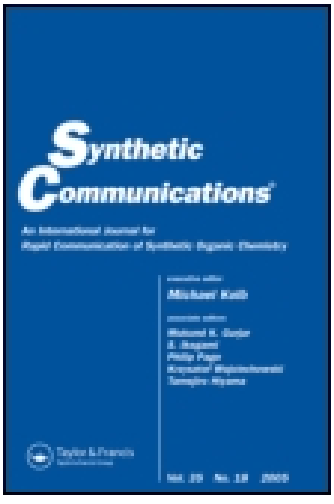

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Montmorillonite K10: An Efficient Catalyst for Solvent-Free Synthesis of 1,5-Benzodiazepine Derivatives

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Montmorillonite K10: An Efficient Catalyst for Solvent-Free Synthesis of 1,5-Benzodiazepine Derivatives

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Abstract: 2,3-Dihydro-1*H*-1,5-benzodiazepines have been synthesized under solvent-free conditions in good yields from *o*-phenylenediamine and ketones catalyzed by montmorillonite K10. This method has advantages of mild reaction conditions, simple operation, and environmental friendliness.

Keywords: 1,5-Benzodiazepine, montmorillonite K10, neat reaction, solid acid, solvent-free reaction

INTRODUCTION

1,5-Benzodiazepine derivatives have received significant attention because of their accessibility, easy functionalization, and potential pharmacological properties including anti-inflammatory, antianxiety, anticonvulsant, and hypnotic activities.[1] It represents a "privileged scaffold" found in compounds active against a variety of target types including peptide hormones,[2a] interleukin converting enzymes,[2b] and inhibitors of mitochondrial F1F0 adenosine triphosphate (ATP) hydrolase.[2c] More recently, the area of biological interest in 1,5-benzodiazepines has been extended to various diseases such as

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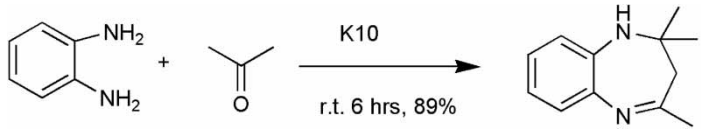
cancer,[3a] viral infection,[3b] and cardiovascular disorders.[3c,d] These derivatives are also used as dyes for acrylic fibers in the photography industry.[4] Because of their wide range of pharmacological activity and industrial and synthetic applications, the synthesis of 1,5-benzodiazepines has received increasing attention. Usually, they are prepared from the condensation of *o*-phenylenediamines with α,β-unsaturated carbonyl compounds, β-haloketones, or ketones catalyzed by BF_3-OEt_2,[5] polyphosphoric acid,[6] $CeCl_3$-NaI/SiO_2,[7] I_2,[8] $ZnCl_2$,[9] SmI_2,[10] $YbCl_3$,[11] and cerium ammonium nitrate (CAN).[12] However, many of them suffer from the drawbacks such as high temperature, drastic conditions, relatively expensive reagents, and nonenvironmental friendliness except for some methods,[13] so there is scope to explore a new, mild, efficient, and green procedure for the synthesis of 1,5-benzodiazepines. We report here a solvent-free and facile method for the synthesis of 1,5-benzodiazepines in the presence of montmorillonite K10 at room temperature.

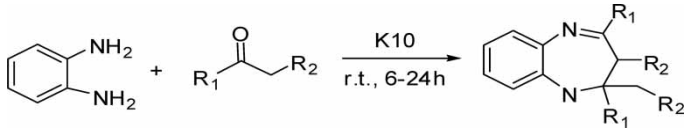
Recently, considerable attention has been devoted to heterogeneous organic transformations utilizing inorganic solid acids.[14a,b] The most obvious merit of heterogeneous catalysis is reducing the use of organic solvent.[14c] Meanwhile, organic synthesis under solvent-free conditions is of great interest in view of growing environmental awareness.[14d,e] Clay is a class of inorganic solid acids, which are cheap and have special catalytic activities for organic reactions under heterogeneous reaction conditions.[15a,b] Montmorillonite K10 is one of the most important inorganic solid acids, which has been extensively reported to promote acid-dependent reactions[15c–f] and as carrier of catalyst.[16] However, to our knowledge, there is no report on the synthesis of 1,5-benzodiazepines catalyzed by montmorillonite K10.

RESULTS AND DISCUSSION

At the initial step, *o*-phenylenediamine (1.0 mmol), acetone (2.5 mmol), and montmorillonite K10 (0.30 g) were mixed at ambient temperature; the corresponding 1,5-benzodiazepine was produced in good yield in 6 h (Scheme 1) without any by-product detected by thin-layer chromatography (TLC) analysis. Encouraged by the result, the reaction was extended to other ketones (Scheme 2), and the expected 1,5-benzodiazepines were obtained in good to excellent yields (Table 1). As shown in Table 1, the acetophenones



Scheme 1.



