comparison with racemic material. Integration of the baseline-separated peaks revealed an enantiomeric excess of 85% which secured the stereospecificity

of the reaction. After deprotection to sulfoximine (*R*)-(−)-**5b** the comparison of the specific optical rotation with the value reported for (*S*)-(+)-**5b**[10b] proved that the nitrene transfer had occurred with retention of configuration. Similarly, the imidation of sulfoxide (*S*)-(−)-**1d** was shown to proceed stereospecifically. The reaction delivered the corresponding sulfoximide (*S*)-(−)-**3d** without deterioration of the enantiomeric excess (62% *ee*). Subsequent deprotection gave the free sulfoximine (*S*)-(−)-**5d** in 72% yield (see Experimental Section).



Scheme 2. Stereospecific imidation of enantiomerically enriched sulfoxides and subsequent deprotection; [a] the deprotection procedure was not optimized (see Experimental Section)

Although the azide was the limiting agent in these reactions it is important to note that the nitrene transfer proceeded almost quantitatively with regard to sulfoxide conversion. The non-converted chiral sulfoxide (*R*)-(+)-**1b** for example was fully recovered from the reaction mixture with no deterioration of the optical purity. The yield based on sulfoxide conversion was determined to be > 80% for most cases.

Mechanistic investigations lag behind the preparative experiments we have carried out so far. As mentioned previously it is very likely that a redox process is involved in the nitrene transfer we studied. If no sulfoxide was added, the major reaction product derived from $BocN_3$ was $BocNH_2$ (vide supra) and an oxidation of Fe^{II} was indicated by the color change of the reaction mixture. This assumption is in accord with the lower yield which was recorded if the reaction was run under aerobic conditions (entry 6, Table 1). In an earlier report[29] it was revealed that aryl azides undergo a reaction with Fe^{II} compounds to yield the corresponding (μ-imido)Fe^{III} complexes. The hydrolysis of a similar complex derived from $BocN_3$ would yield $BocNH_2$ upon hydrolysis and could therefore readily account for the formation of this product. Although we have not yet been able to isolate a putative μ-*N*-Boc-imido complex we postulate its intermediacy based on the above-mentioned analogy. The μ-imido complex is most likely a sluggish nitrene transfer reagent in agreement with the observation that the terminal addition of sulfoxide **1d** to a premixed solution of $BocN_3$ and $FeCl_2$ was inferior to the normal addition mode (entry 8, Table 1). We therefore speculate that a precursor to such a μ-imido complex is responsible for the nitrene transfer. A (nitrene)Fe^{IV} complex[30] is a conceivable intermediate, which is either attacked by the sulfur nucleophile to yield the sulfoximide or by Fe^{II} to yield the μ-imido complex. Whereas Fe^{II} is regenerated upon sulfoxide attack, the μ-imido complex formation should be essentially irreversible and it accounts for the loss of catalytic activity. Further experiments are under way to further prove the described hypothesis.

Reaction with Sulfides

If the nucleophilicity of the sulfur compound is indeed important to guarantee a fast nitrene transfer from an Fe intermediate whose alternate reaction pathway is the formation of a (μ-imido)Fe^{III} complex, it was expected that sulfides would be more efficient in the imidation reaction. At 0°C, however, no reaction was observed upon mixing various sulfides with $BocN_3$ and $FeCl_2$ in CH_2Cl_2. The iron salt did not dissolve and the solution remained almost colorless. Upon warming to room temperature, the reaction commenced and the usual gas evolution was observed. A 1:1:0.5 ratio of sulfide/$BocN_3$/$FeCl_2$ was identified as ideal for an effective nitrene transfer. The results for several sulfides are summarized in Table 3.

Table 3. The Fe^{II}-catalyzed imidation of various sulfides **2** with *tert*-butyloxycarbonyl azide according to Equation a in CH_2Cl_2 as the solvent

Entry	Sulfide	R	R[1]	Product	Yield (%)[a]
1	**2a**	Me	Me	**4a**[b]	27
2	**2b**	Ph	Me	**4b**	82
3	**2d**	Bn	Me	**4d**	87
4	**2e**	*i*Pr	Me	**4e**	44
5	**2f**	*t*Bu	Me	**4f**	6
6	**2g**	Bn	Et	**4g**	90
7	**2h**	Bn	Ph	**4h**	92

[a] Yield of isolated product. − [b] Not stable upon chromatography.

