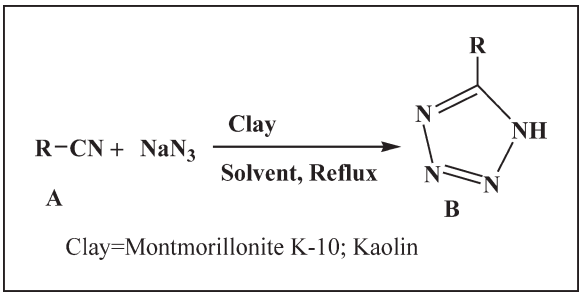
Alireza Najafi Chermahini,[a]* Abbas Teimouri,[b] Fariborz Momenbeik,[a,c] Amin Zarei,[d] Zeinab Dalirnasab,[a] Aseyeh Ghaedi,[a] and Mostafa Roosta[a]

[a]Department of Chemistry, Faculty of Science, Yasouj University, Yasouj 75918-74831, Iran
[b]Department of Chemistry, Payame Noor University (PNU), Isfahan 81395-671, Iran
[c]Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran
[d]Department of Science, Islamic Azad University, Fasa Branch, Fasa, Fars, Iran
*E-mail: najafi@mail.yu.ac.ir or najafy@gmail.com

Received September 27, 2009
DOI 10.1002/jhet.382
Published online 18 June 2010 in Wiley InterScience (www.interscience.wiley.com).



In this study, the possibility of 5-substituted 1-*H*-tetrazoles synthesis using clays as catalyst was investigated. The reaction of a series of aromatic nitriles with sodium azide was catalyzed by montmorillonite K-10 or kaolin clays in water or DMF as solvent. Conventional heating or ultrasonic irradiation was used to promote reaction. The amount of nitrile to sodium azide mole ratio, amount of catalyst, reaction time, and solvent type were optimized. The versatility of this method was checked by using various nitriles, which showed reasonable yields of tetrazole formation. It was found that using nitriles with electron-withdrawing groups result in both higher yields and lower reaction times. The catalysts could be reused several times without significant loss of their catalytic activity. Compared to conventional heating, ultrasonic irradiation reduced reaction times and increased catalyst activity. The present procedure is green and offers advantages, such as shorter reaction time, simple workup, and recovery and reusability of catalyst.

J. Heterocyclic Chem., **47**, 913 (2010).

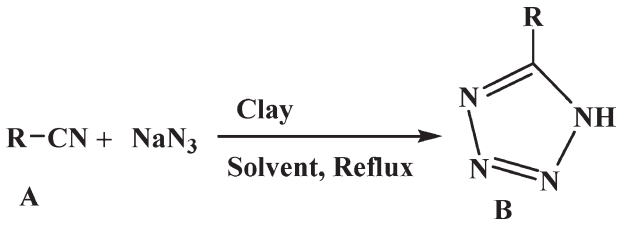
INTRODUCTION

Tetrazoles are important heterocyclic compounds in medicinal chemistry [1–3]. Among them 5-substituted 1-*H*-tetrazoles are often used as metabolically stable surrogates for carboxyl group and for cis-amide bond [4,5]. Also, an enormous number of biologically active compounds are known, which contain tetrazole [6–8]. The [2+3] cycloaddition of nitriles and azides is a common method for the synthesis of tetrazole derivatives. Because of biological importance of tetrazoles, various synthetic methodologies have been developed for their synthesis. In most of these methods, highly toxic and explosive hydrazoic acid generates through activation of the azide by using strong Lewis acids [9,10], expensive and toxic metals [11–13], or amine salts [14]. The ''click'' chemistry approach using zinc catalysis in aqueous solution is a magnificent improvement over previous methods [15,16], but still requires the tedious and time-consuming steps such as removal of zinc salts from the acidic products. Clay-catalyzed organic transformations have been recently developed and obtained great interest as green methods. This has been attributed to their inexpensive nature and special catalytic activity under heterogeneous reaction conditions [17–22]. Acidic clays are suitable replacement of various homogeneous acid catalysts. They have been used in the synthesis of 1,5-benzodiazepines [23], acetonide protection [24], alkylation of benzene [25], Diels-Alder reaction [26], dihydrofuran synthesis [27], and bromination and chlorination of aromatic compounds [28]. In continuing with our research in tetrazole chemistry [29–31] and application of clays in organic transformations [32,33], herein we report a new process for synthesis of 1-*H*-5-substituted tetrazoles using clays as safe, environmentally benign, and inexpensive catalysts.

RESULTS AND DISCUSSION

Synthesis of tetrazoles derivatives under reflux condition. In the reaction between benzonitrile **1a** and sodium azide (Scheme 1), effect of the catalyst amount was investigated. The different catalyst amounts (20, 50, and 100 mg) were used, and it was found that the maximum reaction yield obtained using 50 mg of catalyst. The results show that for K-10 when the catalyst amount

Scheme 1. Clay-catalyzed synthesis of 5-substituted 1-*H*-tetrazoles.



