D] Solventless reactions:

Reactions that occur on absence of any solvents is called solventless (or solvent-free) reactions. There are two experimental conditions employed to carry out the chemical reactions under solvent-free conditions such as (a) reaction on solid support and (b) reaction without any solvent, solid support, or catalyst.

In case of reaction on solid support, the reactants are initially adsorbed either on mineral support (alumina, silica clays) or polymer support (polystyrene, polyethylene glycol) or via their solution in an appropriate organic solvent of low boiling. Then, the solvent is removed and the reaction is carried out in dry media between adsorbed reactants either by MW heating technology or by grinding method. Finally, the products are obtained by elution using diethyl ether or dichloromethane and filtered to eliminate the insoluble solid support.

While the reaction without any solvent, solid support or catalyst can be carried out between neat reactants in quasi-equivalent amount without any adduct. In the case of solid-liquid mixture, the reaction involves either solublization of the solid in the liquid phase or adsorption of liquid on the solid surface as an interfacial reaction. When all the reactants are in solid state, then they require proper mixing or homogeneity which can be achieved by using grinding technology or MW heating methods. Various reactions such as condensation, cycloaddition, rearrangement reactions, oxidation and reduction, etc. are carried out based on this principle.

Two of the Twelve Principles of Green Chemistry are to ‘‘use safer solvents and reaction conditions’’ and to ‘‘prevent waste.’’ These axioms are both directly met by eliminating a reaction medium. A third principle is ‘‘increase energy efficiency’’ is also often addressed. The advantages of solvent-free reaction are:

1. Avoids use of toxic, flammable and volatile organic solvents; minimizes health hazard and environmental impact.

2. There is no reaction medium to collect, purify, and recycle, thus eco-friendly.

3. Product purity is high, so avoids extensive purification using chromatography, only recrystallization is required in some cases; work-up simplified and less tedious.

4. High yield and less time for the completion of reaction due to intimate mixing of the reactants.

5. Process is cost effective as expensive solvents are not needed.

6. Simple workup procedure and no need for specialized equipment.

7. Functional group protection-deprotection can be avoided.

8. Low energy consumption.

9. Reactions are facile, regioselective; more efficient with more selectivity as compared to reactions carried out in solvents.

Drawbacks:

1. Homogenous reactants should mix to a reaction system.

2. Solvents are required during workup (e.g., extraction).

3. Not always possible to find a solventless alternative for solvent-assisted reactions.

4. High viscosity in reaction system may lead to complications.

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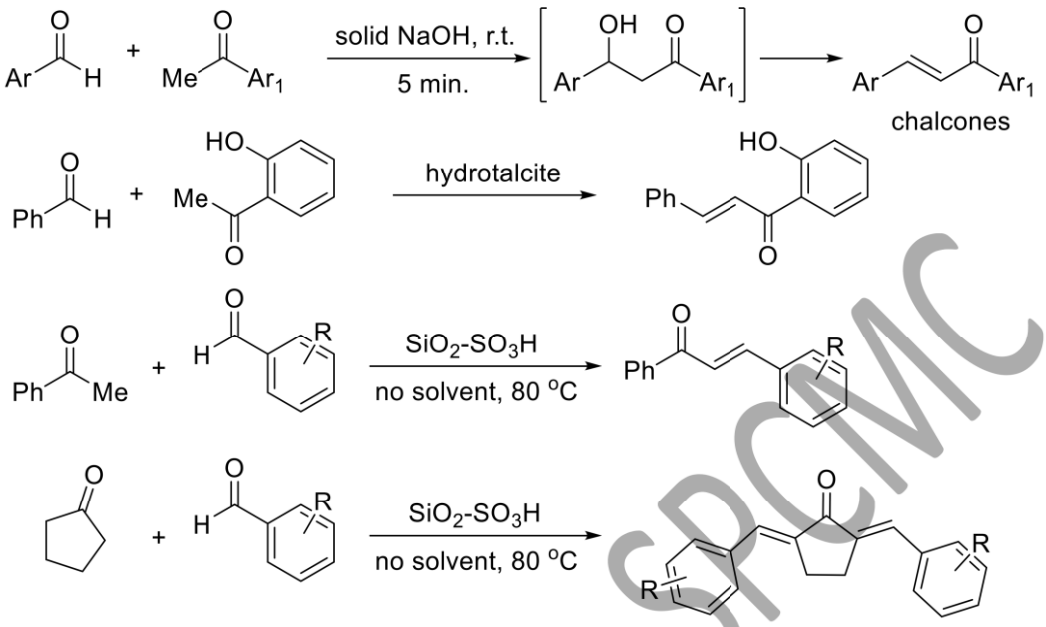
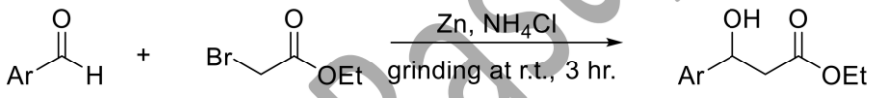
Some examples of solventless reaction:

