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## Graphical Abstract

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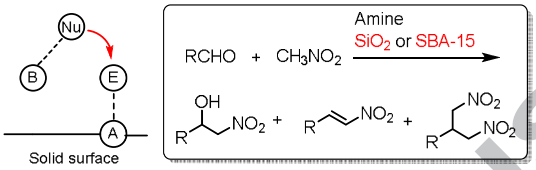

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# Base-catalyzed reactions enhanced by solid acids: Amine-catalyzed nitroaldol (Henry) reactions enhanced by silica gel or mesoporous silica SBA-15

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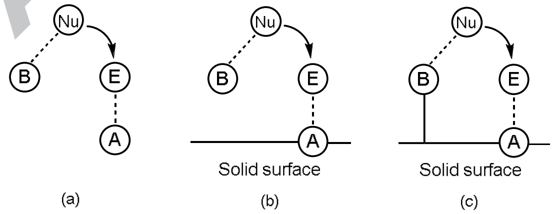
ABSTRACT

The reactions of various aldehydes with $CH_3NO_2$ catalyzed by $Et_3N$, $n\text{-}C_6H_{13}NH_2$, and $Me_2N(CH_2)_2NH_2$ were accelerated by the addition of silica gel to give aromatic (aliphatic) β-nitroalcohols, aromatic nitroalkenes, and aromatic 1,3-dinitroalkanes, respectively. Mesoporous silica SBA-15 showed higher activity than silica gel for the synthesis of aromatic nitroalkenes by the reactions of the corresponding aldehydes with $CH_3NO_2$ catalyzed by $n\text{-}C_6H_{13}NH_2$.

A weak acid can coexist with a weak base in a medium and the rate of reactions is remarkably enhanced by the coordination of the weak acid to the electrophile and the weak base to the nucleophile (Fig. 1a).[1-3] On the other hand, weak base-catalyzed reactions are largely accelerated by the addition of solid acids such as silica gel, mesoporous silica, alumina, and zeolite (Fig. 1b).[4-6] Wide ranges of base-functionalized solid acids have been reported because immobilization is more advantageous from the point of recycling of catalysts (Fig. 1c).[6-14] Although many investigations have been carried out for the reactions depicted in Figs 1a and 1c, very little attention has been paid for the reactions depicted in Fig. 1b. As an example of Fig. 1b, Kubota et al. reported the secondary amine-catalyzed aldol reactions accelerated by mesoporous silica.[4,5] They mentioned that this methodology will provide another simple and efficient way to obtain β-hydroxyketones by aldol reaction. In the experiments conducted by Motokura et al., it can been seen that the mixture of $Et_3N$ and silica-alumina significantly accelerated the Michael reaction of nitrile to α,β-unsaturated ketone.[6]



A: acid, B: base, E: electrophile, Nu: nucleophile

**Figure 1**. Types of cooperative activation by acid and base.

**Table 1**
Base-catalyzed nitroaldol reactions of **1a** in the presence of additives[a]

| Entry | Amine | Additive | Yield (%)[b] |
|---|---|---|---|
| 1 | $Et_3N$ | - | 25 |
| 2 | $Et_3N$ | $SiO_2$ | 64 |
| 3 | $Et_3N$ | $SiO_2$[c] | 71 |
| 4 | $Et_3N$ | $Al_2O_3$ | 64 |
| 5 | $Et_3N$ | Amberlite CG50 | 37 |
| 6 | $Et_3N$ | AcOH[d] | 11 |
| 7 | $Et_3N$ | $MgSO_4$ | 27 |
| 8 | $Et_3N$ | SBA-15 | 35 |
| 9 | $Et_3N$ | MCM-41 | 21 |
| 10 | $i\text{Pr}_2\text{EtN}$ | $SiO_2$ | 54 |
| 11 | Piperidine | $SiO_2$ | 53 |
| 12 | $n\text{-Bu}_2\text{NH}$ | $SiO_2$ | 46 |
| 13 | $PhCH_2NH_2$ | $SiO_2$ | 9 |
| 14 | $n\text{-}C_6H_{13}NH_2$ | $SiO_2$ | 12 |
| 15 | - | $SiO_2$ | 0 |

[a] Aldehyde **1a** (2.0 mmol), amine (0.2 mmol), additive (200 mg), $CH_3NO_2$ (2 mL), room temp, 0.5 h.
[b] Yields were determined by $^1H$ NMR with $CH_2Cl_2$ as the internal standard.
[c] Dried at 120 °C under vacuum for 6 h.
[d] AcOH (0.2 mmol) was used.