Clay=Montmorillonite K-10; Kaolin

increased to 20 and 50 mg, the conversion increased to 45 and 94% and 56 and 95% in water and DMF as solvent, respectively. However for kaolin, increase of catalyst amount from 20 to 50 mg increased the conversion from 27 to 95% and 43 to 94% in water and DMF, respectively. Also, it is obvious that the catalyst amount more than 50 mg has no significant effect on the conversion of benzonitrile to corresponding tetrazole. Any attempts to carry out the reactions in the absence of montmorillonite K-10 and kaolin were failed, and no products were found despite prolonged reaction times, which emphasis the clay catalytic role. To see whether the action of clays is truly catalytic, we reduced the amount of clays in the reaction between sodium azide and benzonitrile from 20 to 10 mg.

Upon our results, it is evident that a low loading of K-10 and kaolin is still effective, although the reactivity was decreased consequently (see Table 1, entries 13, 14). Even 10 mg of K-10 and kaolin afforded the desired product after 24 h in 29 and 40% yields in water and 38 and 17% yields in DMF, respectively. Although the activity of K-10 in DMF was slightly higher than kaolin, but there is no significant difference between specific activities of these two catalysts in both solvents. One important advantage of clays as catalyst is the easy workup of the reaction. After completion of the reaction, simple filtration of the reaction mixture followed by acidification of filtrate result in precipitating the product as a white powder. Another advantage of this method is its large-scale applicability. For this, we examine a run with 30 mmol of benzonitrile in DMF as the solvent, and the results were comparable to those obtained in the small-scale experiments. The effect of solvent was examined using water and DMF. The results showed that DMF because of its higher boiling point is more efficient. However, the use of water as a clean, inexpensive, and universal solvent combines features of both economic and environmental advantages. A close look at Figure 1 reveals that conversion rate of benzonitrile to phenyl tetrazole for both K-10 and kaolin in the DMF is faster. For example, with using montmorillonite K-10 as catalyst after 6 h, benzonitrile conversion was 72 and 53% in DMF and water, respectively. At the same condition, the conversion values for kaolin were 66 and 54% in DMF and water, respectively (see Fig. 1). The variation of the reaction conversion with the amount of sodium azide was studied, and the experimental results are tabulated in Table 1. It is apparent that the reaction conversion increased as the mole ratio of benzonitrile to sodium azide increased from 1:1 to 1:3 (from 50 to 94% and 69 to 95% for K-10 and from 20 to 95% and 27 to 94% for kaolin in DMF and water, respectively).

Table 1

Initial screening of reaction parameters for the formation of tetrazole derivatives.[a]

Entry	Solvent	Benzonitrile/Sodium azide	Catalyst amount (mg)	% Conversion[b]	
1	H_2O	1:1	50	50	20
2	DMF	1:1	50	69	27
3	H_2O	1:3	50	94	95
4	DMF	1:3	50	95	94
5	H_2O	1:3	100	43	13
6	DMF	1:3	100	94	24
7	H_2O	1:3	20	45	27
8	DMF	1:3	20	56	43
9	H2O	1:1	20	30	7
10	DMF	1:1	20	21	12
11	H_2O	1:5	50	74	81
12	DMF	1:5	50	75	78
13	H_2O	1:3	10	29	38
14	DMF	1:3	10	40	17
15	H_2O	1:3	0	0	0
16	DMF	1:3	0	0	0

[a] Reaction time (24 h).
[b] Conversion was calculated using HPLC. Left (K-10) and right (kaolin).

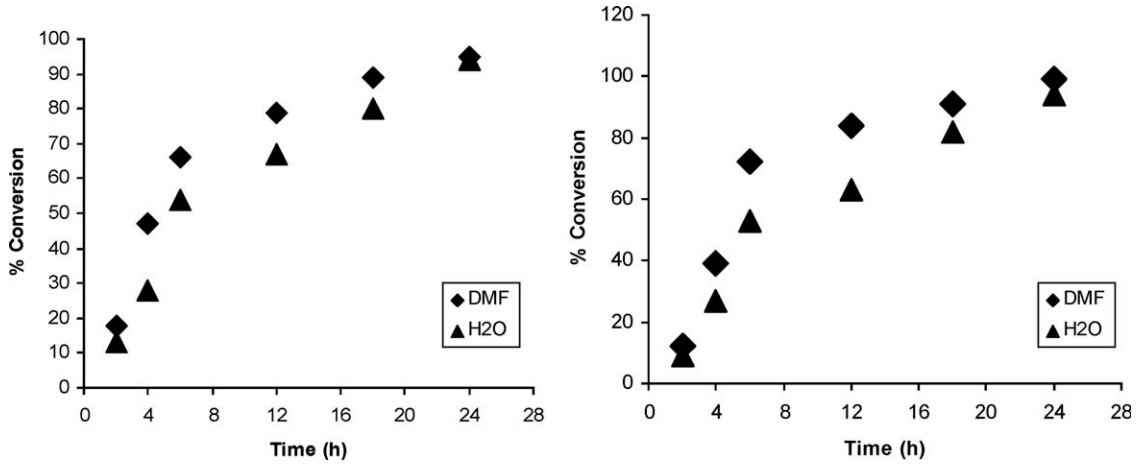


Figure 1. Effect of time on conversion of benzonitrile to phenyl tetrazole in DMF and water under reflux condition using montmorillonite K-10 and kaolin. Condition: 2 mmol benzonitrile and 6 mmol sodium azide.

