Naftolik schiff bazının zeolit katalizörlüğünde iyotlanması

*Murat GÜNDÜZ , Sevim BİLGİÇ

Department of Chemistry, Arts and Science Faculty, Eskisehir Osmangazi University, 26480, Eskişehir

Anahtar Kelimeler:
Aromatik iyotlama,
iodoarenler,
Schiff bazı,
zeolit.

ÖZET

Bu makalede, Naftolik Schiff bazının iyotlanması için basit, direkt ve çevre dostu bir yöntem sunulmuştur. Naftolik Schiff bazı, zeolit varlığında, ılımlı koşullar altında seçici olarak iyotlanmıştır. Bu yöntem diğer aromatik ve hetero aromatik bileşiklerinin iyotlanmasında da uygulanabilir.

Iodination of naphtholic schiff base in zeolite catalyst

Keywords:
Aromatic iodination,
iodoarenes,
Schiff base,
zeolite.

ABSTRACT

In this paper, a simple, direct and environment friendly procedure for the iodination of naphtholic Schiff base is presented. Naphtholic Schiff base was regioselectively iodinated in the presence of zeolite under mild conditions. The procedure has been extended to the iodination of other aromatic and hetero aromatic compounds.

* *Sorumlu yazar (Corresponding author) e-posta: muratgunduz26@gmail.com*

1. Introduction

Iodoarenes are useful intermediates in organic synthesis [1]. Moreover; they are vastly used in the biomedical region owing to their potential ability [2]. Iodoarenes are synthesized by two main ways. Direct methods do not always let to control regioselectivity in electrophilic aromatic substitution reactions containing halogens and are usually carried out in the presence of oxidants and strong mineral acids catalyst such as conc. H_2SO_4 or aq. HCl [3-4]. Indirect methods that involve the Sandmeyer reaction and iododemetallation, contain the use of highly toxic organomercury compounds [4] even if selective.

Direct chlorination and bromination of aromatic compounds are well known. However, the direct and selective iodination of aromatic compounds with molecular iodine is much more difficult owing to lower electrophilic strength of iodine molecule [5].

Therefore, attempts have been made to overcome these disadvantages, by employing recyclable heterogeneous catalysts with a wide variety of reagents and conditions. In this letter, we reported an exceedingly simple, mild, selective and environmentally method of direct aromatic iodination, using the zeolite as catalyst.

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 [6]. In addition zeolites are known for the shape-selective and catalytic behavior the field of petrochemistry and organic transformations [7].

In particular, zeolites have attracted much attention of organic chemists over the last two decades. Due to their regular microporous structure they proved to be useful as a tool for reaction control in organic synthesis [8] 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 [9], transalkylation [10], isomerization [11], halogenations [12], rearrangement [13], oxidation [14], reduction [15], condensation [16] and acylation [17].

Recently, zeolite catalysts have been found to catalyze the selective chlorination [18-19] and bromination [20-21] of a variety of aromatic substrates. However, only a few reports are available on the selective iodination of aromatics over zeolites [22].

Clinoptilolite, used in this study as a catalyst, is one of the most important natural zeolites, since it is found in large deposits worldwide. It is a silica-rich member of the heulandite family [23]. Applications of clinoptilolite as catalysts have been reported in many previous works [24-25].

2. Experimental section

2.1. General procedures

Melting points were taken in open capillaries and uncorrected. IR spectra were recorded on Bruker FT-IR Tensor 27 spectrometer. UV spectra were recorded on Unicam UV2-100/visible spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were determined at Bruker AC 200L and Bruker 400 MHz spectrometer for solution in $CDCl_3$. Mass spectra were recorded on (LC/MS-APCI) Agilent 1100 MSD Instrument. Elemental analyses were 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. Reaction of Schiff base (1b) with iodine in the catalyst of natural zeolite clinoptilolite

