Dumlupınar Üniversitesi Fen Bilimleri Enstitüsü Dergisi
Sayı: 17 Aralık 2008 ISSN - 1302 - 3055

ELECTROPHILIC AROMATIC IODINE SUBSTITUTION OF 1-{[(PHENYL)IMINO]METHYL}NAPHTHALEN-2-OL[1]

Murat GÜNDÜZ*, Sevim BİLGİÇ

University of Eskişehir Osmangazi, Faculty of Arts and Science,
Department of Chemistry, 26480, Eskişehir
e-mail: murat@ogu.edu.tr

Geliş Tarihi:15.04.2008 Kabul Tarihi:06.10.2008

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.

Key Words: *Aromatic iodination, iodoarenes, Schiff base, zeolite, catalyst.*

1-{[(FENİL)İMİNO]METİL}NAFTALEN-2-OL'ÜN ELEKTROFİLİK AROMATİK İYOT SÜBSTİTÜSYONU

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.

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

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]. They 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 concentrated 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].

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 [6-7]. In addition zeolites are known for the shape-selective and catalytic behavior the field of petrochemistry and organic transformations [8].

---

[1] This work was supported by the Eskisehir Osmangazi University Scientific Research Project Commission.

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 [9] 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 [10], transalkylation [11], isomerization [12], halogenations [13], rearrangement [14], oxidation [15], reduction [16], condensation [17] and acylation [18].

Recently, zeolite catalysts have been found to catalyze the selective chlorination [19-20] and bromination [21-22] of a variety of aromatic substrates. However, only a few reports are available on the selective iodination of aromatics over zeolites [23].

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 [24]. Applications of clinoptilolite as catalysts have been reported in many previous works [25-26].

In this letter, we reported an exceedingly simple, mild, selective and environmentally method of direct aromatic iodination, using the zeolite as catalyst. At the end of reactions we found that the iodine was incorporated into the phenyl ring of the naphtholic Schiff base.

2. EXPERIMENTAL SECTION

2.1. General Procedures

All melting points were taken in open capillaries and uncorrected. The IR spectrum was recorded on Bruker FT-IR Tensor 27 spectrometer. ^{1}H and ^{13}C-NMR spectra were determined at Bruker AC 200L and Bruker 400 MHz spectrometer using $CDCl_3$. Mass spectrum was recorded on (LS/MS-APCl) 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 Schiff Base (1)

Schiff base **(1)** was synthesized according to the method of Sawich and coworker [27]. Its structure was determined by IR, UV and ^{13}C-NMR spectra.

2.3. Reaction of Schiff Base (1) with Iodine in the Catalysis of Natural Zeolite Clinoptilolite

Naphtholic Schiff base **(1)** (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 % $Na_2S_2O_3$ solution to remove the excess iodine and was 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 product was purified by preparative TLC (SiO_2/toluen) using toluene as eluent and crystallized from ethanol.

1-{[(4-iodophenyl)imino]methyl}naphthalen-2-ol (2). Yield: 28.2%. mp: 90 °C. Anal. calcd. for $C_{17}H_{12}INO$ (373,19): C, 54.71; H, 3.24; N, 3.75. Found: C, 54.42; H, 3.32; N, 3.51. Mass spectra: m/z : [373.0, 100%], 245.1 [M-HI, 41.6%]$^+$, 227.0 [M-(HI+H_2O), 31.6%]$^+$. IR (KBr) ν_{max} (cm^{-1})**:** 3448, 1612, 1550-1474, 817. ^{13}C-NMR (400 MHz, $CDCl_3$) δ (ppm): 90.8 (C-4′), 114.7 (C-1), 116.9 (C-4a), 118.9 (C-3), 121.6 (C-6), 122.5 (C-6'), 123.8 (C-2′), 127.6 (C-8), 128.2 (C-7), 129.5 (C-5), 136.7 (C-4), 138.7 (C-3'), 143.3 (C-8a), 146.1 (C-5'), 153.2 (C-1'), 155.8 (-CH=N-), 168.7 (C-2). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.11 (2H, d, J=8.0 Hz, H-2′), 7.12 (1H, d, J=6.0 Hz, H-3), 7.36 (1H, t, J=8.0 Hz, H-6), 7.53 (1H, dxt, J≅8.0, 2.0 Hz, H-7), 7.73 (1H, d, J=8.0 Hz, H-