Aldol condensation:

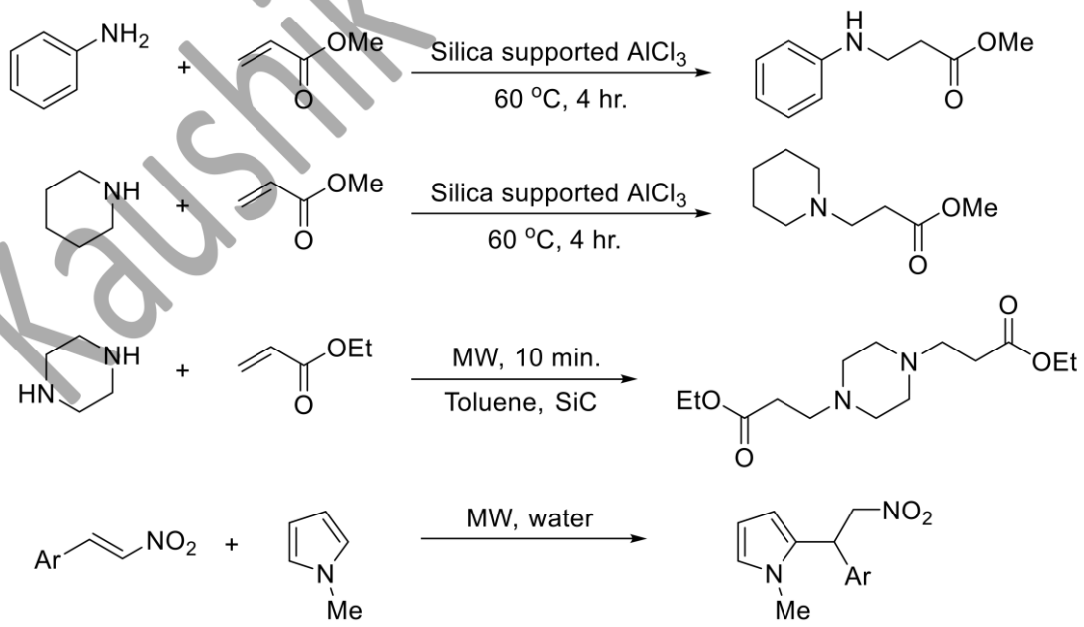


SiO_2-SO_3H: silica supported sulfuric acid

Reformatsky reaction:



Michael addition:



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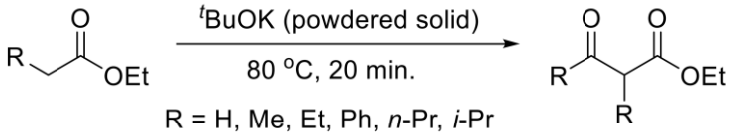
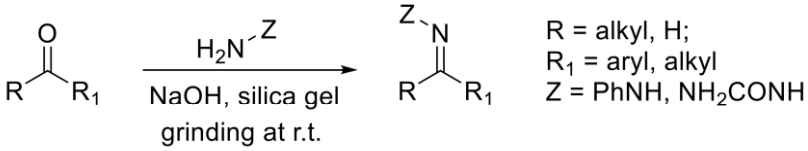
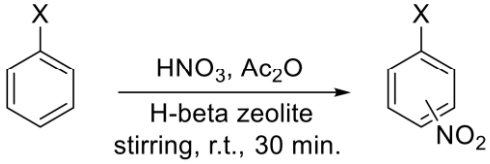
Claisen Condensation:



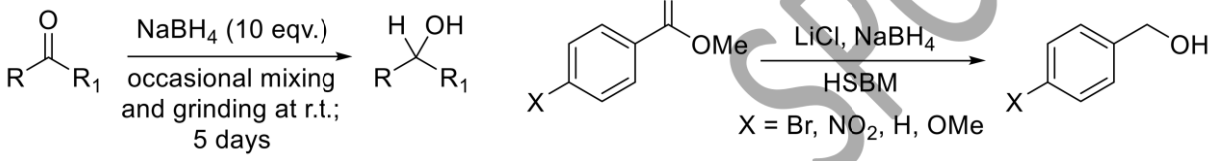
C=N bond formation:

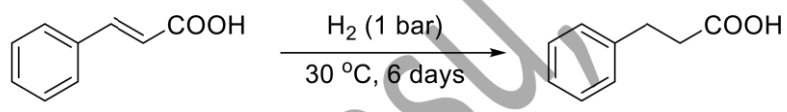


Aromatic electrophilic substitution:

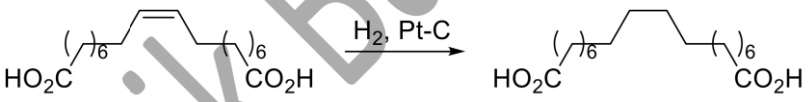


Reduction:

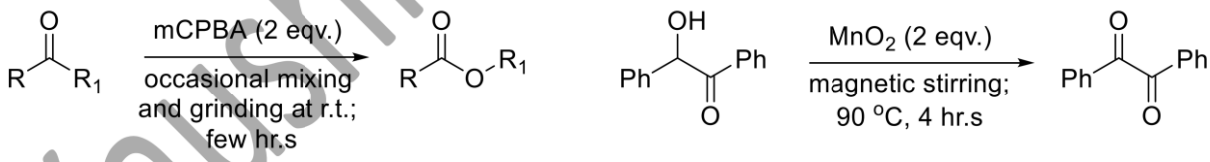


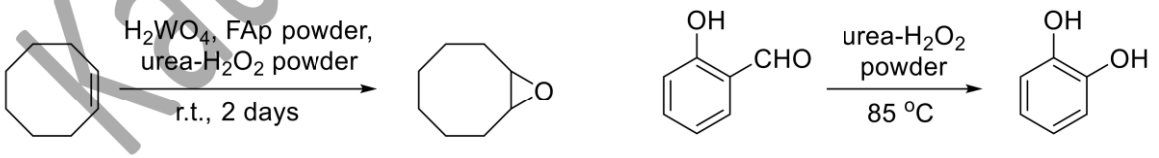


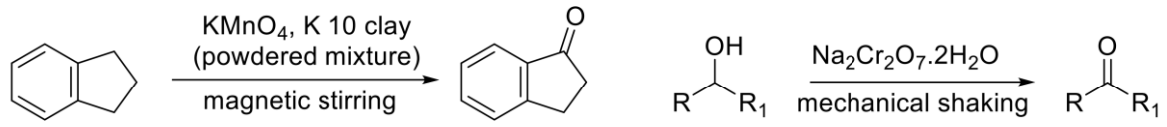
(doped with Pd-complex)



Oxidation:







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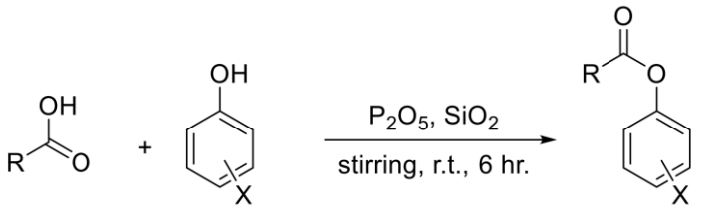
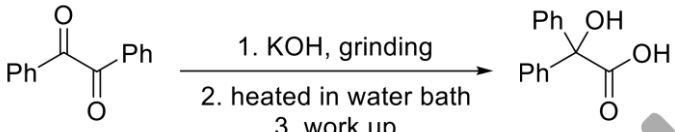
Esterification:

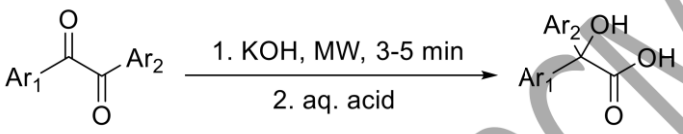


R = Me, Ph; X = H, Me, NO_2

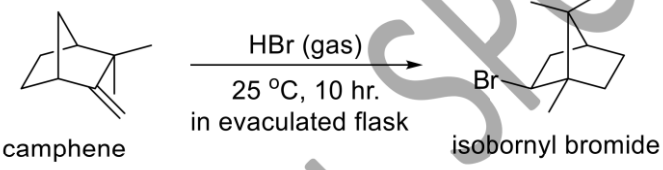
Rearrangement reactions:

Benzil-benzilic acid rearrangement:



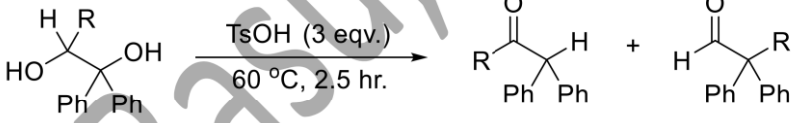


Wagner-Meerwein:

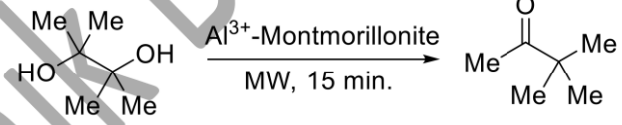


camphene isobornyl bromide

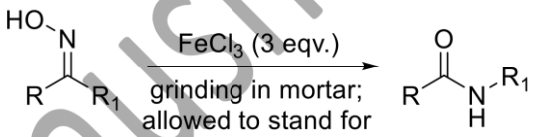
Pinacol-pinacolone:



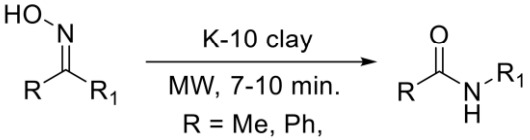
R = Ph, tolyl, 4-methoxyphenyl, 4-chlorophenyl



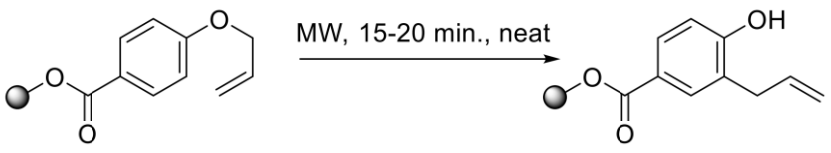
Beckmann:



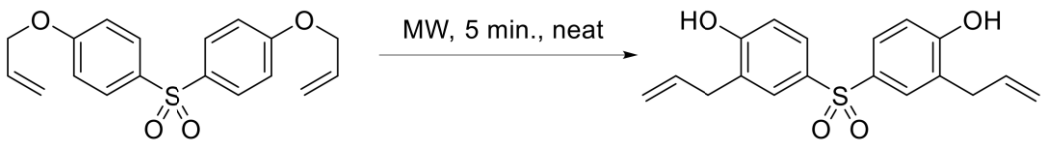
$R = R_1 = -(CH_2)_5-$; R = alkyl R_1 = aryl



Claisen:



loaded with Merrifield resin



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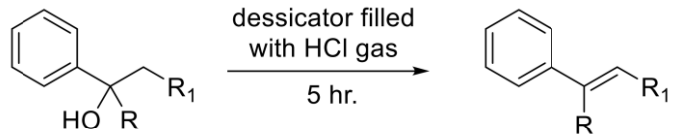
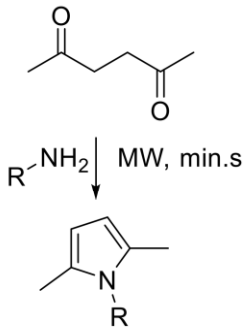
Elimination reaction:



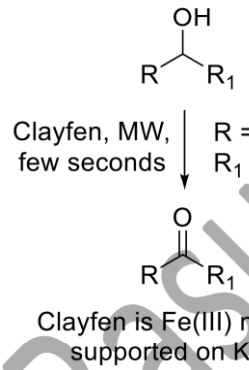
R = Ph, aryl; R_1 = H, alkyl aryl

Microwave-assisted solvent-free reactions are of three different types:

Reaction b/w neat reactants at least one of which is polar that absorbs the MW irradiation

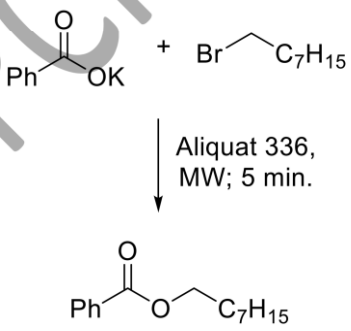


Reaction b/w neat reactants supported on dry media by impregnation on silica, alumina or clay.



Clayfen is Fe(III) nitrate supported on K10

PTC where a liquid regant acts as areactant and the organic phase.



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