

Monograph on Green Chemistry
Laboratory Experiments

Green Chemistry Task Force
Committee, DST

PREFACE

Green Chemistry is an essential part of Chemistry Curriculum. Thus teaching of Green Chemistry in class room and laboratory should go simultaneously. In India although Green Chemistry is being taught in a few colleges and Universities, laboratory experiments remained largely the same as being taught fifty years back. Many of these experiments particularly involving toxic chemicals like liquid bromine, potassium cyanide, benzene, carbon tetrachloride are not at all safe to human health. Thus, a need for a monograph with safe green laboratory experiments is felt by the academic community. The Green Chemistry Task Force Committee shouldered the responsibility of bringing out this monograph.

Efforts are made to demonstrate green experiment for a reaction already taught in the theory class. The classical procedure for a particular reaction was mentioned in all the experiments highlighting the hazardous component in it and then a greener procedure is described. In a particular experiment if the described procedure is not completely (100%) green, it may be improved in the later phase.

During preparation of this monograph discussion meetings at four different regions, Kolkata, Delhi, Chennai and Hyderabad with the teachers of undergraduate and postgraduate colleges were held and suggestions and views of the learned colleagues are carefully considered. The members of the Monograph committee and Task Force committee also provided very valuable comments and suggestions. I am grateful to all the invited teachers and scientists (Professors/Drs. A. K. Sarkar, B. K. Chaudhuri, S. Bhattacharyya, S. Bhar, S. Kumar, I. Sidhwani, S. Dhingra, S. Mehta, A. Srivastava, S. Prakash, K. Mukkanti, Ch P. Rao, K. R. Radhika, M. Chakrabarty, P. Radhakrishna, S. Baskaran, S. Muthusamy, H. S. P. Rao, Ravindranathan, and A. Chakraborty), all the members of the Task Force committee and Monograph committee for their support, co-operation and help to accomplish this task. (If the name of any participating teacher is missed, I beg your apology in advance; it is not intentional)

Task Force Committee

Professor S. Chandrasekaran (Chairman)

Professor M. K. Chaudhuri

Dr. S. Devotta

Dr. P. K. Ghosh

Dr. J. S. Yadav

Dr. S. Bhaduri

Dr. B. B. Lohray

Dr. B. Gopalan

Dr. P. Bhate

Professor B. C. Ranu

Dr. R. Brakaspathy (Member-Secretary)

Monograph Committee

Professor B. C. Ranu (Co-ordinator)

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Professor G. D. Yadav

Professor R. K. Sharma

Dr. S. Bhanumati

Dr. H. Meshram

Professor K. P. Pitchumani

Finally, the mission and efforts of all of us will be successful if this monograph helps to improve the environment of the laboratory and health of young students.

Brindaban C. Ranu
Co-ordinator

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1. Green Chemistry- Definition and Principles

What is Green Chemistry?

Green Chemistry is defined as invention, design, development and application of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to human health and environment.

Principles of Green Chemistry

- 1) It is better to prevent waste than to treat or clean up waste after it is formed.**
- 2) Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.**
- 3) Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.**
- 4) Chemical products should be designed to preserve efficacy of function while reducing toxicity.**
- 5) The use of auxiliary substances (e.g. solvents, separation agents *etc.*) should be made unnecessary wherever possible and, innocuous when used.**

- 6) **Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.**
- 7) **A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.**
- 8) **Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.**
- 9) **Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.**
- 10) **Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.**
- 11) **Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.**
- 12) **Substances and the forms of the substance used in chemical reaction should be chosen so as to minimize the potential of chemical accidents, including releases, explosions, and fires.**

P. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*; Oxford Science Publications, Oxford, **1998**

The objective of this monograph is to suggest modifications of the hazardous Laboratory Experiments, currently practiced by the students in the present syllabus.



Green Guidelines for Teachers and Students in Laboratory

1. Experiments should involve the use of alternative reagents which are not only eco-friendly but also be easily available anywhere in the country in bulk quantities at very cheap price. They should not preferably involve the use of organic solvents (like ether, petroleum ether or ethyl acetate); ethanol and methanol are mostly preferred.
2. Modified Experiments, if possible should not involve sophisticated instrumentation techniques like high-pressure system, evacuated system, inert atmosphere using argon, *etc.* This is in view of the stringent situations in many of the laboratories in most of the institutions of our country, specially, in rural areas.
3. Experiments should avoid tedious experimental procedure like longer reaction time, reaction at high temperature *etc.*
4. All organic chemistry experiments (preparation, separation of mixture of compounds, identification of functional groups *etc.*) should preferably be conducted in semi-micro or micro-scale. Thin-layer chromatography (TLC), spectroscopic techniques (UV, IR and wherever available NMR) should be methods of choice for determining purity, functional groups and structure elucidation.
5. One can use ethyl chloroformate as a substitute for PCl_5 , PCl_3 , POCl_3 or SOCl_2 . The acid is converted to anhydride which can be used for the same purpose
6. Dimethyl carbonate may be used as a suitable substitute for dimethyl sulfate and methyl halides for methylation as the end product is only carbon dioxide
7. Preparation of derivatives on large scale and assessing them could be dispensed with. Instead the student may be asked to report TLC behavior of the compounds prepared.

b) Inorganic Analysis

The conditions of the laboratories for doing inorganic analysis by conventional methods in the under graduate level are at all not eco-friendly. The gases are toxic – causing health-hazards. Insufficiency of exhaust fans remain a big problem. Sometimes experiments are carried out in closed doors – in hot, humid conditions. The labs are not properly ventilated. Students often fall victim of this infrastructure. The acid fumes, which are toxic, pollute the atmosphere. So, a change in outlook must be brought about with the existing systems.

