

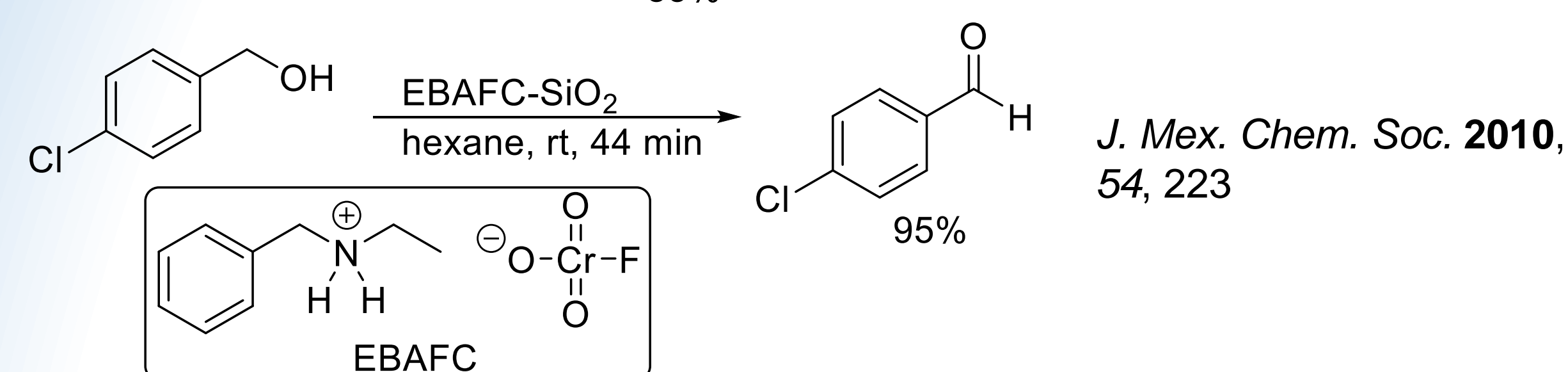
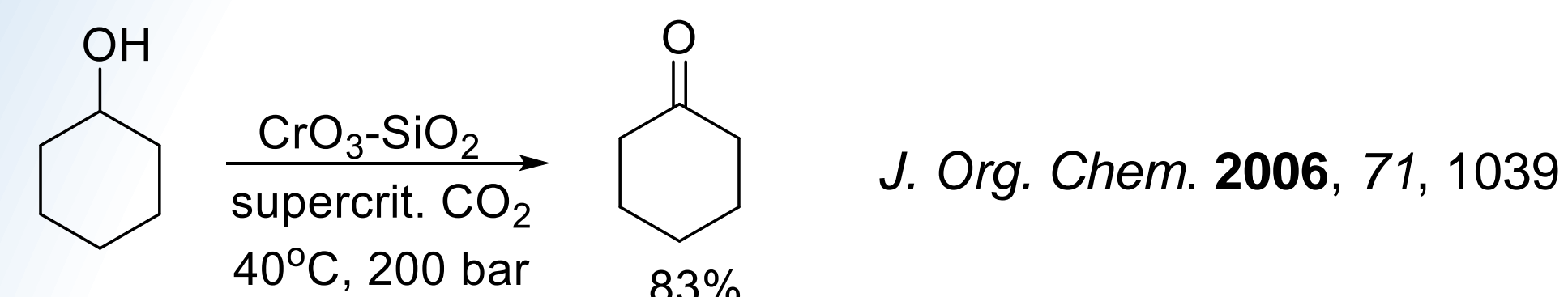
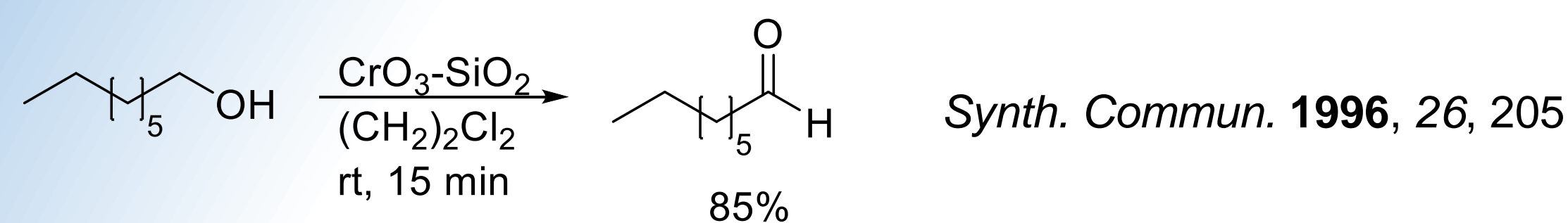
# The Other SiO<sub>2</sub>: Investigating Oxidation of Alcohols using (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in Sand