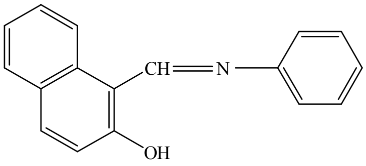
8), 7.76 (2H, d, J=8.0 Hz, H-3′), 7.82 (1H, d, J≅9.0 Hz, H-5), 8.10 (1H, d, J≅8.0 Hz, H-4), 9.35 (1H, s, -CH=N-), 15.20 (1H, s, naphtholic -OH).

3. RESULTS AND DISCUSSION

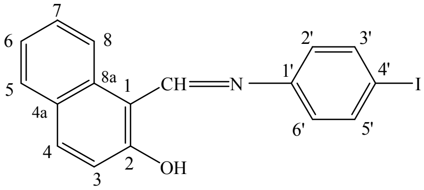
In our previous paper [27] we reported the iodination of 1-(*o*-tolylimino-methyl)-naphthalen-2-ol. At the end of iodination reaction, the iodine was regioselectively substituted to the *para*-position of the phenyl ring with respect to azomethine group. In this letter, when there is no substituent in phenyl ring we investigated the effect on the iodination reaction.

In this work, the naphtholic Schiff base (1) was reacted with iodine in the catalyst of natural zeolite clinoptilolite in order to synthesize iodine substituted Schiff base (2). The isolated product structure was determined by NMR (^{1}H-NMR, ^{13}C-NMR), mass and IR spectra as well as chemical analysis. Under our reaction conditions we found that the iodine was incorporated into the phenyl ring of the naphtholic Schiff base.

Naphtholic Schiff base **(1)** was synthesized according to the method of Sawich and Zetensow [28]. The structure of Schiff base **(1)** was determined by NMR (^{1}H-NMR, ^{13}C-NMR) and IR spectra. The spectroscopic data of the Schiff base **(1)** was in accordance with the literature. A band for the azomethine group (-CH=N-) was observed in IR spectrum approximately in 1625 cm^{-1}.



1-{[(phenyl)imino]methyl}naphthalen-2-ol (1)



1-{[(4-iodophenyl)imino]methyl}naphthalen-2-ol (2)

Then compound **1** was reacted with iodine in the catalyst of natural zeolite clinoptilolite in order the synthesize iodine substituted compound **(2)**. Preparative TLC (SiO_2/toluene) of the crude product **(2)** showed the presence of one compound (R_f=0.24). After preparative TLC (SiO_2/toluene) purification the product was crystallized from alcohol as yellow crystals (mp: 90 °C). Mass spectrum of the compound **(2)** gave a molecular ion peak at 373.0 confirming the $C_{17}H_{12}INO$ structure (Figure 3.1). The chemical analysis of the compound was compatible with the structure $C_{17}H_{12}INO$.

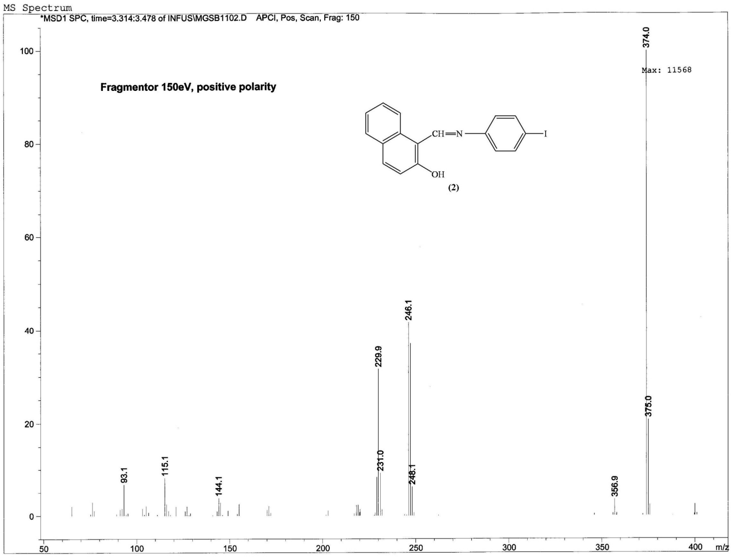


Figure 3.1 Mass spectrum of 1-{[(4-iodophenyl)imino]methyl}naphthalen-2-ol (2).

