ELECTROPHILIC AROMATIC IODINE SUBSTITUTION OF 1-[(p-TOLYLIMINO)METHYL]-NAPHTHALEN-2-OL IN ZEOLITE CATALYST

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ABSTRACT

In this study, the naphtholic Schiff base has been reacted with iodine in the catalyst of natural zeolite clinoptilolite in order to synthesize iodine substituted Schiff base. The isolated product structure has been determined by IR, UV, ¹H-NMR, ¹³C-NMR, Mass spectroscopy and elemental analysis. Under our reaction conditions it’s found that the iodine is substituted to the phenyl ring of the naphtholic Schiff base.

Keywords: Aromatic iodination, electrophilic aromatic substitution, iodoarenes, Schiff base, zeolite, catalyst.

1. INTRODUCTION

Iodoaromatic compounds are valuable and versatile synthetic intermediates in many domains of synthetic organic chemistry, medicine and biochemistry [1-2]. Direct iodination of aromatic compounds is difficult due to the poor electrophilic strength of molecular iodine compared to that of molecular chlorine and bromine. Iodination of aromatic compounds was carried out by using molecular iodine together with a Lewis acid or some strong oxidizing agents such as iodic acid [3], nitric acid, sulfuric acid [4] and hydrogen peroxide [5]. Recently, direct iodination methods have been reported using various iodinium donating reagents, such as n-BuLi-CF₃CH₂I [6], iodine-F-TEDA-BF₄ [7], NH₄I-oxone [8], ICl [9] and iodine-iodic acid [10]. However, most of these methods are required high reaction temperatures for longer reaction times [11], involve toxic heavy metals, harsh conditions and generate complex and hazardous waste [12]. Therefore, attempts have been made to overcome these disadvantages, by employing recyclable heterogeneous catalysts with a wide variety of reagents and conditions. In this work, we reported an exceedingly simple, mild, selective and environmentally method of direct aromatic iodination, using the zeolite as catalyst. At the end of reactions it’s found that the iodine is substituted to the phenyl ring of the naphtholic Schiff base.
Zeolites are crystalline, hydrated aluminosilicates having a fine network of structural cavities and are used in various technological areas, but recently they have found different applications as adsorbents, ion exchangers and catalyst in industry, agriculture, veterinary medicine, sanitation and environmental protection [13-14]. In particular, zeolites have attracted much attention of organic chemists over the last two decades. Due to their regular microporous structure they have been proved to be useful as a tool for reaction control in organic synthesis [15] and zeolites increase the selectivity in electrophilic aromatic substitution reactions containing halogens. The applications of zeolites in organic reactions have been comprehensively reviewed by many researchers. Several catalyst applications of zeolites have been reported in the literature. The potential of zeolites in this field has been demonstrated for a variety of organic reactions such as alkylation [16], trans-alkylation [17] isomerization [18], halogenations [19], rearrangement [20], oxidation [21], reduction [22], condensation [23] and acylation [24]. Recently, zeolite catalysts have been found to catalyze the selective chlorination [25] and bromination [26] of a variety of aromatic substrates. However, only a few reports are available on the selective iodination of aromatics over zeolites [27]. Clinoptilolite, used in this study as a catalyst, is one of the most important natural zeolites, since it is widely found in the world. It is a silica-rich member of the heulandite family [28]. Applications of clinoptilolite as catalysts have been reported in many previous works [29].

2. Experimental Section

2.1. General Procedures

All melting points were taken in open capillaries and uncorrected. IR and UV spectra were recorded on Bruker FT-IR Tensor 27 spectrometer and on Unicam UV2-100/Visible spectrometer. \(^1\)H and \(^13\)C-NMR spectra were determined at Bruker AC 200L and Bruker 400 MHz spectrometer for solution in CDCl\(_3\). Mass spectrum was recorded on (LS/MS-APCI) Agilent 1100 MSD Instrument. The elemental analysis was obtained LECO CHNS 932 Machine. Merck Kieselgel (HF\(_{254}\) type-60) and Kieselgel 40-60 µm type were used for TLC. For analytical work 0.25 mm, for preparative work 0.75 mm plates were used.

2.2. The Synthesis of the Schiff base (3)

Schiff base (3) was synthesized according to the literature. Its structure was determined by IR, UV, \(^1\)H-NMR and \(^13\)C-NMR spectra.