Further increase in mole ratio to 1:5, the benzonitrile conversion decreased slightly to 74 and 75% for K-10 and 81 and 78% for kaolin in the DMF and water, respectively (Table 1, entries 11, 12). This observation suggesting that the excess values of sodium azide may block active sites of catalysts.

The catalytic role of clays in the synthesis of tetrazoles was investigated by two reaction without use of catalysts. The results indicate that no progress was observed. (Table 1, entries 15 and 16).

The effect of time on the product yield using montmorillonite K-10 and kaolin is shown in Figure 1. The conversion increases from 12 to 91% and 9 to 82% as the time increased from 2 to 18 h. With further increase in reaction time to 24 h, formation of phenyl tetrazole marginally increases and reaches to 94 and 95% for K-10 in the water and DMF, respectively. Moreover for kaolin, as the time increased from 2 to 24 h conversion increases from 18 and 13% to 95 and 94% in the water and DMF, respectively.

One of the most important advantages of heterogeneous catalysis over the homogeneous counterpart is the possibility of reusing the catalyst by simple filtration, without loss of activity. The recovery and reusability of the catalyst was investigated in the tetrazole formation with benzonitrile. After completion of the reaction, the catalyst was separated by filtration, washed three times with 5 mL acetone, then with doubly distilled water several times, and dried at 110°C. Then, the recovered catalyst was used in the next run. The results of three consecutive runs showed that the catalyst can be reused several times without significant loss of its activity (see Fig. 2).

Several substituted nitriles reacted with sodium azide to give the corresponding tetrazoles in good yields. Heteroaromatic nitriles such as 2, 3, and 4-pyridinecarbonitriles give the corresponding tetrazoles with excellent yields (Table 2, entries 3–5). Interestingly, phthalonitriles afford the monoaddition product (Table 2, entries 7–9). The nature of the substituents on the nitriles has a significant effect on the tetrazole yield (Table 2). The highest conversions were observed for nitriles with electron-withdrawing substituents (Table 2, entries 1–11).

However, electron-donating groups (*e.g.*, OH and NH_2) were the least reactive ones. With acetylation of 4-hydroxy benazonitrile, the reaction yield was improved, but for acetylated 4-amino benzonitrile even with long reaction times no product was formed (Table 2, entries 14–16). A probable mechanistic pathway for synthesis of tetrazoles from nitriles has been shown in Figure 3. Based on this mechanism, the nitrile activated

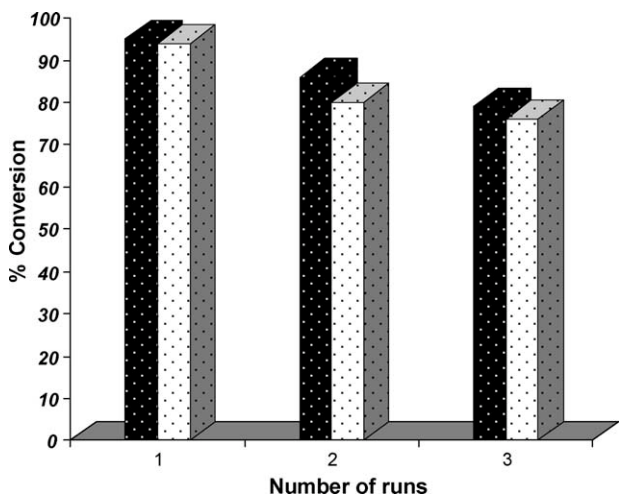
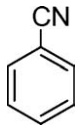
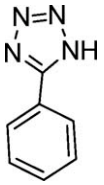
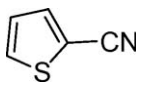
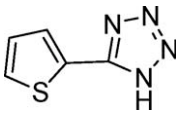
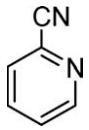
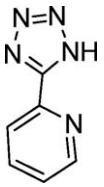
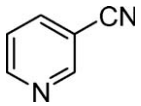
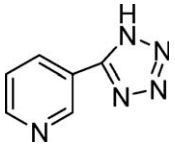
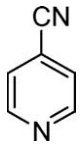
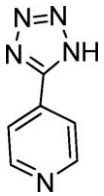
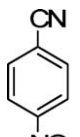
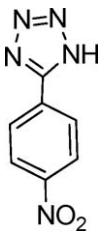
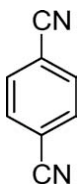
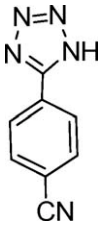


Figure 2. The results obtained from catalyst reuse montmorillonite K10 (black bars) and kaolin (white bars) in the tetrazole formation.

