GREEN CHEMISTRY

SEMESTER-VI
DSE-A3

Dr. Kalyan Kumar Mandal
Associate Professor
Department of Chemistry
St. Paul's C. M. College
Kolkata

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Supercritical Carbon dioxide (Sc CO_2)

Properties of Carbon Dioxide

Carbon dioxide can exist as a solid, liquid or gas.

Gas phase: It is very familiar.

Solid phase: The solid phase is frequently used for cooling applications and is sold as 'DryIce'.

At atmospheric temperature and pressure, the solid CO_2 transforms directly to the gas without passing through the liquid phase.

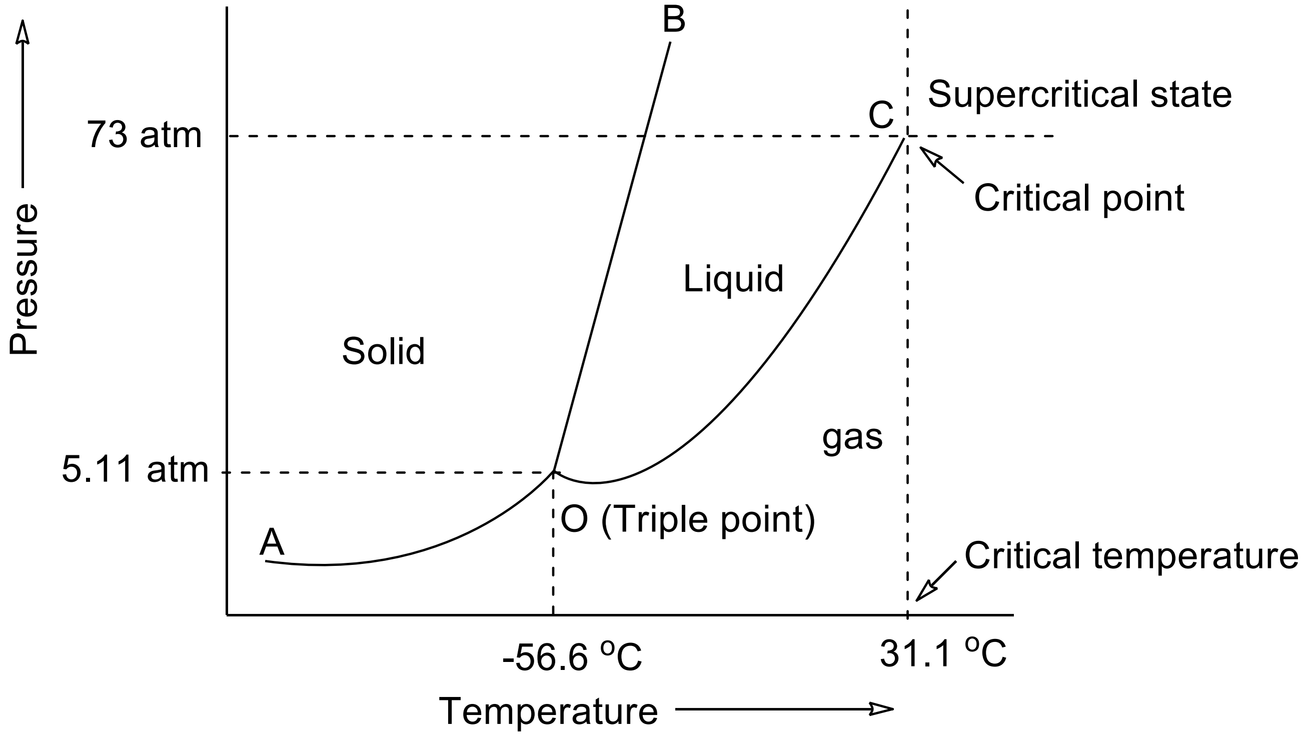
Liquid phase: Under certain conditions (e.g., compression of the gas or heating of solid CO_2 under pressure), liquid carbon dioxide can be formed.

- At the triple point all three phases are in equilibrium. The critical point is important for CO_2 as its critical temperature (31°C) lies close to ambient temperature.
- The critical temperature for a substance is that temperature above which it is impossible to liquify the gas no matter what pressure is applied.
- The upper limit for extraction using liquid carbon dioxide is 31°C as this temperature is the critical temperature of CO_2.
- The lower limit for extraction using liquid carbon dioxide is theorically -56° but there are problems with running an extractor at such low temperatures.

