

# Zinc montmorillonite as a reusable heterogeneous catalyst for the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepine derivatives

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## Abstract

A novel approach for the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines from *o*-phenylenediamines and structurally divergent ketones is described using zinc montmorillonite as catalyst at room temperature. The catalyst can be reused for at least three cycles with consistent activity.

**Keywords:** 2,3-Dihydro-1*H*-1,5-benzodiazepines, zinc montmorillonite, ketones, *o*-phenylenediamines

**CAUTION:** *o*-Phenylenediamines are toxic to work with and hazardous to the environment

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## Introduction

1,5-Benzodiazepine derivatives have received significant attention, and the core is indeed a “privileged scaffold” found in compounds active against a variety of target types including peptide hormones (such as CCK),<sup>1a</sup> interleukin converting enzymes (ICE)<sup>1b</sup> and potassium blockers (I<sub>k</sub>)<sup>1c</sup>. More recently, the area of biological interest of 1,5-benzodiazepines has been extended to various diseases such as cancer,<sup>2a</sup> viral infection (non-nucleoside inhibitors of HIV-1 reverse transcriptase),<sup>2b,2e</sup> cardiovascular disorders.<sup>2c-d</sup> In addition, 1,5-benzodiazepines show antidepressive, antifungal, antibacterial, antifeedant, antiinflammatory, analgesic and anticonvulsant activities.<sup>3</sup> Besides, these derivatives are also used as dyes for acrylic fibre<sup>4</sup> in photography. Moreover, 1,5-benzodiazepines are valuable synthons used for the preparation of other fused ring compounds such as triazolo-, oxadiazolo-, oxazino-, or furanobenzodiazepines.<sup>5</sup> Despite their importance from a pharmacological, industrial and synthetic point of view, comparatively few methods for their preparation are reported in the literature, a great number of which have appeared only very recently employing BF<sub>3</sub>·Et<sub>2</sub>O,<sup>6a</sup> NaBH<sub>4</sub>,<sup>6b</sup> polyphosphoric acid or SiO<sub>2</sub>,<sup>6c</sup> MgO/POCl<sub>3</sub>,<sup>6d</sup> Yb(OTf)<sub>3</sub>,<sup>6e</sup> Al<sub>2</sub>O<sub>3</sub>/P<sub>2</sub>O<sub>5</sub> or AcOH under microwave conditions,<sup>6f,g</sup> Amberlyst-15 in ionic liquid,<sup>6h</sup> CeCl<sub>3</sub>·7H<sub>2</sub>O/NaI supported on silica gel,<sup>6i</sup> InBr<sub>3</sub>,<sup>6j</sup> 1-butyl-3-methylimidazolium bromide ([bmim]Br),<sup>6k</sup> Sc(OTf)<sub>3</sub>,<sup>6l</sup> CAN,<sup>6m</sup> ZnCl<sub>2</sub> under thermal

conditions,<sup>6n</sup> AgNO<sub>3</sub>,<sup>6o</sup> sulfated zirconia,<sup>6p</sup> InCl<sub>3</sub><sup>6q</sup> as catalysts. However, many of these methods have some drawbacks such as low yields of the products,<sup>6a,b</sup> high temperatures,<sup>6c</sup> long reaction times,<sup>6c</sup> and relatively expensive catalysts.<sup>6e,i,j,l,q</sup> Therefore, the search continues for a better catalyst for the synthesis of 1,5-benzodiazepines in terms of operational simplicity, reusability, economic viability.