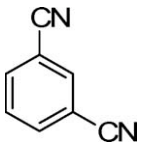
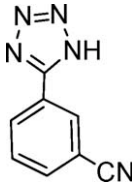
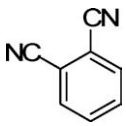
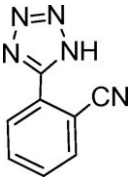
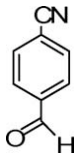
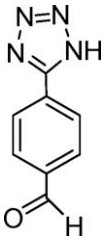
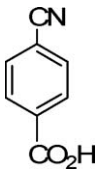
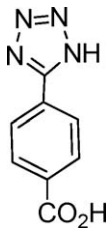
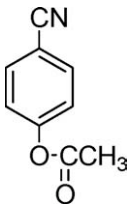
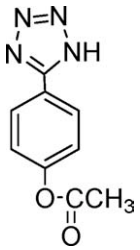
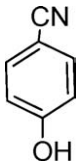
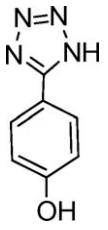
Table 2

Synthesis of 5-substituted 1-*H*-tetrazoles catalyzed by clay.[a,b]

			Yields[c]			
			Montmorillonite K-10		Kaolin	
Entry	Nitrile	Tetrazole	H_2O	DMF	H_2O	DMF
1			80	90	82	90
2			88	96	80	90
3			72	86	74	91
4			88	98	74	96
5			90	95	80	90
6			76	95	91	98
7			88	90	82	95

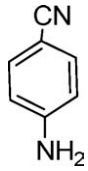
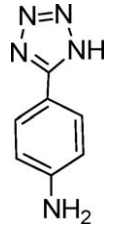
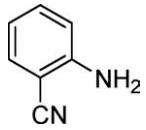
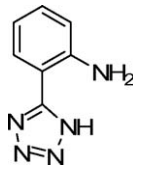
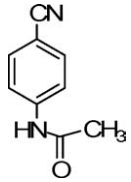
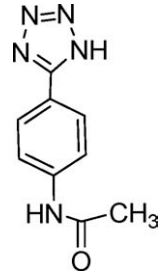
(*Continued*)

Table 2
(*Continued*)

Entry	Nitrile	Tetrazole	Yields[c] Montmorillonite K-10 H_2O	Montmorillonite K-10 DMF	Kaolin H_2O	Kaolin DMF
8			83	95	53	95
9			43	91	53	95
10			55	96	53	56
11			45	64	57	64
12			37	81	30	57
13			>10[d]	30	6	37

(*Continued*)

Table 2
(*Continued*)

			Yields[c]			
			Montmorillonite K-10		Kaolin	
Entry	Nitrile	Tetrazole	H_2O	DMF	H_2O	DMF
14			Trace[d]	Trace	Trace	Trace
15			Trace[d]	Trace	Trace	Trace
16			<10[d]	<10	Trace	Trace

[a] The products were characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectroscopy.
[b] Reaction time (24 h).
[c] Isolated yields after recrystallization.
[d] The product was not isolated.

by clay in the first stage and this activated fragment attacked by azide ion to produce the imidoyl azide. The imidoyl azide then converted to tetrazole derivative.

Synthesis of tetrazole derivatives under ultrasonic irradiation. Ultrasound has been used recently to accelerate a number of synthetically useful reactions [34,35]. The ultrasound effects observed on organic reactions are due to cavitation, a physical process that create, enlarge, and implode gaseous and vaporous cavities in an irradiated liquid. Impulsion of the cavitational bubbles, extreme temperatures, and pressures is generated at the center of the collapsed bubble [36–38]. These effects may enhance liquid–solid mass transfer and cause physicochemical change in the processed medium considerably [39,40]. Advantages and attractive features of sonochemistry led us to explore the effect of ultrasonic waves on this catalytic system. For this reason, reactions were exposed to ultrasonic irradiation using two clay catalysts in the water as the solvent.

The obtained results within reaction conditions are summarized in Table 3. The effect of catalyst amount on reaction times tested, and it was found that with increasing of catalyst amount all reaction times reduced. For example, for phenyl tetrazole with increase of catalyst amounts from 50 to 100 mg, the reaction times reduced from 90 to 40 and 120 to 50 min for montmorillonite and kaolin, respectively (Table 3 entry 1). Again a close look at Table 3 reveals that there is no significant difference between montmorillonite K-10 and kaolin, although the activity of K-10 in water under ultrasound irradiation is slightly higher than kaolin. A comparison of results obtained with nonultrasound reactions (Tables 1 and 2) shows that with ultrasound irradiation the reaction times reduced.