John Lepore, Emily Toy, Dr. Robert Torregrosa

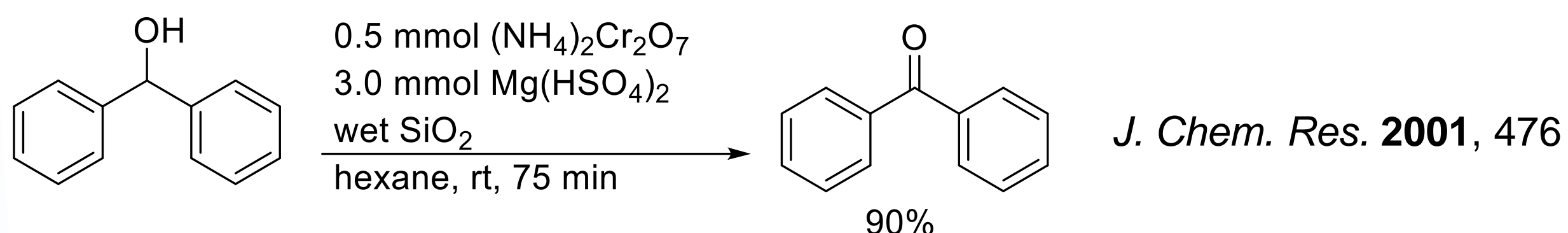
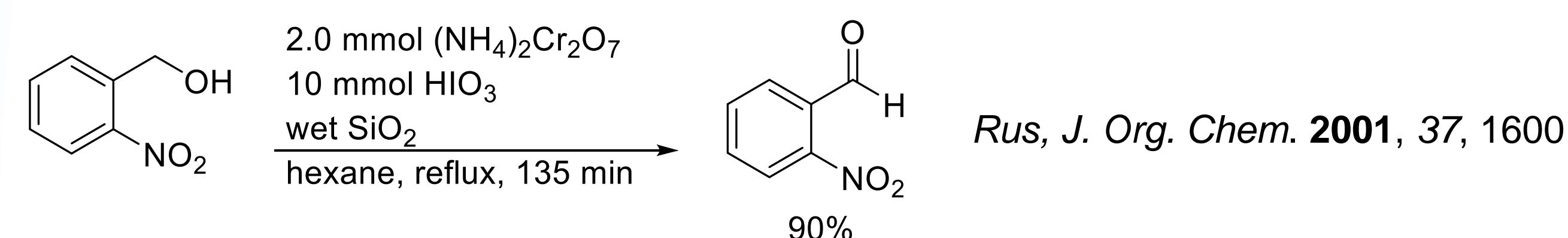
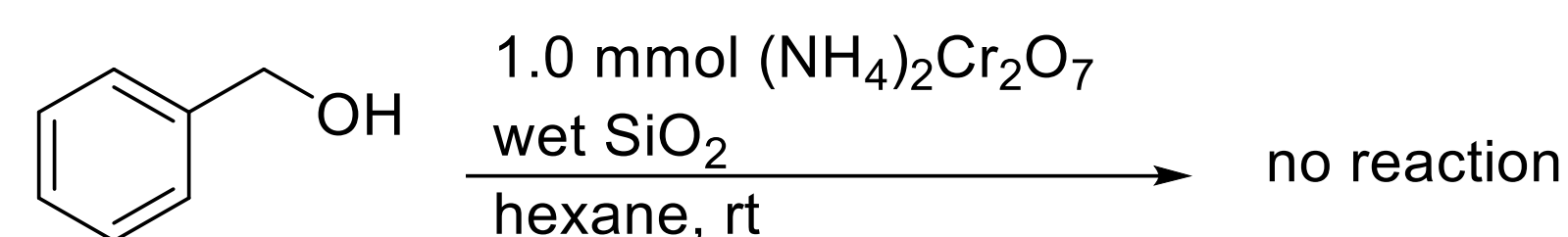
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## Background

Oxidation of primary and secondary alcohols to aldehydes and ketones in the presence of Cr(VI)-based reagents supported in silica gel.

