Zeolite catalyzed efficient synthesis of perimidines at room temperature

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Arylperimidines, **3(a-l)**, were synthesized in good yields by cyclocondensation reaction of 1,8-diamino-naphthalene and aromatic aldehydes in the presence of NaY zeolite as a catalyst. The simple environmentally benign nature, reusability of the catalyst, and the easy work-up reaction are some of the advantages of this protocol.

Key Words: Diaminonaphthalene, perimidine, zeolite.

Introduction

Multi-nuclear N-heterocyclic compounds like perimidines are of wide interest because they exhibit a diverse range of biological activities.[1−4] There are several preparative methods for the synthesis of perimidine derivatives.[5−10] The most commonly method for the preparation of perimidines is the condensation reaction of 1,8-diaminonaphthalene with a carbonyl group, which needs special reagent or force reaction conditions. However, because of the continuing interest in this field, investigation into simple methods for the synthesis of perimidines is important. Recently, the use of inorganic solid acid in organic synthesis has become more popular.[11−15] Among the various solid acid catalysts, zeolites have received increasing attention because of their suitable acidity, insolubility to all organic solvents, thermal stability, and low cost.

Due to the versatile biological properties of perimidine derivatives and as a continuation of our studies on synthesis of perimidines[16,17] we wish to report a clean and simple synthetic method for preparation of 2,3-dihyroperimidines using zeolite as an efficient catalyst.

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Experimental

NaY zeolite was prepared and activated according to the procedure described previously.[18] NMR spectra were recorded on a Bruker 300 MHz spectrometer. IR spectra were performed on a Galaxy FT-IR 500 spectrophotometer. Microanalyses were performed by the Elemental Analyzer (Elemental, Vario EL III) at Arak University. The microanalysis results agreed favorably with the calculated values. Reaction progress was routinely monitored by thin layer chromatography using silica gel F_{254} aluminum sheets (Merck). All chemicals were used as obtained without further purification.

General procedure for preparation of 2-arylperimidines

To a solution of 1,8-diaminonaphthalene (0.02 mmol) and corresponding aromatic aldehyde (0.01 mmol) in ethanol (20 mL) was added NaY zeolite (0.20 g). The mixture was stirred at room temperature for 45-50 h. After the completion of the reaction the catalyst was separated by filtration. Then water (15-20 mL) was added to the filtration and stirred for 5 min. The precipitate was filtered and washed with cold water and air dried. For the catalyst recovery study, the catalyst was washed with ethanol and chloroform after each run, and air dried.

2-Phenyl-2,3-dihydro-1H-perimidine (3a)

Yield 70%, mp 101-103 °C. IR (KBr): ν = 3382, 3359, 3039, 2809, 1598, 1419, cm^{-1}. ^{1}H-NMR (DMSO): δ (ppm) = 5.36 (s, 1H, CH), 6.49-7.62 (m, 13H, CH$_{arom}$, 2NH). ^{13}C-NMR (DMSO): δ (ppm): 66.8, 104.8, 112.9, 115.7, 127.3, 128.4, 128.7, 129.0, 134.8, 142.2, 143.5. Anal calcd for $C_{17}H_{14}N_2$: C, 82.88; H, 5.74; N, 11.37%. Found: C, 82.98; H, 5.50; N, 11.48%.

2-(4-Methylphenyl)-2,3-dihydro-1H-perimidine (3b)

Yield 83%, mp 161-163 °C. IR (KBr): ν = 3385, 3045, 2922, 1602, 1420 cm^{-1}. ^{1}H-NMR (DMSO): δ (ppm) = 2.32 (s, 3H, CH$_3$), 5.31 (s, 1H, CH), 6.47-7.49 (m, 12H, CH$_{arom}$, 2NH). ^{13}C-NMR (DMSO): δ (ppm): 21.3, 66.8, 104.9, 113.1, 115.8, 127.4, 128.4, 129.2, 135.0, 138.3, 139.3, 143.7. Anal calcd for $C_{18}H_{16}N_2$: C, 83.03; H, 6.21; N, 10.76%. Found: C, 83.21; H, 6.18; N, 10.87%.

