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One-pot Tandem Reactions for Direct Conversion of Thiols and Disulfides to Sulfonic Esters, Alcohols to Bis(indolyl)methanes and Synthesis of Pyrroles Catalyzed by *N*-Chloro Reagents

Hojat Veisi,[a,b,*] Meral Ataee,[b] Leila Fatolahi[a] and Shahram Lotfi[a]

[a]*Department of Chemistry, Payame Noor University, 19395-4697 Tehran, I.R. of Iran*

[b]*Department of Chemistry, Islamic Azad University-Saveh Branch, P. 39187-366, Saveh, Iran*

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Abstract: A convenient synthesis of sulfonic esters from thiols and disulfides has been described. *In situ* preparation of sulfonyl chlorides from thiols is accomplished by oxidation with Chloramin-T, *tetra*-butylammonium chloride (*t*-Bu_4NCl) and water. The sulfonyl chlorides are then further allowed to react with phenol derivatives in the same reaction vessel. Also, a facile synthesis of bis(indolyl)methanes from alcohols using TCCA/KBr/wet-SiO_2, and *N*-substituted pyrroles by reaction of hexane- 2,5-dione with primary amines has been accomplished under mild condition with excellent yields.

Keywords: Thiols, sulfonic esters, Bis(indolyl)methanes, pyrroles, *N*-Chloro regents.

INTRODUCTION

Sulfonic esters are a class of sulfonic acid derivatives that have drawn much attention because they are valuable intermediates in organic synthesis and are suitable precursors for sulfonamides [1]. In addition, various sulfonic esters exhibit interesting biological and pharmacological properties [2]. Therefore, it is not surprising that the synthesis of sulfonic esters has always been of great interest to organic chemists. The most typical method for the preparation of sulfonic esters is the reaction of sulfonyl chlorides with alcohols or phenols in the presence of a base [3-10]. However, the preparation of sulfonic esters from phenols has been much less investigated as compared to the preparation of sulfonic esters from alcohols.

The pyrrole ring system is a useful structural element in medicinal chemistry [11] and has found broad application in drug development for antibacterial, antiviral, anti-inflammatory, antitumoral and antioxidant [12] activity and is widely used in materials science [13]. Therefore, preparation of pyrroles is an important reaction for which a wide variety of methods has been developed [14]. One of the general routes for synthesis of pyrroles is the Paal-Knorr reaction which converts γ-diketone to pyrroles by the interaction of primary amines in the presence of various promoting agents such as: montmorillonite KSF [15], microwave irradiation [16], $Bi(NO_3)_3.5H_2O$ [17], $Sc(OTf)_3$ [18], layered zirconium phosphate and zirconium sulfophenyl phosphonate [19], Titanium [20], $TiCl_4/Et_3N$ [21], *p*-TSA [22] and I_2 [15]. Some other methods for synthesis of pyrroles included conjugate addition reactions [23], annulation reactions [24] and aza-Wittig reactions [25, 26]. However, some of these reactions involve the use of excess amounts of acids, hazardous organic solvents, tedious workup, or large amounts of solid catalysts [27], which may not be the preferred choices in view of green chemistry. Hence, an efficient and mild Paal-Knorr condensation is needed for contemporary chemical synthesis. Also, *N*-Halo compounds are versatile reagents and have been employed as potentially reactive intermediates that are widely used in organic synthesis [28].

RESULTS AND DISCUSSION

We would like to present a direct convenient one-pot synthesis of sulfonic esters from thiols and disulfides, and phenols using Chloramin-T/*t*-Bu_4NCl /H_2O under mild conditions (Scheme **1**).

In order to find optimized conditions for the reaction, 4-methyl-thiophenol and phenol were selected as model substrates in acetonitrile at room temperature. After many optimization experiments with respect to the molar ratio of the reactants, reaction time, and possible solvents, the best result was achieved by using the reaction of 4-methyl-thiophenol (1 equiv), with *t*-Bu_4NCl (3 equiv), H_2O (2.5 equiv), and Chloramin-T (2 equiv) in CH_3CN (10 min, rt) with continuous addition of phenol (1.1 equiv, 30 min) and triethylamine (Et_3N, 1.1 equiv) to give the corresponding sulfonic ester in 94% yield (Table **1**, Entry 1). Et_3N was used as base and HCl trapper in the reaction medium.