Inorganic analysis mainly deals with the detection and estimation of basic and acid radicals. For the detection of radicals “Spot-tests” may be introduced.

Although spot reagents are costly, a little amount of the reagents are required. So, it will be cost-effective.

Suggestions for Improvement of Laboratory Atmosphere

1. Direct use of H₂S gas generated from Kipp's apparatus must be avoided.
2. a) H₂S may be generated from the Kipp's apparatus in a fume cupboard (or, in absence of it, in open air) and be dissolved in water. Saturated solution of H₂S is to be prepared and kept in air-tight bottles. This H₂S water is to be supplied in dropping bottles and be used when required.
3. A better alternative for H₂S in inorganic group analysis is highly desirable and efforts should continue to find one.
4. Laboratory remains filled up with acid fumes. Rampant use of conc. acids like HNO₃, HCl must be avoided. Ammonia bottles must always remain tightly corked. Chemical tests using conc. acids or ammonia must be carried out in fume-cupboard. The gases from the exhaust may be passed through alkali solution (preferably lime water) for absorption. The nitrite or nitrate salts of calcium may be used as fertilizer.
5. The laboratory must be provided with sufficient number of exhaust fans.
6. Dissolution of ores/alloys for making solution for quantitative analyses must be carried out in the modified fume cupboard.
7. Fire extinguisher, first aid kit, eye shower should be kept ready in a particular common place. Hand gloves, safety glasses, and aprons must be made compulsory during lab work.
8. **'SPOT TESTS'** must be introduced for the detection of basic as well as acid radicals (Inorganic Analysis).
9. Preliminary experiments leading to the detection of NO₂⁻, NO₃⁻, Br⁻, Cl⁻ should be carried out in test tubes fitted with an outlet (bent tube). Gases issuing out of the tube must pass through alkali solution.
10. Tests with Hg, As, Cd, Pb, Bi, Cr – salts, which are toxic, must be excluded from syllabus meant for the undergraduate general stream students. But these tests may be kept for Hons. Students for demonstration only. For these metal ions 'spot-tests' are only recommended. The waste, after the tests, may be dumped in pits specially designed for waste disposal. Plants that absorb the heavy metals are seeded or transplanted into metal-polluted soil and are cultivated using established phytoremediation practices, if possible. As they become saturated with the metal contaminants, roots or whole plants are harvested for disposal. The plants include water hyacinth, penny wort ("Thankuni" – Hydrocotyle Umbellata L.) duduweed ("Pana" – Lenna Minor L). The roots of Indian mustard are effective in the removal of Cd, Cr, Cu, Ni, Pb, Zn, and sunflower removes Pb, U, ¹³⁷Cs and ⁹⁰Sr from hydroponic solutions.

c) Physical Chemistry Experiments

1. In distribution experiment, the use of chemicals like carbon tetrachloride, benzene should be avoided and can be substituted by toluene or acetic acid in butanol.
2. Experiments involving conductometry, polarimetry, potentiometry, pH metry, colorometry, polarography, spectrophotometry, requires chemicals in very low concentrations and have no negative influence on the health or environment, hence these expt. may not need any change or alterations.
3. If possible, instrumental methods may be introduced from the UG level.

General Comments:

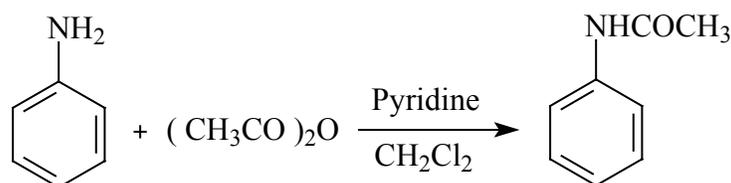
GREEN chemistry experiments are introduced not to drastically replace the conventional ones rather, they are considered complementary to the existing protocols. This not only provides a wider view of various techniques but also imbibes inquest in innovative minds for future development and growth of the subject in general with due emphasis to green chemistry context. The teachers may take periodical tests to judge understanding of the students about the experiments practiced. Wherever possible and feasible, the conventional process should be replaced with the greener ones to transmit the message of this issue.