2-(2-Chlorophenyl)-2,3-dihydro-1H-perimidine (3c)

Yield 50%, mp 116-118 °C. IR (KBr): ν = 3381, 3353, 3046, 2804, 1602, 1418 cm^{-1}. ^{1}H-NMR (DMSO): δ (ppm) = 5.76 (s, 1H, CH), 6.51-7.77 (m, 12H, CH$_{arom}$, 2NH). ^{13}C-NMR (DMSO): δ (ppm): 63.0, 105.0, 112.7, 116.0, 127.3, 127.9, 129.7, 130.3, 130.5, 133.1, 134.8, 138.9, 143.3. Anal calcd for $C_{17}H_{13}N_2Cl$: C, 72.72; H, 4.68; N, 9.98%. Found: C, 72.50; H, 4.74; N, 10.04%.

2-(4-Chlorophenyl)-2,3-dihydro-1H-perimidine (3d)

Yield 57%, mp 158-160 °C. IR (KBr): ν = 3390, 3054, 2800, 1601, 1420, 1039 cm^{-1}. ^{1}H-NMR (DMSO): δ (ppm) = 5.38 (s, 1H, CH), 6.48-7.63 (m, 12H, CH$_{arom}$, 2NH). ^{13}C-NMR (DMSO): δ (ppm): 66.0, 104.9,

112.9, 115.9, 127.4, 128.7, 130.2, 133.4, 134.8, 141.4, 143.2. Anal calcd for $C_{17}H_{13}N_2Cl$: C, 72.72; H, 4.68; N, 9.98%. Found: C, 72.83; H, 4.88; N, 10.11%.

2-(4-Fluorophenyl)-2,3-dihydro-1H-perimidine (3e)

Yield 82%, mp 180-182 °C. IR (KBr): $\nu = 3402, 3041, 2801, 1601, 1410, 1214\ cm^{-1}$. ^{1}H-NMR (DMSO): δ (ppm) = 5.42 (s, 1H, CH), 6.58-7.73 (m, 12H, CH_{arom}, 2NH). ^{13}C-NMR (DMSO): δ (ppm): 66.2, 105.0, 113.0, 115.3, 115.6, 116.0, 127.4, 130.4, 130.5, 134.9, 138.5, 143.5, 161.1, 164.4. Anal calcd for $C_{17}H_{13}N_2F$: C, 77.24; H, 4.97; N, 10.60%. Found: C, 77.41; H, 4.67; N, 10.86%.

2-(2-Nitrophenyl)-2,3-dihydro-1H-perimidine (3f)

Yield 47%, mp 158-160 °C. IR (KBr): $\nu = 3358, 3232, 2853, 1602, 1519, 1416, 1334\ cm^{-1}$. ^{1}H-NMR (DMSO): δ (ppm) = 5.83 (s, 1H, CH), 6.52-8.05 (m, 12H, CH_{arom}, 2NH). ^{13}C-NMR (DMSO): δ (ppm): 61.4, 105.2, 112.5, 116.2, 124.5, 127.4, 130.0, 130.4, 134.0, 134.7, 136.9, 142.5, 149.4. Anal calcd for $C_{17}H_{13}N_3O_2$: C, 70.08; H, 4.51; N, 14.43%. Found: C, 70.19; H, 4.56; N, 14.35%.

2-(3-Nitrophenyl)-2,3-dihydro-1H-perimidine (3g)

Yield 40%, mp 188-190 °C. IR (KBr): $\nu = 3346, 3232, 2854, 1604, 1529, 1417, 1352\ cm^{-1}$. ^{1}H-NMR (DMSO): δ (ppm) = 5.55 (s, 1H, CH), 6.50-8.44 (m, 12H, CH_{arom}, 2NH). ^{13}C-NMR (DMSO): δ (ppm): 65.5, 105.1, 112.9, 116.1, 123.0, 123.7, 127.4, 130.3, 134.8, 135.0, 142.7, 145.0, 148.2. Anal calcd for $C_{17}H_{13}N_3O_2$: C, 70.08; H, 4.51; N, 14.43%. Found: C, 70.15; H, 4.61; N, 14.57%.