To extend the scope of the reaction and to generalize the procedure, we then investigated the generality and versatility of this procedure using a series of structurally different thiols and phenols (commercially available) under these optimized conditions. A combinatorial library (parallel format) of sulfonic esters was smoothly prepared in good to high yields whose results are summarized in Table **1**.

*Address correspondence to this author at the Department of Chemistry, Payame Noor University (PNU), 19395-4697 Tehran, I.R. of Iran;
Fax +98(838)4227463; E-mail: hojatveisi@yahoo.com

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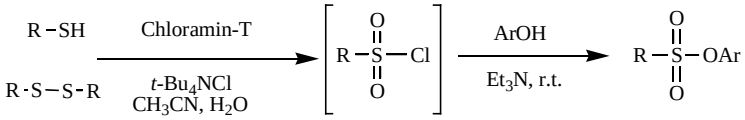
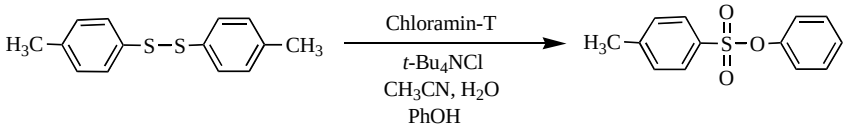


Scheme 1. Convenient one-pot synthesis of sulfonic esters from thiols and disulfides.

Table1. Preparation of Sulfonic Esters from Thiols.

Entry	R	Ar	Yield (%)[a]	Mp/°C	Ref.
1	4-MeC_6H_5	C_6H_5	94	92-94	[10]
2	4-MeC_6H_5	4-$MeOC_6H_5$	92	70-71	[10]
3	4-MeC_6H_5	4-$NO_2C_6H_5$	80	94-95	[8]
4	4-FC_6H_5	C_6H_5	92	oil	[10]
5	Naphtyl	C_6H_5	90	90-92	[10]
6	4-$NO_2C_6H_5$	C_6H_5	90	110	[7]
7	Cyclohexyl	4-$MeOC_6H_5$	85	oil	[10]
8	4-$NO_2C_6H_5$	4-MeC_6H_5	90	99-100	[7]

[a]Products were characterized from their physical properties, comparison with authentic samples and by spectroscopic methods.



Scheme 2. Formation of sulfonic ester from the corresponding disulfide.

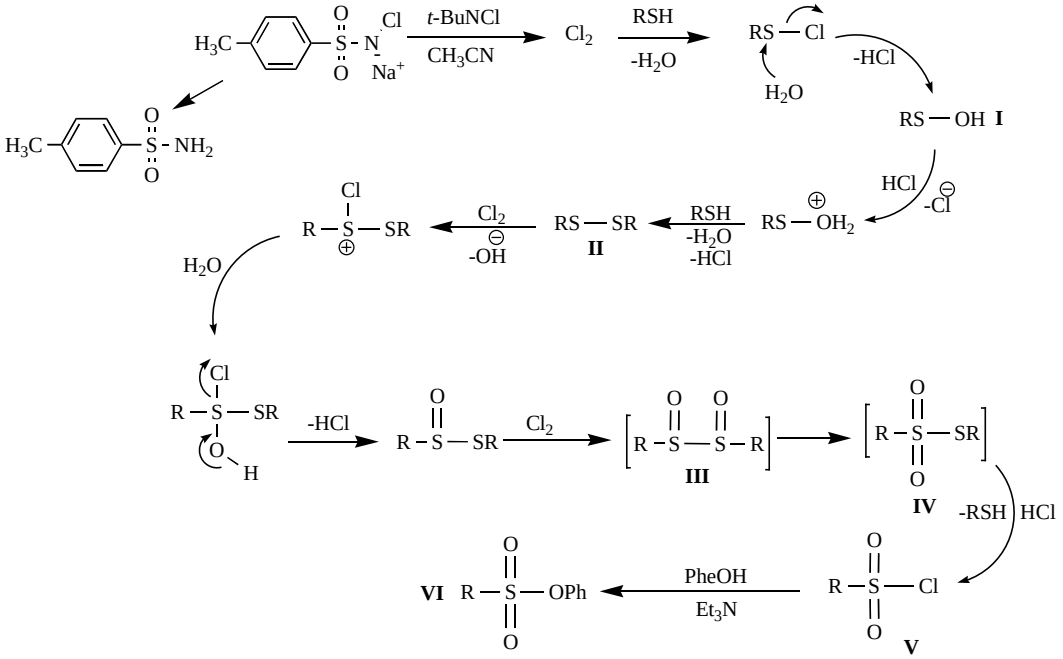
Table 2. Preparation of Sulfonic Esters from Disulfides.