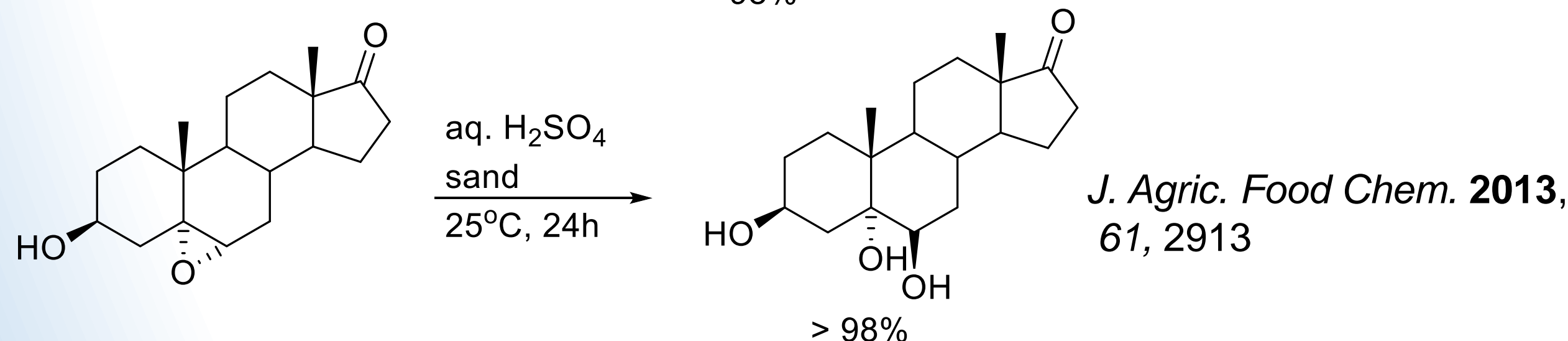
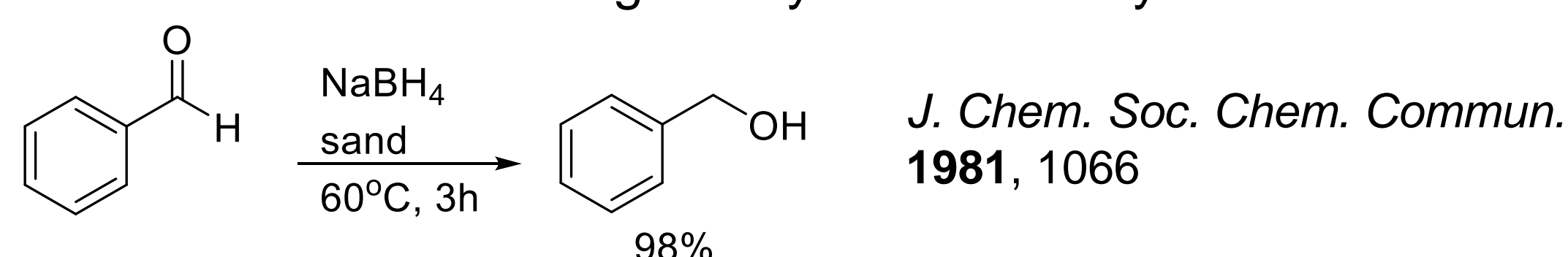


The use of (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in wet silica gel affords products when stoichiometric additives are used.

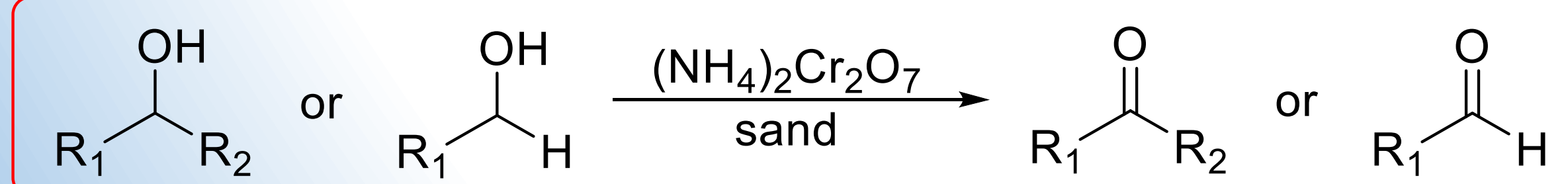


## From silica gel to sand... same SiO<sub>2</sub>

Utilization of sand in organic synthesis is very limited.