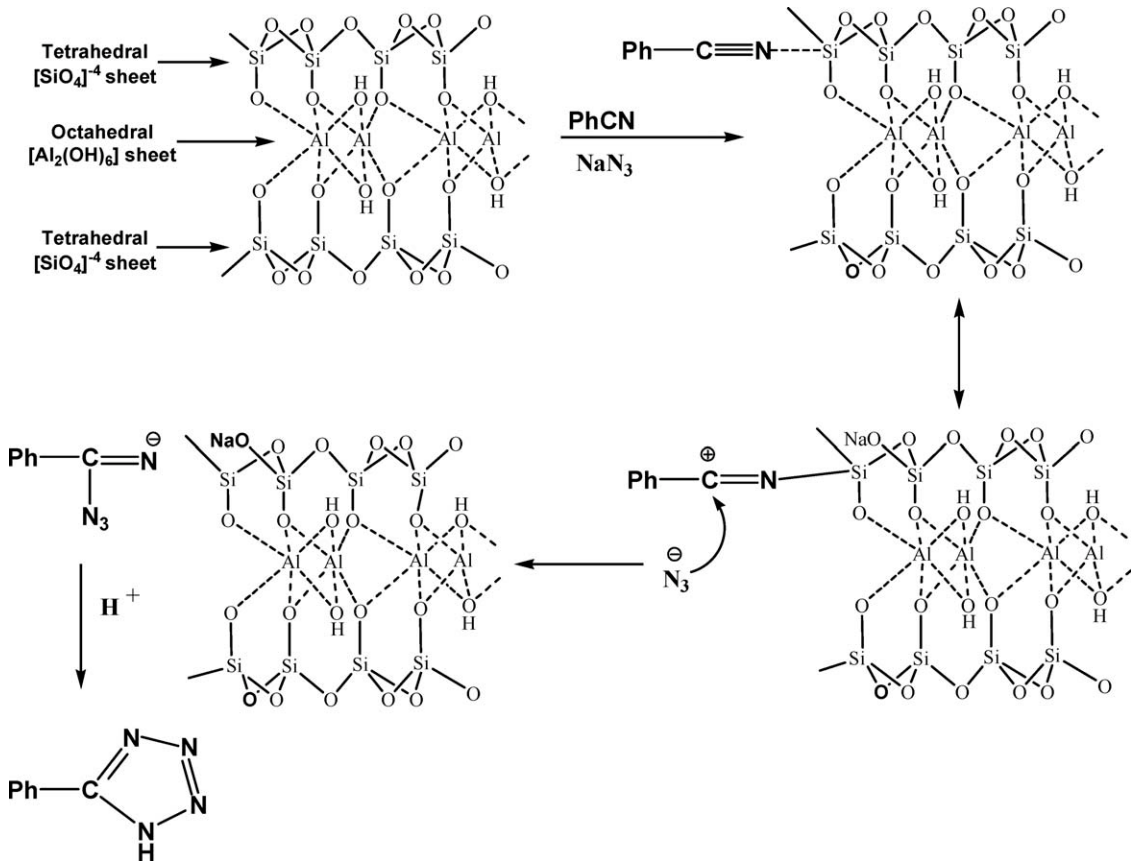


Figure 3. Proposed mechanism for conversion of nitriles to tetrazoles over K-10 clay.

CONCLUSION

In conclusion, we developed a simple, environmentally benign, and efficient method for the preparation of 5-substituted 1-*H*-tetrazoles using clay catalysts. Various nitriles reacted with NaN_3 at 100–130°C to yield the corresponding 5-substituted 1-*H*-tetrazoles with moderate to good yields. This methodology may find widespread use in organic synthesis for the preparation of tetrazoles. The advantages of this catalytic system are as follows: mild reaction condition, high product yields, easy preparation of the catalysts, nontoxicity of the catalysts, and simple and clean workup of the desired products.

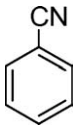
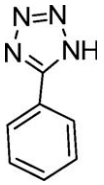
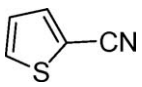
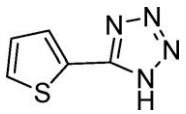
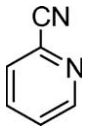
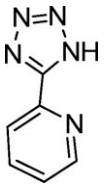
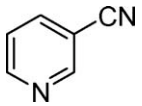
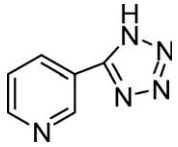
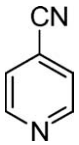
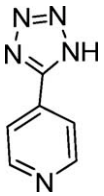
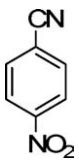
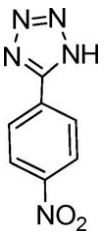
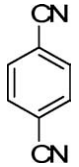
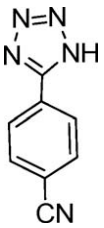
EXPERIMENTAL

Materials and instruments. Montmorillonite K-10, kaolin, sodium azide, and nitriles all were procured from Aldrich and Merck. A JASCO FT/IR-680 PLUS spectrometer was used to record IR spectra using KBr pellets. NMR spectra were recorded on a Bruker 400 Ultrasheild NMR, and DMSO-d_6 was used as a solvent. Melting points reported were determined by open capillary method using a Galen Kamp melting point apparatus and are uncorrected. Mass spectra were recorded on a Shimadzu gas chromatograph mass spectrometer GCMS-QP5050A/Q P5000 apparatus. HPLC analysis was performed using a series 1100 Agilent instrument equipped with Zorbax eclips C_{18} as column, detection at 254 nm, and 30% methanol in water as mobile phase. Reactions under ultrasonic irradiation were performed in an ultrasonic bath with heating system (Tecno-GAZ SPA Ultra Sonic System) at 40 kHz of frequency and 500 W of power. Catalysts were activated before the reaction runs with HCl (2*M*) in the solid to liquid ratio of 1:4 (40 mL, 2*M* HCl for 10 g clay) for a period of 45 min and then filtered. To remove chloride ions, catalysts were washed thoroughly with doubly distilled water and dried in an air oven at 100°C for 6 h.