Naphtholic Schiff base **(1b)** was synthesized according to the method of Sawich and coworker [27]. Schiff bases (5 mmol) were dissolved in anhydrous toluene (150 ml) and were added natural zeolite clinoptilolite (10 g) then I_2 (5 mmol) was added to this solutions. The reaction mixtures were stirred and heated at 100 ^{o}C for 24 hours under a reflux condenser to find optimum reaction conditions. Then zeolite filtered off and filtrate was washed with 10% $Na_2S_2O_3$ solution to remove the excess iodine and were extracted with $CHCl_3$ (30 ml) and dried over anhydrous Na_2SO_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/toluene) using toluene as eluent and crystallized from ethanol.
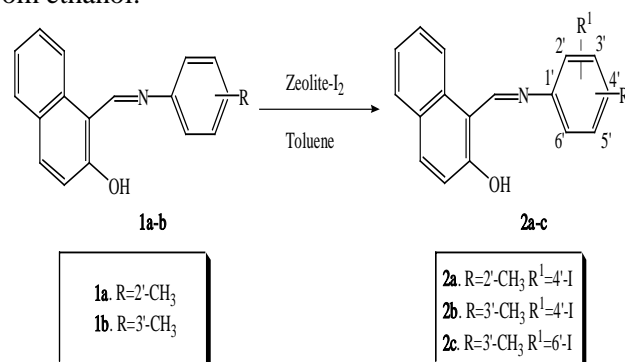
Scheme 1. Aromatic iodination reactions.

1-[(4′-iodo-3′-methyl-phenylimino)-methyl]-naphthalen-2-ol (2b).

Yield: 39.6%. Orange crystals. mp: 97 ^{0}C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 2.50 (3H, s, -CH_3), 6.91

(1H,dxd, J= 8.0 Hz, H-6′), 7.09 (1H, d, J=8.0 Hz, H-3), 7.24 (1H, s, J≅9.0 Hz, H-2′), 7.35 (1H, t, J=8.0 Hz, H-6), 7.53 (1H, t, J=8.0 Hz, H-7), 7.72 (1H, d, J=8.0 Hz, H-5′), 7.81 (1H, d, J=8.0 Hz, H-8), 7.86 (1H, d, J≅8.0 Hz, H-5), 8.10 (1H, d, J=8.0 Hz, H-4), 9.33 (1H, brd.s, -CH=N-), 15.27 (1H, brd.s, naphtholic -OH). ^{13}C-NMR (400 MHz, CDCl$_3$) δ (ppm): 28.2 (-CH$_3$), 97.7 (C-4′), 109.0 (C-1), 118.9 (C-2′), 119.3 (C-3), 121.8 (C-8), 121.9 (C-6′), 123.7 (C-6), 127.5 (C-4a), 128.3 (C-7), 129.4 (C-5), 133.2 (C-8a), 136.7 (C-4), 139.9 (C-5′), 142.9 (C-3′), 146.1 (C-1′), 155.2 (-CH=N-), 169.4 (C-2). IR (KBr) ν$_{max}$ (cm^{-1}): 3361, 1620, 1542-1483, 835, 740. UV (EtOH) λ$_{max}$(log ε) (nm): 286.4 (0.560), 316.8 (0.560), 358.8 (0.396), 443.6 (0.080), 464.0 (0.079). MS: m/z= M$^+$ [388.0], [260.1 (M-HI, 100%)]$^+$, [244.0 (M-C$_{10}$H$_8$O, 22.1%)]$^+$. Anal. calcd for C$_{18}$H$_{14}$INO (387.21): C, 55.83; H, 3.64; N, 3.62. Found: C, 56.49; H, 3.76; N, 3.39.

1-[(6′-iodo-3′-methyl-phenylimino)-methyl]-naphthalen-2-ol (2d).