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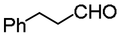
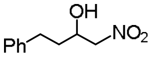
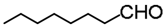
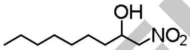
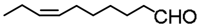
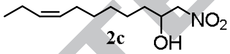
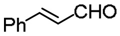
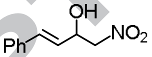
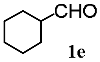
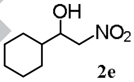
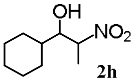
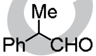
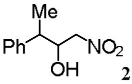
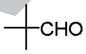
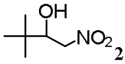
Nitroaldol (Henry) reactions are one of the most important reactions in synthetic organic chemistry which form carbon-carbon bonds.[15-17] In general, aliphatic aldehydes react with nitroalkanes catalyzed by tertially amines to give β-nitroalcohols.[12,18,19] For the reactions of aromatic aldehydes with nitroalkanes catalyzed by tertially amines and primary amines, β-nitroalcohols[20-24] and nitroalkenes are obtained,[7,8,10] respectively. The treatment of ketones with nitroalkanes catalyzed by $H_2N(CH_2)_2NH_2$[25] or $Me_2N(CH_2)_2NH_2$[26] leads to allylic nitro compounds. It was reported that aromatic aldehydes reacted in nitromethane in the presence of both primary and tertially amines-immobilized silica-alumina to give 1,3-dinitroalkanes.[27] β-Nitroalcohols, nitroalkenes, allylic nitro compounds, and 1,3-dinitroalkanes are known to be important synthetic intermediates.

Although numerous amine-immobilized solid acids have been devised for many reactions such as nitroaldol reactions and aldol reactions,[7-10,12-14] different kinds of amine-immobilized solid acids must be synthesized using silane coupling agents (most of them are expensive) for each reaction followed by the determination of nitrogen contents. It was reported that the yields of products decreased on recycling in some cases because of the decomposition of the amine moiety.[28] In this paper, we wish to report that simple physical mixing of various amines and solid acids such as silica gel and mesoporous silica SBA-15 is useful for nitroaldol reactions in which some kinds of amines are required for the synthesis of different types of products.

**Table 2**

$Et_3N$-catalyzed nitroaldol reactions of aliphatic aldehydes **1** enhanced by $SiO_2$[a]

| Entry | Substrate | Time (h) | Product | Yield (%)[b] |
|---|---|---|---|---|
| 1 |  **1a** | 2 |  **2a** | 99 |
| 2[c] | | 96 | | 73 |
| 3[d] | | 96 | | 40 |
| 4[e] | | 96 | | 11 |
| 5 |  **1b** | 3 |  **2b** | 95 |
| 6 |  **1c** | 3 |  **2c** | 99 |
| 7 |  **1d** | 3 |  **2d** | 83 |
| 8 |  **1e** | 6 |  **2e** | 96 |
| 9[f] | | 6 |  **2h** | 80[g] |
| 10 |  **1f** | 5 |  **2f** | 96[h] |
| 11 |  **1g** | 96 |  **2g** | 83 |

[a] Aldehyde **1** (2.0 mmol), $Et_3N$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2 mL), room temp.

[b] Isolated yields.

[c] Aldehyde **1** (2.0 mmol), $Et_3N$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), toluene (4 mL), room temp.

[d] Aldehyde **1** (2.0 mmol), $Et_3N$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), EtOH (4 mL), room temp.

[e] Aldehyde **1** (2.0 mmol), $Et_3N$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), THF (4 mL), room temp.

