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Highly Efficient Sulfimidation of 1,3-Dithianes by Cu(I) Complexes

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Abstract: A series of four Cu(I) complexes were tested for sulfimidation of 1,3-dithianes in the presence of [N-(p-tolysulfonyl)imino]phenyliodinane (PhI = NTs) as the nitrene-transfer agent. Cu(TMPhen)(PPh₃)Br is an efficient catalyst with more than 90% yield of the corresponding product with less reaction time as compared to the literature copper(I) complexes.

Keywords: Cu(I) complexes, 1,3-dithianes, PhI = NTs, sulfimidation

INTRODUCTION

Sulfoxides have emerged as versatile building blocks in the synthesis of pharmaceutical products.^[1] Sulfimides are the nitrogen equivalents of sulfoxides. Unlike sulfoxides, sulfimide use in organic synthesis is rather limited because of the lack of convenient synthetic methods. Sulfimidation is a nitrene-transfer reaction, and various reagents have been employed to achieve this transformation. Classically, sulfimidation of sulfides has been achieved in protic solvents using chloramine-T (the sodium salt of

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N-chloro-*p*-toluenesulfonamide) as the nitrene source, which is cheap and readily available. The first formed chlorosulfonium salt can be prone to hydrolysis, and the corresponding sulfoxide is often a by-product.^[2] To circumvent this problem, metal catalysts and [N-(*p*-tolysulfonyl)imino]phenyliodinane (PhI = NTs) as nitrene source were used in sulfimination.^[3] Evans et al. have reported PhI = NTs to be an effective asymmetric nitrene-transfer reagent to alkenes in the presence of a catalytic amount of Cu(I) salt together with a chiral 4,4'-disubstituted bis(oxazoline) ligand.^[4] Takada and coworkers reported enantioselective synthesis of chiral sulfimides using chiral copper(I)-bis(oxazoline) complex as a catalyst.^[5] Nishikori and Katsuki have used chiral Mn(III) and Ru(II) salen complexes for enantioselective sulfimination of 1,3-dithianes to get up to 99% enantiomeric pure compounds.^[6] However, with these salen catalysts, the reaction time is longer, and the synthesis of catalyst is also tedious.

On the other hand, utilization of either Cu(I) or Cu(II) salts in the sulfimination of 1,3-dithianes has well documented in the literature.^[7] The most common Cu(I) salts used in sulfimination are Cu(OTf), Cu(PF₆), CuCl, [Cu(NCMe)₄]BF₄, or Cu(CH₃CN)₄PF₆ and Cu(II) salts are Cu(OTf)₂ or Cu(acac)₂. Recently, we reported sulfimination of 1,3-dithianes by micro-encapsulated copper(II) acetylacetonate and Cu(acac)₂ immobilized in ionic liquids using PhI = NTs.^[8] All these methods involve either lower yields or high reaction times. We are interested in using Cu(I) complexes for sulfimination of 1,3-dithianes to further improve the reaction yields as well as to reduce the reaction time. Most copper(I) salts are insoluble in organic solvents, and hence, the reactions are often heterogeneous and require high reaction temperatures. For this reason, we have chosen four Cu(I) complexes for sulfimination. They are Cu(PPh₃)₃Br (**1**), Cu(Phen)(PPh₃)Br (**2**), Cu(neocup)(PPh₃)Br (**3**), and Cu(TMPhen)(PPh₃)Br (**4**). All four Cu(I) complexes are applied for the sulfimination reaction, and results are presented herein. Earlier, we used Cu(PPh₃)₃Br, Cu(Phen)(PPh₃)Br, and Cu(neocup)(PPh₃)Br complexes for triarylamine synthesis.^[9] Complexes **1**, **2**, and **3** were synthesized according to the reported procedure.^[10]

EXPERIMENTAL

IR spectra were recorded on a Nicolet-740 FT IR spectrometer. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz and Varian Gemini 200 spectrometer at 200 MHz. Chemical shifts are given in parts per million (ppm) with respect to internal TMS for all recorded NMR spectra, and *J* values are quoted in hertz (Hz). Mass spectra were recorded on VG Micromass-7070 H spectrometer at 70 eV. Reactions were monitored on 0.25-mm E. Merck precoated silica-gel plates (60 F₂₅₄). Starting materials were used from commercial samples without purification.