In the IR spectrum there were (-CH=N-) and -OH groups at 1612 cm^{-1} and 3448 cm^{-1}. Signals at 1550-1474 cm^{-1} and 817 cm^{-1} supported aromatic structure and *para*-disubstituted phenyl ring (Figure 3.2).

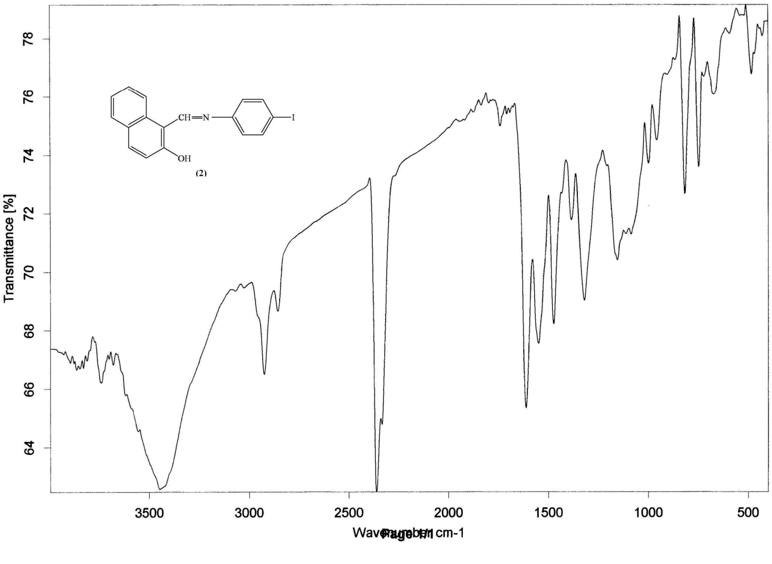


Figure 3.2 IR Spectrum of 1-{[(4-iodophenyl)imino]methyl}naphthalen-2-ol **(2)** (KBr).

The ^{13}C-NMR spectral data are also in complete accord with assigned structure **(2)** (Figure 3.3). ^{13}C-NMR spectrum of the product showed a peak at 90.8 ppm which can be attributed to the iodine substituted carbon. Signal at 155.8 ppm was assigned to azomethine carbon. In ^{13}C-NMR spectra observed 11 -CH and 6 -C- signals. It was thought that, small 6 peak signals at 114.7, 168.7, 116.9, 143.3, 153.2 and 90.8 ppm were assigned to C-1, C-2, C-4a, C-8a, C-1′ and C-4′ carbons which not to include hydrogen. -CH signals at 118.9, 136.7, 129.5, 121.6, 128.2 and 127.6 ppm marked to C-3, C-4, C-5, C-6, C-7 and C-8 carbons in naphtyl ring. It was understood that, remaining signals at 123.8, 138.7, 146.1 and 122.5 ppm were belonging to C-2′, C-3′, C-5′ and C-6′ aromatic carbons in phenyl ring of naphtholic Schiff base.