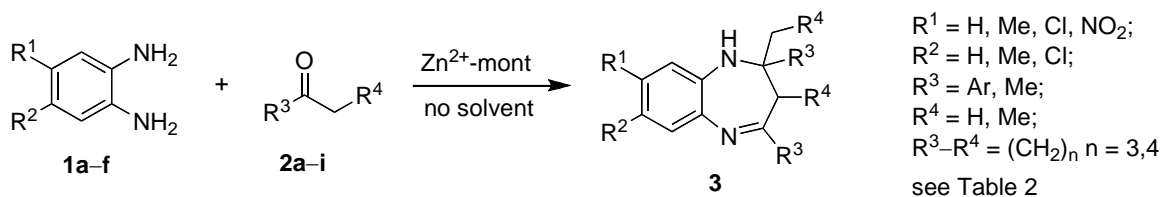
The increasing demand for cleaner processes promoted by stringent environment laws requires use of eco-friendly and selective catalysts. Use of inexpensive and non-polluting reagents is highly desirable in recent years and the use of clays as catalyst supports has received considerable attention.<sup>7</sup> Academic and industrial interest has focused on the use of acid activated montmorillonite K10-supported zinc chloride (zinc montmorillonite, Zn<sup>2+</sup>-mont); use of this remarkable material has been first reported in 1989.<sup>8</sup> Examples for Zn<sup>2+</sup>-mont-mediated organic reactions such as alkylation, preparation of 1,1-diacetates from aldehydes, hydroamination, 3-aza-Cope rearrangement etc. are well documented in the literature.<sup>9</sup>

In continuation of our interest in developing novel synthetic methodologies, particularly carbon-carbon, carbon-heteroatom bond formations,<sup>6m,10</sup> and in the use of montmorillonites as environmentally friendly reagents for organic synthesis, we undertook a study of the utility of Zn<sup>2+</sup>-mont as catalyst for the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines (Scheme 1). However, to the best of our knowledge, there are no earlier reports on the preparation of 2,3-dihydro-1*H*-1,5-benzodiazepines using Zn<sup>2+</sup>-mont to date.

## Results and Discussion

At first, we have evaluated the feasibility of the reaction of *o*-phenylenediamine (**1a**, 1 mmol) and acetophenone (**2a**, 2.2 mmol) using various zinc salts (Table 1) at ambient temperature to afford the corresponding 2,3-dihydro-1*H*-1,5-benzodiazepine **3a**. Some of the examined zinc salts worked as reasonable catalysts, e.g., ZnBr<sub>2</sub>, ZnCl<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, etc., while some salts such as zinc hydroxyapatite, Zn metal (granulated), Zn dust and ZnSO<sub>4</sub> were not effective. Notably, Zn<sup>2+</sup>-mont (Table 1, entry 8) exhibited superior catalytic activity compared to the unsupported salts such as ZnBr<sub>2</sub>, ZnCl<sub>2</sub> in terms of regeneration and ease of disposal of the used catalyst. Furthermore, the corresponding homogeneous catalyst (e.g., ZnCl<sub>2</sub>) is least preferred by the industry, because it generates problems such as environmental pollution, handling, safety, corrosion, and tedious work up.

Encouraged by these results, we studied different reaction parameters. The optimum product yield was obtained with a 1:2.2 ratio of *o*-phenylenediamines **1** to ketones **2**. No reaction was observed when *o*-phenylenediamine **1a** reacted with acetophenone **2a** under similar conditions in the absence of Zn<sup>2+</sup>-mont as promoter even after stirring for 2 days.



### Scheme 1

**Table 1.** Comparison of Zn salts as catalysts for the cyclocondensation reaction of *o*-phenylenediamine **1a** with acetophenone **2a**

| Entry | Catalyst                                | Reaction time [h] | Isolated yield (%) |
|-------|---|-------------------|--------------------|
| 1     | Zn(OAc) <sub>2</sub> ·2H <sub>2</sub> O | 24                | 35                 |
| 2     | Zn(NO <sub>3</sub> ) <sub>2</sub>       | 24                | 55                 |
| 3     | Zn(l-proline) <sub>2</sub>              | 36                | 42                 |
| 4     | ZnBr <sub>2</sub>                       | 24                | 68                 |
| 5     | Zn-hydroxyapatite                       | 24                | trace              |
| 6     | Zn (granulated)                         | 48                | 0                  |
| 7     | ZnCl <sub>2</sub>                       | 12                | 72                 |
| 8     | Zn <sup>2+</sup> -mont                  | 12                | 81                 |
| 9     | Zn (dust)                               | 48                | trace              |
| 10    | Zn(OTf) <sub>2</sub>                    | 24                | 48                 |
| 11    | ZnSO <sub>4</sub>                       | 48                | trace              |

After establishing optimized reaction conditions, we synthesized a variety of biologically relevant 2,3-dihydro-1*H*-1,5-benzodiazepines **3** using Zn<sup>2+</sup>-mont at room temperature (Table 2). In all cases, the reactions were clean and complete within 4–24 h.