Yield: 22.7%. Orange crystals. mp: 107 ^{0}C. ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm): 2.41 (3H, s, -CH$_3$), 6.84 (1H, d, J≅8.0 Hz, H-4′), 7.11 (1H, s, H-2′), 7.20 (1H, d, J=9.0 Hz, H-5′, H-3), 7.36 (1H, t, J=8.0 Hz, H-6), 7.54 (1H, t, J=9.0 Hz, H-7), 7.77 (1H, d, J=8.0 Hz, H-5), 7.81 (1H, d, J=8.0 Hz, H-8), 8.19 (1H, d, J=8.0 Hz, H-4), 9.36 (1H, brd.s, -CH=N-), 15.01 (1H, brd.s, naphtholic -OH). ^{13}C-NMR (400 MHz, CDCl$_3$) δ (ppm): 21.1 (-CH$_3$), 91.2 (C-6′), 109.3 (C-1), 119.2 (C-3), 120.8 (C-6), 123.7 (C-2′), 127.5 (C-8), 127.8 (C-7), 128.1 (C-5), 128.96 (C-4a), 129.43 (C-4′), 133.1 (C-4), 136.1 (C-8a), 136.1 (C-3′), 139.4 (C-5′), 139.9 (C-1′), 157.4 (-CH=N-), 165.9 (C-2). IR (KBr) ν$_{max}$ (cm^{-1}): 3450, 1617, 1546-1463, 813, 736. UV (EtOH) λ$_{max}$(log ε) (nm): 288.4 (0.738), 316.8 (0.376), 338.8 (0.376), 359.6 (0.419), 462.4 (0.090). MS: m/z= M$^+$ [388.0], [260.1 (M-HI, 39.3%)]$^+$, [106.1 (C$_8$H$_{10}$, 100%)]$^+$. Anal. calcd for C$_{18}$H$_{14}$INO (387.21): C, 55.83; H, 3.64; N, 3.62. Found: C, 56.02; H, 4.17; N, 2.97.

3. Results and discussion

In our previous paper [26] we reported the iodination of 1-(*o*-tolylimino-methyl)-naphthalen-2-ol (2a). At the end of iodination reaction, the iodine was regioselectively substituted to the *para*-position of the phenyl ring with respect to azomethine group. In particular, compound 2a have proved to be very promising. In this letter, when the *meta*-position is blocked with a methyl substituent, we wished to explore the effect on the iodination reaction.

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 (1b) was synthesized according to the method of Sawich and Zetensow (1956). The structure of Schiff base was determined by IR, UV, ^{1}H-NMR and ^{13}C-NMR spectra. The spectroscopic data of compound 1b 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 compound 1b was reacted with iodine in the catalyst of natural zeolite clinoptilolite in order the synthesize iodine substituted compounds (2b and 2c). Preparative TLC (SiO$_2$/toluene) of the crude products showed the presence of two compounds as 2b (R$_f$=0.25, mp: 97 ^{o}C) and 2c (R$_f$=0.46, mp: 107 ^{o}C). After preparative TLC (SiO$_2$/toluene) purification, the products were crystallized from alcohol as orange crystals. The products (2b and 2c) were characterized by elemental analyses, IR, UV, ^{1}H-NMR, ^{13}C-NMR and mass spectroscopy. Mass spectrum of the compounds (2b and 2c) showed the molecular ion peaks at 388 and confirmed the C$_{18}$H$_{14}$INO structure (Figure 1 and Figure 5). The elemental analyses of the compounds were compatible with the structure C$_{18}$H$_{14}$INO.

Absorption bands for -OH group at 3361 cm^{-1} and azomethine group at 1620 cm^{-1} were observed in the IR spectrum of the 1-[(4′-iodo-3′-methylphenylimino)methyl]-naphthalen-2-ol (2b). Signals at 1542-1483 cm^{-1} supported aromatic structure. The ^{13}C-NMR spectral data are also in complete accord with assigned structure (Figure 2). From ^{13}C-NMR spectrum of the product (2b), we understood from signal at 97.7 ppm that the iodine was substituted to C-4′ carbons of phenyl ring. In addition, -CH$_3$ carbon was observed at 28.2 ppm in the ^{13}C-NMR spectrum. Signal at 155.2 ppm was thought to be belonging to azomethine carbon. In the ^{13}C-NMR spectrum observed 10 -CH and 7 -C- signals. It was thought that, small 6 peak signals at 169.4, 146.1, 142.9, 133.2, 127.5 and 109.0 ppm were belonging to in turn in order C-2, C-1′, C-3′, C-8a, C-4a and C-1 carbons which not to include hydrogen. -CH signals in the naphtyl ring at 119.3, 121.8, 123.7, 128.3, 129.4 and 136.7 ppm marked to be belonging to C-3, C-8, C-6, C-7, C-5 and C-4 carbons. It was understood that, remaining signals at 118.9, 121.9 and 139.96 ppm were belonging to C-6′, C-2′and C-5′ aromatic carbons in the phenyl ring of naphtholic Schiff base. In the ^{1}H-NMR spectrum of the compound, two 1-proton singlets at 15.27 ppm and 9.33 ppm were assigned to naphtholic -OH and azomethine proton. 3-protons signal at 2.50 ppm was attributed to the methyl protons (Figure 3). Aromatic protons were marked from enlarged spectrum of aromatic region (Figure 4). 1-proton doublets at 7.09, 7.81, 7.86 and 8.10 ppm were belonging was marked as to be