Scheme 2. **3a**, $R_1 = C_6H_5$, $R_2 = H$; **3b**, $R_1 = CH_3$, $R_2 = H$; **3c**, $R_1 = p\text{-Cl-}C_6H_4$, $R_2 = H$; **3d**, $R_1 = p\text{-}NO_2\text{-}C_6H_4$, $R_2 = H$; **3e**, $R_1 = p\text{-}CH_3\text{-}C_6H_4$, $R_2 = H$; **3f**, $R_1 = m\text{-}NO_2\text{-}C_6H_4$; **3g**, $R_1 = CH_3CH_2$, $R_2 = H$; and **3h**, $R_1 + R_2 = C_4H_8$.

gave good yields (83–90%), whereas 3-pentanone and cyclohexanone gave moderate yields (75% and 64%, respectively). The structures of all products were confirmed by comparison of their spectral data and the literature reported. Furthermore, X-ray analysis of compound **3c** was carried out (Fig. 1). From the packing diagram, it is obvious that there is a hydrogen bond -N-H···N- between molecules, which formed a chain in the cell unit. To our knowledge, this is the first report of the single-crystal structure of **3c**.

In conclusion, we have developed a practical, clean procedure for the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines at room temperature in the presence of montmorillonite K10. The advantages of the present protocol are mild conditions and easy workup. Furthermore, the catalyst is environmentally friendly and inexpensive.

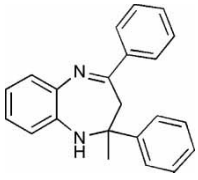
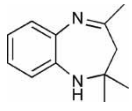
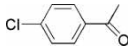
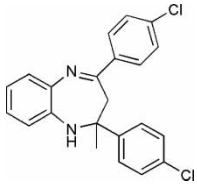
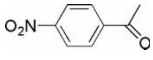
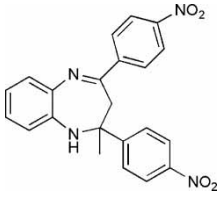
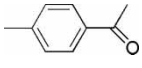
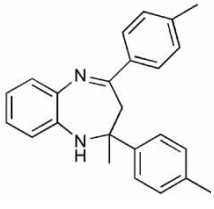
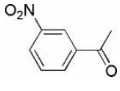
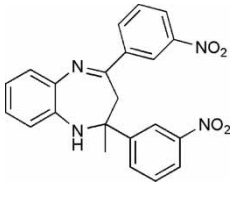
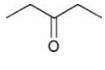
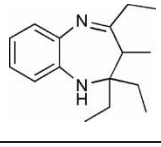
EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova-400 spectrometer, and trimethyl silane (TMS) was used as internal standard. Mass spectra were taken on a Micromass spectrometer. Elemental analyses were carried out on a Carlo Erba EA 1110-CHNOS instrument.

General Procedure for the Synthesis of 1,5-Benzodiazepine

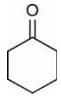
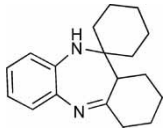
Acetone (0.15 g, 2.5 mmol) was added to a mixture of phenylenediamine (0.11 g, 1.0 mmol) and montmorillonite K10 (0.30 g). They stood still for the appropriate time. When the reaction was complete (monitored by TLC, ethyl acetate–petroleum ether (1:4, v/v) as eluent), 5 mL of acetone was added and filtered; the filtrate was evaporated to dryness. The residue was subjected to column chromatography over silica gel using petroleum ether–acetone (4:1) as eluent to afford pure **3b** (0.17 g). The recovered catalyst was washed by acetone (3 × 5 mL), activated by keeping in the oven for 2 h at 120 °C, and directly used in the next experiments.

Table 1. Synthesis of 1,5-benzodiazepines catalyzed by K10

Entry	Ketone	Product	Number	Time (h)	Yield[a] (%)
1			**3a**	24	90
2			**3b**	6	90
3			**3c**	24	87
4			**3d**	24	85
5			**3e**	24	90
6			**3f**	24	83
7			**3g**	24	75

(*continued*)

Table 1. Continued

Entry	Ketone	Product	Number	Time (h)	Yield[a] (%)
8			**3h**	10	64

[a]Isolated yield.

Spectral Data of Products

2,2-Dimethyl-4-phenyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3a): Mp 150–152 °C (lit.[9] 150–152 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.83–7.60 (m, 14H, ArH), 3.52 (s, 1H, NH), 2.96–3.15 (d, 2H, $J = 13.2$ Hz), 1.76 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.2 (C═N), 148.0, 140.5, 139.9, 130.2, 128.8, 128.5, 127.5, 126.7, 125.9, 122.1, 121.9, 74.2, 43.5, 30.3.

2,2,4-Trimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3b): Mp 136–138 °C (lit.[9] 137–138 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.12–7.14 (m, 1H, ArH), 6.96–7.01 (m, 2H, ArH), 6.72–6.74 (m, 1H, ArH), 2.97 (s, 1H, NH), 2.37 (s, 3H, CH_3), 2.22 (s, 2H, CH_2), 1.34 (s, 6H, $2CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.1 (C═N), 141.1, 138.3, 127.1, 125.9, 122.5, 122.2, 68.9, 45.4, 30.8, 30.2.