Supercritical Carbon dioxide (Sc CO_2)

Phase Diagram for Carbon Dioxide

CO_2 can exist in different states depending on the temperature and pressure of its surroundings.
A phase diagram provides a graphic representation to the states of CO_2 under various pressures and temperatures as shown below.



[Figure is not to scale]

Supercritical Carbon dioxide (Sc CO_2)

- At room temperature and normal pressure (1 atm), CO_2 exists in the gaseous state. However, if pressure is increased, CO_2 becomes liquid.
- At the triple point (point 'O' in the diagram; -56°C and 5.1 atm), CO_2 exists as gas, liquid and solid simultaneously.
- The triple point pressure of CO_2 is higher than that of the atmospheric pressure. Consequently, when solid CO_2 is heated, it vaporises directly without passing through the liquid state.
- At point C (31.1 ^{o}C and 73 atm), CO_2 exists as super critical fluid. At this point, liquid and gaseous phase of CO_2 co-exist.
- By compressing CO_2 kept at above its critical temperature, a dense fluid, known as the supercritical CO_2, is obtained which does not represent the true liquid or the gaseous state.
- In the supercritical state, CO_2 has a viscosity similar to that of a gas and density similar to that of a liquid.
- In the phase diagram, AOB indicates solid phase, BOC indicates liquid phase and AOC (right side) indicates the gas phase of CO_2.
- Important uses and applications of supercritical carbon dioxide:

  (1) Use of supercritical carbon dioxide for dry cleaning.

  (2) Use of supercritical carbon dioxide as solvent for organic reactions.

Supercritical Carbon dioxide (Sc CO_2)

Properties of supercritical carbon dioxide

- Chemically inert;
- Non-toxic;
- Easily available at high purities;
- Fire suppressing capacity and relatively low temperature of the process allows most compounds to be extracted;
- Recyclable and reusable;
- Solubility of many extracted compounds in CO_2 varies with pressure, permitting selective extraction;
- Separation of the products from the starting materials is much easier with the Sc-CO_2 solvent than with the traditional organic solvents.

Supercritical Carbon dioxide (Sc CO_2)

Uses of supercritical carbon dioxide

(1) It is used as dry-clening agent over traditional solvents as hydrocarbons, including perchloroethylene (PERC, $Cl_2C=CCl_2$).

(2) It is used for extraction of caffeine from coffee bean leaves.

(3) It is used in polymerization, foaming of polymer, etc.

(4) It can be used as the mobile phase or eluent in Sc-CO_2 chromatography to separate chemically closed molecules or mixtures like chiral compounds efficiently.

(5) It has a varied solvating strength that allows for selective extractions.

(6) It can be used to remove organochloride pesticides from agricultural crops without adulterating the desired constituent from the plant matters.

(7) The relatively low critical temperature and low reactivity of CO_2 allows extraction of the desired product without altering or decomposing the product.

(8) It is used for cleaning of semiconductor chips, preparation of nono-particles, synthesis of organometallic compounds, enzymatic compounds, etc.

Supercritical Carbon dioxide (Sc CO_2)

Advantages of supercritical carbon dioxide

(1) Chemically inert reaction medium;

(2) CO_2 is non - toxic and environmentally benign.

(3) The properties of SC CO_2 are intermediate between that of a liquid and gas.

(4) Solvent properties of SC CO_2 (e.g. dielectric constant, solubility parameter, viscosity and density) can be altered via manipulation of temperature and pressure.

(5) increase of the reaction rate and selectivity

(6) Increased efficiency

(7) A prolonged catalyst life span due to the high solubility of the coke precursors enabling their easy extraction

(8) The possibility of its usage in hetereogenious catalysis and regeneration of zeolite catalysts

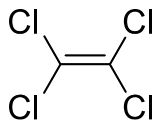
(9) The tunable extraction power by altering pressure and temperature

(10) Simplear product isolation from the media, post reaction

Commercial application of Supercritical Carbon dioxide (Sc CO_2)

(1) Supercritical carbon dioxide (Sc CO_2) in cleaning industry (dry cleaning

- Articles of clothing made from fabrics cannot be washed in water and require a dry-cleaning process. In fact, a liquid solvent is actually used in dry cleaning for removing dirt and stains.
- Perchloroethylene (PERC) is used as solvent in drycleaning.