2. Organic preparations (Undergraduate Level)

Experiment: UG-1

ACETYLATION OF PRIMARY AMINE (Preparation of acetanilide)

Conventional Procedure:



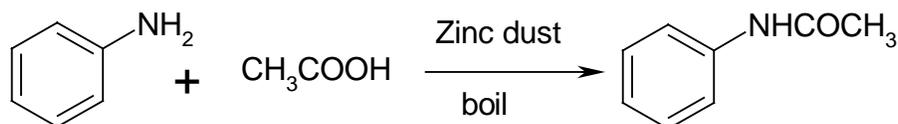
Non-green Components:

Use of chlorinated solvent like CH₂Cl₂

Pyridine is also not eco-friendly

Acetic anhydride leaves one molecule of acetic acid unused (not atom-economic)

Alternative Green Procedure:



Chemicals Required:

Aniline	- 10 ml (10.2 g)
Glacial acetic acid	- 30 ml
Zinc dust	- 0.5 g

A mixture of aniline (10 ml) and zinc dust (0.5 g) in acetic acid (30 ml) in a 100 ml round bottom flask was heated over a gentle flame using water condenser. Heating was continued for about 2 hrs. The reaction mixture was then carefully poured in cold water (100 ml) in a 250 ml beaker with cooling and vigorous stirring. The shining crystals of acetanilide were separated slowly. After 15 min. the acetanilide crystals were collected by filtration. The solid crystals were washed over the Buchner funnel with water and the product was dried (yield, 10 gm). It

was crystallized in boiling water. (If necessary, decolorizing charcoal may be used), m.p. 114 °C.

Yield: 10 g (91%)

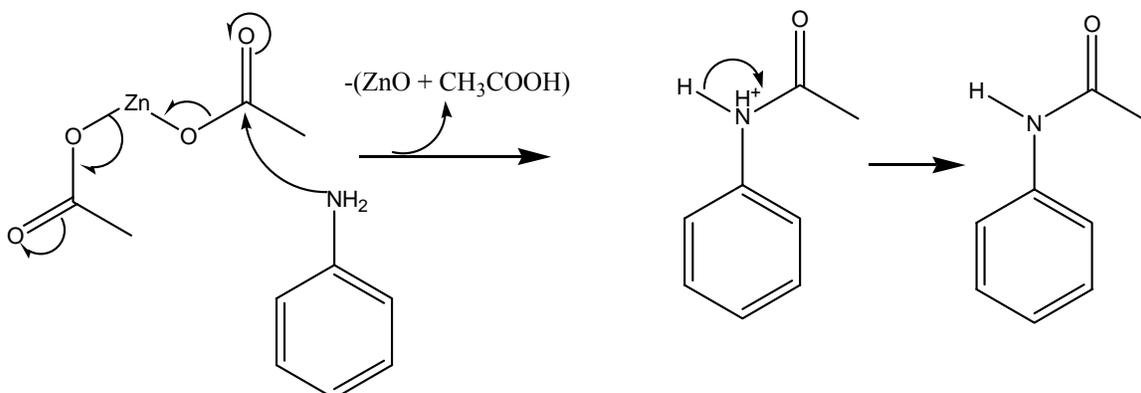
Green Context:

Avoids use of acetic anhydride (usage banned in some states, due to its utility in narcotic business)

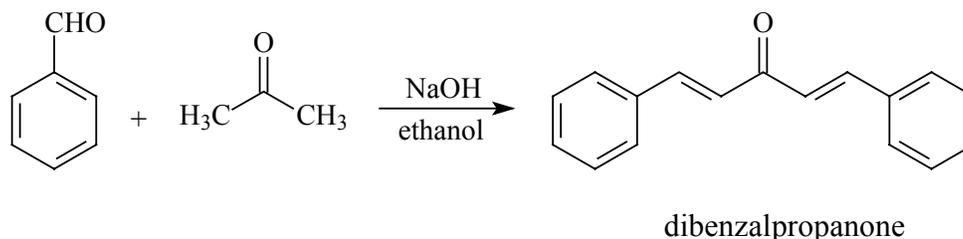
Minimizes waste by-products

Avoids hazardous solvent

Mechanism:



H. Meshram, ICT, Hyderabad, Private Communication

Experiment: UG-2**BASE CATALYZED ALDOL CONDENSATION
(Synthesis of dibenzalpropanone)****Chemicals Required:**

Acetone – 1 ml (0.83 g)

Benzaldehyde – 3.8 ml (3.9 g)

