# Acidic Alumina as a Useful Heterogeneous Catalyst in the Michael Reaction of β-Dicarbonyl Derivatives with Conjugated Nitroalkenes

Roberto Ballini,*[a] Raimondo Maggi,[b] Alessandro Palmieri,[a] Giovanni Sartori[b]

[a] Green Chemistry Group, Dipartimento di Scienze Chimiche, Università, Via S. Agostino 1, 62032 Camerino (MC), Italy
Fax +39(0737)402297; E-mail: roberto.ballini@unicam.it

[b] Clean Synthetic Methodologies Group, Dipartimento di Chimica Organica e Industriale, Università, Consorzio Interuniversitario 'La Chimica per l'Ambiente' (INCA), UdR di Parma 2, Viale G.P. Usberti 17A, 43100 Parma, Italy

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**Abstract:** Addition of a variety of 1,3-dicarbonyl derivatives to conjugated nitroalkenes was efficiently performed under heterogeneous catalysis by acidic alumina in the presence of a minimum amount of solvent ($Et_2O$, 0.5 mL/mmol). The procedure allows satisfactory to good yields of a diastereomeric mixture (~1:1) of polyfunctionalized adducts. Moreover, work-up can be avoided since the reaction mixture can be directly charged into a chromatographic column for immediate purification.

**Key words:** acidic alumina, conjugated nitroalkenes, Michael reaction, heterogeneous catalysis, eco-friendly synthesis

Nitro-olefins are excellent Michael acceptors owing to both their low propensity for 1,2-addition and to the strong anion-stabilizing ability of the nitro group. Furthermore, the conjugate addition of 1,3-dicarbonyl derivatives to electron-poor alkenes is one of the best strategies for the formation of new C–C bonds. In this context, nitroalkenes, thanks to the electron-withdrawing power of the nitro group[1] and to the possibility of converting the nitro group into other functionalities,[2] provides access to polyfunctionalized derivatives that are useful building blocks for the synthesis of important nitrogen-containing bioactive agrochemical and pharmaceutical compounds.[3]

Usually, the conjugate addition of 1,3-dicarbonyl derivatives to nitro-olefins is performed in a homogeneous solution of the reactants in an organic solvent using soluble catalysts;[4] the use of AgOTf–$PPh_3$ complex in water as reaction medium,[5] and of a polymer-anchored metal catalyst in highly toxic solvents such as dioxane or chloroform,[6] have also been reported.

In recent years, a range of heterogeneous catalysts have successfully been used to carry out various chemical transformations; however, environmental and economical constraints mean that there is still an urgent need to redesign and improve these important processes. In this framework, heterogeneous catalysis plays a fundamental role.[7]

During our studies on the application of heterogeneous catalysts for fine chemical preparation,[8,9] we found that acidic alumina, in a minimum amount of diethyl ether, constitutes a new and convenient heterogeneous catalyst that is able to promote the conjugate addition of β-dicarbonyl compounds **1** to nitroalkenes **2**.

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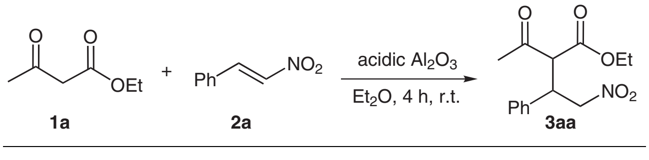
In order to find optimum conditions for the reaction, we investigated a range of substrate-to-catalyst ratios using the addition of ethyl acetoacetate (**1a**) to β-nitrostyrene (**2a**) as a model. As reported in Table 1, the best result (91% yield) was obtained using an alumina-to-substrate ratio of 0.5.

**Table 1** Effect of Catalyst-to-Substrate Ratio on the Preparation of **3aa**



| Ratio of $A1_2O_3$ (g) to **1a** (mmol) | Yield (%)[a] |
|---|---|
| 0.4 | 88 |
| 0.5 | 91 |
| 0.6 | 89 |

[a] Yield of pure, isolated **3aa**.

A number of different dicarbonyl derivatives **1** and nitro-olefins **2** were chosen in order to assess the reaction conditions. All reactions were carried out by mixing stoichiometric amounts of starting material (1 mmol) and acidic $Al_2O_3$ (0.5 g), in the presence of a minimum amount of diethyl ether (0.5 mL/mmol) in order to favor the mixing of **1** with **2**, since the starting materials were predominantly solid compounds. The reactions proceeded in satisfactory to good yields (46–91%), at room temperature, in short reaction times (usually 2–4 h, see Table 2).