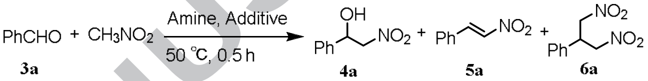
[f] $CH_3CH_2NO_2$ (2mL) was used instead of $CH_3NO_2$.

[g] The *anti* : *syn* ratio of **2h** determined by $^1$H-NMR analysis was 46 : 54.

[h] The *anti* : *syn* ratio of **2f** determined by $^1$H-NMR analysis was 80 : 20.

First, we examined nitroaldol reactions of 3-phenylpropanal (**1a**) catalyzed by various amines in the presence of some additives at room temperature for 0.5 h in $CH_3NO_2$. The results are shown in Table 1. When $Et_3N$ was employed, the addition of silica gel or alumina largely increased the yields of 1-nitro-4-phenyl-2-butanol (**2a**) (entries 1, 2, and 4). The use of dried silica gel increased the yield of **2a** to some extent (entry 3). We employed silica gel without drying in order to simplify the recycling procedure in the present study. The addition of Amberlite CG50 (methacrylic resin, hydrogen form) and SBA-15 resulted in the small increase of the yields of **2a** (entries 5 and 8). When MCM-41 was employed, the yield of **2a** did not increase (entry 9). The reactions catalyzed by primary amines such as $PhCH_2NH_2$ and $n$-$C_6H_{13}NH_2$ were very slow (entries 13 and 14). In the absence of amines, the reaction did not occur (entry 15).

During the reactions, adsorption of amines such as $Et_3N$ and $n$-$C_6H_{13}NH_2$ by silica gel, alumina, SBA-15, and MCM-41 was observed,[29] which was confirmed by $^1$H-NMR spectroscopy and TLC of the filtrate. In the cases of SBA-15 and MCM-41, $Et_3N$ and $n$-$C_6H_{13}NH_2$ completely disappeared in the filtrate. The adsorbed $Et_3N$ and $n$-$C_6H_{13}NH_2$ were recovered by the elution of the solid acids with toluene, EtOAc, and acetone.



**3a** **4a** **5a** **6a**

**Table 3**

Base-catalyzed nitroaldol reactions of **3a** in the presence of additives[a]

| Entry | amine | Additive | Yield (%)[b] | | |
|---|---|---|---|---|---|
| | | | **4a** | **5a** | **6a** |
| 1 | $Et_3N$ | - | 15 | 0 | 0 |
| 2 | $Et_3N$ | $SiO_2$ | 59 | 0 | 10 |
| 3 | $Et_3N$ | $Al_2O_3$ | 29 | 0 | 0 |
| 4 | $Et_3N$ | Amberlite CG50 | 14 | 0 | 0 |
| 5 | $Et_3N$ | AcOH[c] | 2 | 0 | 0 |
| 6 | $Et_3N$ | $MgSO_4$ | 12 | 0 | 0 |
| 7 | $Et_3N$ | SBA-15 | 19 | 0 | 0 |
| 8 | $Et_3N$ | MCM-41 | 10 | 0 | 0 |
| 9 | - | $SiO_2$ | 0 | 0 | 0 |
| 10 | $i$Pr$_2$EtN | $SiO_2$ | 52 | 0 | 8 |
| 11 | Piperidine | $SiO_2$ | 35 | 8 | 6 |
| 12 | $n$-Bu$_2$NH | $SiO_2$ | 40 | 19 | 5 |
| 13 | $PhCH_2NH_2$ | $SiO_2$ | 0 | 46 | 0 |
| 14 | $n$-$C_6H_{13}NH_2$ | $SiO_2$ | 0 | 72 | 0 |
| 15 | $n$-$C_6H_{13}NH_2$ | - | 0 | 33 | 0 |
| 16 | $n$-$C_6H_{13}NH_2$ | $Al_2O_3$ | 4 | 51 | 0 |
| 17 | $n$-$C_6H_{13}NH_2$ | Amberlite CG50 | 0 | 35 | 0 |
| 18 | $n$-$C_6H_{13}NH_2$ | AcOH[c] | 0 | 58 | 0 |
| 19 | $n$-$C_6H_{13}NH_2$ | $MgSO_4$ | 0 | 35 | 0 |
| 20 | $n$-$C_6H_{13}NH_2$ | SBA-15 | 0 | 88 | 0 |
| 21 | $n$-$C_6H_{13}NH_2$ | MCM-41 | 0 | 80 | 0 |

[a] Aldehyde **3a** (2.0 mmol), amine (0.2 mmol), additive (200 mg), $CH_3NO_2$ (2 mL), 50 °C, 0.5 h.

