

Combination of HNaX Zeolite and Diphenyl Sulfide as Regioselectivity Enhancer in Chlorination of Toluene

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Abstract

A catalytic combination of HNaX zeolite and diphenyl sulfide (DPS) has been used to enhance regioselective *para* chlorination of toluene by sulfuryl chloride as chlorinating agent.

Keywords: Zeolite, regioselective, *para* chlorination, sulfuryl chloride, diphenyl sulfide

1. Introduction

The isomerically pure chloroaromatics are very valuable materials. They can serve as intermediates in the synthesis of compounds such as pesticides and pharmaceuticals.

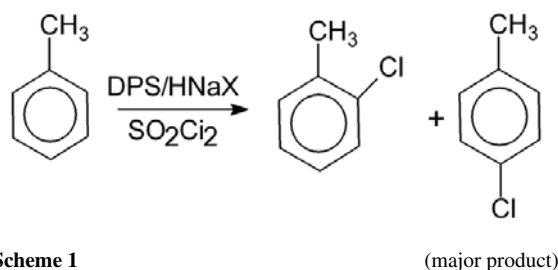
Unfortunately, the conventional methods for chlorination of aromatics in many cases result in mixtures of regioisomers, which are difficult to separate. During the past few years, considerable efforts have been devoted to the development of more efficient and selective aromatic chlorinations including use of different reagent types, solvents, and catalysts.¹⁻⁴

One of the conventional catalysts used in this regard is AlCl_3 . Watson has used diphenyl sulfide (DPS) together with aluminum chloride as a catalyst in regioselective *para*-chlorination of activated aromatic compounds by sulfuryl chloride as chlorinating agent.⁵

A disadvantage of the use of catalysts such as aluminum chloride is that they are destroyed during work-up, produce a corrosive acidic by-product, and present a disposal problem. Therefore, there is considerable need to devise reactions, which avoid the use of such Lewis acid catalysts. Zeolites have been investigated as catalysts in electrophilic aromatic substitution reactions such as chlorination, as alternatives for Lewis acids. Namely, they have the potential to remedy some of the liabilities of the classical Lewis acids.⁶⁻⁷ Although the research has mostly focused on the reactive aromatic compounds like phenol, zeolites such as NaK-L and ZSM-5 have also been used in recent years as catalysts for regioselective chlorination of relatively inactive compounds such as toluene.⁸⁻⁹ Partially protonated Faujasite X (HNaX) is far superior to amor-

phous silica and other zeolites in terms of efficiency and regioselectivity. For instance, the combination of a bulky chlorinating agent (*tert*-butyl hypochlorite) and HNaX zeolite has been reported for *para* regioselective chlorination of toluene.¹⁰ However, some of the drawbacks of this method are the high catalyst/reagent weight ratio and use of toxic solvents.

In the present paper we were interested in the use of a catalytic combination of HNaX zeolite and diphenyl sulfide (DPS) in solvent free regioselective *para* chlorination of toluene by sulfuryl chloride (Scheme 1).



Scheme 1

(major product)

2. Results and Discussion

Sulfuryl chloride is a well-known and easily accessible chlorinating agent for chlorination of aromatic compounds. However, the greatest drawback of this compound is its lack of regioselectivity to *ortho* or *para* isomers in aromatic chlorinations.¹¹

To overcome this problem, the effect of the catalysts such as HNaX and DPS in the chlorination of toluene by

sulfuryl chloride to make such chlorination regioselective to *para* isomer and at the same time to provide a high reaction yield, was studied. In a first attempt, SO_2Cl_2 was gently added to the mixture of toluene and HNaX catalyst over a period of half an hour at ambient temperature and the reaction was allowed to go on for 4 hours at this temperature. The obtained product mixture and analyzed by gas chromatography revealed to contain approximately equal amounts of *para* and *ortho* isomers.

Diphenyl sulfide has been previously used as a catalyst in the phenol chlorination using SO_2Cl_2 . Under these conditions, the diphenylsulfur dichloride formed during the course of the reaction makes the chlorinating agent bulky and increases its selectivity toward formation of *para* isomer.¹² Our results also indicate that diphenyl sulfide catalyzed chlorination of toluene using sulfuryl chloride somewhat increases reaction selectivity and yield. Furthermore, the combination of HNaX zeolite and DPS as a catalyst in the chlorination of toluene by sulfuryl chloride in the present work results in remarkable increases in selectivity and yield of monochloro products. The results are illustrated in Table 1.