PERC

Environmental problem associated with PERC for drycleaning clothes

(1) Disposal of perchloroethylene, a suspected carcinogen, can contaminate ground water.

(2) PERC when released into the atmosphere rises to the stratosphere region, where it gets decomposed into chlorine radical by the action of UV rays of the sun. The chlorine radicals are responsible for depleting the ozone layer.

$$\text{PERC} \xrightarrow{\text{UV rays}} Cl^{\bullet}$$

$$O_3 + Cl^{\bullet} \longrightarrow O_2 + ClO^{\bullet}$$

$$ClO^{\bullet} + [O] \longrightarrow Cl^{\bullet} + O_2$$

Net reaction : $O_3 + [O] \longrightarrow 2O_2$

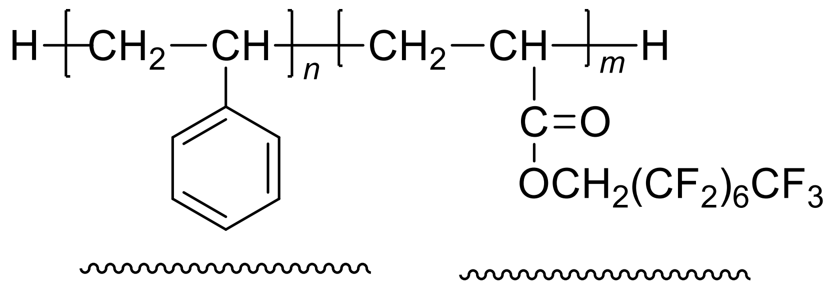
Alternative solvent used in drycleaning clothes

Use of liquid or super critical carbon dioxide (CO_2) as the cleaning solvent

Commercial application of Supercritical Carbon dioxide (Sc CO_2)

Role of Sc CO_2 in drycleaning cloths in presence of surfactants

- Most greases and oils (from cloths) is very insoluble in CO_2. A surfactant is used to increase the solubility of oils and grease in CO_2.
- Supercritical carbon dioxide is used as a solvent with the surfactant (fluorocarbon based) co-polymer) composed of 'CO_2 – philic' segments (which are attracted to CO_2) and 'CO_2 – phobic' segments (which are not attracted to CO_2).
- The 'CO_2 - phobic' segment can be made lipophilic (attracted to fats, oils and grease) or hydrophilic (attracted to water).
- When this polymer is placed in a medium of supercritical or liquid CO_2, it assembles into a micelle structure. The "CO_2 - philic" segments surrounds or encase the "CO_2 - phobic" segments.



"CO_2 - phobic" chain segment

"CO_2 - philic" chain segment

Surfactant molecule for Sc CO_2 solvent

- The miscelle structure can encase materials such as greases and oil in the inner "CO_2 - phobic" area of the micelle structure and allow them to be washed away by the CO_2 solvent.

Commercial application of Supercritical Carbon dioxide (Sc CO_2)

(2) Decaffeination of coffee using Sc CO_2

- The extraction is carried out at low temperature and in the absence of organic solvent.
- **Steps:**

  1st step : Caffeine is extracted from coffee by Sc CO_2 using water.

  2nd step : The extracted components are separated from Sc CO_2 by releasing the pressure over CO_2.

Advantages : (1) A very little waste is formed in this extraction process.

(2) This process is economically and environmentally sustainable.

(3) Sc CO_2 in polymer and plastic industry

Disadvantages of Sc CO_2

(1) It is not a very suitable solvent for high-molecular compounds and the majority of polar compounds.

(2) It is not very much suitable for the reaction which passes through polar transition state.

(3) It is very suitable in small scale (laboratory scale) reactions but not so suitable for most of the commercial scale/industrial processes.