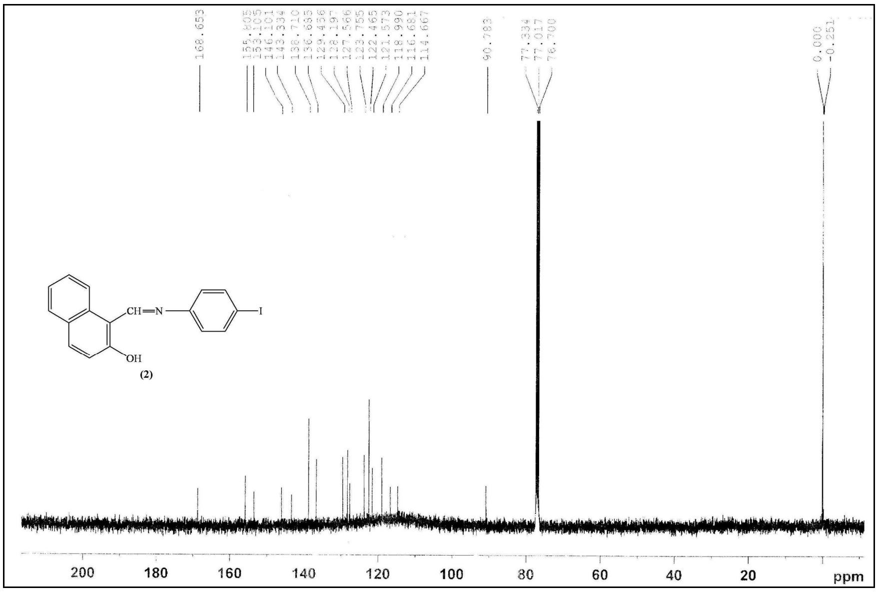


Figure 3.3 ^{13}C-NMR Spectrum of 1-{[(4-iodophenyl)imino]methyl}naphthalen-2-ol **(2)** ($CDCl_3$).

Halogens prefer as selective *para*-position in the catalysis of zeolite [29-31]. From the ^{1}H-NMR spectrum of the product it was clear that the substitution occurred to the *para*-position of the phenyl ring with respect to the azomethine group (Figure 3.4). In the ^{1}H-NMR spectrum observed typical *para*-splitting. This result supported the literature. Two 1-proton singlets at 15.20 ppm and 9.35 ppm were assigned to naphtholic -OH and azomethine proton in ^{1}H-NMR spectrum of the compound. Aromatic protons were marked from enlarged spectrum of aromatic region (Figure 3.5). 1-proton doublets at 8.10, 7.82, 7.73 and 7.12 ppm were assigned to the H-4, H-5, H-8 and H-3 protons respectively. It was thought that doublets of the two 2-protons at 7.11 and 7.76 ppm were belonging to H-2′ and H-3′ protons. Furthermore, 1-proton triplet at 7.36 ppm and 1-proton triplet of doublets at 7.53 ppm were assigned to H-6 and H-7 protons.

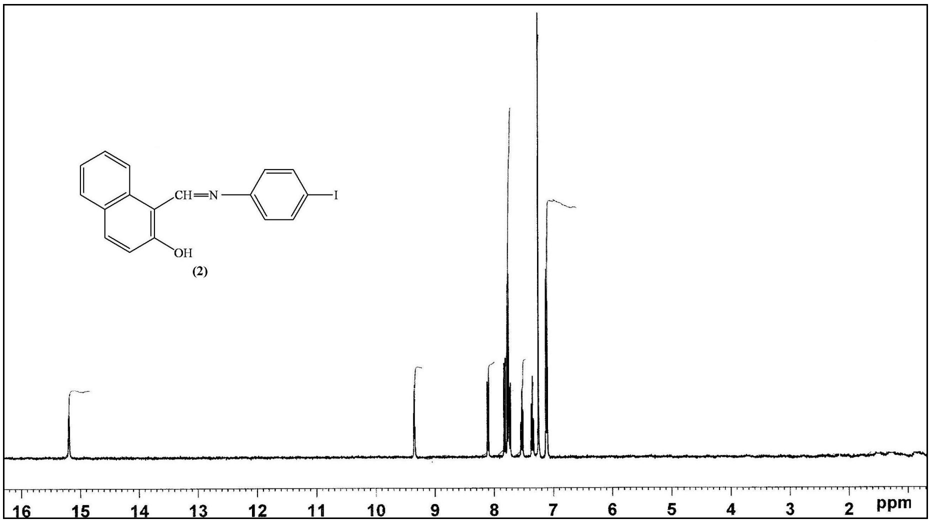


Figure 3.4 ^{1}H-NMR Spectrum of 1-{[(4-iodophenyl)imino]methyl}naphthalen-2-ol **(2)** ($CDCl_3$).