[b] Yields were determined by $^1$H NMR with acetone as the internal standard.

[c] AcOH (0.2 mmol) was used.

Next, various aliphatic aldehydes **1a-g** involving **1c** and **1d** which possess the double bond in a molecule were treated with a catalytic amount of $Et_3N$ in the presence of silica gel at room temperature in $CH_3NO_2$ to give the corresponding β-nitroalcohols **2a-g** in good to excellent yields (Table 2). The order of reactivities of aldehydes was primary > secondary > tertially. It was possible to apply $CH_3CH_2NO_2$ to the reaction of **1e** to give compound **2h** in good yield (entry 9). When 1.1 equiv. of $CH_3NO_2$ was used in toluene, EtOH, or THF, the reactions proceeded quite slowly (entries 2-4).

Table 3 summarizes the results for nitroaldol reactions of benzaldehyde (**3a**) catalyzed by various amines in the presence of some additives at 50 °C for 0.5 h in $CH_3NO_2$. The addition of silica gel to $Et_3N$-catalyzed nitroaldol reactions remarkably increased the yield of 2-nitro-1-phenylethanol (**4a**) (entries 1 and 2). When mesoporous silica SBA-15 and MCM-41 were used, significant increases in the yields of **4a** were not observed (entries 7 and 8). In the absence of $Et_3N$, the reaction did not occur at all (entry 9). On the other hand, the use of primary amines such as $PhCH_2NH_2$ and $n$-$C_6H_{13}NH_2$ gave nitroalkene **5a** (entries 13 and 14). When SBA-15 and MCM-41 were added, the reactions proceeded faster than that of silica gel (entries 14, 20, and 21). It is noteworthy that SBA-15 and MCM-41 accelerated the reactions catalyzed by $n$-$C_6H_{13}NH_2$, whilst they did not enhance the rates of the reactions by $Et_3N$. It might be attributed to the steric hindrance between $Et_3N$ and weakly acidic sites[29] of mesoporous silica although the detailed mechanism is not clear at the present time. Interestingly, AcOH was effective for the formation of **5a** catalyzed by $n$-$C_6H_{13}NH_2$ (entry 18). It was reported that $NH_4OAc$ was a good catalyst for the synthesis of aromatic nitroalkenes[30]

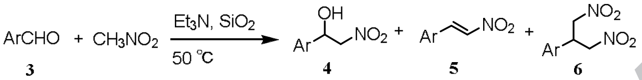


**Table 4**
$Et_3N$-catalyzed nitroaldol reactions of aromatic aldehydes **3** enhanced by $SiO_2$[a]

| Entry | Ar | Time (h) | Yield (%)[b] | | |
|---|---|---|---|---|---|
| | | | **4** | **5** | **6** |
| 1 | Ph (**3a**) | 2 | 80 | 2 | 13 |
| 2[c] | | 17 | 0 | 18 | 8 |
| 3 | 4-$ClC_6H_5$ (**3b**) | 1 | 81 | 0 | 11 |
| 4 | 2-$ClC_6H_5$ (**3c**) | 0.5 | 97 | 0 | 0 |
| 5 | 4-$BrC_6H_5$ (**3d**) | 1 | 78 | 0 | 14 |
| 6 | 4-$NCC_6H_5$ (**3e**) | 0.5 | 89 | 0 | 9 |
| 7 | 4-$O_2NC_6H_5$ (**3f**) | 0.5 | 93 | 0 | 7 |
| 8 | 4-$MeC_6H_5$ (**3g**) | 3 | 63 | 1 | 18 |
| 9[c] | | 17 | 0 | 0 | 7 |
| 10[d] | | 17 | 9 | 0 | 3 |
| 11[e] | | 17 | 8 | 0 | 0 |
| 12[f] | | 24 | 46 | 0 | 0 |
| 13 | 2-Naphthyl (**3h**) | 3 | 64 | 0 | 19 |
| 14 | 4-$MeOC_6H_5$ (**3i**) | 6 | 31 | 0 | 20 |
| 15[g] | | 64 | 38 | 4 | 16 |