Entry	Disulfide (R)	Sulfonic ester (Ar)	Yield (%)[a]
1	4-MeC_6H_5	C_6H_5	90
2	4-MeC_6H_5	4-$MeOC_6H_5$	95
3	4-MeC_6H_5	4-$NO_2C_6H_5$	92
4	4-FC_6H_5	C_6H_5	80
5	Naphtyl	C_6H_5	92
6	4-$NO_2C_6H_5$	C_6H_5	90
7	Cyclohexyl	4-$MeOC_6H_5$	95

[a]Products were characterized from their physical properties, comparison with authentic samples and by spectroscopic methods.

An investigation into the mechanistic aspects of oxidative chlorination of thiols showed the corresponding disulfide as the main intermediate in this transformation. In order to further verify the mediation of the disulfides in the oxidative chlorination of thiols, reactions were repeated with a range of symmetrical disulfides for the synthesis of sulfonic esters (Scheme **1**, **2**). After optimizing the reaction in order to identify conditions that consistently produced excellent yields of sulfonic esters, we found that the best reaction conditions required the presence of Chloramin-T (1.2 equiv), *t*-Bu_4NCl (1.5 equiv), H_2O (1.5 equiv) and disulfide (1 mmol) in acetonitrile at room temperature. The generality and the scope of the reaction were investigated and the results of the study are summarized in Table **2**. As shown, all reactions resulted in the formation of the corresponding sulfonic esters in excellent yields with high purity. This shows that successive oxidation of the sulfur atom, followed by S–S bond cleavage and subsequent chlorination, occurs during the direct conversion of thiols into the corresponding sulfonyl chlorides and subsequently to sulfonic esters.

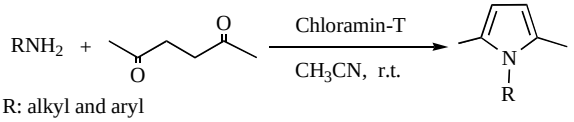
A possible mechanism for this transformation is shown in Scheme **3** [29i]. Molecular chlorine generated from Chloramin-T and *t*-Bu_4NCl affects the oxidative chlorination. It is reasonable to assume that the thiol will chlorinates in the presence of chlorine. Therefore, the mechanism proceeding



Scheme 3. The possible mechanism for this transformation.

through hydroxylation of thiol leads to the formation of sulfenic acid (I), which gives the corresponding symmetric disulfide (II). Then the successive oxidation of both sulfur atoms of the disulfide molecule by chlorine produces the intermediate (III) that undergoes rapid isomerization to the thiosulfonate (IV), which can easily furnish sulfonyl chloride (V). Then, the sulfonyl chloride (V) reacts with phenol to form the corresponding sulfonic esters (VI).

In continuation of our works, we wish to report our preliminary results on the synthesis of pyrroles from a γ-diketone and primary amines with Chloramin-T as catalyst under mild condition with excellent yields (Scheme **4**).



R: alkyl and aryl

Scheme 4. Synthesis of pyrroles from γ-diketone and primary amines.