In contrast to the sulfoxide system an excess of the sulfur nucleophile is not neccessary for a good conversion. This result reflects the higher reactivity of sulfides, which allows them to compete more successfully than sulfoxides against the Fe^{II} nucleophile in the reaction with the putative (nitrene)Fe^{IV} complex. The amount of catalyst could be lowered to 0.1 equiv. without a significant reduction in yield, provided a higher sulfide/$BocN_3$ ratio was chosen. Again, as in the sulfoxide case, a bulky substituent at the sulfur atom strongly inhibits attack of the nitrene transfer reagent (sulfide **2f**, entry 5). Dimethyl sulfide (**2a**) reacted cleanly but the resulting sulfimide **4a** proved to be unstable and could not be purified by chromatography.

Attempts to induce a reaction at 0°C were initiated in order to find possible ligands which solubilize the Fe^{II} salt and, by this means, accelerate the reaction. For these experiments a 2.5:1:0.25 ratio of sulfide/$BocN_3$/$FeCl_2$ was found most suitable. After some unsuccessful trials (among others using sulfimides as possible ligands) DMF[27] and acetyl acetone emerged as ideal candidates for the desired pur-

pose. Acetyl acetone was superior in most cases and Table 4 provides the results obtained with this ligand.

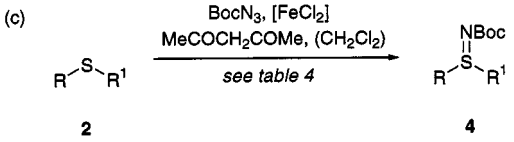


Table 4. Catalysis of the imidation of various sulfides **2** with *tert*-butyloxycarbonyl azide by $FeCl_2$/acetyl acetone according to Equation c [a] Yield of isolated product.

Entry	Sulfide	R	R^1	Product	Yield (%)[a]
1	**2b**	Ph	Me	**4b**	90
2	**2d**	Bn	Me	**4d**	61
3	**2e**	*i*Pr	Me	**4e**	36
4	**2f**	*t*Bu	Me	**4f**	4
5	**2g**	Bn	Et	**4g**	67
6	**2h**	Bn	Ph	**4h**	57

[a] Yield of isolated product. − [b] Not stable upon chromatography.

As the ligand had to be removed by chromatography the reaction of dimethyl sulfide (**2a**) was not studied. Except for sulfimide **4f** the sulfimide yields are moderate to good. The synthetically interesting sulfimide **4b**, which should be suited as a methylene transfer reagent,[31] was formed in excellent yield. Based on these results work is currently in progress aimed at chiral ligands that can induce an enantioselective nitrene transfer to sulfides.

Summary and Conclusion

N-Boc-substituted sulfoximides and sulfimides were synthesized by an $FeCl_2$-promoted nitrene transfer to sulfoxides and sulfides in CH_2Cl_2 as the solvent. In order to ensure a reasonable nitrene transfer an excess sulfoxide was required. The mass balance with regard to sulfoxide was very good and unchanged sulfoxide was fully recovered without significant losses. The conversion of sulfoxides into sulfoximides proceeded stereospecifically under retention of configuration. The removal of the Boc group was facile and sulfoximines were readily available. A (nitrene)Fe^{IV} complex is postulated as an intermediate in these reactions, whose attack by a sulfoxide yields the corresponding sulfoximide whereas an attack by solvated $FeCl_2$ yields a (μ-imido)Fe^{III} complex. The latter complex is assumed to be catalytically inactive and yields $BocNH_2$ upon hydrolysis. The more nucleophilic sulfides reacted more readily in the nitrene transfer reaction than sulfoxides. A 1:1 ratio of sulfide/$BocN_3$ was satisfactory to ensure moderate to good yields in the presence of 0.5 equiv. $FeCl_2$ at room temperature. It was shown that the addition of a suitable ligand facilitates a nitrene transfer at 0°C presumably by coordinating to $FeCl_2$ and thus solubilizing it in CH_2Cl_2

Experimental Section

General: All reactions involving water-sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under Ar. Dichloromethane was distilled from calcium hydride under Ar. Common solvents (*tert*-butyl methyl ether, pentane, and methanol) were distilled prior to use. $BocN_3$,[22][23] the sulfoxides **1b**−**1h**,[32] and the sulfides **2b**, **2d**−**2g**[33] were prepared according to literature procedures. All other reagents and solvents were used as received. − Melting points (uncorrected): Reichert hot bench. − IR: Bruker IFS 88 FT-IR or Nicolet 510 M FT-IR. − MS: Varian CH7 (EI). − GC: Hewlett-Packard HP 6890 series GC systems, column HP-1 (crosslinked methyl siloxane, 30 m). − ^1H and ^{13}C NMR: Bruker ARX-200, Bruker AC-300, Bruker AM-400, Bruker HMX-500. Chemical shifts are reported relative to tetramethylsilane as an internal reference. $CDCl_3$ was used unless noted otherwise. − Elemental analysis: Varian Elementar vario EL. − TLC: Merck aluminium sheets (0.2 mm silica gel 60 F_{254}), a pentane/*tert*-butyl methyl ether mixture was used; detection by UV or by coloration with ceric ammonium molybdate (CAM). − Column chromatography: Merck silica gel 60 (70−230 mesh).