Electronically divergent acetophenones **2a–e** were employed for the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines **3** in moderate to excellent yields (55–90%). Three new products **3ac**, **3ad**, and **3ae** were characterized by IR, NMR, MS and elemental analyses (see Supporting Information). Benzodiazepines **3** were the only products isolated besides starting materials. The procedure was extended to four aliphatic ketones **2f–i**. The reaction of *o*-phenylenediamines **1a–f** with acetone (**2f**) was performed under similar conditions with good yields of the corresponding 2,3-dihydro-1*H*-1,5-benzodiazepines **3af–ff** (62–80%). It is noteworthy that in the reaction with the unsymmetrical ketone 2-butanone (**2g**) ring formation occurred regioselectively forming a single product **3ag** (78%). Cyclopentanone (**2h**) and cyclohexanone (**2i**) also reacted well affording moderate yields of the corresponding fused benzodiazepines **3ah** and **3ai**, respectively. The melting points observed for products **3ah** and

**3ai** match those reported earlier<sup>6b</sup> but not those given in a recent paper.<sup>6j</sup> The catalyst could be reused for at least three cycles after activation at 120 °C for 1 h; there was a slight decrease in activity after the third use in the reaction forming **3aa** (78%). The mechanism of the reaction probably involves an intramolecular imine-enamine cyclization promoted by Zn<sup>2+</sup>-mont as already reported by Jung and coworkers when using polyphosphoric acid or silica.<sup>6c</sup>

## Conclusions

A novel and efficient method for the synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines **3** is described using the solid acid catalyst Zn<sup>2+</sup>-mont at ambient temperature. The easy work-up procedure, inexpensive recyclable catalyst and good yields make this method a valid contribution to existing methodologies.

**Table 2.** Zn<sup>2+</sup>-mont-Catalyzed synthesis of 2,3-dihydro-1*H*-1,5-benzodiazepines **3** via cyclocondensation of *o*-phenylenediamines **1** and ketones **2**