Accordingly, treatment of 1,4-diketone with aniline in the presence of a catalytic amount of Chloramin-T afforded 2,5-dimethyl-*N*-phenylpyrrole in 80% yield under solvent-free condition (Scheme **4**). In continuation, we investigated the effect of solvents on this reaction. Several solvents including acetonitrile, dichloromethane, chloroform, water and ethanol were investigated during the course of this study. These experiments show that CH_3CN is a better solvent than the rest ones tested (97% yield).

These results promoted us to investigate the scope and the generality of these new protocols for various amines (aliphatic and aromatic) under optimized conditions. In the same manner, a variety of amines were coupled with 1,4-diketone in the presence of a catalytic amount of Chloramin-T at room temperature to give the corresponding pyrroles in good to excellent yields (Table **3**). The less basic aromatic amines require only slightly more time than the more basic amino compounds, and both lead to high yields of the pyrrole products.

As shown in Table **3**, aromatic amines with electron donating groups (Table **3**, entries 6, 7, 10) or electron-withdrawing group (Table **3**, entries 8, 9) are both effective in the Paal-Knorr reaction. Due to the good results obtained, we found that, the present protocol that was also applied to less nucleophilic aromatic amines.

Having these results in hand, several amines including monocyclic, bicyclic aromatic, aliphatic, benzylic, diamines and triamine, have been subjected to the above-mentioned optimized conditions, and the results are also presented in Table **3**. It is evident that our methodology is reasonably general and can be applied to several amines. The other starting material hexane- 2,5-dione, was commercially available (Scheme **4**). The yields of products are also shown in Table **3**.

As shown in Table **3**, a series of aromatic amines bearing either electron-withdrawing or electron releasing groups on the aromatic ring was investigated. The substituent group on the phenyl ring did not make any difference in the Paal-Knorr reaction. Morever, we also examined the Paal-Knorr reaction of aliphatic amines with hexane- 2,5-dione (Table **3**, Entries 14-17). Similarly, the corresponding products were obtained in excellent yield.

We found this method is selective for preparation of pyrrole containing aromatic rings with functional groups such as chlorine (Table **3**, entry 5), and carboxylic acids (Table **3**, entry 9).

Our experiments also indicated that Chloramin-T is a reusable catalyst and after three runs, the catalytic activity of the catalyst was almost the same as that of fresh catalyst. Also, to compare this method with previously published

Table 3. Pyrroles Derivatives Produced from Paal-Knorr Condensation with Chloramin-T at Room Temperature.

Entry	Amine (1)	Time	Yield (%)[a]
1	C_6H_5-NH_2	2 h	90
2	C_6H_5-CH_2NH_2	5 min.	98
3	4-MeO-C_6H_4-CH_2NH_2	10 min.	96
4	H_2NCH_2-C_6H_4-CH_2NH_2 (*p*)	10 min.	92
5	4-Cl-C_6H_4-NH_2	2.5 h	80
6	4-OMe-C_6H_4-NH_2	3 h	85
7	4-Me-C_6H_4-NH_2	2 h	90
8	3-CF_3-C_6H_4-NH_2	3 h	85
9	4-COOH-C_6H_4-NH_2	4 h	70
10	H_2N-C_6H_4-NH_2 (*p*)	45 h	85
11	H_2N-C_6H_4-NH_2 (*m*)	5.5 h	80
12	Naphthalen-1-amine	3..5 h	82
13	Naphthalene-1,5-diamine	5 h	75
14	Cyclopentanamine	15 min.	96
15	H_2N-CH_2CH_2-NH_2	20 min.	96
16	HN-(CH_2CH_2-NH_2)$_2$	25 min.	92
17	N-(CH_2CH_2-NH_2)$_3$	1.5 min.	96