[a] Aldehyde **3** (2.0 mmol), $Et_3N$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2 mL), 50 °C.
[b] Isolated yields.
[c] Aldehyde **3** (2.0 mmol), $Et_3N$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), toluene (4 mL), 90 °C.
[d] Aldehyde **3** (2.0 mmol), $Et_3N$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), EtOH (4 mL), 75 °C.
[e] Aldehyde **3** (2.0 mmol), $Et_3N$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), THF (4 mL), 60 °C.
[f] Aldehyde **3** (2.0 mmol), $Et_3N$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), 50 °C (neat conditions).
[g] Without $SiO_2$.

Table 4 shows the results for nitroaldol reactions of various aromatic aldehydes catalyzed by $Et_3N$ enhanced by silica gel at 50 °C in $CH_3NO_2$. The reactions of compounds **3a-f** gave the corresponding β-nitroalcohols **4a-f** in good yields, respectively (entries 1 and 3-7). In the cases of **3g-i** which possess electron-donating substituents on the benzene ring or possess the naphthalene ring, compounds **4g-i** were obtained in moderate to low yields with the formation of 18-20% of 1,3-dinitroalkanes **6g-i** (entries 8, 13, and 14). 1,3-Dinitroalkanes **6** were reported to form *via* Michael addition of $CH_3NO_2$ to **5** catalyzed by tertially amines such as $Et_3N$.[31,32] When 1.1 equiv. of $CH_3NO_2$ was used in toluene, EtOH, or THF, the reactions proceeded quite slowly (entries 2 and 9-11).

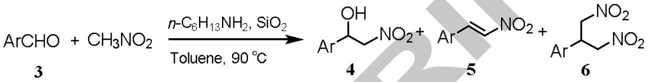


**Table 5**
$n$-$C_6H_{13}NH_2$-catalyzed nitroaldol reactions of aromatic aldehydes **3** enhanced by $SiO_2$ or SBA-15[a]

| Entry | Ar | Time (h) | Yield (%)[b] | | |
|---|---|---|---|---|---|
| | | | **4** | **5** | **6** |
| 1[c] | Ph (**3a**) | 1.5 | 4 | 80 | 14 |
| 2 | | 4 | 0 | 90 | 0 |
| 3[d] | | 4 | 0 | 0 | 0 |
| 4[e] | | 2 | 0 | 91 | 0 |
| 5[f] | | 10 | 0 | 45 | 0 |
| 6[g] | | 10 | 0 | 0 | 0 |
| 7[c] | 4-$ClC_6H_5$ (**3b**) | 1 | 4 | 81 | 1 |
| 8 | | 4 | 0 | 82 | 0 |
| 9[e] | | 2 | 0 | 83 | 0 |
| 10 | 2-$ClC_6H_5$ (**3c**) | 3 | 0 | 93 | 0 |
| 11[c] | 4-$O_2NC_6H_5$ (**3f**) | 4 | 49 | 25 | 24 |
| 12 | | 8 | 0 | 87 | 0 |
| 13[e] | | 6 | 0 | 80 | 0 |
| 14 | 4-$F_3CC_6H_5$ (**3j**) | 10 | 0 | 85 | 0 |
| 15[c] | 4-$MeC_6H_5$ (**3g**) | 3 | 0 | 61 | 35 |
| 16 | | 6 | 0 | 80 | 3 |
| 17[c] | 4-$MeOC_6H_5$ (**3i**) | 3 | 0 | 37 | 46 |
| 18 | | 6 | 0 | 84 | 4 |
| 19[e] | | 3 | 0 | 99 | 0 |
| 20 | 2-Thienyl (**3k**) | 6 | 0 | 80 | 4 |
| 21 | 2-Furyl (**3l**) | 6 | 0 | 90 | 0 |
| 22[e] | | 3 | 0 | 89 | 0 |