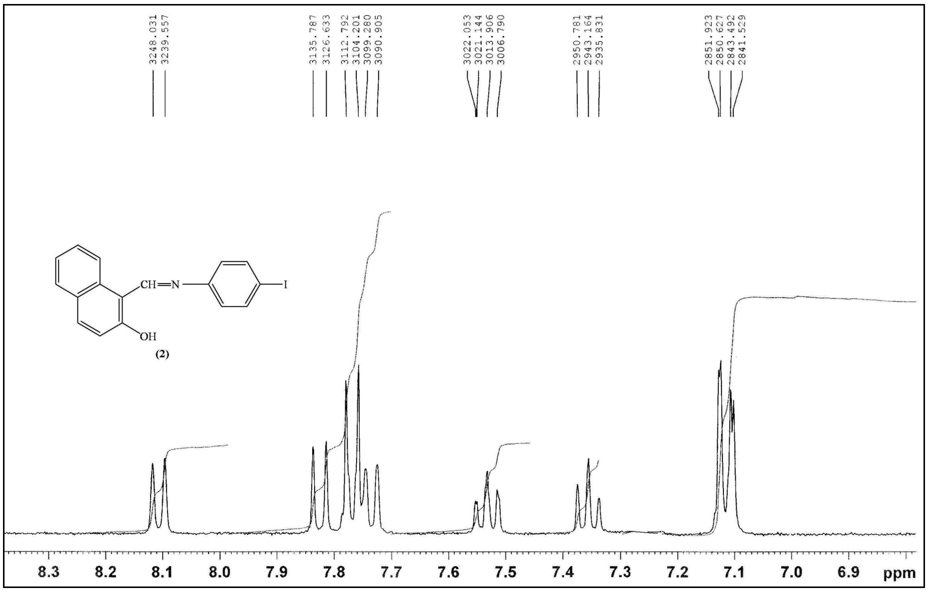


Figure 3.5 ^{1}H-NMR Spectrum of 1-{[(4-iodophenyl)imino]methyl}naphthalen-2-ol **(2)** (Aromatic Region Enlarged).

These spectroscopic data and chemical analysis where in accordance with 1-{[(4-iodophenyl)imino]-methyl}naphthalen-2-ol **(2)**.

Finally, aniline Schiff base **(1)** over zeolite catalyst took place with regioselectivity and only mono-iodination was found to occur. Iodination was *para*-directed when possible; otherwise it occurred in the *ortho*-position.

ACKNOWLEDGEMENT

This work was supported by the Eskisehir Osmangazi University Scientific Research Project Commission (grant No. 200419036).

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”, Wiley-VCH: Weinheim, Germany, 358-372 (1998).

[3] Skulski, L., “Organic iodine (I, III, V) chemistry: 10 years of development at the Medical University of Warsaw, Poland (1990-2000)”, ***Molecules***, 5: 1331-1371 (2000).

[4] Merkushev, E.B., “Advances in the synthesis of iodoaromatic compounds”, ***Synthesis***, 923 (1988).

[5] Chiappe, C. and Pieraccini, D., “Regioselective iodination of arenes in ionic liquids mediated by selectfluor^{TM} reagent F-TEDA-BF$_4$”, ***Arkivoc***, xi: 249-255 (2002).

[6] Colella, C., “Ion exchange equilibria in zeolite materials”, ***Mineralium Deposita***, 31 (6): 554–562 (1996).

[7] Mumpton, F.A., ***Proc. Natl. Acad. Sci.***, 96: 3463 (1999).

[8] Dyer, A., “An Introduction to Zeolite Molecular Sieves”, Wiley & Sons, Chichester, 88-92 (1988).

[9] Jansen, J.C., Karge, H.G., Weitkamp, J., ***Advanced Zeolite Science and Application; Studies in Surface Science and Catalysis***, Elsevier, Amsterdam, 85: 244-256, (1994).