The complexes $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (**1**), $\text{Cu}(\text{Phen})(\text{PPh}_3)\text{Br}$ (**2**), and $\text{Cu}(\text{neocup})(\text{PPh}_3)\text{Br}$ (**3**) were synthesized according to procedures reported in the literature.^[10]

Synthesis of $\text{Cu}(\text{TMPhen})(\text{PPh}_3)\text{Br}$ (**4**)

Copper(I) bromide (1.98 g, 2.13 mmol) was dissolved in 150 ml of chloroform. To this, 0.51 g (2.13 mmol) of 3,4,7,8-tetramethyl-1,10-phenanthroline were added. The colorless solution immediately changed to red. The reaction mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure to get a yellow solid. The solid material was recrystallized from chloroform and diethyl mixture to get desired compound (1.23 g, 80% yield). ^1H NMR (CDCl_3 , 200 MHz): δ 1.83 (s, 6H, CH_3), 2.17 (s, 6H, CH_3), 7.24–7.70 (m, 19H, Ar-H). ^{13}C NMR (CDCl_3): δ 30.67, 128.18, 129.25, 130.49, 131.86, 133.55. ^{31}P NMR (CDCl_3): δ –2.77, –30.17. IR (KBr): ν 3045, 1585, 1517, 1479, 1434, 1383, 1093, 820, 748, 696, 524, and 527 cm^{-1} . Anal. calc. for $\text{C}_{34}\text{H}_{31}\text{BrN}_2\text{CuP}$: C, 63.60; H, 4.87; N, 4.36; Br, 12.45; P, 4.92. Found: C, 62.34; H, 5.27; N, 4.95; Br, 10.95; P, 2.31.

Typical Experimental Procedure

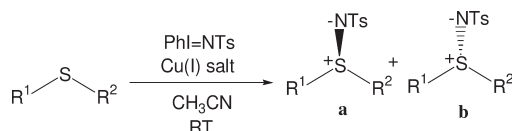
$\text{Cu}(\text{TMPhen})(\text{PPh}_3)\text{Br}$ (0.018 g, 0.028 mmol), methyl phenyl sulfide (0.062 g, 0.5 mmol), and $\text{PhI} = \text{NTs}$ (0.186 g, 0.5 mmol) were added to acetonitrile (5 ml), and the reaction mixture was stirred at room temperature for the time shown in Table 1. The reaction was monitored by the disappearance of $\text{PhI} = \text{NTs}$ from the reaction mixture. After completion of the reaction, the solvent was removed under reduced pressure to get the solid material (Scheme 1). The obtained solid material was subjected to silica-gel column chromatography and eluted with hexane/ethyl acetate (80/20, v/v) to afford the pure product as a white solid. Yield 0.132 g (90%). Mp 131°C

Table 1. Sulfimination of sulfides with $\text{PhI} = \text{NTs}$ using various Cu(I) catalysts^a

Entry	Catalyst	Reaction time (h)	Yield (%) ^b
1	$\text{Cu}(\text{PPh}_3)_3\text{Br}$	2	80
2	$\text{Cu}(\text{Phen})(\text{PPh}_3)\text{Br}$	2.5	78
3	$\text{Cu}(\text{neocup})(\text{PPh}_3)\text{Br}$	4	82
4	$\text{Cu}(\text{TMPhen})(\text{PPh}_3)\text{Br}$	1.5	90

^aSulfide (0.5 mmol), $\text{PhI} = \text{NTs}$ (0.5 mmol), catalyst (5 mol%) in 5 ml of acetonitrile at rt.

^bIsolated yields.



Scheme 1.

(lit.^[11]: 131–132°C). ¹H NMR (CDCl₃, 300 MHz): δ 2.34 (s, 3H, CH₃), 2.81 (s, 3H, CH₃), 7.12–7.71 (m, 9H, Ar-H); IR (KBr): ν 3030, 2928, 1597, 1447, 1279, 1142, 1090, 963, 756, 662, 575 cm⁻¹. Anal. calc. for C₁₄H₁₅NO₂S₂: C, 57.31; H, 5.15; N, 4.77; S, 21.84. Found: C, 57.35; H, 5.17; N, 4.75; S, 21.60.