General procedure for preparation of tetrazoles under reflux condition. The procedure for the synthesis of the tetrazole **2a** (Scheme 1) is representative. In a round bottom flask, benzonitrile (0.2 g, 2 mmol), sodium azide (0.4 g, 6mmol), montmorillonite K-10 (50 mg), and DMF or water (20 mL) were charged. Then, the reaction mixture was refluxed for 24 h. The progress of reaction (after 2, 4, 6, 12, 18, and 24 h) was followed by HPLC and TLC (75:25 ethyl acetate/*n*-hexane). After that the reaction was cooled to room temperature, and insoluble material was filtered and washed with doubly distilled water and acetone to separate the catalyst. The solution was acidified with HCl (5 mL, 12*M*). The precipitate was collected, dried, and recrystallized from water/ethanol to afford pure 5-phenyl-1*H*-tetrazole (**1b**) as a white powder weight, mp = 212–214°C; 0.26 g (90% yield). ^{1}H NMR (DMSO-d_6, 400

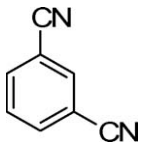
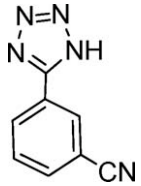
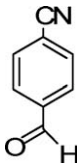
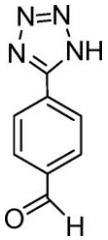
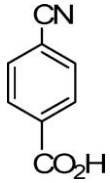
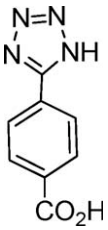
Table 3

Preparation of tetrazole derivatives under ultrasound irradiation using clays as catalyst.

			Reaction times			
			K-10 amount		Kaolin amount	
Entry	Nitrile	Tetrazole	50 mg	100 mg	50 mg	100 mg
1			90	40	120	50
2			130	110	150	120
3			240	160	220	160
4			240	180	240	210
5			200	180	220	200
6			300	200	320	210
7			320	180	300	220

(*Continued*)

Table 3
(*Continued*)

Entry	Nitrile	Tetrazole	Reaction times			
			K-10 amount		Kaolin amount	
			50 mg	100 mg	50 mg	100 mg
8			300	200	280	220
9			180	150	180	160
10			180	150	180	170

Reaction progress followed by TLC.
Temperature: 70°C.
Reaction times in min.
Solvent H_2O with 5–6 drops of DMF.
Nitrile/Sodium azide ratio 1:3.

MHz): 7.6–8.1 ppm (m, 5H); ^{13}C NMR (DMSO-d_6, 100 MHz); 124.5, 127.4, 129.9, 131.7, 155.8; MS (70 eV) *m/z*: 146, 118, 103, 91, 77, 63, 39; IR (KBr) υ: 3054, 2981, 2914, 2837, 2794, 2701, 2610, 1608, 726 cm^{-1}; HPLC retention time R_t = 14.7 min.

5-(Thiophen-2yl)-1*H*-tetrazole (2b). White solid; mp = 201–203°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 7.1 (t, J = 4 Hz, 1H), 7.6 (d, J = 4 Hz, 1H), 7.7 (d, J = 4 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz); 149, 134, 130, 125 ppm; MS (70 eV) *m/z*: 154, 152, 124, 109, 97, 69, 45; IR (KBr) υ: 3108, 3093, 3076, 2952, 2890, 2789, 2685, 1505, 1434, 964 cm^{-1}; R_t = 9.62 min.

2-(1-H-tetrazole-5-yl) pyridine (3b). White solid; mp = 208–210°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 7.4 (t, J = 6.4 Hz, 1H), 7.8 (t, J = 6.4 Hz, 1H), 8.0 (t, J = 8.0 Hz, 1H), 8.5 (d, J = 3.2 Hz, 1H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz); 167, 158, 149, 137, 124, 121 ppm; MS (70 eV) *m/z*: 147, 119, 105, 91, 78, 51; IR (KBr) υ: 3278, 3181, 2929, 1662, 1578, 1390, 923 cm^{-1}; R_t = 9.78 min.

3-(1-H-tetrazole-5-yl) pyridine (4b). White solid; mp = 238–240°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 9.1 (s, 1H), 8.8 (d, J = 3.8 Hz, 1H), 8.3 (d, J = 3.8 Hz, 1H), 7.6 (1H, m); ^{13}C NMR (DMSO-d_6, 100 MHz); 165, 153, 150, 136, 126, 123; IR (KBr) υ: 3080, 2950, 2890, 2850, 2761, 1480, 1200 cm^{-1}; R_t = 9.50 min.

4-(1-H-tetrazole-5-yl) pyridine (5b). White solid; mp = 254–258°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 8.0 (d, J = 7.8 Hz, 2H), 8.8 (d, J = 7.8 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz); 165, 149, 134, 121 ppm; MS (70 eV) *m/z*: 147, 119, 92, 78, 62, 50; IR (KBr) υ: 3080, 3060, 3028, 2955, 2917, 2832, 2751, 2689, 1608, 1581, 1492, 1065, 784 cm^{-1}; R_t = 8.16 min.