| <b>1</b> | R <sup>1</sup>  | R <sup>2</sup> | <b>2</b> | R <sup>3</sup>                    | R <sup>4</sup> | Reaction time [h] | <b>3</b>  | Yield <sup>a</sup> (%) | mp [°C] | mp lit. [°C] | lit. |
|----------|-----------------|----------------|----------|-----------------------------------|----------------|-------------------|-----------|------------------------|---------|--------------|------|
| <b>a</b> | H               | H              | <b>a</b> | Ph                                | H              | 12                | <b>aa</b> | 81 <sup>b</sup>        | 152     | 150–152      | 6l   |
| <b>a</b> | H               | H              | <b>b</b> | 4-MeC <sub>6</sub> H <sub>4</sub> | H              | 10                | <b>ab</b> | 78                     | 98–99   | 98–99        | 6m   |
| <b>a</b> | H               | H              | <b>c</b> | 4-ClC <sub>6</sub> H <sub>4</sub> | H              | 10                | <b>ac</b> | 90                     | 143–145 | –            | –    |
| <b>a</b> | H               | H              | <b>d</b> | 4-BrC <sub>6</sub> H <sub>4</sub> | H              | 16                | <b>ad</b> | 76                     | 145–146 | –            | –    |
| <b>a</b> | H               | H              | <b>e</b> | 4-IC <sub>6</sub> H <sub>4</sub>  | H              | 12                | <b>ae</b> | 55                     | 143–144 | –            | –    |
| <b>b</b> | Me              | H              | <b>a</b> | Ph                                | H              | 24                | <b>ba</b> | 75                     | 90      | 92           | 6k   |
| <b>c</b> | Me              | Me             | <b>a</b> | Ph                                | H              | 18                | <b>ca</b> | 68                     | 114     | 114–116      | 6g   |
| <b>c</b> | Me              | Me             | <b>b</b> | 4-MeC <sub>6</sub> H <sub>4</sub> | H              | 24                | <b>cb</b> | 72                     | 102–103 | 102–103      | 6m   |
| <b>d</b> | Cl              | Cl             | <b>a</b> | Ph                                | H              | 10                | <b>da</b> | 85                     | 158–160 | 158–160      | 6m   |
| <b>d</b> | Cl              | Cl             | <b>b</b> | 4-MeC <sub>6</sub> H <sub>4</sub> | H              | 12                | <b>db</b> | 66                     | 179–180 | 179–180      | 6m   |
| <b>d</b> | Cl              | Cl             | <b>c</b> | 4-ClC <sub>6</sub> H <sub>4</sub> | H              | 12                | <b>dc</b> | 82                     | 199–200 | 199–200      | 6m   |
| <b>a</b> | H               | H              | <b>f</b> | Me                                | H              | 5                 | <b>af</b> | 77                     | 121     | 120–121      | 6b   |
| <b>b</b> | Me              | H              | <b>f</b> | Me                                | H              | 7                 | <b>bf</b> | 67                     | 126     | 127–129      | 6j   |
| <b>c</b> | Me              | Me             | <b>f</b> | Me                                | H              | 8                 | <b>cf</b> | 62                     | 113     | 112–114      | 6j   |
| <b>d</b> | Cl              | Cl             | <b>f</b> | Me                                | H              | 5                 | <b>df</b> | 78                     | 92–94   | 92–94        | 6m   |
| <b>e</b> | Cl              | H              | <b>f</b> | Me                                | H              | 4                 | <b>ef</b> | 80                     | 90      | 90–92        | 6j   |
| <b>f</b> | NO <sub>2</sub> | H              | <b>f</b> | Me                                | H              | 10                | <b>ff</b> | 64                     | 116     | 113–114      | 6j   |
| <b>a</b> | H               | H              | <b>g</b> | Et                                | H              | 8.5               | <b>ag</b> | 78                     | 137     | 137–139      | 6j   |
| <b>a</b> | H               | H              | <b>h</b> | (CH <sub>2</sub> ) <sub>3</sub>   |                | 12                | <b>ah</b> | 55                     | 74      | 72–74        | 6b   |
| <b>a</b> | H               | H              | <b>i</b> | (CH <sub>2</sub> ) <sub>4</sub>   |                | 14                | <b>ai</b> | 68                     | 98      | 97–99        | 6b   |

<sup>a</sup> Isolated yields after column chromatography. <sup>b</sup> Yield after third use of the same catalyst sample: 78%.

## Experimental Section

Zn<sup>2+</sup>-mont was prepared according to the literature procedure.<sup>9d</sup> All reagents were obtained from commercial sources and used without further purification. Solvents for chromatography were distilled before use. <sup>1</sup>H and <sup>13</sup>C NMR spectra of CDCl<sub>3</sub> solutions were recorded on Varian FT-200 MHz (Gemini) and Bruker UXNMR FT-300 MHz (Avance) instruments. Electron-impact (EI) mass spectra were recorded on a VG 7070H Micromass mass spectrometer at 200 °C, 70 eV. Elemental analyses were performed by Elementar analyzer Vario EL. Melting points were recorded on an Electrothermal melting point apparatus. The IR spectra (using KBr pellets) were obtained with a Perkin Elmer 240-C instrument. The reactions were monitored by TLC using pre-coated plates (Merck, silica gel 60F-254 on glass). Column chromatography was performed using Acme silica gel (100–200 mesh).