[a] Aldehyde **3** (2.0 mmol), $n$-$C_6H_{13}NH_2$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), toluene (4 mL), 90 °C.
[b] Isolated yields.
[c] Aldehyde **3** (2.0 mmol), $n$-$C_6H_{13}NH_2$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2 mL), 50 °C.
[d] Without $SiO_2$.
[e] SBA-15 (200 mg) was used instead of $SiO_2$
[f] Aldehyde **3** (2.0 mmol), $n$-$C_6H_{13}NH_2$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), EtOH (4 mL), 75 °C.
[g] Aldehyde **3** (2.0 mmol), $n$-$C_6H_{13}NH_2$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2.2 mmol), THF (4 mL), 60 °C.

We investigated the reactions of various aromatic aldehydes **3** catalyzed by $n$-$C_6H_{13}NH_2$ enhanced by silica gel at 50°C in $CH_3NO_2$ (Table 5). Because the yields of nitroalkenes **5** decreased in some cases (entries 11, 15, and 17), we carried out the reactions using 1.1 equiv. of $CH_3NO_2$ at 90 °C in toluene. Toluene was a superior solvent than EtOH and THF (entries 2, 5, and 6). Nitroalkenes **5** were obtained in good yields for all examined cases in toluene (entries 2, 8, 10, 12, 14, 16, 18, 20, and 21). Without silica gel, compound **5** was not obtained at all (entry 3). When SBA-15 was used in toluene, the reactions proceeded faster than those of silica gel to give **5** in good yields in every case (entries 2, 4, 8, 9, 12, 13, 18, 19, 21, and 22).

As shown in Table 6, the use of $Me_2N(CH_2)_2NH_2$ in the presence of silica gel at 50°C for 1 h in $CH_3NO_2$ led to the main formation of 1,3-dinitroalkane **6a** (entry 1). In this case, the $NH_2$ group of $Me_2N(CH_2)_2NH_2$ would catalyze the formation of compound **5a** from **3a** *via* **4a**. The $Me_2N$ group would promote the formation of compound **4a** from **3a** and compound **6a** from **5a**.[31,32] Because $Me_2N(CH_2)_2NH_2$ possesses both $NH_2$ and $Me_2N$ groups in a molecule, compound **6a** could become the major product. In the absence of silica gel, the reaction was considerably slow (entry 2). When $Et_3N$ and $n$-$C_6H_{13}NH_2$ were employed instead of $Me_2N(CH_2)_2NH_2$, lower yield (55%) of **6a** compared to that of $Me_2N(CH_2)_2NH_2$ (73%) was obtained accompanied by 21 and 15% yields of compounds **4a** and **5a**, respectively (entry 3). The addition of SBA-15 and MCM-41 resulted in the lower yields of **6a** than that of silica gel (entries 1, 4, and 5).

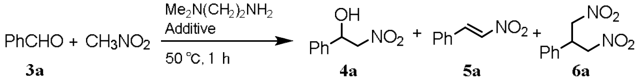


**Table 6**

$Me_2N(CH_2)_2NH_2$-catalyzed reactions of **3a** in the presence of solid supports[a]

| Entry | Additive | Yield (%)[b] | | |
|---|---|---|---|---|
| | | **4a** | **5a** | **6a** |
| 1 | $SiO_2$ | 0 | 23 | 73 |
| 2[c] | - | 18 | 32 | 18 |
| 3[d] | $SiO_2$ | 21 | 15 | 55 |
| 4 | SBA-15 | 0 | 55 | 43 |
| 5 | MCM-41 | 0 | 53 | 46 |

[a] Aldehyde **3a** (2.0 mmol), $Me_2N(CH_2)_2NH_2$ (0.2 mmol), additive (200 mg), $CH_3NO_2$ (2 mL), 50 °C, 1h.

[b] Yields were determined by $^1H$ NMR with acetone as the internal standard..