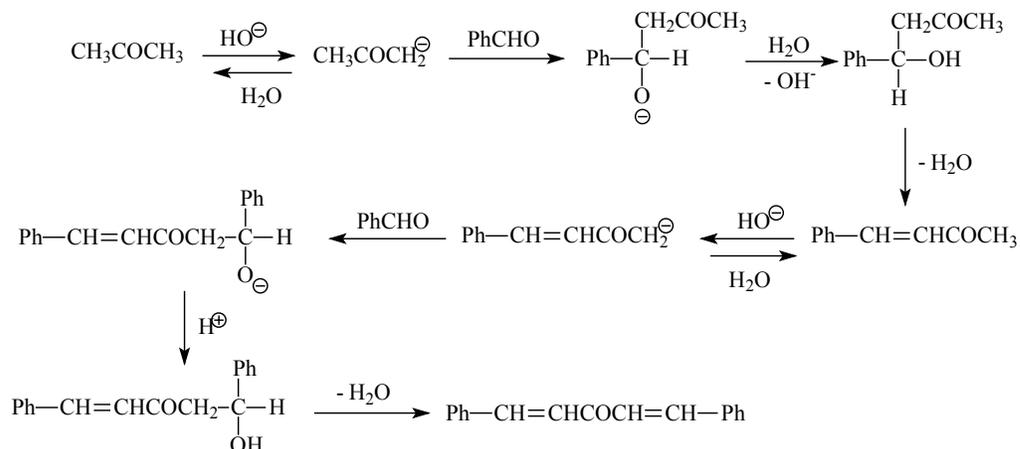
NaOH – 30 ml of 10 % soln

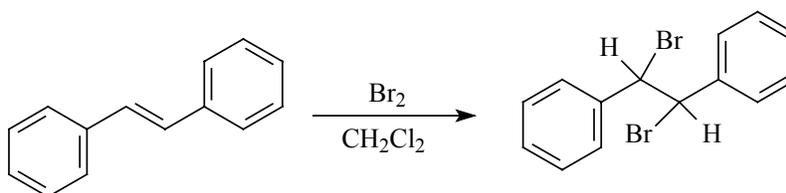
In a conical flask fitted with a cork, benzaldehyde (1 ml), acetone (3.8 ml) and methylated spirit (or alcohol) (15 ml) were shaken together for 2 minutes. To it was added 10% sodium hydroxide solution and shaken vigorously for 10 minutes with simultaneous pressure release. The reaction mixture was cooled in ice and the pale yellow solid was filtered through a filter paper, washed with water, dried, collected, weighed and recrystallized from ethanol, m. p. (120-122 °C).

Yield: 3 g (90%)**Green context:**

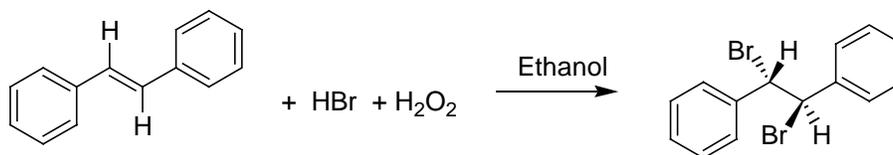
Hazardous organic solvents are avoided

Reagents are non-toxic

Mechanism

Experiment : UG-3**HALOGEN ADDITION TO C=C BOND
(Bromination of *trans*-stilbene)****Conventional Procedure:****Non-green Component:**

Use of liquid bromine
Chlorinated solvents

Green Procedure 1¹:**Chemicals Required:**

<i>trans</i> -Stilbene	- 1.8 g
HBr in water	- 5.2 ml
30% Hydrogen peroxide	- 7 ml
Ethanol	- 10 ml

Trans-stilbene (1.80 g) in ethanol (10 ml) was refluxed. The aqueous solution of HBr (33%) (5.2 ml) and hydrogen peroxide (H₂O₂, 30%) (7 ml) were added from a dropping funnel sequentially to this refluxing solution of stilbene. The colourless solution became deep orange in colour. Within 15 minutes, the orange colour disappeared. This indicates the bromination of stilbene. The solution

was allowed to cool down. During this the precipitate due to stilbene dibromide separated out. The precipitate was filtered, recrystallized and dried.

Melting point (m.p.): 237 °C

Yield: 2.4 g (70%)

Alternative Procedure²:

Chemicals Required:

<i>trans</i> -Stilbene	- 1.8 g
Glacial Acetic acid	- 20 ml
Sodium bromide	- 3 g
Sodium bromate	- 1 g

To a solution of *trans*-stilbene in acetic acid was added a mixture of sodium bromide and sodium bromate at room temperature with stirring by a glass rod. The reaction mixture was then stirred occasionally with a glass rod for 1 hour. The developed light brown colour disappeared. The acetic acid in the reaction mixture was then neutralized by sodium hydroxide solution. The precipitate of stilbene dibromide separated out. This was filtered and dried.

Yield: 2.6 g (80%)

Green Context:

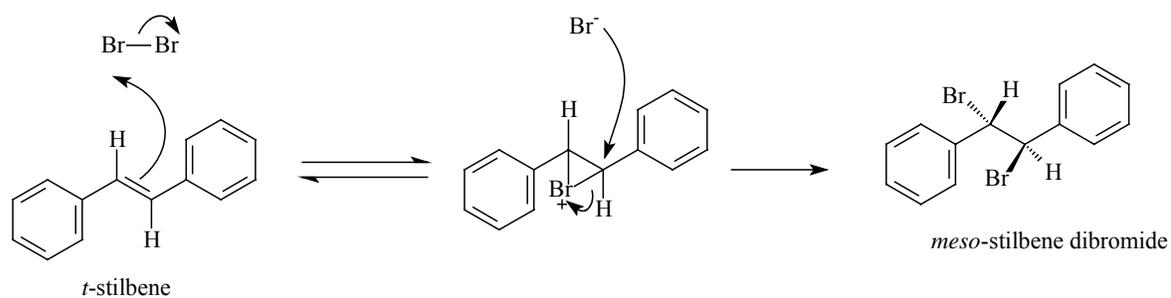
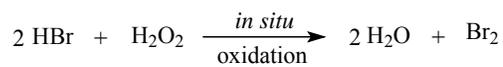
Corrosive liquid bromine is avoided
Atom efficient