4-(4-Chlorophenyl)-2,2-dimethyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3c): Mp 147–149 °C (lit.[17] 143–144 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.84–7.53

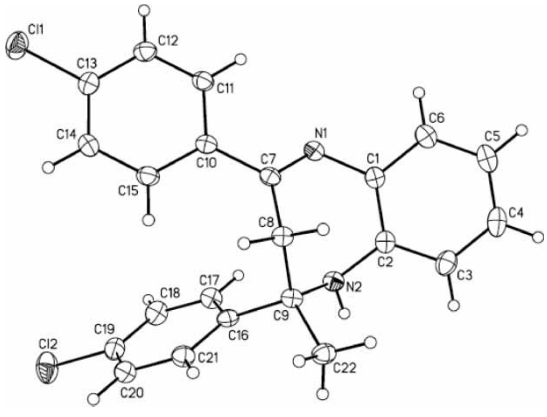


Figure 1. X-ray analysis of compound **3c**.

(m, 12H, ArH), 3.43 (s, 1H, NH), 2.87–3.09 (dd, 2H, $J_1 = 12$ Hz, $J_2 = 12.8$ Hz), 1.74 (s, 3H, CH_3).

2,2-Dimethyl-4-(4-nitrophenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine (3d): Mp 154–155 °C (lit.[12] 156–158 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.90–8.08 (m, 12H, ArH), 3.64 (s, 1H, NH), 2.99–3.32 (m, 2H, CH_2), 1.85 (s, 3H, CH_3). $C_{22}H_{18}N_4O_4$ (402.13) calcd.: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.37; H, 4.47; N, 14.01.

2,2-Dimethyl-4-*p*-tolyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3e): Mp 99–101 °C (lit.[12] 98–99 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.81–7.59 (m, 12H, ArH), 3.52 (s, 1H, NH), 2.96–3.11 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 1.74 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.1 (C=N), 145.5, 140.8, 140.5, 138.7, 137.4, 137.2, 129.5, 129.3, 129.0, 127.6, 126.6, 125.7, 122.1, 122.0, 73.9, 43.3, 30.3, 21.8, 21.4.

2,2-Dimethyl-4-(3-nitrophenyl)-2,3-dihydro-1*H*-1,5-benzodiazepine (3f): Mp 164–166 °C (lit.[17] 151–153 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.92–8.48 (m, 12H, ArH), 3.56 (s, 1H, NH), 2.99–3.28 (m, 2H, CH_2), 1.87 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.6 (C=N), 149.6, 148.7, 141.0, 139.8, 137.6, 133.0, 132.4, 130.0, 129.7, 129.4, 127.9, 124.9, 122.9, 122.7, 122.0, 121.3, 104.0, 74.6, 43.3, 37.6, 30.4. HRMS (m/z): calcd. for $C_{22}H_{18}N_4O_4$ 402.1328; found 402.1295.

2,2,4-Triethyl-3-methyl-2,3-dihydro-1*H*-1,5-benzodiazepine (3g): Mp 140–141 °C (lit.[8b] 142–144 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.59–7.34 (m, 4H, ArH), 3.85 (s, 1H, NH), 2.81–2.83 (m, 1H), 2.49–2.57 (m, 2H), 1.52–1.56 (m, 2H), 1.20–1.37 (m, 4H), 0.68–0.96 (m, 10H).

10-Spirocyclohexane-2,3,4,10,11,11a-hexahydro-1*H*-dibenzo[b,e][1,4] diazepine (3h): Mp 134–136 °C. (lit.[8b] 137–139 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.99–7.33 (m, 4H, ArH), 3.80 (br, 1H, NH), 2.87–3.24 (m, 3H), 1.55–2.75 (m, 16H). HRMS (m/z): calcd. $C_{18}H_{24}N_2$ 268.1939, found 268.1929.

Crystallographic Data for 3c

Crystals from acetone-petroleum, $C_{22}H_{18}C_{l2}N_2$, $Mr = 381.28$, monoclinic, space group $P2_1/c$, $a = 14.095(3)$, $b = 9.9845(15)$, $c = 14.859(3)$ Å, $\beta = 116.728(3)^\circ$, $V = 1867.7(6)$ Å^3, $Z = 4$, $Dc = 1.356$ g cm^{-3}, μ(Mo$K\alpha$) = 0.355 mm^{-1}. $F(000) = 792$, T = 213(2) K, crystal dimensions: 0.48 × 0.38 × 0.20 mm^3, Rigaku Mercury CCD, Mo$K\alpha$ radiation, $\lambda = 0.71070$ Å, $\theta_{max} = 25.35^\circ$, 17639 measured reflections: 3404 unique, 3103 with $I > 2\sigma(I)$. The final refinement converged to $R = 0.0432$ and $wR = 0.0940$. X-ray data has been deposited at the Cambridge Crystallographic Data Center, deposition number CCDC 621740. Copies of the data can be obtained free of charge on application to

CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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