Benzyl *N*-*tert*-Butyloxycarbonyl Methyl Sulfoximine (3d). − Typical Procedure A: 1 mmol of $BocN_3$ (143 mg) and 5 mmol of benzyl methyl sulfoxide[32a] (**1d**) (780 mg) were dissolved in 0.75 mL of dry CH_2Cl_2 at 0°C. After addition of 1 mmol of $FeCl_2$ (126 mg) nitrogen started to evolve. The reaction mixture was warmed to room temperature and stirred overnight. It was subsequently poured into 5 mL of water and the aqueous layer was extracted with CH_2Cl_2 (5 × 3 mL). The combined organic layers were washed with water and dried with $MgSO_4$. After filtration, the solvent was removed and the residue was purified by column chromatography (pentane/*tert*-butyl methyl ether, 20:80). 188 mg (70%) of **3d** was obtained as a white solid. R_f = 0.35 (*tert*-butyl methyl ether). − M.p. 62−64°C. − IR (KBr): $\tilde{\nu}$ = 1659 cm^{-1} (w, C=O), 1285 (s, C−O−C), 1174 (s, C−O−C). − ^1H NMR (300 MHz): δ = 1.67 [s, 9 H, $C(CH_3)_3$], 3.07 (s, 3 H, SCH_3), 4.87 (d, ^2J = 14.2 Hz, 1 H, CH*H*), 4.97 (d, ^2J = 14.0 Hz, 1 H, C*H*H), 7.57 (s, 5 H, arom. H). − ^{13}C NMR (75.5 MHz): δ = 28.1 [$C(CH_3)_3$], 37.9 (SCH_3), 59.4 (SCH_2), 80.5 [$C(CH_3)_3$], 127.6 (arom. C), 129.2 (arom. C), 129.5 (arom. C), 130.8 (arom. C), 158.5 (C=O). − MS (70 eV); *m*/*z* (%): 213 (67) [$C_9H_{11}NO_3S^+$], 154 (18)[$C_8H_{10}OS^+$] 91 (100) [$C_7H_7^+$], 57 (33) [$C_4H_9^+$]. − $C_{13}H_{19}NO_3S$ (269.35): calcd. C 57.97, H 7.11, N 5.20; found C 57.73, H 7.35, N 5.09.

(*S*)-(−)-Benzyl *N*-*tert*-Butyloxycarbonyl Methyl Sulfoximine (3d): Enantiomerically enriched (62% *ee*) material was prepared according to procedure A from (*S*)-(−)-benzyl methyl sulfoxide[28] (**1d**). − $[\alpha]_D^{25}$ = −50.7 (*c* = 1.1, acetone).

(*S*)-(−)-Benzyl Methyl Sulfoximine (5d): The enantiomerically enriched sulfoximide (*S*)-(−)-**3d** (0.65 mmol, 177 mg) was treated with 0.5 mL of CF_3COOH in 3 mL of CH_2Cl_2 at 0°C. The mixture was warmed to room temperature and the volatiles were removed by azeotropic distillation with toluene. The residue was dissolved in water and neutralized with aqueous Na_2CO_3 solution. The aqueous layer was extracted with CH_2Cl_2 (4 × 4 mL). The combined organic layers were dried with $MgSO_4$. Upon removal of the solvent 80 mg of (*S*)-(−)-**5d** (72%) remained. − $[\alpha]_D^{25}$ = −7.6 (*c* = 0.9, acetone). − All other analytical data are identical to those reported in the literature for racemic **5d**.[10c]

***N*-*tert*-Butyloxycarbonyl Dimethyl Sulfoximine (3a):**[16] The reaction was carried out as described in typical procedure A starting from dimethyl sulfoxide (**1a**). 102 mg (58%) of **3a** was obtained as a white solid. The analytical data were in full agreement with those reported in the literature.[16a]