[10] Reddy, K.S.N., Rao, B.S. and Shiralkar, V.P., “Reforming of pyrolysis gasoline over platinum-alumina catalysts containing MFI type zeolites”, ***Appl. Catal.***, 95: 53-63 (1993).

[11] Pradhan, A.R. and Rao, B.S., “Transalkylation of di-isopropylbenzenes over large pore zeolites”, ***Appl. Catal.***, 106: 143-153 (1993).

[12] Weigert, F.J., U.S. Patent, 4,593,124 (1986).

[13] Singh, A.P. and Kale, S.M., U.S. Patent, 5,892,138 (1999).

[14] Singh, A.P., Bandyopadhyay, R. and Rao, B.S., “Vapour phase Beckmann Rearrangement of cyclohexanone oxime over SAPO-11 molecular sieve”, ***Appl. Catal***., 136: 249-263 (1996).

[15] Thangaraj, A., Sivasanker S. and Ratnasamy, P., “Evidence for the simultaneous incorporation of Al and Ti in MFI structure (Al-TS-1)”, ***Zeolites***, 135-137 (1992).

[16] Iwamoto, M., Yashiro, H., Tandaa, K. and Mizumo, N., “Removal of nitrogen monoxide through a novel catalytic process”, ***J. Phys. Chem.***, 95(9): 3727-3730 (1991).

[17] Tobias, M.A., U.S. Patent, 3,728,408 (1973).

[18] Venkateshan, C., Jaimol, T., Moreau, P., Finiels, A., Ramaswamy, A.V. and Singh, A.P., “Liquid phase selective benzoylation of chlorobenzene to 4,4′-dichlorobenzophenone over zeolite H-beta”, ***Catal. Lett.***, 75: 119-123 (2001).

[19] Ratnasamy, P., Singh, A.P. and Sharma, S., “Halogenation over zeolite catalysts”, ***Appl. Catal. A***, 135: 25-55 (1996).

[20] Roy, S.C., Rana, K.K., Guin, C. and Banerjee, B., “Ceric ammonium nitrate catalyzed mild and efficient α-chlorination of ketones by acetyl chloride”, ***Arkivoc***, ix: 34-38 (2003).

[21] 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).

[22] Csunderlik, C., Bercean, V., Peter, F. and Badea, V., “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).

[23] 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).

[24] Szostak, R., “Handbook of Molecular Sieves”, Springer, New York, 342-356 (1982).

[25] Tihmillioglu, F. and Ulku, S., “Use of clinoptilolite in ethanol dehydration”, ***Sep. Sci. Tech.***, 31: 2855-2865 (1996).

[26] Linares, C.F., Goldwasser, M.R., Machado, F.J., Rivera, A., Rodriguez-Fuentes, G. and Barrault, J., “Advantages of base exchanged natural clinoptilolite as a catalyst for the Knoevenagel reaction “, ***Microporous Mesoporous Mater.***, 41: 69-77 (2000).

[27] 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).

[28] Sawich, A. and Zetensow, J.V., ***Astron. Fiz. Khim.*** Spit Syn, I., 1: 233-242 (1956).

[29] Young, L.B., Butter, S.A., Kaeding, W. and Young, W., “Shape selective reactions with zeolite catalysts III. Selectivity in xylene isomerization, toluene-methanol alkylation, and toluene disproportionation over ZSM-5 zeolite catalysts “, ***J. Catal.*** 1982, 76: 418-432 (1982).

[30] Miyake, K., Sekizawa, K., Hironaka, T., Nakano, M., Fujii, S. and Tsutsumi, Y., **“**Selective *para*-bromination of phenyl acetate under the control of zeolites, bases, acetic anhydride or metal acetates in the liquid phase“ ***Stud. Surf. Sci. Catal.***, 28: 747-758 (1986).

[31] Ratnamasy, P., Singh, A.P. and Sharma, S., “Halogenation over zeolite catalysts” ***Applied Catalysis A***, 135: 25-55 (1996).