Water is the only byproduct in HBr- H₂O₂ method and in NaBr- NaBrO₃ method sodium acetate is formed along with water.

HBr-H₂O₂ mixture and bromide-bromate couple offer *in situ* oxidation of Br⁻ to molecular bromine.

Caution:

Care must be taken while handling the solution of hydrogen bromide and hydrogen peroxide.

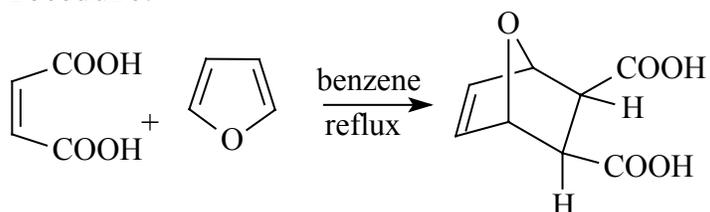
Mechanism:

1. L. C. McKenzie, L. M. Huffman, and J. E. Hutchison, *Journal of Chemical Education.*, **2005**, *82*, 306.

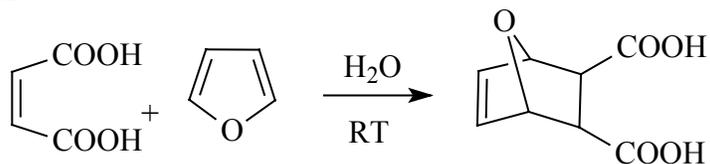
2. Unpublished Results, B. C. Ranu, S. Adimurthy, and P. K. Ghosh

Experiment: UG-4

[4+2] CYCLOADDITION REACTION
(Diels-Alder reaction between furan and maleic acid)

Conventional Procedure:**Non-green Component:**

Use of benzene which is one of the most toxic solvents

Green Procedure:**Chemicals required:**

Furan : 1.75 g

Maleic acid : 1.1 g

A mixture of furan (1 g), maleic acid (2 g) in water (10 ml) was shaken or stirred for 2-3 hrs at room temperature. The adduct formed, was filtered, washed with water, dried and recrystallized from aqueous ethanol, m.p. 138-140 °C

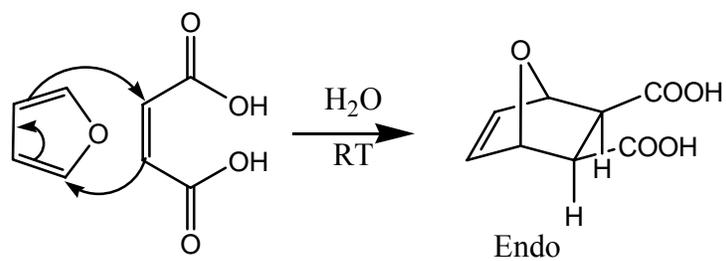
Yield: 2.1 g (80%)

Green Context:

Reaction carried out in aqueous medium avoiding benzene

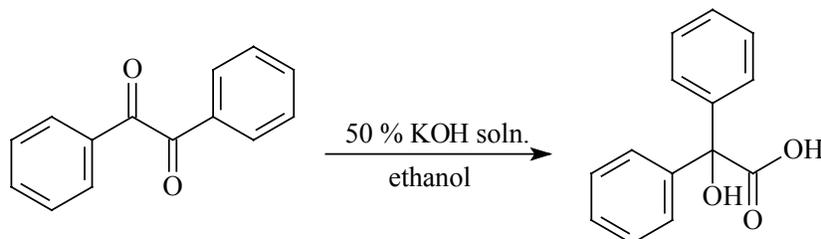
Efficient at room temperature itself

100% atom efficient

Mechanism:

R.B. Woodward and H. Baer, *J. Am. Chem. Soc.* **1948**, 70, 1161.