***N*-*tert*-Butyloxycarbonyl Methyl Phenyl Sulfoximine (3b):** The reaction was carried out as described in typical procedure A starting from methyl phenyl sulfoxide[32a] (**1b**). 188 mg (74%) of **3b** was

obtained as a white solid. – R_f = 0.26 (*tert*-butyl methyl ether). – M.p. 65–67°C. – IR (KBr): $\tilde{\nu}$ = 1666 cm^{-1} (s, C=O), 1278 (s, C–O–C), 1159 (s, C–O–C), 748 (s, C–S). – ^1H NMR (200 MHz): δ = 1.35 [s, 9 H, $C(CH_3)_3$], 3.21 (s, 3 H, SCH_3), 7.49–7.66 (m, 3 H, arom. H). 7.87–7.96 (m, 2 H, arom. H). – ^{13}C NMR (50 MHz): δ = 27.6 [$C(CH_3)_3$], 44.3 (SCH_3), 80.2 [$C(CH_3)_3$], 127.0 (arom. C), 129.2 (arom. C), 132.4 (arom. C), 138.5 (arom. C), 157.1 (C=O). – MS (70 eV); *m/z* (%): 182 (9) [$C_8H_8NO_2S^+$], 140 (11) [$C_7H_8SO^+$], 77 (22) [$C_6H_5^+$], 56 (45) [$C_4H_8^+$]. – $C_{12}H_{17}NO_3S$ (255.33): calcd. C 56.45, H 6.71, N 5.48; found C 56.45, H 6.81, N 5.41.

(*R*)-(–)-*N-tert*-Butyloxycarbonyl Methyl Phenyl Sulfoximine (3b): Enantiomerically enriched (85% *ee*) material was prepared according to procedure A from (*R*)-(+)-methyl phenyl sulfoxide[28] (**1b**). – $[\alpha]_D^{25}$ = –52.9 (*c* = 1.0, acetone).

(*R*)-(–)-Methyl Phenyl Sulfoximine (5b): The sulfoximine was obtained from (*R*)-(–)-**3b** in 63% yield following the procedure described for (*S*)-(–)-**5d** above. – $[\alpha]_D^{25}$ = –28.1 (*c* = 1.2, acetone). – The value reported for (*S*)-(+)-**5b** (93.5% *ee*)[10b] is $[\alpha]_D^{25}$ = +34.1 (*c* = 2.0, acetone). All other analytical data are identical to those reported in the literature for racemic **5b**.[10c]

***N-tert*-Butyloxycarbonyl 4-Methoxyphenyl Methyl Sulfoximine (3c):** The reaction was carried out as described in typical procedure A starting from 4-methoxyphenyl methyl sulfoxide[32a] (**1c**). 239 mg (84%) of **3c** was obtained as a white solid. – R_f = 0.19 (*tert*-butyl methyl ether). – M.p. 106–108°C. – IR (KBr): $\tilde{\nu}$ = 1665 cm^{-1} (s, C=O), 1274 (s, C–O–Ar), 1251 (s, C–O–C), 1157 (s, C–O–C). – ^1H NMR (200 MHz): δ = 1.27 [s, 9 H, $C(CH_3)_3$], 3.12 (s, 3 H, SCH_3), 3.77 (s, 3 H, OCH_3), 6.96 (d, ^3J = 9.0 Hz,2 H, arom. H), 7.80 (d, ^3J = 9.0 Hz, 2 H, arom. H). – ^{13}C NMR (50 MHz): δ = 28.0 [$C(CH_3)_3$], 45.1 (SCH_3), 55.7 (OCH_3), 80.3 [$C(CH_3)_3$], 114.8 (arom. C), 129.5 (arom. C), 129.6 (arom. C), 157.7 (arom. C), 163.7 (C=O). – MS (70 eV); *m/z* (%): 212 (53) [$C_9H_{10}NO_3S^+$], 170 (18) [$C_8H_{10}SO^+$], 107 (13) [$C_7H_8O^+$], 57 (47) [$C_4H_9^+$]. – $C_{13}H_{19}NO_4S$ (285.36): calcd. C 54.47, H 6.71, N 4.91; found C 54.45, H 6.51, N 4.68.

***N-tert*-Butyloxycarbonyl Isopropyl Methyl Sulfoximine (3e):** The reaction was carried out as described in typical procedure A starting from isopropyl methyl sulfoxide[32a] (**1e**). 119 mg (54%) of **3e** was obtained as a white solid. – R_f = 0.22 (*tert*-butyl methyl ether). – M.p. 50°C. – IR (KBr): $\tilde{\nu}$ = 1657 cm^{-1} (s, C=O), 1274 (s, C–O–C), 1171 (s, C–O–C), 789 (s, C–S), 763 (s, C–S). – ^1H NMR (200 MHz): δ = 1.38 (d, ^3J = 6.8 Hz, 3 H, CH_3CHCH_3), 1.40 (d, ^3J = 6.8 Hz, 3 H, CH_3CHCH_3), 1.40 [s, 9 H, $C(CH_3)_3$], 3.00 (s, 3 H, SCH_3), 3.55 (sept, ^3J = 6.8 Hz, 1 H, CH_3CHCH_3). – ^{13}C NMR (50 MHz): δ = 15.3 (CH_3CHCH_3), 15.9 (CH_3CHCH_3), 26.8 (SCH_3), 28.0 [$C(CH_3)_3$], 54.5 (CH_3CHCH_3), 80.0 [$C(CH_3)_3$], 158.6 (C=O). – MS (70 eV); *m/z* (%): 148 (24) [$C_5H_{10}NO_2S^+$], 106 (50) [$C_4H_{10}S^+$], 57 (57) [$C_4H_9^+$], 43 (87) [$C_3H_7^+$]. – $C_9H_{19}NO_3S$ (221.32): calcd. C 48.84, H 8.65, N 6.33; found C 48.73, H 8.55, N 6.15.