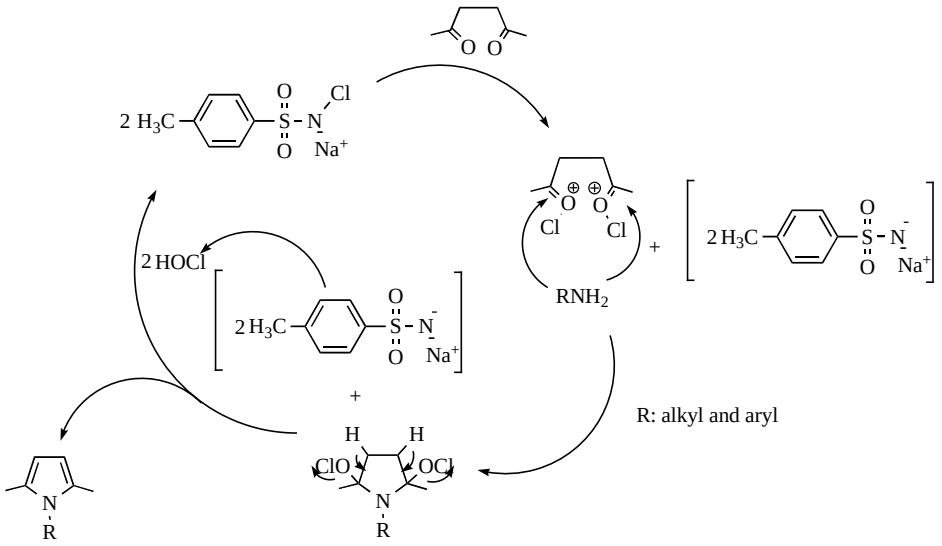
[a] Products were characterized on the basis of their physical properties, comparison with authentic samples and by spectroscopic methods.

Table 4. Reaction Times and Yield for Previously Published Methods.

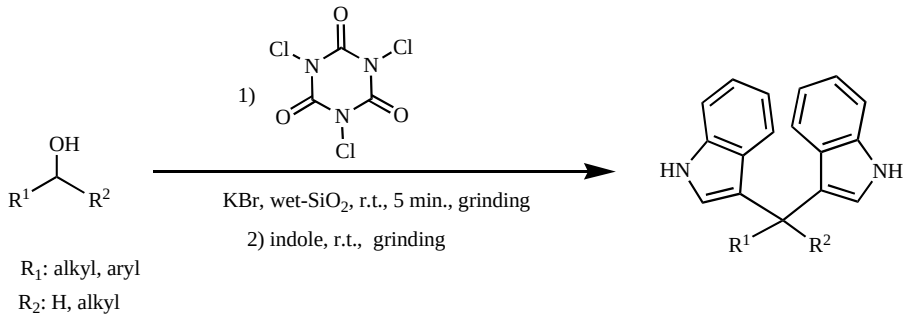
Substrate	Conditions	Reaction time	Yield (%)
Benzylamine	Montmorillonite, KSF	10 h	95 [15]
Benzylamine	I_2	0.5 h	92 [15]
Benzylamine	$Bi(NO_3)_3.5H_2O$	10 h	95 [17]
Benzylamine	Microwave	0.5 min	90 [16]
Benzylamine	α-$Zr(KPO_4)_2$	2 h	78 [19]
1-Naphthylamine	$Sc(OTf)_3$	40 min	90 [18]
1-Naphthylamine	Montmorillonite, KSF	11 h	83 [15]
1-Naphthylamine	I_2	1 h	85 [15]
1-Naphthylamine	$Bi(NO_3)_3.5H_2O$	11 h	83 [17]
2-aminopyridine	$Bi(NO_3)_3.5H_2O$	25 h	70 [17]
2-aminopyridine	Montmorillonite, KSF	25 h	70 [15]
2-aminopyridine	I_2	1 h	78 [15]

methods for the synthesis of *N*-substituted pyrroles with benzylamine, naphthylamine and 2-aminopyridine, we carried out the following studies, as shown in Table **4**. These results clearly demonstrate that this procedure is a good system for the preparation of *N*-alkyl and *N*-aryl-2, 5-dimethylpyrroles.

Since Chloramin-T contains a halogen atom that is attached to the nitrogen atoms, it is quite possible that Cl^+ released *in situ* can act as catalyst in the reaction medium. In Scheme **5**, the suggested mechanism for synthesis of pyrroles with Chloramin-T is shown.