2.3. Reaction of Schiff Base (3) with Iodine in the Catalyst of Natural Zeolite Clinoptilolite

Naphtholic Schiff base (3) (5 mmol) was dissolved in anhydrous toluene (150 ml) and was added natural zeolite clinoptilolite (10 g) then I\(_2\) (5 mmol) was added to this solutions. The reaction mixture were stirred and heated at 100 °C for 24 hours under a reflux condenser to find optimum reaction conditions. Then this mixture was treated with 10% Na\(_2\)SO\(_4\) solution to remove the excess iodine and was extracted with CHCl\(_3\) (30 ml) and dried over anhydrous Na\(_2\)SO\(_4\). The reaction medium pH was approximately 5.0-5.5. After evaporation of the solvent in vacuo crude products were purified by preparative TLC (SiO\(_2\)/toluen) using toluene as eluent and crystallized from ethanol.

1-[{(2’-iodo-4’-methyl-phenylimino)-methyl-NAPHTHALENO-2-ol (4) Yield: 57.4%. Yellow crystals. mp: 141 °C. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 2.37 (3H, s, -CH\(_3\)), 7.21 (1H, d, J=9.0 Hz, H-6’), 7.21 (1H, d, J=9.0 Hz, H-5’), 7.25 (1H, d, J=6.0 Hz, H-3), 7.37 (1H, t, J=8.0 Hz, 8.0 Hz, H-6), 7.54 (1H, dtx, J\(\geq\)9.0 Hz, 9.0 Hz, 1.0 Hz, H-7), 7.77 (1H, d, J\(\geq\)8.0 Hz, H-8), 7.80 (1H, s, H-3’), 7.85 (1H, d, J=9.0 Hz, H-5), 8.17 (1H, d, J=9.0 Hz, H-4), 9.39 (1H, s, -CH=N-), 15.00 (1H, s, naphtholic -OH). \(^13\)C-NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 20.46 (-CH\(_3\)), 95.58 (C-2’), 109.27 (C-1), 118.03 (C-3), 119.18 (C-6’), 120.68 (C-6), 123.65 (C-8), 127.79 (C-4a), 128.03 (C-7), 129.41 (C-5), 130.28 (C-3’), 133.03 (C-8a), 135.89 (C-4), 138.24 (C-4’), 140.09 (C-5’), 146.66 (C-1’), 157.07 (-CH=N-), 165.55 (C-2), IR (KBr) \(\nu_{\text{max}}\) (cm\(^{-1}\)) : 3447, 1611, 1577, 1513, 1420, 1379, 1276, 1187, 1158, 1066, 980, 722. UV (EtOH) \(\lambda_{\text{max}}\) (log \(e\)) (nm): 287.6 (0.970), 312.8 (0.779), 366.4 (0.562), 442.4 (0.207), 463.6 (0.196) . MS: m/z = M\(^+\) [388.0]. Anal. calcd for C\(_{13}\)H\(_{13}\)INO (387.21): C, 54.71; H, 3.24; N, 3.75. Found: C, 54.10; H, 3.69; N, 3.41.

3. Results and Discussion

In our previous paper [30] we reported the iodination of 1-phenyliminomethyl-naphthalene-2-ol (1). At the end of iodination reaction, the iodine was regionselectively substituted to the para-position of the phenyl ring with respect to azomethine group. In particular, compound 2 have been proved to be very promising. In this work, when the para- position is blocked with a methyl substituent, we wished to explore the effect on the iodination reaction.
Absorption bands for -OH group at 3447 cm\(^{-1}\) and azomethine group at 1611 cm\(^{-1}\) were observed in the IR spectrum of the 1-[\(\text{[2'-iodo-4'-methylphenylimino]methyl}\)-naphthalen-2-ol (4). Signals at 1557-1467 cm\(^{-1}\) supported aromatic structure (Figure 2).

The \(^{13}\text{C}-\text{NMR}\) spectral data are also in complete accord with assigned structure (Figure 4). \(^{13}\text{C}-\text{NMR}\) spectrum of the product (4) showed a peak at 95.58 ppm which can be attributed to the iodine substituted carbon. In addition, -CH\(_3\) carbon was observed at 20.46 ppm in the \(^{13}\text{C}-\text{NMR}\) spectrum. Signal at 157.07 ppm were assigned to azomethine carbon. In the \(^{13}\text{C}-\text{NMR}\) spectrum was observed 10 -CH and 7 -C- signals. It was thought that, small 6 peak signals at 165.55, 146.66, 138.24, 133.03, 127.79 and 109.27 ppm were assigned to C-2, C-1’, C-4’, C-8a, C-4a and C-1 carbons respectively which not to include hydrogen. -CH signals in the naphthyl ring at 118.03, 120.68, 123.65, 128.03, 129.41 and 135.89 ppm marked to be belonging to C-3, C-6, C-8, C-7, C-5 and C-4 carbons. It was understood that, remaining signals at 119.18, 130.28 and 140.09 ppm were assigned to C-6’, C-5’ and C-3’ aromatic carbons in the phenyl ring of naphtholic Schiff base.