***tert*-Butyl *N-tert*-Butyloxycarbonyl Methyl Sulfoximine (3f):** The reaction was carried out as described in typical procedure A starting from *tert*-butyl methyl sulfoxide[32a] (**1f**). 24 mg (10%) of **3f** of was obtained as a colorless oil. – R_f = 0.31 (*tert*-butyl methyl ether). – IR (film): $\tilde{\nu}$ = 1722 cm^{-1} (s, C=O), 1241 (s, C–O–C), 1191 (s, C–O–C), 721 (s, C–S). – ^1H NMR (300 MHz): δ = 1.47 [s, 9 H, $SC(CH_3)_3$], 1.48 [s, 9 H, $OC(CH_3)_3$], 3.20 (s, 3 H, SCH_3). – ^{13}C NMR (50 MHz): δ = 23.6 [$SC(CH_3)_3$], 28.7 [$OC(CH_3)_3$], 33.0 [$SC(CH_3)_3$], 60.7 (SCH_3), 80.4 [$OC(CH_3)_3$], 160.0 (C=O). – MS (70 eV); *m/z* (%): 236 (0.4) [$M^+ = C_{10}H_{21}NO_3S^+$], 136 (34) [$C_6H_{12}NOS^+$], 57 (100) [$C_4H_9^+$]. – $C_{10}H_{21}NO_2S$ (235.35): calcd. C 51.03, H 8.99, N 5.95; found C 50.89, H 8.63, N 5.66.

Benzyl *N-tert*-Butyloxycarbonyl Ethyl Sulfoximine (3g): The reaction was carried out as described in typical procedure A starting from benzyl ethyl sulfoxide[32a] (**1g**). 268 mg (95%) of **3g** was obtained as a white solid. – R_f = 0.47 (*tert*-butyl methyl ether). – M.p. 107–109°C. – IR (KBr): $\tilde{\nu}$ = 1643 cm^{-1} (s, C=O), 1276 (s, C–O–C), 1159 (s, C–O–C), 884 (s, S–N), 797 (s, S–N). – ^1H NMR (200 MHz): δ = 1.32 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3) 1.47 [s, 9 H, $C(CH_3)_3$], 3.02 (q, ^3J = 7.5 Hz, 2 H, CH_2CH_3), 4.64 (d, ^2J = 14.3 Hz, 1 H, CH*H*), 4.78 (d, ^2J = 14.3 Hz, 1 H, C*H*H), 7.36 (s, 5 H, arom. H). – ^{13}C NMR (50 MHz): δ = 6.3 (CH_2CH_3), 28.1 [$C(CH_3)_3$], 44.3 (CH_2CH_3), 56.6 (CH_2Ph), 80.3 [$C(CH_3)_3$], 125.6 (arom. C), 129.0 (arom. C), 129.1 (arom. C), 130.4 (arom. C), 158.7 (C=O). – MS (70 eV); *m/z* (%): 227 (16) [$C_{10}H_{13}NO_3S^+$], 91 (100) [$C_7H_7^+$], 57 (40) [$C_4H_9^+$], 29 (9) [$C_2H_5^+$]. – $C_{14}H_{21}NO_3S$ (283.39): calcd. C 59.34, H 7.47, N 4.94; found C 59.08, H 7.55, N 4.73.