D. C. Rideout and R. Breslow, *J. Am. Chem. Soc.* **1980**, 102, 7816.

Experiment: UG-5**REARRANGEMENT REACTION - III
(Benzil Benzilic acid rearrangement)****Conventional Procedure:****Alternate Green Procedure:****Preparation of Benzilic Acid in Solid State under Solvent-free Condition:****Chemicals Required:**

Benzil : 1 g
 Sodium hydroxide or potassium hydroxide: 1 g
 Conc. Hydrochloric acid

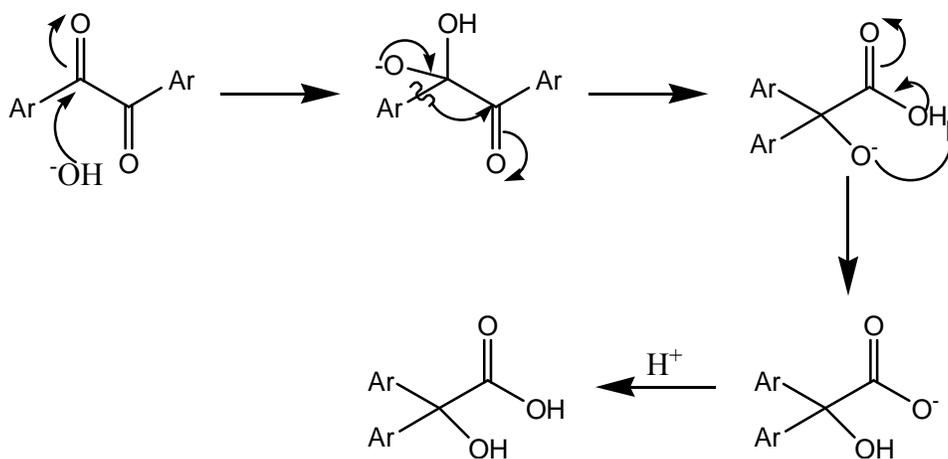
Benzil (1 g) was thoroughly grounded with solid NaOH or KOH (1 g) in a dry mortar with the help of a pestle to make an easy flowing powder. This material was subsequently taken in a dry conical flask fitted with a piece of cotton at its mouth and heated on a boiling water-bath for 20 minutes. Then it was cooled to room temperature, dissolved in minimum amount of water (unreacted benzil, if any, was removed simply by filtration) and the aqueous solution was acidified with conc. HCl with thorough cooling in ice. The precipitated benzilic acid was filtered, washed with cold water and crystallized from hot water, if needed.

M.p. 149-151 °C

Yield : 0.86 g (80%.)

Green Context:

- Solvent-free procedure
- Atom efficient

Mechanism:

Note: This experiment may be practiced in UG level too

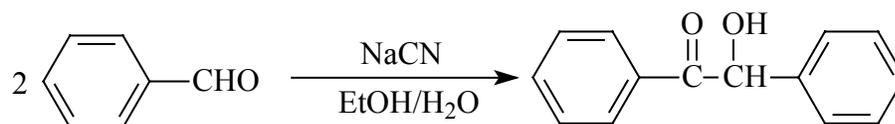
K. Tanaka and F. Toda, *Chem. Rev.*, **2000**, *100*, 1045.

3. Organic Preparations (Postgraduate Level)

Experiment: PG-1

COENZYME CATALYZED BENZOIN CONDENSATION (Thiamine hydrochloride catalyzed synthesis of benzoin)

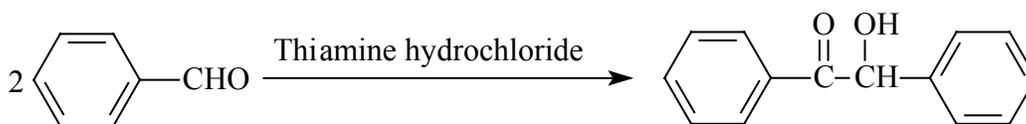
Conventional Procedure:



Non-green Component:

Involves the use of highly poisonous sodium cyanide

Alternate Green Procedure:



Chemicals Required:

Benzaldehyde	- 10 g
Thiamine hydrochloride	- 1.75 g
Sodium hydroxide	- 5 ml (2 M)
Ethanol	- 15 ml

The thiamine hydrochloride (1.75 g) was dissolved in water (about 5 ml) in a 50 ml round bottom flask. Ethanol (95%, 15 ml) was added and the solution was cooled by swirling the flask in an ice water bath. Meanwhile, sodium hydroxide solution (5 ml) was cooled in a small conical flask in an ice bath. Then over a period of about 10 min the sodium hydroxide solution was added dropwise to the thiamine solution. Fresh benzaldehyde (10 ml) was added to the reaction mixture. The mixture was heated gently on a water bath for about 90 min. The mixture was cooled to room temperature and then in ice bath to induce crystallization of the

benzoin. If product separated as oil, the mixture was reheated until it was once again homogeneous. Then it was allowed to cool more slowly than before. Scratching of the flask with a glass rod may induce crystallization.