[c] **3a** was recovered in 30%.

[d] $Et_3N$ (0.2 mmol) and $n$-$C_6H_{13}NH_2$ (0.2 mmol) were used instead of $Me_2N(CH_2)_2NH_2$.

Table 7 shows the results for $Me_2N(CH_2)_2NH_2$-catalyzed reactions of various aromatic aldehydes enhanced by silica gel at 50°C in $CH_3NO_2$. Aromatic aldehydes **3a**, **3g-i**, **3k**, and **3l** were converted into the corresponding 1,3-dinitroalkanes **6a**, **6g-i**, **6k**, and **6l** in good yields, respectively (entries 1 and 5-9). Compounds **6** are known to be important building blocks for various functionalized compounds such as 1,3-diamines, heterocycles, and carbohydrate derivatives, and furthermore, for biologically active substrates involving HIV-protease activity inhibitors and NMDA receptor antagonists.[31] In the cases of **3b** and **3f** which possess electron-withdrawing groups on the benzene ring, the yields of **6b** and **6f** were low because of the formation of β-nitroalcohols **4b** and **4f**, respectively (entries 3 and 4). The decrease in the yields of **6b** and **6f** has been also reported in the case of both primary and tertially amines-immobilized silica-alumina.[27]

Silica gel and SBA-15 could be recycled five times without any significant loss of activities for the synthesis of compounds **2a** and **4a**-**6a** (see Supplementary data).

In conclusion, we clarified that the amine-catalyzed nitroaldol reactions were largely accelerated by the addition of silica gel or SBA-15. Although it is impossible to reuse amines, solid acids can be recycled without significant loss of activity. The synthesis of different types of amine-functionalized solid acids is unnecessary for each reaction. Various kinds of amines and solid acids can be employed easily depending on an individual purpose. The procedure will be applied for various base-catalyzed organic transformations as well as nitroaldol reactions and furthermore, it is especially useful in laboratories.

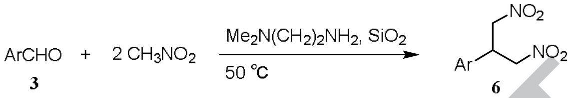


**Table 7**

$Me_2N(CH_2)_2NH_2$-catalyzed reactions of aromatic aldehydes **3** enhanced by $SiO_2$[a]

| Entry | Ar | Time (h) | Yield (%)[b] |
|---|---|---|---|
| 1 | Ph (**3a**) | 4 | 75 |
| 2[c] | | 24 | 22[d] |
| 3 | 4-$ClC_6H_5$ (**3b**) | 24 | 32[e] |
| 4 | 4-$O_2NC_6H_5$ (**3f**) | 24 | 11[f] |
| 5 | 4-$MeC_6H_5$ (**3g**) | 4 | 77 |
| 6 | 2-Naphthyl (**3h**) | 4 | 75 |
| 7 | 4-$MeOC_6H_5$ (**3i**) | 8 | 72 |
| 8 | 2-$MeOC_6H_5$ (**3l**) | 8 | 70 |
| 9 | 2-Thienyl (**3k**) | 8 | 70 |

[a] Aldehyde **3** (2.0 mmol), $Me_2N(CH_2)_2NH_2$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (2 mL), 50 °C.

[b] Isolated yields.

[c] Aldehyde **3** (2.0 mmol), $Me_2N(CH_2)_2NH_2$ (0.2 mmol), $SiO_2$ (200 mg), $CH_3NO_2$ (4.4 mmol), toluene (4 mL), 90 °C.

[d] Compound **5a** was obtained in 47% yield

[e] Compound **4b** was obtained in 26% yield

[f] Compound **4f** was obtained in 56% yield

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## Supplementary data

Supplementary data (general experimental procedures, data of IR and NMR spectra of the products, and recycle experiments) associated with this article can be found, in the online version.

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**Highlights**

* Amine-catalyzed nitroaldol reactions were accelerated by silica gel or SBA-15.

* SBA-15 showed higher activity than silica gel for the synthesis of nitroalkenes.

* Various kinds of amines and solid acids can be easily employed.