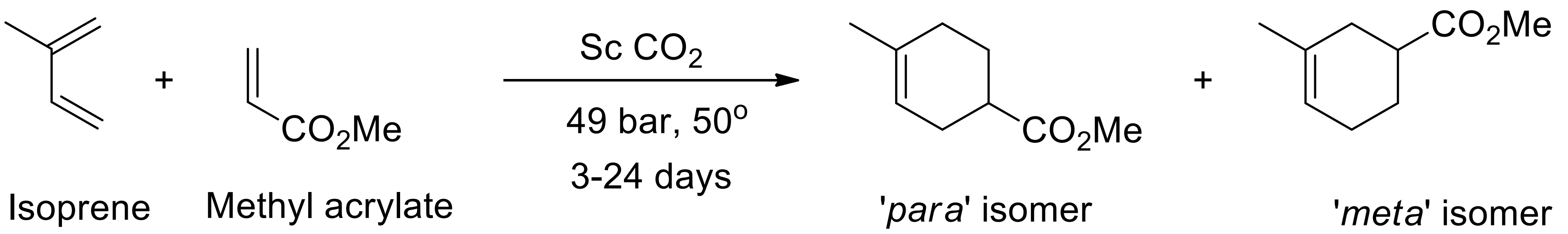
(4) The reactions in Sc CO_2 can be carried out in 'batch processes' but it cannot be carried out in 'continuous process', for large production.

(5) The reaction in Sc CO_2 require uneconomically high process pressure to solvate polar, inorganic or high molecular-weight materials and it needs to design and manufacture of appropriate costly equipment.

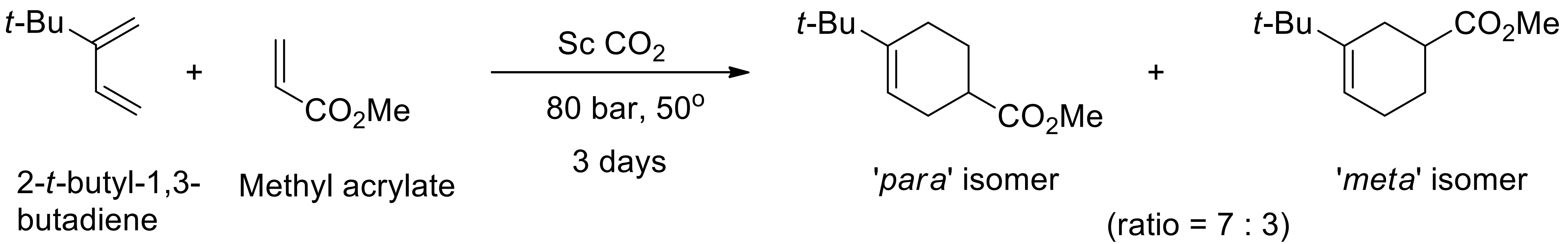
Reaction in Supercritical Carbon dioxide

(1) Diels-Alder reaction

(a) Diels-Alder reaction of isoprene and methylacrylate to produce *'para'* and *'meta'* isomers

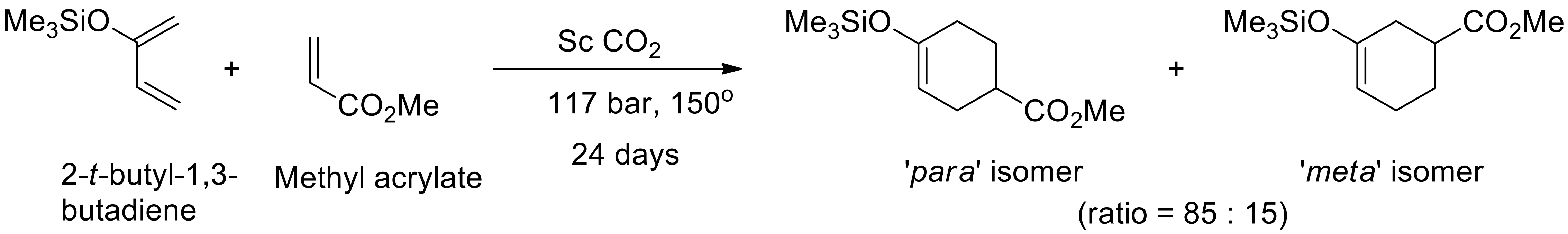


(b) Diels-Alder reaction of 2-*t*-butyl-1,3-butadiene and methyl acrylate to produce *'para'* and *'meta'* isomers



Reaction in Supercritical Carbon dioxide

(c) Diels-Alder reaction of 2-*t*-butyl-1,3-butadiene and methyl acrylate to produce *'para'* and *'meta'* isomers