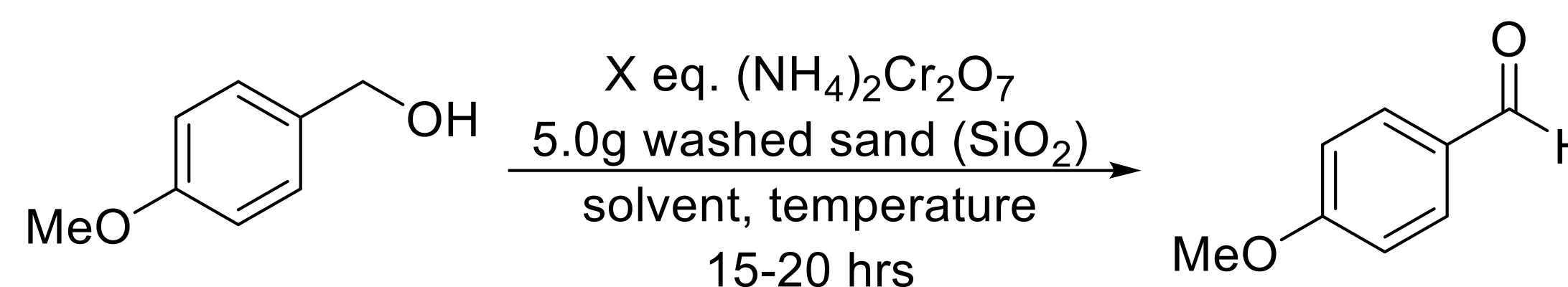
## Exploring Cr-based Oxidation Reactions In the Presence of Sand



- Sand is cheaper (\$32.00/500 g – Fisher) than silica gel (\$698.00/500g – Fisher).
- Sand is less harmful than silica gel (known irritant).
- Sand is abundant in nature and has many practical uses such as geology and construction.
- Sand does not affect separation of mixtures in column chromatography unlike silica gel.
- Sand is not difficult to handle and easily accessible.
- Sand is also SiO<sub>2</sub> and should possess similar characteristic profile and activity just like silica gel.