Yield - 6 g (30%)

Melting point of benzoin - 135 °C

Caution:

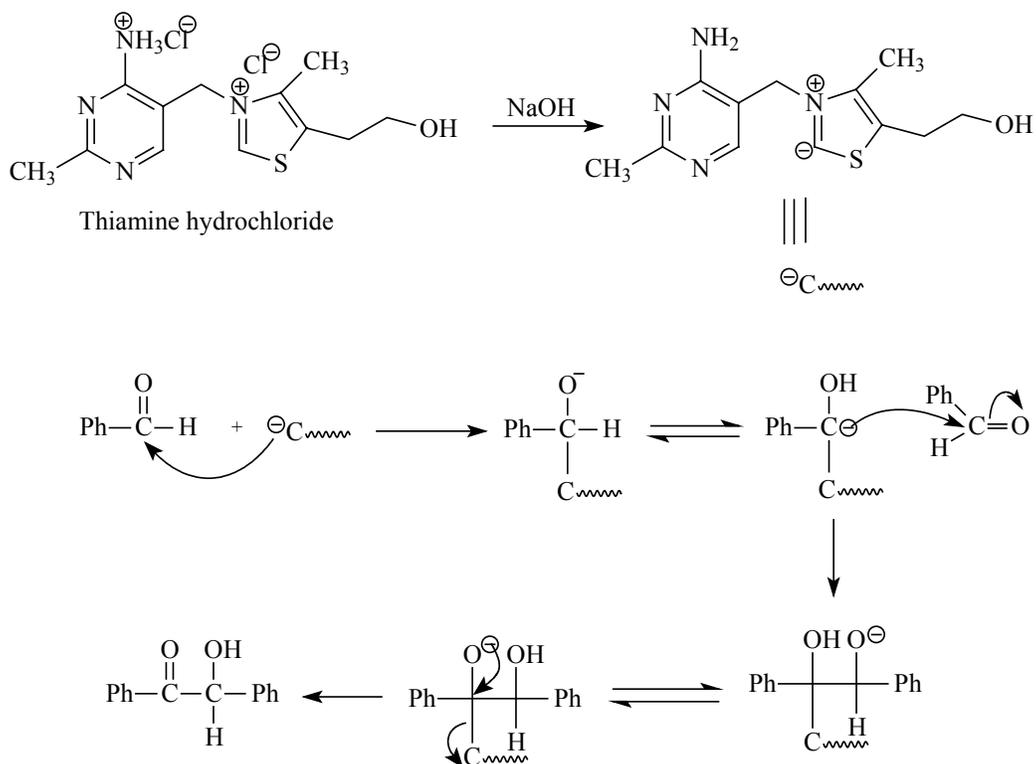
Benzaldehyde used in the experiment should be free of benzoic acid

Thiamine hydrochloride should be kept in refrigerator when it is not in use.

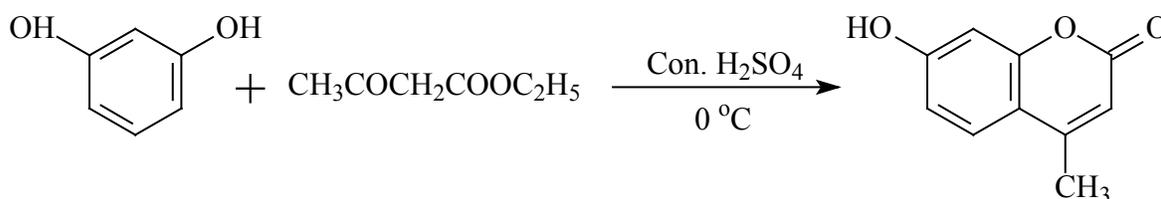
Green Context:

- Hazardous and poisonous cyanide ion is replaced by thiamine hydrochloride.
- Reaction is effected at a lower temperature.

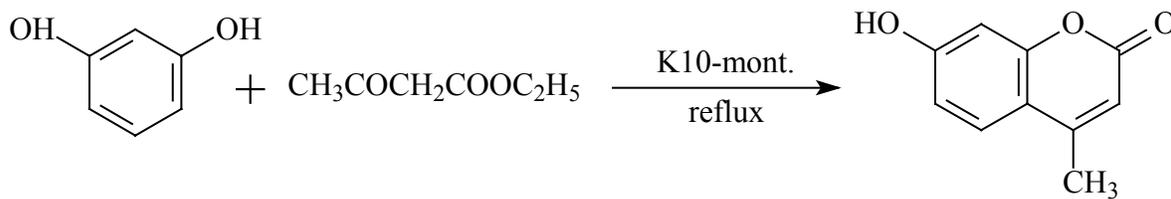
Mechanism:



P.,D. L. Lampman, G. M.Chriz, *Introduction to organic lab technique*; College Publishing, New York, **1982** experiment no 40

Experiment: PG-2**PECHMANN CONDENSATION FOR COUMARIN SYNTHESIS
(Clay catalyzed solid state synthesis of 7-hydroxy-4-methylcoumarin)****Conventional Procedure:****Non-green Component:**

Use of corrosive conc. Sulfuric acid.