belonging to H-3, H-8, H-5 and H-4 protons respectively. It was thought that doublet of the 1-proton at 7.72 and 1-proton double doublet at 6.91 ppm were belonging to H-5′ and H-6′ protons in the phenyl ring of compound **2b**. Furthermore, two 1-proton triplets at 7.35 and 7.53 ppm and 1-proton singlet at 7.24 ppm were assigned to H-6, H-7 and H-2′ protons. It was understood from the above from the above described spectroscopic data and chemical analysis that, the structure was 1-(4′-iodo-3′-methylphenylimino-methyl)-naphthalen-2-ol **(2b)**.

^{1}H-NMR and ^{13}C-NMR spectral data of compound **2c** compatible with compound **2b** (Figure 6 and Figure 7). Finally, *o*-CH$_3$ Schiff base **(2a)** over zeolite catalyst took place with regioselectivity and only mono-iodination was found to occur. When the *meta*-position was blocked with a methyl substituent, iodination was occurred in the *para*- and *ortho*- positions to phenyl ring of naphtholic Schiff base.
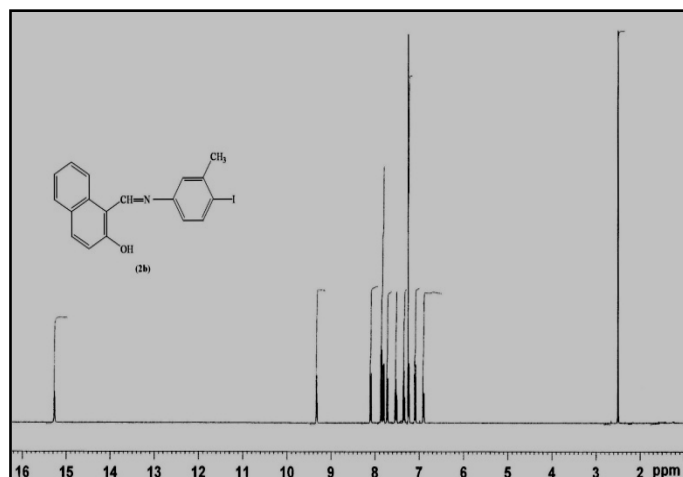

Figure 3. ^{1}H-NMR Spectrum of 1-[(4′-iodo-3′-methylphenylimino)methyl]-naphthalen-2-ol **(2b)** (CDCl$_3$)
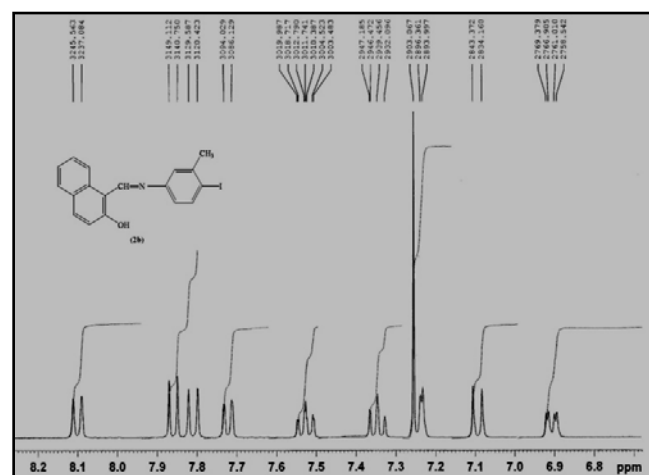