Benzyl *N-tert*-Butyloxycarbonyl Phenyl Sulfoximine (3h): The reaction was carried out as described in typical procedure A starting from benzyl phenyl sulfoxide[32b] (**1h**). 132 mg (40%) of **3h** was obtained as a white solid. – R_f = 0.67 (*tert*-butyl methyl ether). – M.p. 102°C. – IR (KBr): $\tilde{\nu}$ = 1665 cm^{-1} (s, C=O), 1285 (s, C–O–C), 1169 (s, C–O–C), 754 (s, C–S), 689 (s, C–S). – ^1H NMR (200 MHz): δ = 1.36 [s, 9 H, $C(CH_3)_3$], 4.63 (s, 1 H, CH_2Ph), 6.85–6.89 (m, 2 H, arom. H), 7.08–7.23 (m, 3 H, arom. H), 7.49–7.60 (m, 3 H, arom. H), 7.33–7.40 (m, 2 H, arom. H). – ^{13}C NMR (50 MHz): δ = 28.1 [$C(CH_3)_3$], 62.1 (CH_2Ph), 80.6 [$C(CH_3)_3$], 127.1 (arom. C), 128.5 (arom. C), 128.7 (arom. C), 129.0 (arom. C), 129.1 (arom. C), 131.2 (arom. C), 133.7 (arom. C), 135.5 (arom. C), 158.0 (C=O). – MS (70 eV); *m/z* (%): 275 (10) [$C_{14}H_{13}NO_3S^+$], 91 (100) [$C_7H_7^+$], 77 (29) [$C_6H_5^+$], 57 (60) [$C_4H_9^+$].

Benzyl *N-tert*-Butyloxycarbonyl Methyl Sulfimine (4d). – Typical Procedure B: 1 mmol of $BocN_3$ (143 mg) and 1 mmol of benzyl methyl sulfide[33a] (**2d**) (140 mg) were dissolved in 0.75 mL of dry CH_2Cl_2. After addition of 0.5 mmol of $FeCl_2$ (67 mg), nitrogen started to evolve and the mixture was stirred overnight at room temperature. The reaction mixture was poured into 5 mL of water and the aqueous layer was extracted with CH_2Cl_2 (5 × 3 mL). The combined organic layers were washed with water and were dried with $MgSO_4$. After filtration, the solvent was removed and the residue was purified by column chromatography (CH_2Cl_2/methanol, 100:0 → 80:20). 220 mg (87%) of **4d** was obtained as a colorless oil which crystallized upon standing. – R_f = 0.21 (CH_2Cl_2/methanol, 98:2). – M.p. 55–56°C. – IR (KBr): $\tilde{\nu}$ = 1616 cm^{-1} (s, C=O), 1287 (s, C–O–C), 1159 (s, C–O–C), 698 (s, C–S). – ^1H NMR(300 MHz): δ = 1.51 [s, 9 H, $C(CH_3)_3$], 2.50 (s, 3 H, SCH_3), 4.02 (d, ^2J = 12.7 Hz, 1 H, CH*H*), 4.44 (d, ^2J = 12.7 Hz, 1 H, C*H*H), 7.32–7.44 (m, 5 H, arom. H). – ^{13}C NMR (75.5 MHz): δ = 28.1 [$C(CH_3)_3$], 28.5 (SCH_3), 53.0 (CH_2Ph), 78.3 [$C(CH_3)_3$], 128.3 (arom. C), 128.7 (arom. C), 128.8 (arom. C), 129.9 (arom. C), 164.2 (C=O). – MS (70 eV); *m/z* (%): 253 (0.1) [$M^+ = C_{13}H_{19}NO_2S^+$], 91 (100) [$C_7H_7^+$], 57 (36) [$C_4H_9^+$]. – $C_{13}H_{19}NO_2S$ (253.53): calcd. C 61.63, H 7.56, N 5.53; found C 61.54, H 7.52, N 5.51.

***N-tert*-Butyloxycarbonyl Dimethyl Sulfimine (4a):** The reaction was carried out as described in typical procedure B starting from dimethyl sulfide (**2a**). 47 mg (27%) of **4a** was obtained as a white solid. – R_f = 0.12 (CH_2Cl_2/methanol, 98:2). – M.p. 70°C. – ^1H NMR (200 MHz): δ = 1.39 [s, 9 H, $C(CH_3)_3$], 1.59 (s, 6 H, SCH_3). – ^{13}C NMR (75.5 MHz): δ = 28.3 [$C(CH_3)_3$], 33.1 (SCH_3), 78.7 [$C(CH_3)_3$], 164.5 (C=O). – MS (70 eV); *m/z* (%): 177 (0.2) [M^+ =

$C_7H_{15}NO_2S^+$], 121 (28) [$C_3H_7NO_2S^+$], 104 (100) [$C_3H_6NOS^+$], 62 (85) [$C_2H_6S^+$], 57 (62) [$C_4H_9^+$]. − $C_7H_{15}NO_2S$ (177.26): calcd. C 47.43, H 8.53, N 7.90; found C 47.20, H 8.40, N 7.75.