Compounds **3** were obtained as diastereomeric mixtures (~1:1) and, although β-keto esters **1a** and **1b** seem to be more reactive than the 1,3-diketones **1c** and **1d**, a variety of both dicarbonyl derivatives **1** and conjugated nitroalkenes **2** (aliphatics, aromatics and heteroaromatics) could be efficiently employed under these mild acidic conditions. Finally, we addressed the problem of catalyst recycling: at the end of the reaction of **1a** with **2a**, the mixture was extracted with ethyl acetate, filtered and washed with ethyl acetate. The catalyst was dried and reused with comparable yields (1st cycle: 91%, 2nd cycle: 88%, 3rd cycle:

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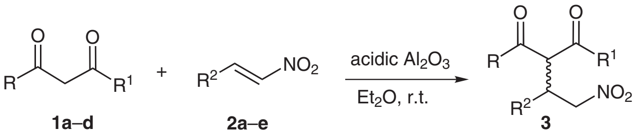
**Table 2** Conjugate Addition of β-Dicarbonyl Derivatives to Conjugated Nitroalkenes



| β-Dicarbonyl derivative **1** | | | Nitroalkene **2** | | Product | Time (h) | Yield (%)[a] |
|---|---|---|---|---|---|---|---|
| R | $R^1$ | | $R^2$ | | | | |
| Me | EtO | **1a** | Ph | **2a** | **3aa** | 4 | 91 |
| Me | EtO | **1a** | $p$-$ClC_6H_4$ | **2b** | **3ab** | 4 | 80 |
| Me | EtO | **1a** | $p$-$NO_2C_6H_4$ | **2c** | **3ac** | 4 | 75 |
| Me | EtO | **1a** | 2-furyl | **2d** | **3ad** | 3 | 87 |
| Me | EtO | **1a** | $n$-$C_5H_{11}$ | **2e** | **3ae** | 4 | 62 |
| Ph | EtO | **1b** | 2-furyl | **2d** | **3bd** | 3 | 88 |
| Ph | EtO | **1b** | $n$-$C_5H_{11}$ | **2e** | **3be** | 4 | 62 |
| Me | Me | **1c** | Ph | **2a** | **3ca** | 2 | 84 |
| Me | Me | **1c** | $p$-$ClC_6H_4$ | **2b** | **3cb** | 4 | 60 |
| Me | Me | **1c** | $p$-$NO_2C_6H_4$ | **2c** | **3cc** | 3 | 46 |
| Me | Me | **1c** | 2-furyl | **2d** | **3cd** | 2 | 64 |
| Ph | Me | **1d** | Ph | **2a** | **3da** | 3 | 84 |
| Ph | Me | **1d** | $p$-$NO_2C_6H_4$ | **2c** | **3dc** | 4 | 57 |

[a] Yield of pure, isolated product **3**.

84%). The slightly decrease in yield upon repeated use, is probably ascribable to a gradual deposition of tar compounds on the catalyst surface which, after three cycles, begins to hamper access of the substrate to the catalytic sites.

In conclusion, we have reported an eco-friendly, heterogeneous methodology for the Michael-addition of β-dicarbonyl derivatives to nitro-olefins. This procedure works well using a minimum amount of solvent (diethyl ether) and affords, in satisfactory to good yields, the corresponding Michael adducts without the need for any quenching or extraction; the reaction mixture can be directly charged, after evaporation of the solvent, into a chromatography column for immediate purification.