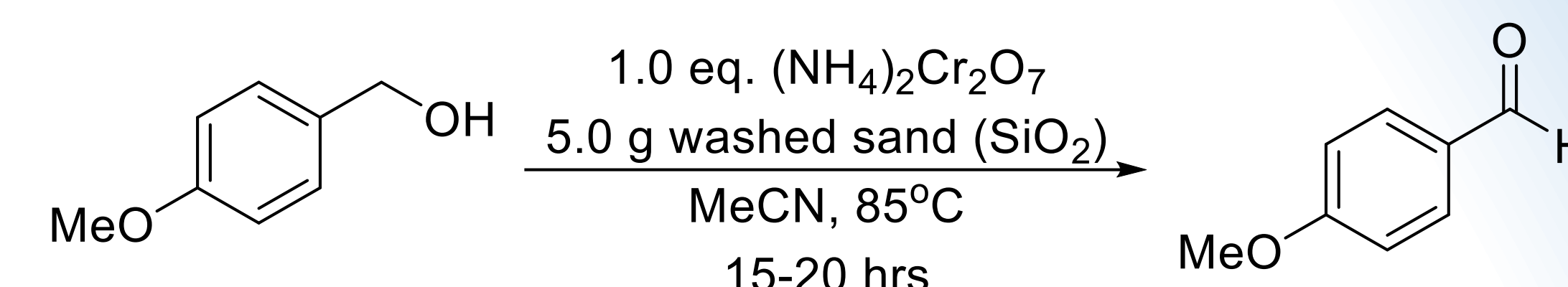
## Method Development

### Part 1: Reaction Conditions



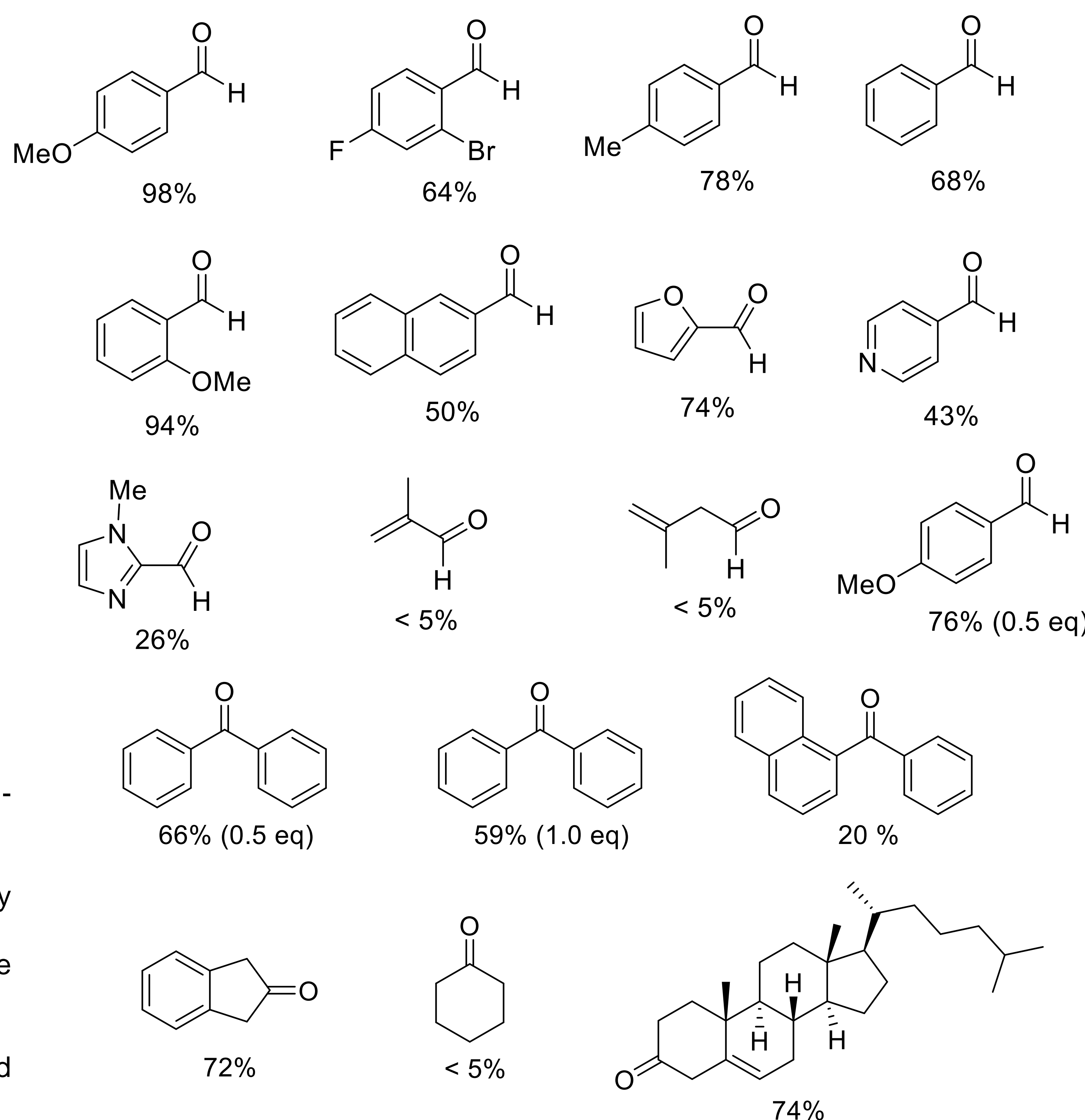
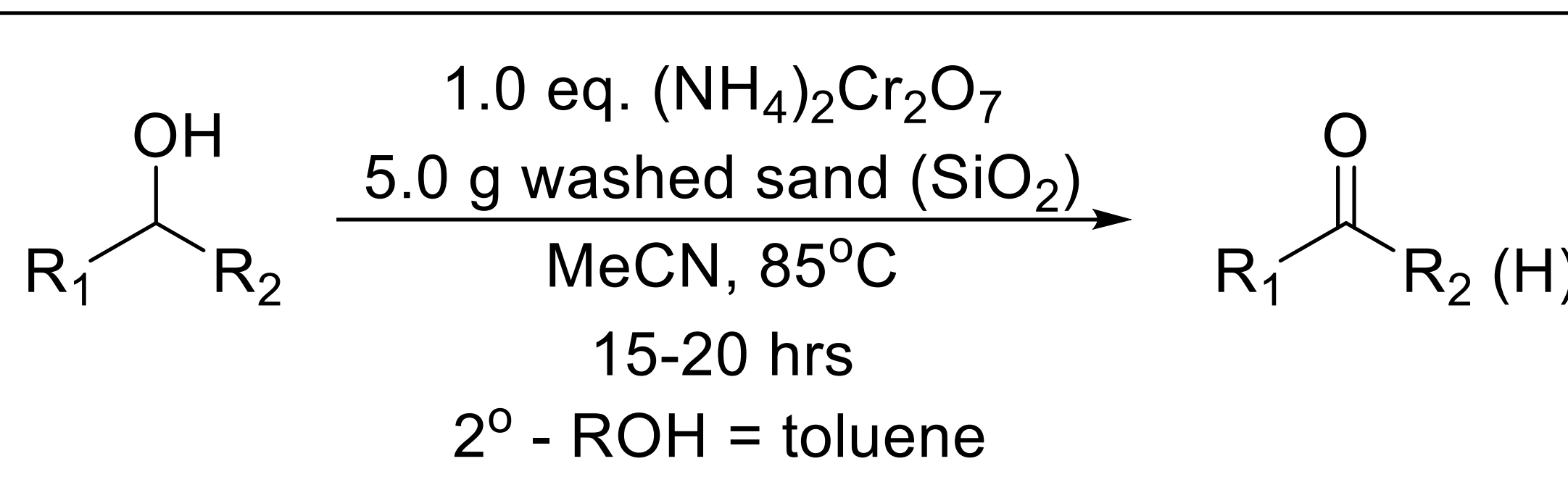
|   | X   | solvent                         | Temp (°C) | % Conversion ( <sup>1</sup> H-NMR) |
|---|-----|---------------------------------|-----------|------------------------------------|
| 1 | 1.0 | CH <sub>2</sub> Cl <sub>2</sub> | 25        | 2                                  |
| 2 | 1.0 | CH <sub>2</sub> Cl <sub>2</sub> | 45        | 16                                 |
| 3 | 1.0 | THF                             | 60        | 51                                 |
| 4 | 1.0 | MeCN                            | 85        | >98                                |
| 5 | 1.0 | toluene                         | 110       | 78                                 |
| 6 | 1.0 | benzene                         | 80        | 20                                 |
| 7 | 2.0 | CH <sub>2</sub> Cl <sub>2</sub> | 50        | 5                                  |
| 8 | 2.5 | MeCN                            | 85        | R-CHO + R-CO <sub>2</sub> H        |