Figure 4. ^{1}H-NMR Spectrum of 1-[(4′-iodo-3′-methylphenylimino)methyl]-naphthalen-2-ol **(2b)** (Aromatic Region Enlarged)
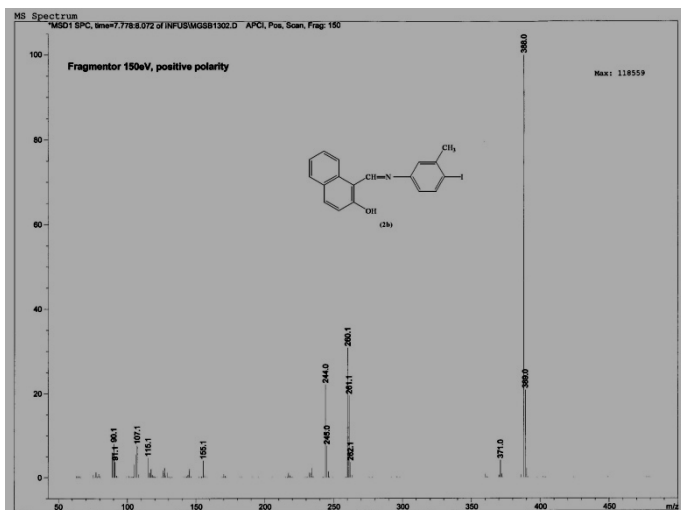

Figure 1. Mass Spectrum of 1-[(4′-iodo-3′-methylphenylimino)methyl]-naphthalen-2-ol **(2b)**
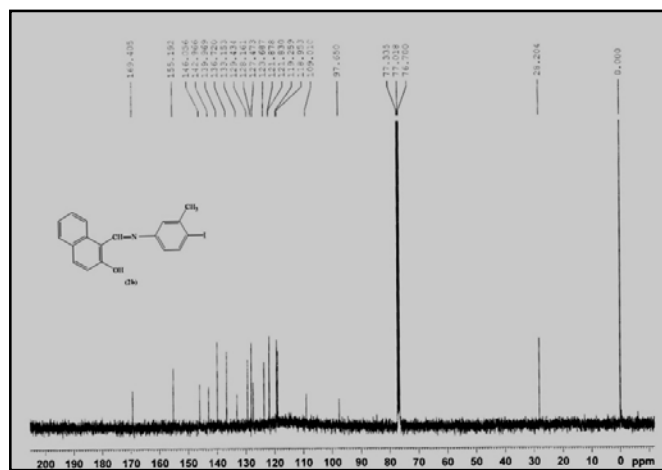

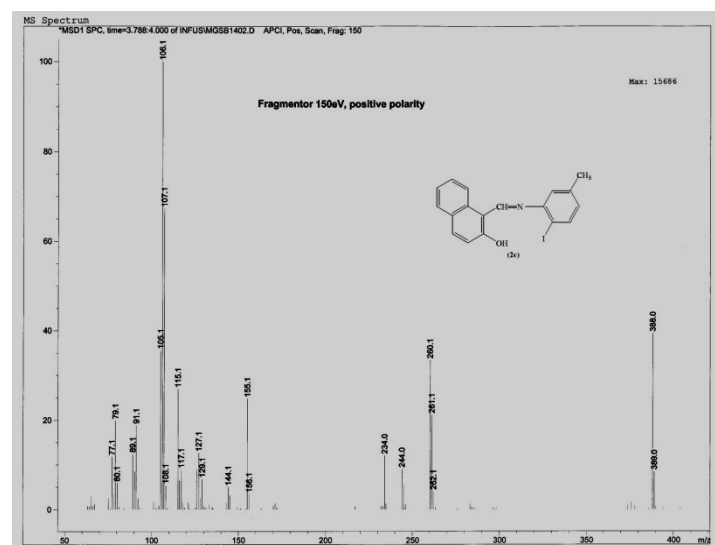**Figure 2.** ^{13}C-NMR Spectrum of 1-[(4′-iodo-3′-methylphenylimino)methyl]-naphthalen-2-ol **(2b)** (CDCl$_3$)