Role of Sc CO_2

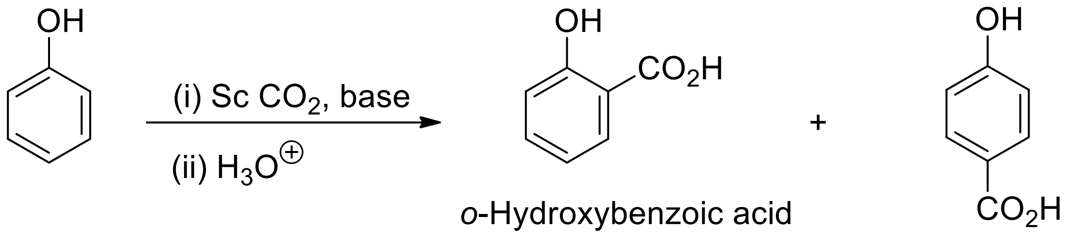
(1) The reactions are more regioselective than that of conventional solvents.

(2) The reaction produces both '*para*' and '*meta*' like products with *meta* selectivity.

Reaction in Supercritical Carbon dioxide

(2) Kolbe-Schmitt reaction

- This is a direct carboxylation reaction in supercritical CO_2. *o*-Hydroxybenzoic acid leads to the production of aspirin.
- The *ortho*-and *para* selectivity between isomers of hydroxy benzoic acids are observed. The reaction produces both *ortho*- and *para* isomer as mixture of products.

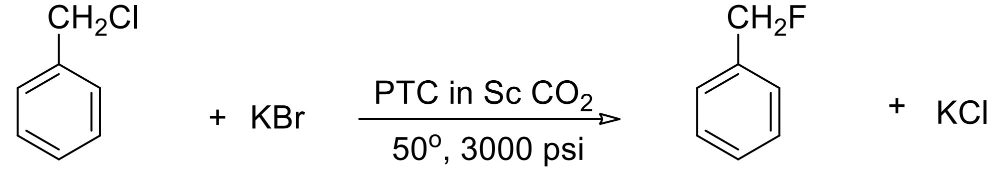


o-Hydroxybenzoic acid (Salicylic acid)

p-Hydroxybenzoic acid

(3) Bromination reaction: Displacement of a chlorinated aromatics

- Phase transfer catalysed reaction of benzyl chloride with potassium bromide in presence of PTC catalyst in supercritical CO_2 gives benzyl bromide.



Benzyl chloride

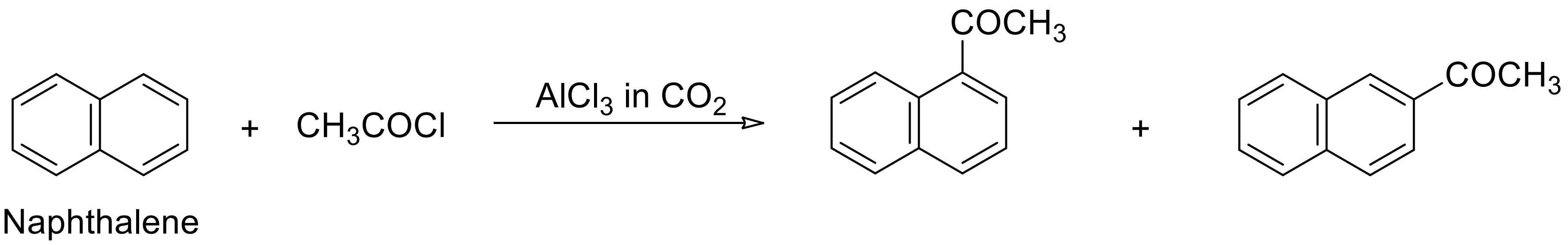
Benzyl chloride

- PTC used in this reaction is tetra-*n*-heptammonium bromide or 18-crown-6.