Table 1: Chlorination of toluene by sulfuryl chloride under different catalytic conditions

Entry	Catalyst	Catalyst Amount(g)	<i>para/ortho</i> Ratio	Yield ^a
1	No catalyst	–	0.93	35
2	HNaX	0.5	0.94	50
3	DPS	0.5	1.7	62.5
4	NaX+DPS	1 ^b	1.2	57
5	HNaX+DPS	1 ^b	6	72.4

^a yield of monochloro products

^b equal amounts of catalysts

As shown in Table 1, when a co-catalyst system of diphenyl sulfide and HNaX zeolite is used in chlorination of toluene by sulfuryl chloride, the *para/ortho* ratio and monochloro product yields increase from 0.93 to 6 and from 50 to 72.4%, respectively.

The mechanism of the reaction is proposed to proceed by the reaction of sulfuryl chloride with diphenyl sulfide to form diphenylsulfur dichloride (**2**), which seems to complex with HNaX zeolite to form the active chlorinating agent **3** as shown in Scheme 2.

Therefore, the chlorination of toluene is *para* regioselective because **3** is a bulky reagent, subjected to the

chlorination at the more readily accessible *para* position. In fact, such chlorinating complex has been previously proposed to result from AlCl_3 reacting with diphenylsulfur dichloride, in the *para* regioselective chlorination of phenols.¹² HNaX zeolite (H-Z) possesses Bronsted acid characteristic and causes electrophilic aromatic chlorination (like AlCl_3).¹¹ Therefore, it is reasonable to assume that it is capable of complex formation with diphenylsulfur dichloride to form **3** as a *para* regioselective chlorinating agent (Scheme 2).

The second major point that needs to be explained from Table 1 is the remarkable increase in the reaction yield when a combination of HNaX zeolite and DPS as a co-catalyst system is used. This seems to originate from the polarization of the rapidly forming complex **3**, which renders it more electrophilic and more inclined to undergo nucleophilic attack. In addition, relative reduction of yield in entry 4 in Table 1 can be attributed to the radical chain chlorination, typical of NaX zeolite catalyzed reactions, which favors chlorination in the alkyl chain and thus suppresses ring chlorination.¹³

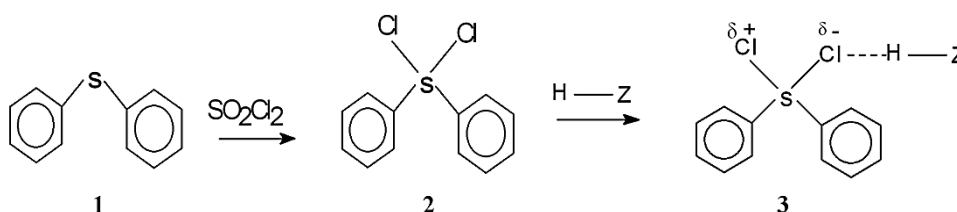
3. Experimental

Toluene was obtained from Fluka and dried using 4A zeolite. Diphenyl sulfide, sulfuryl chloride, ammonium chloride, and NaX zeolite powder were purchased from Aldrich.

Sulfuryl chloride was distilled prior to use and the colorless fraction (bp: 68–70 °C) was used. Analyses of products were performed with a gas chromatographic system equipped with a FID detector and a capillary column (length: 30 m, inside diameter: 0.32 mm, stationary phase: CP SIL-5). Product identifications were performed by comparing retention times with those of authentic commercial samples. Yields were determined using internal standards.

3. 1. General Procedure for the Preparation of Partially Proton-exchanged Sodium Zeolite (HNaX)

Partially proton-exchanged sodium zeolite was obtained using a standard method¹⁰ by refluxing NaX zeolite (3 g) for one hour in a 1M ammonium chloride solution (30 ml), followed by washing with distilled water to



Scheme 2

remove chloride and then drying in a furnace at 500°C for 5 hrs.

3. 2. General Procedure for Chlorination of Toluene

Sulfuryl chloride (8.4 g, 62 mmol) was gradually added over a period of 30 min to a mixture of toluene (5.2 g, 56 mmol) and catalyst (0.5–1 g) as indicated in Table 1, while the solution was gently stirred at 20–25 °C in a 50 ml flask. Following SO₂Cl₂ addition, the reaction was allowed to continue at this temperature for 4 hours. The reaction mixture was then degassed at reduced pressure and analyzed by GC.

An identical procedure was followed in the catalyst free chlorination, except no catalyst was used.

4. Conclusions

In summary, we have successfully applied a novel catalytic combination including HNaX zeolite and diphenyl sulfide to achieve remarkable enhancement of *para/ortho* ratio in chlorination of toluene using sulfuryl chloride. Meanwhile, this method offers some advantages in terms of simplicity of performance, mild reaction con-

ditions, and solvent free reaction, avoiding use of Lewis acid catalysts.

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Povzetek

V prispevku je predstavljena zmes HNaX zeolita in difenilsulfida kot katalizatorja za izboljšanje regiosektivnega kloriranja toluena s sulfuril kloridom na *para* mestu aromatskega obroča.