Scheme 5. The suggested mechanism for synthesis of pyrroles with TCCA.



Scheme 6. Conversion of alcohols to bis(indolyl)methanes in one-pot.

In continuation of our interest in the application of *N*-halo reagents in organic synthesis [28], we interested to find a good way to conversion of alcohols to bis(indolyl) methanes in one-pot. Therefore, we report the use of trichloroisocyanuric acid (TCCA)/KBr/wet-SiO_2/indole as an catalytic system to oxidation conversion of alcohols to bis(indolyl)methanes under solid-state conditions by pulverization-activation method at room temperature with excellent yields (Scheme **6**).

For our initial optimization studies, benzyl alcohol was chosen as the model substrate. A mixture of benzyl alcohol (1mmol), KBr (0.12 mmol) and wet SiO_2 (0.2 g) was stirred for 5 min., followed by addition of indole (2 mmol) which afforded the corresponding bis(indolyl)methane in 90% yield under solid state conditions with pestle in a mortar (Table **5**, entriy 1).

These results promoted us to investigate the scope and the generality of this new protocol for various alcohols under optimized conditions. As shown in Table **6**, a series of aromatic, aliphatic and heterocyclic alcohols underwent oxidation and electrophilic substitution reaction with indole smoothly to afford a wide range of substituted bis(indolyl) methanes in good to excellent yields.

A plausible mechanism for the oxidation is shown in Scheme **7** based on our observation and obtained results, catalytic activity of KBr and insitu generation of HOCl by the use of trichloroisocyanuric acid in the presence of water. The oxidation of bromide ion by HOCl would give hypobromous acid and subsequent oxidation of alcohols by β-elimination of HCl affords aldehydes and ketones. Then, This aldehyde or ketone reacts with indole in the presence of HCl to form a bis(indolyl)methane.

CONCLUSION

In conclusion, we have developed a facile and efficient methodology using one-pot tandem reactions for the direct conversion of thiols and disulfides to sulfonic esters, alcohols to bis(indolyl)methanes, and synthesis of *N*-substituted pyrroles using *N*-chloro regents. The advantages of the method include (*i*) short reaction times, (*ii*) high yields, and (*iii*) easy work-up.

EXPERIMENTAL

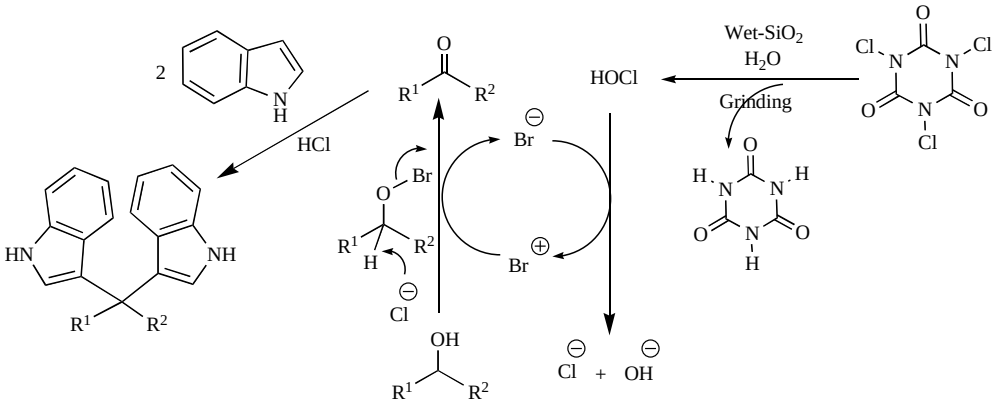
General Procedures for the Conversion of Thiols to Sulfonic Esters

To a stirred mixture of of thiol (1 mmol), *t*-Bu_4NCl (3 equiv), and water (2.5 mmol) in CH_3CN (5 mL) at 0 °C, Chloramin-T (2 equiv) was added in portions over 1-2 min. After 30 min, a solution of phenol (1.1 mmol) in triethylamine (1.1 mmol) was added to the reaction mixture over 1-

Table 6. Synthesis of bis(indolyl)methanes from alcohols.