***N*-*tert*-Butyloxycarbonyl Methyl Phenyl Sulfimine (4b):** The reaction was carried out as described in typical procedure B starting from methyl phenyl sulfide[33a] (**2b**). 195 mg (82%) of **4b** was obtained as a white solid. − R_f = 0.48 (CH_2Cl_2/methanol, 95:5). − M.p. 82−83°C. − IR (KBr): $\tilde{\nu}$ = 1627 cm^{-1} (s, C=O), 1281 (s, C−O−C), 1160 (s, C−O−C), 748 (s, C−S). − ^1H NMR (300 MHz): δ = 1.39 [s, 9 H, $C(CH_3)_3$], 2.72 (s, 3 H, SCH_3), 7.44−7.48 (m, 3 H, arom. H). 7.67−7.70 (m, 2 H, arom. H). − ^{13}C NMR (75.5 MHz): δ = 28.6 [$C(CH_3)_3$], 36.0 (SCH_3), 79.1 [$C(CH_3)_3$], 126.2 (arom. C), 130.0 (arom. C), 132.2 (arom. C), 137.3 (arom. C), 164.6 (C=O). − MS (70 eV); *m*/*z* (%): 239 (1) [M^+ = $C_{12}H_{17}NO_2S^+$], 124 (100) [C_7H_8S], 77 (14) [$C_6H_5^+$], 57 (53) [$C_4H_9^+$]. − $C_{12}H_{17}NO_2S$ (239.33): calcd. C 60.22, H 7.16, N 5.85; found C 60.04, H 6.85, N 5.89.

***N*-*tert*-Butyloxycarbonyl Isopropyl Methyl Sulfimine (4e):** The reaction was carried out as described in typical procedure B starting from isopropyl methyl sulfide[33a] (**2e**). 90 mg (40%) of **4e** was obtained as a colorless oil. − R_f = 0.07 (CH_2Cl_2/methanol, 98:2). − IR (film): $\tilde{\nu}$ = 1627 cm^{-1} (s, C=O), 1288, (s, C−O−C), 787 (s, C−S), 754 (s, C−S). − ^1H NMR (300 MHz): δ = 1.22 (d, ^3J = 6.8 Hz, 3 H, CH_3CHCH_3), 1.25 (d, ^3J = 6.8 Hz, 3 H, CH_3CHCH_3), 1.35 [s, 9 H, $C(CH_3)_3$], 2.42 (s, 3 H, SCH_3), 3.07 (sept, ^3J = 6.8 Hz, 1 H, CH_3CHCH_3). − ^{13}C NMR (75.5 MHz): δ = 15.7 (CH_3CHCH_3), 16.4 (CH_3CHCH_3), 26.9 (SCH_3), 28.3 [$C(CH_3)_3$], 48.7 (CH_3CHCH_3), 78.3 [$C(CH_3)_3$], 165.0 (C=O). − MS (70 eV); *m*/*z* (%): 205 (2) [M^+ = $C_9H_{19}NO_2S^+$], 90 (26) [$C_5H_{10}S$], 57 (100) [$C_4H_9^+$]. − $C_9H_{19}NO_2S$ (205.32): calcd. C 52.65, H 9.33, N 6.82; found C 52.41, H 9.49, N 6.99.

***tert*-Butyl *N*-*tert*-Butyloxycarbonyl Methyl Sulfimine (4f):** The reaction was carried out as described in typical procedure B starting from *tert*-butyl methyl sulfide[33a] (**2f**). 13 mg (6%) of **4f** was obtained as a colorless oil. − R_f = 0.13 (CH_2Cl_2/methanol, 98:2). − M.p. 103−104°C. − IR (KBr): $\tilde{\nu}$ = 1642 cm^{-1} (s, C=O), 1271 (s, C−O−C), 1158 (s, C−O−C), 831 (s, C−S), 744 (s, C−S). − ^1H NMR (200 MHz): δ = 1.25 [s, 9 H, $SC(CH_3)_3$], 1.37 [s, 9 H, $OC(CH_3)_3$], 2.34 (s, 3 H, SCH_3). − ^{13}C NMR (50 MHz): δ = 23.6 [$SC(CH_3)_3$], 25.3 (SCH_3), 28.3 [$OC(CH_3)_3$], 53.9 [$SC(CH_3)_3$], 78.2 [$OC(CH_3)_3$], 165.5 (C=O). − MS (70 eV); *m*/*z* (%): 163 (0.1) [$C_6H_{13}NO_2S^+$], 146 (5) [$C_6H_{12}NOS^+$], 57 (100) [$C_4H_9^+$]. − $C_{10}H_{21}NO_2S$ (219.35): calcd. C 54.75, H 9.65, N 6.38; found C 54.55, H 9.10, N 6.12.