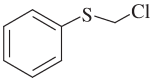
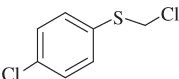
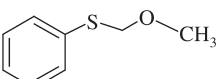
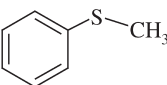
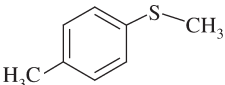
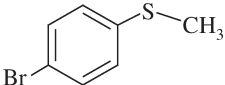
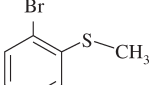
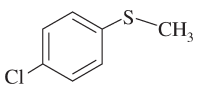
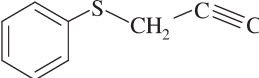
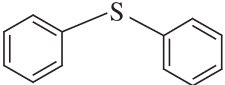
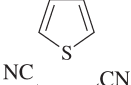
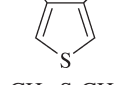
Results and Discussion

In this article, we report a highly efficient sulfimination of 1,3-dithianes by using a series of four Cu(I) complexes with PhI = NTs as nitrene-transfer agent. The catalysts **1**, **2**, and **3** were synthesized and characterized according to the reported procedure in the literature,^[10] whereas catalyst **4** was accomplished by copper(I) bromide and 3,4,7,8-tetramethyl-1,10-phenanthroline in chloroform, and the characterization of the complex was satisfactory.

Initially, the catalytic activity of all four copper(I) complexes were examined for sulfimination of methyl phenyl sulfide using PhI = NTs as nitrene source at room temperature in acetonitrile solvent. The results are presented in Table 1. From Table 1, it is clear that the reaction time of sulfimination of methyl phenyl sulfide follows the order 3 > 2 > 1 > 4, whereas yield follows the order 4 > 3 > 1 > 2. Hence, we decided to use the catalyst **4** for variety of 1,3-dithianes for sulfimination.

Under optimized conditions, a variety of 1,3-dithianes (including both aromatic and aliphatic sulfides) underwent reaction with PhI = NTs using 5 mol% of Cu(TMPhen)(PPh₃)Br (**4**) catalyst. The results are summarized in Table 2. Both aliphatic and aromatic sulfides gave more than 70% yields. Aliphatic sulfides undergo sulfimination faster than aromatic sulfides (entries 13, 14, and 15). Aromatic sulfides bearing electron-releasing groups (entry 5) are more reactive than those bearing electron-withdrawing groups in the sulfimination reaction. But, in the sulfimination of thiophene (entry 9), the yield is very low and reaction rate is also slow, whereas in the case of 3,4-dicyano thiophene (entry 10), sulfimination did not occur even after 10 h under these conditions, probably due to the electron-withdrawing nature of the cyano group. The present catalytic system for sulfimination is highly efficient when compared to other catalytic systems reported in the literature. The preparation of catalyst is straightforward and not air sensitive. We have achieved sulfimination of aliphatic 1,3-dithianes with high yields (93%, entry 12), and the reaction time is only 0.5 h. In contrast, as sulfimination of

Table 2. Sulfinidation of sulfides with PhI = NTs using Cu(TMPhen)(PPh₃)Br^a

Entry	Sulfides	Reaction time (h)	Yield (%) ^b
1		5	71
2		5	81
3		4	85
4		1.5	89
5		2	92
6		5	85
7		4	70
8		4.5	73
9		0.5	93
10		4	81
11		3	55
12		10	—
13	CH ₃ -S-CH ₃	0.5	90
14	Cl-CH ₂ -CH ₂ -S-CH ₃	0.5	91
15	CH ₃ (CH ₂) ₃ S(CH ₂) ₃ CH	0.5	93

^aSulfide (0.5 mmol), PhI = NTs (0.5 mmol), catalyst **4** (5 mol%) in 5 ml of acetonitrile at rt.^bIsolated yields.

existing catalytic systems were achieved only up to 70%, and the reaction time was around 20 h.

In conclusion, four Cu(I) complexes were used as catalysts for sulfimidation of 1,3-dithianes in the presence of $\text{PhI} = \text{NTs}$ as nitrene-transfer agent. The catalyst $\text{Cu}(\text{TMPhen})(\text{PPh}_3)\text{Br}$ shows good performance in sulfimidation. We have achieved the sulfimidation up to 93% with this system. Currently, the application of these Cu(I) complexes to other reactions such as aziridination, aza Michael reaction, and asymmetric sulfimidation is under way.

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