Supporting Information

**Kinetic measurements used to determine the nucleophilicity  
of mesoionic pyridine-derived olefins in THF**

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**Data storage system:**

Folder and file names AEM-xxx refer to individual experiments and are identical to those in this Supporting Information.

The folders contain

* txt files with absorbance vs. time data [raw data]
* exp files used for the *k*obs determination [evaluated data]
* pdf files with results of the *k*obs determination [evaluated data].

**Kinetics**

The kinetics of reactions of **1a** with different electrophiles (structures are shown in Figure S1) in anhydrous THF were monitored by stopped-flow UV/vis spectrophotometry on an Applied Photophysics SX.20 instrument. In all measurements, the decrease of the absorption of **1a** at 625 nm was followed. The temperature of the drive syringes, the flow circuit, and the observation cell was maintained constant at 20 °C (± 0.2 °C) by use of a circulating bath cryostat. All solutions were prepared in flame-dried Schlenk tubes under an atmosphere of dry argon.



**Figure S1**. Electrophiles employed in the kinetic studies.

**1a** + diethyl 2-(4-cyanobenzylidene)malonate (**3a**)

*AEM-643*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [**3a**]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 4.00 × 10-3 | 6.94 × 101 |
| 1.00 × 10-3 | 6.00 × 10-3 | 1.03 × 102 |
| 1.00 × 10-3 | 8.00 × 10-3 | 1.33 × 102 |
| 1.00 × 10-3 | 1.00 × 10-2 | 1.68 × 102 |
| *k*2 = 1.63 × 104 M-1 s-1 | | |

**1a** + diethyl 2-benzylidenemalonate (**3b**)

*AEM-513*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [**3b**]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 1.00 × 10-2 | 1.13 × 101 |
| 1.00 × 10-3 | 2.00 × 10-2 | 1.89 × 101 |
| 1.00 × 10-3 | 3.00 × 10-2 | 2.68 × 101 |
| 1.00 × 10-3 | 4.00 × 10-2 | 3.35 × 101 |
| 1.00 × 10-3 | 6.00 × 10-2 | 5.25 × 101 |
| *k*2 = 8.17 × 102 M-1 s-1 | | |

**1a** + diethyl 2-(4-methylbenzylidene)malonate (**3c**)

*AEM-512*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [**3c**]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 1.00 × 10-2 | 5.32 × 100 |
| 1.00 × 10-3 | 2.00 × 10-2 | 1.04 × 101 |
| 1.00 × 10-3 | 3.00 × 10-2 | 1.48 × 101 |
| 1.00 × 10-3 | 4.00 × 10-2 | 1.85 × 101 |
| 1.00 × 10-3 | 6.00 × 10-2 | 2.74 × 101 |
| *k*2 = 4.35 × 102 M-1 s-1 | | |

**1a** + diethyl 2-(4-methoxybenzylidene)malonate (**3d**)

*AEM-509*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [**3d**]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 1.00 × 10-2 | 2.74 × 100 |
| 1.00 × 10-3 | 2.00 × 10-2 | 5.08 × 100 |
| 1.00 × 10-3 | 3.00 × 10-2 | 8.82 × 100 |
| 1.00 × 10-3 | 4.00 × 10-2 | 1.09 × 101 |
| 1.00 × 10-3 | 6.00 × 10-2 | 1.75 × 101 |
| *k*2 = 2.96 × 102 M-1 s-1 | | |

**1a** + diethyl 2-(4-dimethylaminobenzylidene)malonate (**3e**)

*AEM-631*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [**3e**]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 3.57 × 10-2 | 1.36 × 100 |
| 1.00 × 10-3 | 7.14 × 10-2 | 2.63 × 100 |
| 1.00 × 10-3 | 1.07 × 10-1 | 4.32 × 100 |
| 1.00 × 10-3 | 1.43 × 10-1 | 5.56 × 100 |
| 1.00 × 10-3 | 1.79 × 10-1 | 6.62 × 100 |
| *k*2 = 3.75 × 101 M-1 s-1 | | |

**1a** + acrylonitrile (ACN)

*AEM-629; [a] only one kinetic run each.*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [ACN]0 (M) | *k*obs (s-1)[a] |
| 1.00 × 10-3 | 5.00 × 10-3 | 8.20 × 101 |
| 1.00 × 10-3 | 1.10 × 10-2 | 1.90 × 102 |
| 1.00 × 10-3 | 1.40 × 10-2 | 2.45 × 102 |
| 1.00 × 10-3 | 1.70 × 10-2 | 3.04 × 102 |
| *k*2 = 1.84 × 104 M-1 s-1 | | |

**1a** + *N*,*N*-diphenylcarbodiimide (PhNCNPh)

*AEM-528*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [PhNCNPh]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 5.00 × 10-3 | 9.04 × 100 |
| 1.00 × 10-3 | 2.00 × 10-2 | 3.76 × 101 |
| 1.00 × 10-3 | 3.00 × 10-2 | 5.90 × 101 |
| 1.00 × 10-3 | 4.00 × 10-2 | 8.30 × 101 |
| *k*2 = 2.10 × 103 M-1 s-1 | | |

**1a** + *tert*-butyl acrylate (**5**)

*AEM-525*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [**5**]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 1.00 × 10-2 | 1.43 × 101 |
| 1.00 × 10-3 | 2.00 × 10-2 | 3.30 × 101 |
| 1.00 × 10-3 | 3.00 × 10-2 | 4.94 × 101 |
| 1.00 × 10-3 | 4.00 × 10-2 | 6.90 × 101 |
| 1.00 × 10-3 | 5.00 × 10-2 | 8.92 × 101 |
| *k*2 = 1.86 × 103 M-1 s-1 | | |

**1a** + ethyl cinnamate (**4**)

*AEM-515*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [**4**]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 1.00 × 10-1 | 9.34 × 100 |
| 1.00 × 10-3 | 2.00 × 10-1 | 1.68 × 101 |
| 1.00 × 10-3 | 3.00 × 10-1 | 2.52 × 101 |
| *k*2 = 7.93 × 101 M-1 s-1 | | |

**1a** + cinnamonitrile (**11**)

*AEM-630*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [CMN]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 1.20 × 10-1 | 8.04 × 100 |
| 1.00 × 10-3 | 2.40 × 10-1 | 1.64 × 101 |
| 1.00 × 10-3 | 3.60 × 10-1 | 2.45 × 101 |
| 1.00 × 10-3 | 4.80 × 10-1 | 3.29 × 101 |
| 1.00 × 10-3 | 6.00 × 10-1 | 3.89 × 101 |
| *k*2 = 6.52 × 101 M-1 s-1 | | |