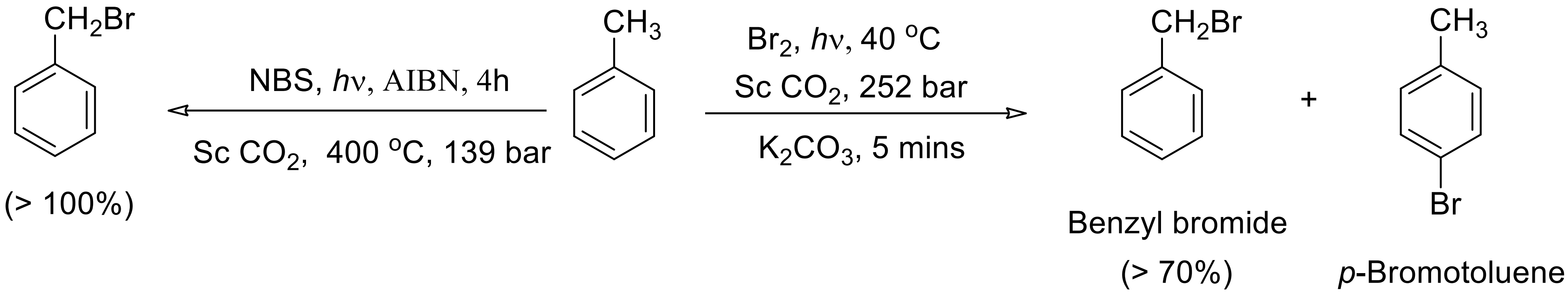
Reaction in Supercritical Carbon dioxide

(4) Friedal-Crafts reaction

- Friedal-Crafts reaction fcan be carried out in Sc CO_2.



(5) Free-radical bromination in Sc CO_2 solvent

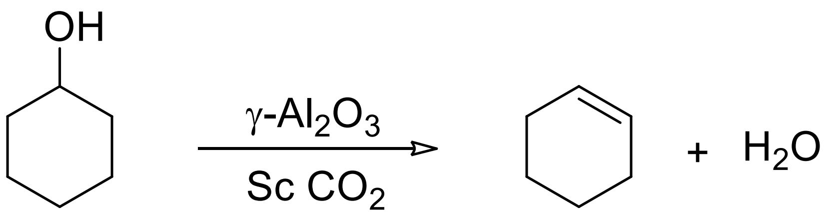


Reaction in Supercritical Carbon dioxide

(6) Synthesis of *o*-cyclohexylphenol using Sc CO_2 as solvent

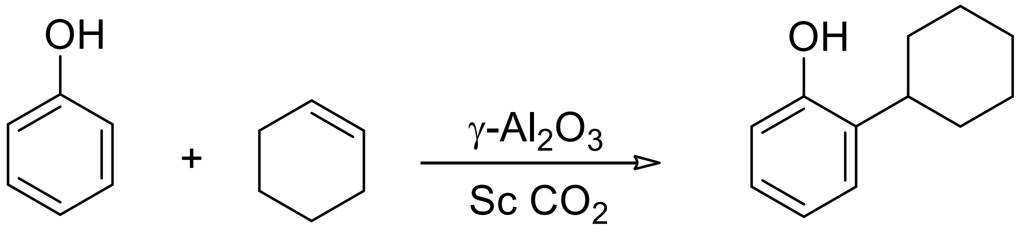
- Cyclohexene being a costly reagent cannot be used as such but it is prepared from the dehydration of cyclohexanol.
- Water produced in the reaction deactivates alumina, so a water scavenger is used.

Reaction 1



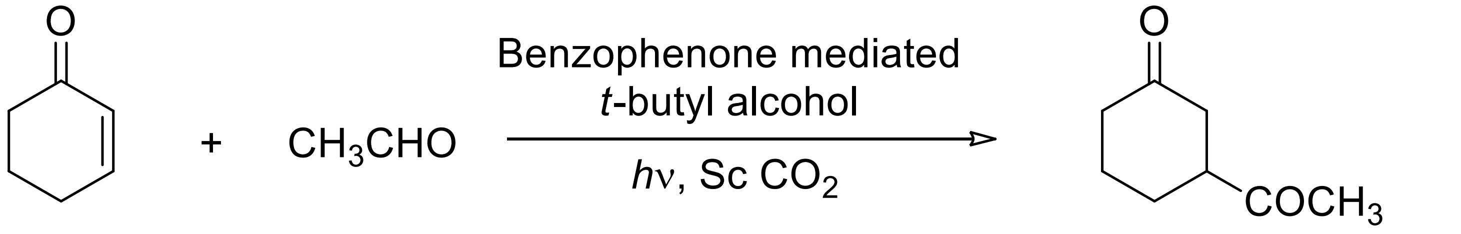
Cyclohexanol Cyclohexene

Reaction 2



Phenol *o*-Cyclohexylphenol

(7) Photochemical reaction in Sc CO_2 as solvent



Cyclohex-2-en-1-one 3-Acetylcyclohexanone