5-(4-Nitrophenyl)-1H-tetrazole (6b). White solid; mp = 218–220°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 8.1 (d, J = 8 Hz, 2H), 8.2 (d, J = 8 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz); 156, 130, 128, 124 ppm; MS (70 eV) *m/z*: 191, 163, 149, 134, 90, 63; IR (KBr) υ: 3103, 2914, 2853, 2752, 2621, 1605, 1526, 1487, 861 cm^{-1}; R_t = 11 min.

4-(1H-tetrazole-5-yl)benzonitrile (7b). White solid; mp = 258–260°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 8.0 (d, J = 7.8 Hz, 2H), 8.2 (d, J = 7.8 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz); 160, 135, 132, 130, 126, 114 ppm; MS (70 eV) *m/z*: 171, 143, 129, 103, 62; IR (KBr) υ: 3100, 2848, 2750, 2250, 1480, 781 cm^{-1}; R_t = 7.47 min.

3-(1H-tetrazole-5-yl)benzonitrile (8b). White solid; mp = 214–216°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 7.7–8.1 (5H, m); ^{13}C NMR (DMSO-d_6, 100 MHz); 164, 134, 133, 132, 131, 129, 115 ppm; MS (70 eV) *m/z*: 171, 143, 102, 62; IR (KBr) υ: 3113, 2981, 2780, 2442, 2237, 1476, 870, 780 cm^{-1}; R_t = 8.0 min.

2-(1H-tetrazole-5-yl)benzonitrile (9b). White solid; mp = 208–210°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 7.6 (t, J = 6.8 Hz, 1H), 7.7 (t, J = 6.8 Hz, 1H), 7.8 (m, 2H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz); 166, 140, 136, 133, 132, 128, 126, 118, ppm; MS (70 eV) *m/z*: 171, 143, 129, 115, 88, 76, 62, 57; IR (KBr) υ: 3096, 2531, 2110, 2023, 1632, 1436, 845 cm^{-1}; R_t = 12 min.

4-(1H-tetrazole-5-yl)benzaldehyde (10b). White solid; mp = 180–182°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 7.9 (d, J = 7.2 Hz, 2H), 8.0 (d, J = 7.2 Hz, 2H), 9.1 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz); 188, 156, 138, 131, 129, 128 ppm; MS (70 eV) *m/z*: 174, 146, 130, 116, 102, 90, 57, 43; IR (KBr) υ: 3015, 2924, 2854, 2713, 2612, 1667, 1440, 776 cm^{-1}; R_t = 6.4 min.

4-(1H-tetrazole-5-yl) benzoic acid (11b). White solid; mp = 248–250°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 7–8 (m, 4H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz); 188, 166, 138, 131, 129, 128 ppm; MS (70 eV) *m/z*: 190, 174, 146, 130, 116, 102, 90, 75, 57; (KBr) υ: 3600–3000 (br), 2500, 1760, 1500, 1480, 780 cm^{-1}; R_t = 6.9 min.

4-(1H-tetrazole-5-yl)phenyl acetate (12b). White solid; mp = 212–214°C; ^{1}H NMR (DMSO-d_6, 400 MHz): 7.9 (d, J = 7.4 Hz, 2H), 7.7 (d, J = 7.4 Hz, 2H), 2.59 (s, 3H); ppm; ^{13}C NMR (DMSO-d_6, 100 MHz); 170, 164, 152, 131, 128, 124, 22 ppm; MS (70 eV) *m/z*: 204, 189, 173, 160, 145, 130, 102, 90; (KBr) υ: 3097, 2925, 2865, 2700, 2625, 1678, 1580, 1269, 843 cm^{-1}; R_t = 12.84 min.

General procedure for preparation of tetrazoles under ultrasonic irradiation. In a round bottom flask, benzonitrile (0.2 g, 2 mmol,), sodium azide (0.4 g, 6mmol), and DMF or water (20 mL) were charged. The flask was suspended into the ultrasonic bath at the reaction temperature (333 K). Then, 50 mg of catalyst (montmorillonite K-10 or kaolin) was added and the reaction time measured. The flask was suspended at the center of the bath. The progress of the reaction was monitored by TLC. After that the reaction was cooled to room temperature, and product was recovered as mentioned.

Acknowledgment. Support from Yasouj University (YU) is gratefully acknowledged. The authors thank the faculty members in the Instrumental Analysis Center of Isfahan Payame Noor University for the measurements of mass spectra.

REFERENCES AND NOTES

[1] Meier, H. R.; Heimgartner, H. In Methoden der Organischen Chemie (Houben-Weyl); Schumann, E., Ed.; Georg Thieme: Stuttgart, 1994; Vol. E8d, p 664.

[2] Herr, R. J. Bioorg Med Chem 2002, 10, 3379.

[3] Butler, R. N. In Comprehensive Heterocyclic Chemistry; Katritzky, A. R., Ress, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, UK, 1996; Vol. 4, p 621.

[4] Yu, K. L.; Johnson, R. L. J Org Chem 1987, 52, 2051.