**Table 3** Spectroscopic Data of Michael Adducts **3**

| Compd | IR (nujol, $cm^{-1}$) | $^1H$ NMR (400 MHz, $CDCl_3$) | $^{13}C$ NMR (100 MHz, $CDCl_3$) | Elemental analysis |
|---|---|---|---|---|
| **3aa**<br>solid<br>diastereomeric mixture | 1563, 1737 | 0.99 (t, $J$ = 7.3 Hz, 1.5 H), 1.27 (t, $J$ = 7.3 Hz, 1.5 H), 2.05 (s, 1.5 H), 2.29 (s, 1.5 H), 3.96 (q, $J$ = 7.3 Hz, 1 H), 4.02 (d, $J$ = 9.4 Hz, 0.5 H), 4.11 (d, $J$ = 9.8 Hz, 0.5 H), 4.14–4.29 (m, 2 H), 4.74 (d, $J$ = 6.4 Hz, 1 H), 4.79–4.85 (m, 1 H), 7.15–7.22 (m, 2 H), 7.24–7.38 (m, 3 H) | 13.9, 14.2, 30.3, 30.6, 42.5, 42.8, 61.8, 62.1, 62.2, 62.5, 78.0, 78.1, 128.1, 128.2, 128.5, 128.6, 129.2, 129.4, 136.6, 136.7, 167.1, 167.7, 200.6, 201.4 | Anal. Calcd for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.13; N, 5.02<br>Found: C, 60.89; H, 6.41; N, 4.78 |
| **3ab**<br>solid<br>diastereomeric mixture | 1560, 1720 | 1.04 (t, $J$ = 7.3 Hz, 1.5 H), 1.27 (t, $J$ = 7.3 Hz, 1.5 H), 2.09 (s, 1.5 H), 2.30 (s, 1.5 H), 3.94–4.02 (m, 1.5 H), 4.07 (d, $J$ = 9.8 Hz, 0.5 H), 4.13–4.27 (m, 2 H), 4.66–4.86 (m, 2 H), 7.12–7.18 (m, 2 H), 7.26–7.31 (m, 2 H) | 13.9, 14.2, 30.3, 30.5, 41.8, 42.0, 61.7, 61.9, 62.3, 62.6, 77.7, 77.9, 129.3, 129.4, 129.5, 129.6, 134.4, 134.5, 135.1, 135.2, 166.8, 167.5, 200.1, 201.0 | Anal. Calcd for $C_{14}H_{16}ClNO_5$: C, 53.60; H, 5.14; N, 4.46<br>Found: C, 53.98; H, 5.45; N, 4.19 |