### Part 2: Experiment Conditions

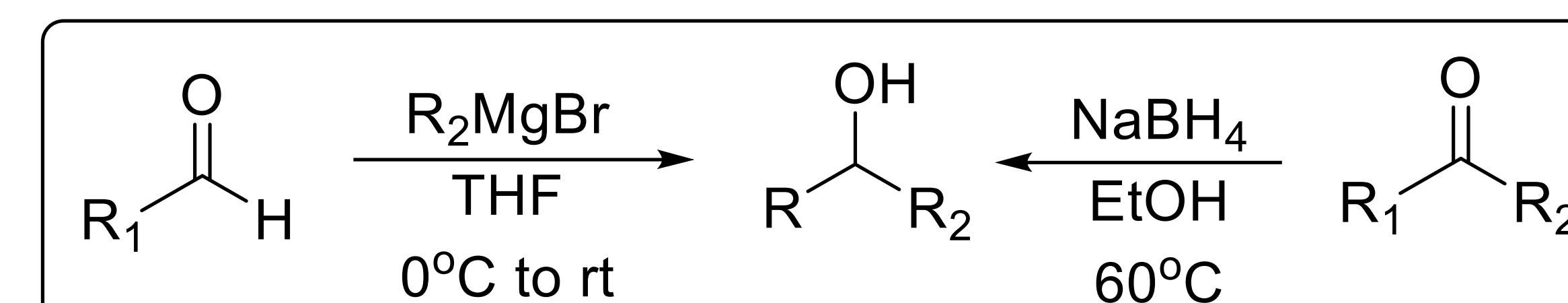


|   | Experiment Conditions  | % Conversion ( <sup>1</sup> H-NMR) |
|---|--|------------------------------------|
| 1 | switched to Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>                               | 67                                 |
| 2 | used 10 g sand   | >98                                |
| 3 | used 1.0 g sand  | 91                                 |
| 4 | equal amounts of sand and (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> | 79                                 |
| 5 | “activating” Cr-SiO <sub>2</sub> mixture for 4 hrs at 100°C                              | 81                                 |
| 6 | no sand added  | R-CHO + R-CO <sub>2</sub> H        |
| 7 | with 5 drops of conc. HCl  | R-CHO + R-CO <sub>2</sub> H        |
| 8 | switched to silica gel   | 72                                 |

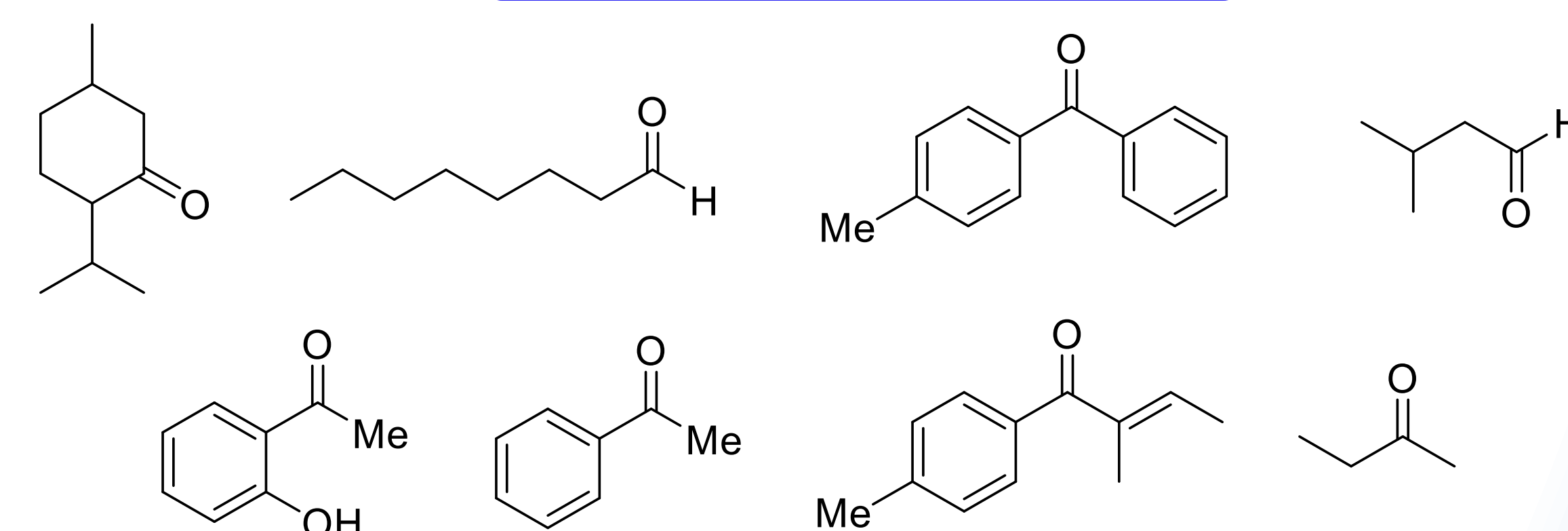
## Substrate Scope



## Preparation of 2° ROH



## Pending Results



## Conclusions

1. Sand is a good alternative to silica gel towards oxidation reactions.
2. (Simple) aryl benzyl alcohols tend to oxidize easily to aldehydes and ketones compared to allyl alcohols.
3. Heat is necessary for oxidation reactions to occur (as opposed to room temperature Cr-silica gel reactions).
4. The differences in yield between silica gel and sand may presumably indicate differences in terms of their crystallinity, morphology, porosity, and nature of Si-surface with Cr.
5. Additives are not required to carry out Cr-sand oxidations.

## Acknowledgements

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