[5] Zabrocki, J.; Smith, D.; Dunbar, J. B., Jr.; Iijima, H.; Marshall, G. R. J Am Chem Soc 1988, 110, 5875.

[6] Davis, B.; Brandstetter, T. W.; Smith, C.; Hackett, L.; Winchester, B. G.; Fleet, G. W. J. Tetrahedron Lett 1995, 36, 7507.

[7] Burg, D.; Hameetman, L.; Filippov, D. V.; van der Marel, G. A.; Mulder, G. J. Bioorg Med Chem Lett 2002, 12, 1579.

[8] Hayashi, R.; Jin, X.; Cook, G. R. Bioorg Med Chem Lett 2007, 17, 6864.

[9] Duncia, J. V.; Pierce, M. E.; Santella, J. B., III. J Org Chem 1991, 56, 2395.

[10] Kumar, A.; Narayanan, R.; Shechter, H. J Org Chem 1996, 61, 4462.

[11] Curran, D. P.; Hadida, S.; Kim, S.-Y. Tetrahedron 1999, 55, 8997.

[12] Hajra, S.; Sinha, D.; Bhowmick, M. J Org Chem 2007, 72, 1852.

[13] Kantam, M. L.; Balasubrahmanyam, V.; Shiva Kumar, K. B. Synth Commun 2006, 36, 1809.

[14] Amantini, D.; Beleggia, R.; Fringuelli, F.; Pizzo, F.; Vaccoro, L. J Org Chem 2004, 69, 2896.

[15] Demko, Z. P.; Sharpless, K. B. J Org Chem 2001, 66, 7945.

[16] Himo, F.; Demko, Z. P.; Noodleman, L.; Sharpless, K. B. J Am Chem Soc 2002, 124, 12210.

[17] Balogh, M.; Laszlo, P. Organic Chemistry Using Clays; Springer: Berlin, 1993.

[18] Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. J Am Chem Soc 2005, 127, 9674.

[19] Choudary, B. M.; Bhaskar, V.; Kantam, M. L.; Rao, K. K.; Raghavan, K. V. Green Chem 2000, 2, 67.

[20] Ballini, R.; Bosica, G.; Maggi, R.; Ricciutelli, M.; Righi, P.; Sartori, G.; Sartorio, R. Green Chem 2001, 3, 178.

[21] Jankovic, L.; Komadel, P. J Catal 2003, 218, 227.

[22] Laszlo, P. Pure Appl Chem 1990, 62, 2027.

[23] Heravi, M. M.; Derikvand, F.; Ranjbar, L. A.; Oskooie, H. A. Heteroatom Chem 2008, 19, 215.

[24] Shaikh, N. S.; Bhor, S. S.; Gajare, A. S.; Deshpande, V. H.; Wakharkar, R. D. Tetrahedron Lett 2004, 45, 5395.

[25] (a) Yadav, J. S.; Subba Reddy, B. V.; Satheesh, G. Tetrahedron Lett 2004, 45, 3673; (b) Sabu, K. R.; Sukumar, R.; Lalithambika, M. Bull Chem Soc Jpn 1993, 66, 3535.

[26] Dintzner, M. R.; Little, A. J.; Pacilli, M.; Pileggi, D. J.; Osner, Z. R.; Lyons, T. W. Tetrahedron Lett 2007, 48, 1577.

[27] Leite, L.; Stonkus, V.; Edolfa, K.; Ilieva, L.; Plyasova, L.; Zaikovskii, V. Appl Catal A 2006, 311, 86.

[28] Hirano, M.; Monobe, H.; Yakabe, S.; Morimoto, T. J Chem Res (S) 1998, 662.

[29] Dabbagh, H. A.; Chermahini, A. N.; Banibairami, S. Tetrahedron Lett 2006, 47, 3929.

[30] Dabbagh, H. A.; Chermahini, A. N.; Teimouri, A. Heteroatom Chem 2006, 17, 416.

[31] Chermahini, A. N.; Esfahani, M. N.; Dalirnasab, Z.; Dabbagh, H. A.; Teimouri, A. J Mol Struct (Theochem) 2007, 820, 7.

[32] Dabbagh, H. A.; Chermahini, A. N.; Teimouri, A. Dyes Pigments 2007, 73, 239.

[33] Dabbagh, H. A.; Chermahini, A. N.; Teimouri, A. Appl Catal B 2007, 76, 24.

[34] Fillion, H.; Luche, J.-L. In Synthetic Organic Sonochemistry; Luche, J.-L., Ed.; Plenum Press: New York, 1998; pp 63–100.

[35] Gedanken, A. Ultrason Sonochem 2004, 11, 47.

[36] Margulis, M. A. High Energy Chem 2004, 38, 135.

[37] Capelo, J. L.; Maduro, C.; Vilhena, C. Ultrason Sonochem 2005, 12, 225.

[38] Run, M.; Wu, S.; Wu, G. Microporous Mesoporous Mater 2004, 74, 37.

[39] Miller-Ihli, N. J.; Fresenius, J. Anal Chem 1993, 345, 482.

[40] Margulis, M. A. In Advances in Sonochemistry; Mason, T. J., Ed.; JAI Press: London, 1990; Vol.1, pp 231–287.