**Table 3** Spectroscopic Data of Michael Adducts **3** (continued)

| Compd | IR (nujol, cm$^{-1}$) | $^1$H NMR (400 MHz, $CDCl_3$) | $^{13}$C NMR (100 MHz, $CDCl_3$) | Elemental analysis |
|---|---|---|---|---|
| **3ac**<br>solid<br>diastereomeric mixture | 1561, 1726 | 1.05 (t, *J* = 7.3 Hz, 1.8 H), 1.28 (t, *J* = 7.3 Hz, 1.2 H), 2.14 (s, 1.2 H), 2.33 (s, 1.8 H), 3.99 (dq, *J* = 1.3, 7.3 Hz, 1.2 H), 4.04 (d, *J* = 9.4 Hz, 0.4 H), 4.13 (d, *J* = 9.8 Hz, 0.6 H), 4.24 (dq, *J* = 1.3, 7.3 Hz, 0.8 H), 4.28–4.41 (m, 1 H), 4.77 (d, *J* = 6.5 Hz, 1.2 H), 4.84–4.90 (m, 0.8 H), 7.39–7.45 (m, 2 H), 8.14–8.20 (m, 2 H) | 14.0, 14.2, 30.3, 30.5, 42.0, 42.1, 61.5, 61.6, 62.6, 62.9, 77.1, 77.4, 124.3, 124.5, 129.3, 129.4, 144.2, 144.4, 147.9, 149.7, 166.5, 167.2, 199.6, 200.5 | Anal. Calcd for $C_{14}H_{16}N_2O_7$: C, 51.85; H, 4.97; N, 8.64<br>Found: C, 54.38; H, 5.30; N, 8.21 |
| **3ad**<br>viscous oil<br>diastereomeric mixture | 1559, 1741[a] | 1.17 (t, *J* = 7.3 Hz, 1.5 H), 1.27 (t, *J* = 7.3 Hz, 1.5 H), 2.16 (s, 1.5 H), 2.29 (s, 1.5 H), 4.04–4.27 (m, 3 H), 4.28–4.39 (m, 1 H), 4.77–4.83 (m, 2 H), 6.16–6.19 (m, 1 H), 6.26–6.30 (m, 1 H), 7.31–7.34 (m, 1 H) | 14.1, 14.2, 30.1, 30.6, 36.5, 36.6, 59.6, 59.9, 62.4, 62.5, 75.8, 75.9, 108.5, 108.8, 110.8, 110.9, 142.8, 142.9, 149.9, 150.1, 167.1, 167.5, 200.5, 201.1 | Anal. Calcd for $C_{12}H_{15}NO_6$: C, 53.53; H, 5.62; N, 5.20<br>Found: C, 53.31; H, 5.32; N, 5.51 |
| **3ae**<br>oil<br>diastereomeric mixture | 1563, 1737[a] | 0.81–0.90 (m, 3 H), 1.18–1.47 (m, 11 H), 2.28 (s, 1.5 H), 2.29 (s, 1.5 H), 2.76–2.92 (m, 1 H), 3.72 (d, *J* = 6.4 Hz, 0.5 H), 3.76 (d, *J* = 7.7 Hz, 0.5 H), 4.17–4.25 (m, 2 H), 4.41–4.71 (m, 2 H) | 14.1, 14.2, 22.5, 22.6, 26.5, 26.6, 29.6, 30.2, 31.6, 31.7, 36.6, 36.7, 60.2, 60.6, 62.1, 62.2, 76.1, 76.7, 168.2, 168.3, 202.0, 202.2 | Anal. Calcd for $C_{13}H_{23}NO_5$: C, 57.13; H, 8.48; N, 5.12<br>Found: C, 57.41; H, 8.80; N, 4.88 |
| **3bd**<br>viscous oil<br>diastereomeric mixture | 1563, 1722[a] | 1.03–1.09 (m, 1.5 H), 1.14–1.20 (m, 1.5 H), 3.97–4.07 (m, 1 H), 4.13–4.20 (m, 1 H), 4.48–4.65 (m, 1 H), 4.79–4.84 (m, 1 H), 4.92–5.03 (m, 2 H), 6.10–6.19 (m, 1 H), 6.21–6.30 (m, 1 H), 7.20–7.23 (m, 0.5 H), 7.31–7.35 (m, 0.5 H), 7.42–7.52 (m, 2 H), 7.55–7.65 (m, 1 H), 7.91–7.96 (m, 1 H), 7.98–8.04 (m, 1 H) | 14.0, 14.1, 37.2, 37.3, 54.2, 55.1, 62.3, 62.4, 75.9, 76.0, 108.8, 108.9, 110.7, 128.8, 128.9, 129.0, 129.1, 134.1, 134.4, 135.8, 135.9, 142.7, 142.9, 149.9, 150.0, 167.2, 167.5, 192.8, 193.0 | Anal. Calcd for $C_{17}H_{17}NO_6$: C, 61.63; H, 5.17; N, 4.23<br>Found: C, 61.88; H, 5.41; N, 4.01 |
| **3be**<br>oil<br>diastereomeric mixture | 1554, 1718[a] | 0.81–0.91 (m, 3 H), 1.12–1.52 (m, 11 H), 2.96–3.09 (m, 1 H), 4.11–4.24 (m, 2 H), 4.56–4.68 (m, 2 H), 4.70–4.80 (m, 1 H), 7.47–7.53 (m, 2 H), 7.56–7.65 (m, 1 H), 7.92–8.02 (m, 2 H) | 14.2, 22.6, 26.6, 26.7, 29.5, 30.3, 31.6, 31.7, 37.3, 37.4, 54.6, 55.3, 61.7, 62.2, 76.5, 76.7, 128.9, 129.0, 129.1, 129.2, 134.2, 134.3, 136.2, 136.3, 168.4, 168.5, 194.1, 194.5 | Anal. Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18<br>Found: C, 64.01; H, 7.19; N, 4.42 |
| **3ca**<br>solid<br>mp 110–112 °C | 1560, 1738 | 1.92 (s, 3 H), 2.27 (s, 3 H), 4.18–4.27 (m, 1 H), 4.36 (d, *J* = 10.7 Hz, 1 H), 4.60–4.64 (m, 2 H), 7.15–7.20 (m, 2 H), 7.24–7.35 (m, 3 H) | 29.8, 30.7, 43.0, 70.9, 78.4, 128.1, 128.8, 129.5, 136.2, 201.3, 202.0 | Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62<br>Found: C, 62.90; H, 6.29; N, 5.29 |
| **3cb**<br>solid<br>mp 125–127 °C | 1567, 1733 | 1.96 (s, 3 H), 2.28 (s, 3 H), 4.18–4.26 (m, 1 H), 4.32 (d, *J* = 11.1 Hz, 1 H), 4.58–4.61 (m, 2 H), 7.12 (d, *J* = 8.5 Hz, 2 H), 7.30 (d, *J* = 8.5 Hz, 2 H) | 29.9, 30.6, 42.3, 70.6, 78.1, 129.5, 129.7, 134.6, 134.7, 200.8, 201.6 | Anal. Calcd for $C_{13}H_{14}ClNO_4$: C, 55.04; H, 4.97; N, 4.94<br>Found: C, 55.47; H, 5.19; N, 4.77 |
| **3cc**<br>solid<br>mp 128–130 °C | 1566, 1727 | 1.98 (s, 3 H), 2.29 (s, 3 H), 4.17–4.28 (m, 1 H), 4.33 (d, *J* = 10.9 Hz, 1 H), 4.56–4.62 (m, 2 H), 7.38–7.44 (m, 2 H), 8.13–8.22 (m, 2 H) | 30.0, 30.5, 42.4, 70.7, 78.0, 124.4, 129.4, 144.5, 148.1, 200.8, 201.6 | Anal. Calcd for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80; N, 9.52<br>Found: C, 52.78; H, 4.51; N, 9.81 |
| **3cd**<br>waxy solid | 1570, 1732 | 2.06 (s, 3 H), 2.25 (s, 3 H), 4.28–4.40 (m, 2 H), 4.64 (d, *J* = 5.6 Hz, 2 H), 6.13–6.16 (m, 1 H), 6.26–6.29 (m, 1 H), 7.32–7.34 (m, 1 H) | 30.1, 31.4, 37.4, 68.6, 76.6, 109.6, 111.6, 143.6, 150.3, 201.6, 202.2 | Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48; N, 5.86<br>Found: C, 55.49; H, 5.77; N, 5.59 |