In the \(^{1}\text{H}-\text{NMR}\) spectrum of the compound (4), two 1-proton singlets at 15.00 ppm and 9.39 ppm were assigned to naphtholic -OH and azomethine proton. 3-protons signal at 2.37 ppm was attributed to the methyl protons. Aromatic protons were marked from enlarged spectrum of aromatic region (Figure 6). 1-proton doublets at 7.25, 7.77, 7.85 and 8.17 ppm were assigned to H-3, H-8, H-5 and H-4 protons respectively. It was thought that doublets of the 2-protons at 7.21 ppm were assigned to H-6’ and H-5’ protons. Furthermore, 1-proton triplet at 7.37 ppm, 1-proton triplet of doublets at 7.53 ppm and 1-proton singlet at 7.80 ppm were assigned to H-6, H-7 and H-3’ protons. All these results suggested that the compound was 1-[\(\text{[2'-iodo-4'-methylphenylimino]methyl}\)-naphthalen-2-ol (4).

Finally, the reaction took place with regioselectivity and only mono-iodination was obtained. Iodination was occurred in the ortho-position to phenyl ring of naphtholic Schiff base since the para-position was blocked with a methyl substituent. It is observed that the iodine substituted in the realized electrophilic aromatic iodine reactions is combined to ortho-position in the phenyl ring according to the position of azomethine group which phenyl ring is combined. According to these results, the effective group in orientation has been azomethine group, the -OH group in naphthalene ring has affected the orientation of the group which will be substituted to phenyl ring and the second substituent in the phenyl ring, (-CH\(_3\)), has very limited contribution for orientation.

The iodination of the naphtholic Schiff base over zeolite catalyst took place with high regioselectivity and only mono-iodination was found to occur. Iodination was para-directed when possible; otherwise it occurred in the ortho-position.

In this work, naphtholic Schiff base (3) was synthesized according to the literature [28]. The structure of Schiff base (3) was determined by IR, UV, \(^{1}\text{H}-\text{NMR}\) and \(^{13}\text{C}-\text{NMR}\) spectra. The spectroscopic data of the Schiff base (3) was in accordance with the literature. A band for the azomethine group (-CH=N-) was observed in the IR spectrum approximately in 1625 cm\(^{-1}\).

Then naphtholic Schiff base (3) was reacted with iodine in the catalyst of natural zeolite clinoptilolite in order the synthesize iodine substituted compound (4). Preparative TLC (SiO\(_2\)/toluene) of the crude product (4) showed the presence of one compound (R\(_f\)=0.23). After preparative TLC (SiO\(_2\)/toluene) purification, the product was crystallized from alcohol as yellow crystals (mp: 141 °C). This product (4) was synthesized with a different method previously [31]. The product (4) was characterized by elemental analysis, IR, UV, \(^{1}\text{H}-\text{NMR}, \(^{13}\text{C}-\text{NMR}\) and mass spectroscopy.

Mass spectrum of the compound (4) showed the molecular ion peak at 388 and confirmed the C\(_{18}\)H\(_{14}\)I\(_{3}\)NO structure (Figure 1). The chemical analysis of the compound was compatible with the structure C\(_{18}\)H\(_{14}\)I\(_{3}\)NO.
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Figure 1. Mass Spectrum of 1-[(2'-iodo-4'-methylphenylimino)methyl]-naphthalen-2-ol (4)

Figure 2. IR Spectrum of 1-[(2'-iodo-4'-methylphenylimino)methyl]-naphthalen-2-ol (4) (KBr)
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Figure 3. UV Spectrum of 1-[2′-iodo-4′-methylphenylimino)methyl]-naphthalen-2-ol (4) (EtOH)

Figure 4. 13C-NMR Spectrum of 1-[2′-iodo-4′-methylphenylimino)methyl]-naphthalen-2-ol (4) (CDCl3)
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Figure 5. $^1$H-NMR Spectrum of 1-[(2'-iodo-4'-methylphenylimino)methyl]-naphthalen-2-ol (4) (CDCl$_3$)

Figure 6. $^1$H-NMR Spectrum of 1-[(2'-iodo-4'-methylphenylimino)methyl]-naphthalen-2-ol (4) (Aromatic Region Enlarged)
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5. References

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