2-Naphthyl-2,3-dihydro-1H-perimidine (3h)

Yield 65%, mp 165-167 °C. IR (KBr): $\nu = 3396, 3045, 1602, 1419\ cm^{-1}$. ^{1}H-NMR (DMSO): δ (ppm) = 5.99 (s, 1H, CH), 6.51-8.01 (m, 15H, CH_{arom}, 2NH). ^{13}C-NMR (DMSO): δ (ppm): 66.5, 104.8, 113.0, 115.7, 125.7, 126.0, 126.2, 127.3, 128.8, 129.6, 131.6, 134.2, 135.0, 136.4, 144.0. Anal calcd for $C_{21}H_{16}N_2$: C, 85.13; H, 5.41; N, 9.46%. Found: C, 85.34; H, 5.30; N, 9.61%.

2-(2,3-Dihydro-1H-perimidine-2-yl)phenol (3i)

Yield 95%, mp 189-191 °C. IR (KBr): $\nu = 3351, 3327, 3051, 2971, 1602, 1492, 1415, 1248\ cm^{-1}$. ^{1}H-NMR (DMSO): δ (ppm) = 5.65 (s, 1H, CH), 6.52-7.47 (m, 12H, CH_{arom}, 2NH), 9.69 (s, 1H, OH). ^{13}C-NMR (DMSO): δ (ppm): 61.3, 105.1, 112.9, 115.9, 119.4, 127.3, 127.6, 128.8, 129.6, 134.9, 143.7, 155.9. Anal calcd for $C_{17}H_{14}N_2O$: C, 77.83; H, 5.39; N, 10.68%. Found: C, 77.59; H, 5.48; N, 10.84%.

4-(2,3-Dihydro-1H-perimidine-2-yl)phenol (3j)

Yield 40%, mp 161-163 °C. IR (KBr): $\nu = 3396, 3331, 3045, 1600, 1517, 1412, 1252\ cm^{-1}$. ^{1}H-NMR (DMSO): δ (ppm) = 5.24 (s, 1H, CH), 6.46-7.42 (m, 12H, CH_{arom}, 2NH), 9.50 (s, 1H, OH). ^{13}C-NMR (DMSO): δ (ppm):

66.8, 104.7, 112.9, 115.3, 115.6, 127.3, 129.6, 132.4, 134.9, 143.9, 158.2. Anal calcd for $C_{17}H_{14}N_2O$: C, 77.83; H, 5.39; N, 10.68%. Found: C, 77.71; H, 5.35; N, 10.71%.

2-Bromo-2-(2,3-dihydro-1H-perimidine-2-yl)phenol (3k)

Yield 88%, mp 164-166 °C. IR (KBr): $\nu = 3347, 3285, 3047, 2860, 1604, 1491, 1419, 1245$ cm^{-1}. ^{1}H-NMR (DMSO): δ (ppm) = 5.63 (s, 1H, CH), 6.52-7.55 (m, 11H, CH$_{arom}$, 2NH), 10.14 (s, 1H, OH). ^{13}C-NMR (DMSO): δ (ppm): 60.5, 105.1, 110.6, 112.8, 116.0, 118.1, 127.4, 130.3, 131.3, 132.1, 134.8, 143.3, 155.2. Anal calcd for $C_{17}H_{13}BrN_2O$: C, 59.84; H, 3.85; N, 8.21%. Found: C, 60.06; H, 3.80; N, 8.47%.

N-[4-(2,3-Dihydro-1H-perimidine-2-yl)phenyl]N,N-dimethylamine (3l)

Yield 68%, mp 49-52 °C. IR (KBr): $\nu = 3389, 3356, 3040, 2891, 1599, 1527, 1478$ cm^{-1}. ^{1}H-NMR (DMSO): δ (ppm) = 2.91 (s, 6H, 2CH$_3$), 5.24 (s, 1H, CH), 6.47-7.43 (m, 12H, CH$_{arom}$, 2NH). ^{13}C-NMR (DMSO): δ (ppm): 19.0, 56.5, 66.8, 104.6, 112.5, 113, 115.5, 127.3, 129.1, 129.6, 135.0, 144.0, 151.4. Anal calcd for $C_{19}H_{19}N_3$: C, 78.85; H, 6.63; N, 14.52%. Found: C, 78.68; H, 6.73; N, 14.59%.