**Table 3** Spectroscopic Data of Michael Adducts **3** (continued)

| Compd | IR (nujol, cm$^{-1}$) | $^1$H NMR (400 MHz, CDCl$_3$) | $^{13}$C NMR (100 MHz, CDCl$_3$) | Elemental analysis |
|---|---|---|---|---|
| **3da** solid diastereomeric mixture | 1571, 1728 | 1.92 (s, 1.8 H), 2.21 (s, 1.2 H), 4.38–4.46 (m, 0.4 H), 4.48–4.56 (m, 0.6 H), 4.62–4.71 (m, 1 H), 4.75 (dd, *J* = 4.2, 13.2 Hz, 0.6 H), 4.83 (dd, *J* = 8.5, 12.8 Hz, 0.4 H), 5.14–5.21 (m, 1 H), 7.11–7.20 (m, 2 H), 7.23–7.36 (m, 3 H), 7.38–7.44 (m, 0.8 H), 7.46–7.52 (m, 1.2 H), 7.53–7.58 (m, 0.4 H), 7.60–7.65 (m, 0.6 H), 7.78–7.82 (m, 0.8 Hz), 7.98–8.03 (m, 1.2 H) | 28.7, 30.0, 43.5, 43.6, 64.9, 65.6, 78.3, 78.4, 128.2, 128.3, 128.4, 128.8, 129.1, 129.2, 129.3, 129.5, 134.3, 134.7, 136.2, 136.3, 136.5, 136.7, 194.0, 194.3, 201.1, 201.9 | Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50<br>Found: C, 70.01; H, 5.79; N, 4.28 |
| **3dc** solid diastereomeric mixture | 1569, 1722 | 1.94 (s, 1.8 H), 2.22 (s, 1.2 H), 4.36–4.44 (m, 0.4 H), 4.46–4.61 (m, 0.6 H), 4.63–4.87 (m, 2 H), 5.14–5.21 (m, 1 H), 7.37–7.42 (m, 2 H), 7.43–7.53 (m, 2 H), 7.57–7.68 (m, 1 H), 7.91–8.07 (m, 2 H), 8.15–8.24 (m, 2 H) | 28.8, 30.1, 43.4, 43.6, 64.8, 65.5, 78.4, 78.5, 124.5, 124.6, 128.6, 128.7, 128.8, 128.9, 129.3, 129.5, 133.3, 133.4, 136.7, 136.8, 144.4, 144.6, 147.9, 148.1, 194.1, 194.3, 200.9, 201.7 | Anal. Calcd for $C_{18}H_{16}N_2O_6$: C, 60.67; H, 4.53; N, 7.86<br>Found: C, 61.01; H, 4.74; N, 7.55 |

[a] The IR spectra of compounds **3ad**, **3ae**, **3bd** and **3be** were obtained under neat conditions.

$^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ at 400 MHz and 100 MHz, respectively, on a Varian Mercury Plus 400 spectrometer. Chemical shifts are expressed in ppm downfield from TMS. IR spectra were collected on a Perkin-Elmer FT-IR Paragon 500 spectrometer. Elemental analyses were performed using a C, H, N Analyzer model 185 from Hewlett-Packard. All reactions were monitored by TLC.

### General Procedure

To a stirred solution of β-dicarbonyl compound **1** (1 mmol) and nitroalkene **2** (1 mmol) in Et$_2$O (0.5 mL), acidic alumina (0.5 g) was added. The resulting heterogeneous mixture was stirred at r.t. for the selected time (see Table 2). After evaporation of the solvent under vacuum, the system was charged directly into a silica gel column (cyclohexane–EtOAc) to give the pure product **3**.

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