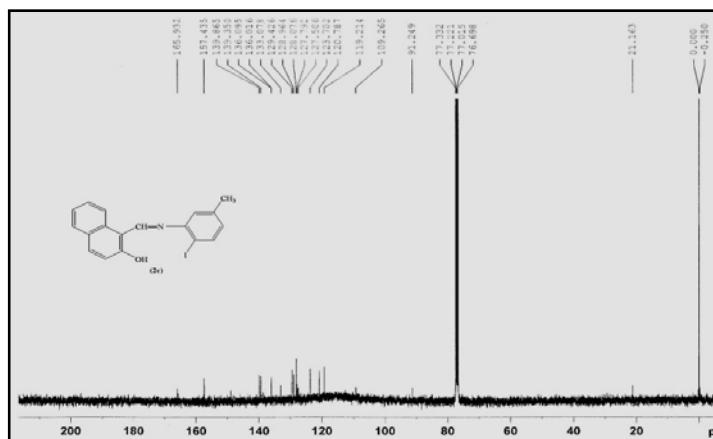**Figure 5.** Mass Spectrum of 1-[(6′-iodo-3′-methylphenylimino)methyl]-naphthalen-2-ol **(2c)**

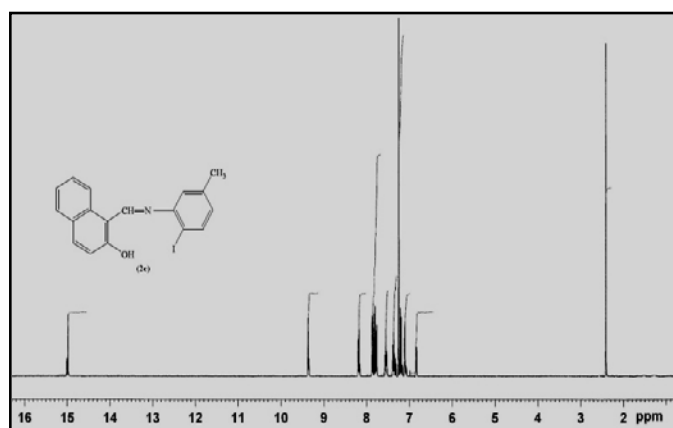**Figure 6.** ^{13}C-NMR Spectrum of 1-[(6′-iodo-3′-methylphenylimino)methyl]-naphthalen-2-ol **(2c)** (CDCl₃)

Figure 7. ^{1}H-NMR Spectrum of 1-[(6′-iodo-3′-methylphenylimino)methyl]-naphthalen-2-ol **(2c)** (CDCl₃)
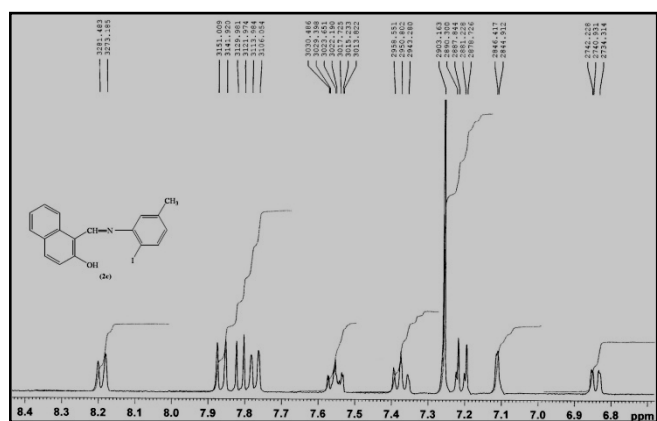

Figure 8. ^{1}H-NMR Spectrum of 1-[(6′-iodo-3′-methylphenylimino)methyl]-naphthalen-2-ol **(2c)** (Aromatic Region Enlarged)