Entry	Carbonyl Compound	Time (min)	Yield (%)[a]	Mp °C
1	Benzyl alcohol	10	90	124-125
2	4-methyl-Benzyl alcohol	12	90	94-95
3	2-methoxy-Benzyl alcohol	8	92	134-136
4	4-methoxy-Benzyl alcohol	8	90	190-192
5	2-bromo-Benzyl alcohol	12	85	110-112
6	4-chloro-Benzyl alcohol	10	89	76-78
7	2-chloro-Benzyl alcohol	12	85	70-72
8	furan-2-yl-methanol	10	80	>300
9	4-hydroxy-Benzyl alcohol	15	90	123-125
10	4-nitro-Benzyl alcohol	15	86	218-220
11	3-nitro-Benzyl alcohol	15	80	258-260
12	4-(*N*,*N*-dimethyl)-Benzyl alcohol	12	75	224-226
13	Cinnamyl alcohol	10	85	98-100
14	thiophen-2-yl-methanol	12	80	151-154
15	Pentanol	15	75	121-123
16	1-phenylethanol	10	90	165–167
17	1-(4-nitrophenyl)ethanol	10	89	190-192
18	cyclohexanol	12	90	115-116

[a] Products were characterized from their physical properties, comparison with authentic samples and by spectroscopic methods.



Scheme 7. Plausible mechanism.

2 min. The resulting mixture was stirred at room temperature for 90 min. until TLC showed complete disappearance of starting material (Table **2**). The reaction mixture was then diluted with water (10 mL) and extracted with EtOAc (3X10 mL). The combined ethyl acetate extracts were dried with $MgSO_4$ and concentrated under reduced pressure to give the corresponding sulfonic ester as the only product.

General Procedures for the Conversion of Disulfides to Sulfonic Esters

To a stirred mixture of thiol (1 mmol), *t*-Bu_4NCl (3 equiv), and water (2.5 mmol) in CH_3CN (10 mL) at 0 °C, Chloramin-T (1.2 equiv) was added in portions over 1-2 min. After 30 min, a solution of phenol (1.1 mmol) in triethylamine (1.1 mmol) was added to the reaction mixture over 1-2 min. The resulting mixture was stirred at room temperature for 60 min. until TLC showed complete disappearance of starting material (Table **2**). The reaction mixture was then diluted with water (10 mL) and extracted with EtOAc (3X10 mL). The combined ethyl acetate extracts were dried with $MgSO_4$ and concentrated under reduced pressure to give the corresponding sulfonic ester as the only product.

General Procedure for the Synthesis of Pyrroles with Chloramin-T

To a solution of amine 1 (1 mmol) and 2,5-hexanedione 2 (1 mmol) in CH_3CN (3 mL) Chloramin-T (0.05 mmol) was added at room temperature. The mixture was allowed to stir at this temperature for the period time specified in Table 3. The reaction was monitored by TLC (3:1 n-hexane/acetone).

After completion of the reaction, the solvent was evaporated. Then CH_2Cl_2 (10 mL) was added and the catalyst was removed by filtration. Evaporation of the solvent under reduced pressure gave the products. Further purification was achieved by thin layer chromatography using n-hexane/ acetone (70: 30) as the solvent system to afford the pyrroles.

Synthesis of bis(indolyl)methanes from Alcohols

A mixture of KBr (0.12 mmol), benzylalcohole (1 mmol), TCCA (0.4 mmol) and wet SiO_2 (0.2 g) was taken and ground with pestle in a mortar for an appropriate time at room temperature, followed by addition of 2 mmol indole. After completion of the reaction (monitored by TLC, hexane/acetone 4:1), the reaction mixture was washed with CH_2Cl_2 (20 mL). Anhyd Na_2SO_4 (2g) was added to the filtrate and was filtered off after 20 min. CH_2Cl_2 was removed. The resulting crude material was purified by recrystalization from ethanol-water to afford pure products.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflict of interest.

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