Results and discussion

The reactions were carried out at room temperature for 45-50 h by taking a 2:1 mol ratio mixture of 1,8-diaminonaphthalene **1** and the aromatic aldehyde **2** in the presence of NaY zeolite in ethanol to give 2,3-dihydro-1H-perimidines (**Figure**) in suitable yields. However, aliphatic aldehydes such as formaldehyde or acetaldehyde were also examined under the same conditions, but the responding products were isolated in trace amounts.
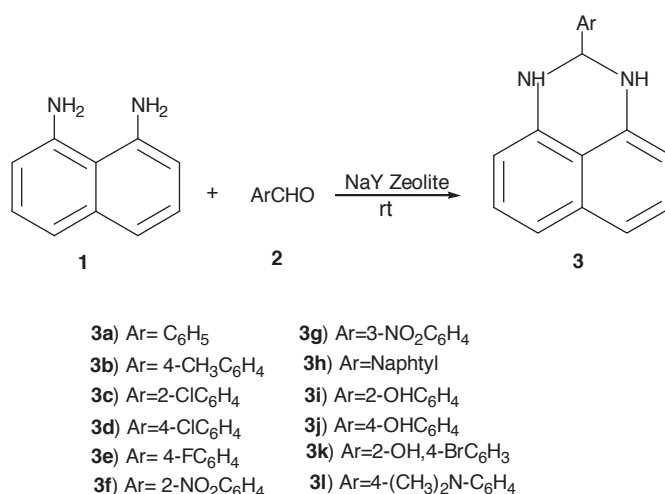

3a) Ar= C_6H_5 **3g)** Ar=3-NO$_2$C$_6$H$_4$
3b) Ar= 4-CH$_3$C$_6$H$_4$ **3h)** Ar=Naphtyl
3c) Ar=2-ClC$_6$H$_4$ **3i)** Ar=2-OHC$_6$H$_4$
3d) Ar=4-ClC$_6$H$_4$ **3j)** Ar=4-OHC$_6$H$_4$
3e) Ar= 4-FC$_6$H$_4$ **3k)** Ar=2-OH,4-BrC$_6$H$_3$
3f) Ar= 2-NO$_2$C$_6$H$_4$ **3l)** Ar=4-(CH$_3$)$_2$N-C$_6$H$_4$

Figure. Reaction of 1,8-diaminonaphthalene and the aromatic aldehydes in the presence of NaY zeolite at room temperature.

For optimization of the amount of catalyst required for this reaction, and also the reusability of the catalyst, 2-hydroxybenzaldehyde was used as a model compound and different amounts of catalyst were tested under the same conditions. An amount of catalyst less than 12 W% could catalyze the reaction, but it needed a longer reaction time. On the other hand, an amount of catalyst over 12 W% did not improve the yield of product (Table 1).

Table 1. Reaction of 1,8-diaminonaphthalene with 2-hydroxybenzaldehyde using different amounts of catalyst.

Entry	W% catalyst	Yield %
1	2	55
2	5	75
3	8	80
4	10	90
5	12	95
6	15	95

All reactions were carried out at room temperature for 45 h.

The catalyst was recovered and used up to 4 times and its activity did not show a significant decrease after 4 runs (Table 2).

Table 2. Catalyst recovery study in reaction of 1,8-diaminonaphthalene with 2-hydroxybenzaldehyde.

Entry	Time (h)	Yield %
1	45	95
2	45	80
3	48	65
4	>50	30

Reusability of an environmentally friendly catalyst, easy procedure, and the purity of products in comparison to the classical methods[19,20] are some of the features of this process.

The ^{1}H- and ^{13}C-NMR spectra as well as the elemental analyses data of all synthesized compounds are consistent with the expected structures. The ^{1}H-NMR spectra of arylperimidines **3** consist of a multiplet at downfield shift resulting from the aromatic protons and two NH groups, respectively. The signal of 2 NH groups appears as a broad signal in the same range as those of the aromatic protons. The CH perimidine ring signal appears at 5.31-5.99 ppm depends on the Ar group.

Conclusion

NaY zeolite was employed as an efficient catalyst for C-C bond formation reaction between 1,8-diaminonaphthalene and aromatic aldehydes. The attractive features of this procedure are good conversion, reusability of catalyst, and easy work-up, making it a useful procedure for the synthesis of 2-aryl-2,3-dihydroperimidines.

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