Benzyl *N*-*tert*-Butyloxycarbonyl Ethyl Sulfimine (4g): The reaction was carried out as described in typical procedure B starting from benzyl ethyl sulfide[33b] (**2g**). 240 mg (90%) of **4g** was obtained as a colorless oil. − R_f = 0.20 (CH_2Cl_2/methanol, 98:2). − IR (film): $\tilde{\nu}$ = 1615 cm^{-1} (s, C=O), 1292 (s, C−O−C), 1166 (s, C−O−C), 835 (s, C−S),700 (s, C−S). − ^1H NMR (200 MHz): δ = 1.48 [s, 9 H, $C(CH_3)_3$], 1.30 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 2.68−2.88 (m, 2 H, CH_2CH_3), 4.03 (d, ^2J = 12.7 Hz, 1 H, CHH), 4.33 (d, ^2J = 12.7 Hz, 1 H, CHH), 7.29−7.38 (m, 5 H, arom. H). − ^{13}C NMR (50 MHz): δ = 7.7 (CH_2CH_3), 28.2 [$C(CH_3)_3$], 37.7 (CH_2CH_3), 51.3 (CH_2Ph), 78.4 [$C(CH_3)_3$], 128.8 (arom. C), 129.0 (arom. C), 130.0 (arom. C), 164.8 (C=O). − MS (70 eV); *m*/*z* (%): 211 (19)[$C_{10}H_{13}NO_2S^+$], 91 (100) [$C_7H_7^+$], 57 (100) [$C_4H_9^+$], 29 (48) [$C_2H_5^+$]. − $C_{14}H_{21}NO_2S$ (219.35): calcd. C 62.89, H 7.92, N 5.24; found C 62.61, H 7.70, N 5.29.

Benzyl *N*-*tert*-Butyloxycarbonyl Phenyl Sulfimine (4h): The reaction was carried out as described in typical procedure B starting from benzyl phenyl sulfide (**2h**). 289 mg (92%) of **4h** was obtained as a white solid. − R_f = 0.23 (CH_2Cl_2/methanol, 98:2). − M.p. 81−83°C. − IR (KBr): $\tilde{\nu}$ = 1644 cm^{-1} (s, C=O), 1268 (s, C−O−C), 1166 (s, C−O−C), 759 (s, C−S). − ^1H NMR (200 MHz): δ = 1.48 [s, 9 H, $C(CH_3)_3$], 4.07 (d, ^2J = 12.25 Hz, 1 H, CHH), 4.52 (d, ^2J = 12.5 Hz, 1 H, CHH), 6.95−6.98 (m, 2 H, arom. H), 7.17−7.29 (m, 3 H, arom. H), 7.35−7.54 (m, 5 H, arom. H). − ^{13}C NMR (50 MHz): δ = 28.3 [$C(CH_3)_3$], 57.4 (CH_2Ph), 78.9 [$C(CH_3)_3$], 127.4 (arom. C), 128.4 (arom. C), 128.6 (arom. C), 128.8 (arom. C), 129.2 (arom. C), 130.4 (arom. C), 132.1 (arom. C), 133.3 (arom. C), 164.4 (C=O). − MS (70 eV); *m*/*z* (%): 259 (5) [$C_{14}H_{13}NO_2S^+$], 215 (9) [$C_{13}H_{13}NS^+$], 200 (1) [$C_{13}H_{12}S^+$], 91 (100) [$C_7H_7^+$] 77 (4) [$C_6H_5^+$], 57 (41) [$C_4H_9^+$]. − $C_{18}H_{21}NO_2S$ (315.43): calcd. C 68.54, H 6.71, N 4.44; found C 68.33, H 6.94, N 4.37.

Procedure for the Nitrene Transfer to Sulfides in the Presence of Acetyl Acetone. − Typical Procedure C: 1 mmol of $BocN_3$ (143 mg) and 2.5 mmol of sulfide **2** were dissolved in 0.75 mL of dry CH_2Cl_2 and the mixture was cooled to 0°C. At this temperature 0.25 mmol of $FeCl_2$ (34 mg) was added. Upon addition of 0.13 mL of acetyl acetone (1.3 mmol) the color of the solution turned from brown to red and nitrogen evolved. After stirring for 5 h at 0°C, the reaction mixture was poured into 5 mL of water and the aqueous layer was extracted with CH_2Cl_2 (5 × 3 mL). The combined organic layers were washed with water and dried with $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was purified by column chromatography (CH_2Cl_2/methanol, 100:0 → 80:20). The sulfimides **4** were obtained in the yields which are summarized in Table 4.

Acknowledgments

This work was supported by the Fonds der Chemischen Industrie and by the Graduiertenkolleg "Metallorganische Chemie" (scholarship to C. K.).

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Received November 17, 1998
[O98520]