**CAUTION:** *o*-phenylenediamines are toxic to work with and hazardous to the environment.

### Typical procedure

A mixture of an *o*-phenylenediamine **1** (1.0 mmol), a ketone **2** (2.2 mmol) and Zn<sup>2+</sup>-mont (50 mg) was vigorously stirred at room temperature for the time specified in Table 2. After completion of the reaction, the reaction mixture was diluted with ethyl acetate (5 mL), the catalyst was filtered off and washed with ethyl acetate (2×5 mL). The combined filtrates were concentrated under reduced pressure to afford the crude product **3**, which was further purified by column chromatography (silica gel; ethyl acetate/*n*-hexane 1:4). All products **3** were recrystallized from ethanol and characterized by comparison of the NMR and mass spectra with those of authentic samples.<sup>6</sup> See also Supporting Information for **3ac**, **3ad**, and **3ae**.

**2,4-Bis(4-chlorophenyl)-2-methyl-2,3-dihydro-1H-1,5-benzodiazepine (3ac).** Pale yellow crystals, mp 143–145 °C. IR (KBr):  $\tilde{\nu}$  3269, 1636, 1593, 765 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.70 (s, 3H), 2.79 (d, *J* = 13.28 Hz, 1H), 2.97 (d, *J* = 13.28 Hz, 1H), 3.25 (br s, NH, 1H), 6.68–6.75 (m, 1H), 6.92–7.02 (m, 1H), 7.12–7.20 (m, 5H), 7.38–7.52 (m, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  29.7, 42.8, 73.4, 121.4, 121.9, 126.6, 127.0, 128.2, 128.3, 128.6, 133.0, 137.5, 137.7, 139.8, 145.8, 165.9. ESI MS: *m/z* = 381 (100), 350 (9), 102 (41), 85 (5). Anal. Calc. for C<sub>22</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub> (381.30): C, 69.30; H, 4.76; N, 7.35; Found: C, 69.29; H, 4.78; N, 7.31.

**2,4-Bis(4-bromophenyl)-2-methyl-2,3-dihydro-1H-1,5-benzodiazepine (3ad).** Yellow solid, mp 145–146 °C. IR (KBr):  $\tilde{\nu}$  3325, 1640, 1589, 1198, 574 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  1.72 (s, 3H), 2.65 (br s, NH, 1H), 2.87 (d, *J* = 12.84 Hz, 1H), 3.00 (d, *J* = 13.60 Hz, 1H), 6.97–6.98 (m, 1H), 7.00–7.04 (m, 6H), 7.18–7.24 (m, 1H), 7.45–7.48 (m, 4H). EI MS: *m/z* = 470 (5), 458 (5), 350 (7.5), 313 (8.7), 273 (15), 186 (65), 173 (25), 141 (43.7), 108 (100), 80 (50), 53 (18.7). Anal. Calc. for C<sub>22</sub>H<sub>18</sub>Br<sub>2</sub>N<sub>2</sub> (470.20): C, 56.20; H, 3.86; N, 5.96; Found: C, 56.19; H, 3.89; N, 5.92.

**2,4-Bis(4-iodophenyl)-2-methyl-2,3-dihydro-1H-1,5-benzodiazepine (3ae).** Pale yellow crystals, mp 143–144 °C. IR (KBr):  $\tilde{\nu}$  3259, 1636, 1579, 462 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz,

CDCl<sub>3</sub>):  $\delta$  1.71 (s, 3H), 2.85 (d,  $J = 13.60$  Hz, 1H), 2.99 (d,  $J = 12.84$  Hz, 1H), 3.32 (br s, NH), 6.73–6.75 (m, 1H), 6.98–7.03 (m, 2H), 7.21–7.33 (m, 5H), 7.53–7.58 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  30.3, 43.4, 74.1, 93.4, 97.4, 122.1, 122.5, 127.3, 128.2, 129.2, 129.3, 137.8, 138.0, 139.4, 140.4, 147.6, 166.8. ESI MS:  $m/z = 565$  (100), 377 (20), 379 (13), 321 (38), 212 (14), 133 (53), 102 (20), 85 (16), 74 (58). Anal. Calc. for C<sub>22</sub>H<sub>18</sub>I<sub>2</sub>N<sub>2</sub> (564.20): C, 46.83; H, 3.22; N, 4.97; Found: C, 46.79; H, 3.19; N, 5.01.

### [Supplementary Information Available](#)

Proofs of evidence for Spectral data for compounds **3ac**, **3ad**, **3ae**.

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