Acknowledgement

References

1. Fanta P.E., The Ullmann Synthesis of Biaryls, Synthesis, 9-21, 1974.
2. Diederich, F. and Stang, P.J., Metal-Catalyzed Cross-Coupling Reactions 2nd ed., Wiley-VCH: Weinheim, 348-359, 1998.
3. Skulski, L., Organic Iodine (I, III, and V) Chemistry", Molecules, 5, 1331-1371, 2000.
4. Merkushev, E.B., Advances in the Synthesis of Iodoaromatic Compounds, Synthesis, 923-925, 1988.
5. Chiappe, C. and Pieraccini, D., Regioselective Iodination of Arenes in Ionic Liquids Mediated by Selectfluor[TM] Reagent F-TEDA-BF₄, Arkivoc, xi, 249-255, 2002.
6. Delgado, F., et al., Characterization and Application of a New Natural Catalyst, Arkivoc, xi, 118-131, 2003.
7. Dyer, A., An Introduction to Zeolite Molecular Sieves, Wiley & Sons, Chichester, 149, 1988.
8. Jansen, J.C., et al., Advanced Zeolite Science and Application; Studies in Surface Science and Catalysis, Elsevier, Amsterdam, Vol. 85, 244, 1994.
9. Reddy, K.S.N., et al., Reforming of Pyrolysis Gasoline over Platinum-alumina Catalysts Containing MFI Type Zeolites, Appl. Catal., 95, 53-63, 1993.
10. Pradhan, A.R. and Rao, B.S., "Transalkylation of Di-isopropylbenzenes over Large Pore Zeolites, Appl. Catal., 106, 143-153, 1993.
11. Weigert, F.J., U.S. Patent, 4 593 124, 1986.
12. Singh, A.P. and Kale, S.M., U.S. Patent, 5 892 138, 1999.
13. Singh, A.P., et al., Vapour Phase Beckmann Rearrangement of Cyclohexanone Oxime over SAPO-11 Molecular Sieve, Appl. Catal., 136, 249-263, 1996.
14. Thangaraj, A., et al., Evidence for the Simultaneous Incorporation of Al and Ti in MFI Structure (Al-TS-1), Zeolites, 135-137, 1992.
15. Iwamoto, M., et al., Removal of Nitrogen Monoxide through a Novel Catalytic Process, J. Phys. Chem., 95:(9), 3727-3730, 1991.
16. Tobias, M.A., U.S. Patent, 3 728 408, 1973.
17. Venkateshan, C., et al., Liquid Phase Selective Benzoylation of Chlorobenzene to 4,4′-dichlorobenzophenone over Zeolite H-beta, Catal. Lett., 75, 119-123, 2001.
18. Ratnasamy, P., et al., Halogenation over Zeolite Catalysts, Appl. Catal. A, 135, 25-55, 1996.
19. Roy, S.C., et al., Ceric Ammonium Nitrate Catalyzed Mild and Efficient α-chlorination of Ketones by Acetyl Chloride, Arkivoc, ix, 34-38, 2003.

20. Gnaim, J.M. and Sheldon, R.A., Regioselective Bromination of Aromatic Compounds with Br_2/SO_2Cl_2 over Microporous Catalysts, Tetrahedron Lett., 46, 4465-4468, 2005.

21. Csunderlik, C., et al., Facile Bromination of the Benzene Ring During the Cyclisation of the 1H-3-methyl-4-ethoxycarbonyl-5-arylidenehydrazonopyrazoles to the 3-substituted-aryl-1H-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazoles, Arkivoc, ii, 133-141, 2002.

22. Kale, S.M., Halogenation and Isomerization Reactions of Aromatics over K-L, H-beta and H-ZSM-5 Zeolite Catalysts, Ph.D. thesis, Catal. Div. Nat. Chem. Lab., University of Pune, India. 2002.

23. Szostak, R., Handbook of Molecular Sieves, Van Nostrand Reinhold, New York, 145-154, 1992.

24. Arcoya, A. X., et al., Effect of Iron on the Deactivation of Ni/Clinoptilolite Catalysts by Thiophene Poisoning, J. Chem. Tech. Biotechnol., 68, 171-176, 1997.

25. Allahverdiev, A. I., et al., Isomerization of α-pinene over Clinoptilolite, J. Catal., 185, 352-362, 1999.

26. Gündüz, M. and Bilgiç, S., 1-(N-para-iyodo-orto-metilfeniliminometil)-2-naftol'ün Sentezi, Anadolu Üniversitesi Bilim ve Teknoloji Dergisi, 8:(2), 159-165, 2007.

27. Sawich, A. and Zetensow, J.V., Astron. Fiz. Khim. Spit Syn, I., 1, 233, 1956.