Alternate Green Procedure:**Chemicals Required:**

Resorcinol - 1.1 g
Ethyl acetoacetate - 1.35 g
K10-montmorillonite- 1.5 g

Resorcinol (1.1 g) was dissolved completely in ethyl acetoacetate (1.35 g) in a 50 ml dry round bottom flask. K10-montmorillonite clay (1.5 g) was added to this homogeneous mixture and mixed thoroughly using a glass rod. The reaction mixture finally appeared as a paste. It was placed on a hot water bath and heated gently for 3-4 h. After completion of the reaction, mixture was cooled to room temperature and 7-hydroxy-4-methylcoumarin was extracted with ether by vigorous shaking. The clay was separated by filtration through Whatmann 4 filter paper. Separation with ether was repeated for 2 times. Finally the filtrate was evaporated and the product is obtained as a white solid.

Yield : 1.5 g (85%)

Melting point of 7-hydroxy-3-coumarin- 180 °C

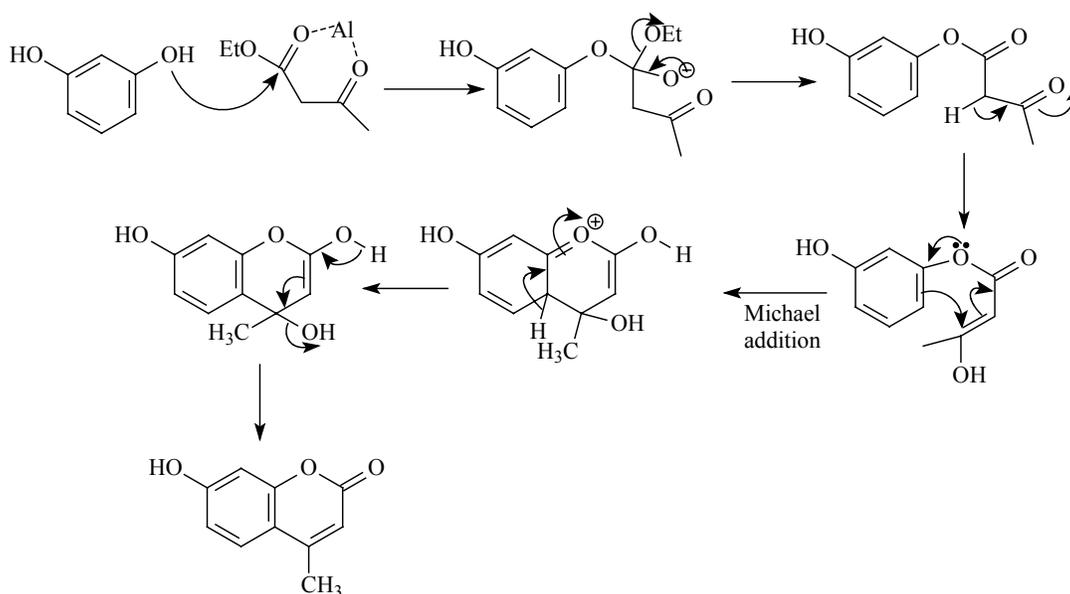
Green Context:

- Strong and corrosive H_2SO_4 is avoided.
- A solid acid catalyst K10 montmorillonite is employed.
- Reaction is carried out in solid state avoiding use of solvents.
- Catalyst can be reused.
- Largely reduced reaction time.
- Ice-bath conditions during addition is avoided.

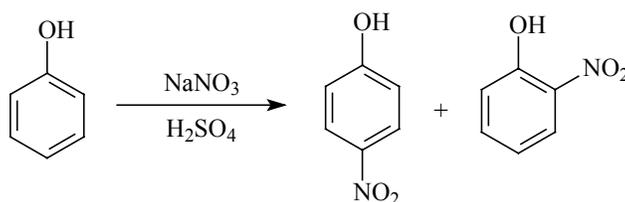
Note:

When refluxed on a heating mantle, the yield increases significantly.

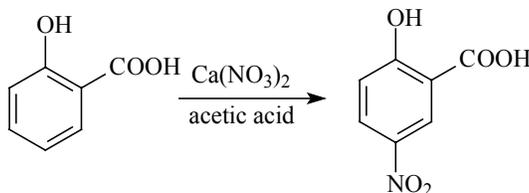
Mechanism:



Greener approach to undergraduate chemistry experiments, ACS publications, 2002, p 25.

Experiment: PG-3**ELECTROPHILIC AROMATIC SUBSTITUTION REACTION-I
(Nitration of phenol)****Conventional Procedure:****Non-green Component:**

Involves use of Con. Sulfuric acid

Alternative Green Procedure:**Chemicals Required:**

Calcium nitrate tetrahydrate - 1.5 g

Acetic acid - 5 ml

Salicylic acid - 1 g

Calcium nitrate (1.5 g) was dissolved in warm acetic acid (5 ml) and salicylic acid (1 g) was added to it. Then the mixture was heated in a boiling water bath (maintained at > 80 °C) for 1 min. Salicylic acid was dissolved completely and the solution became dark red. It was immediately poured into a 10 ml of ice cold water. The resultant turbid dark red solution was placed in a refrigerator. After four hours, the yellow crystals that separated were washed free of acid with minimum amount of ice cold water and then dried.

Yield: 0.66 g (50 %)

m.p. of 4-nitrosalicylic acid = 234 °C

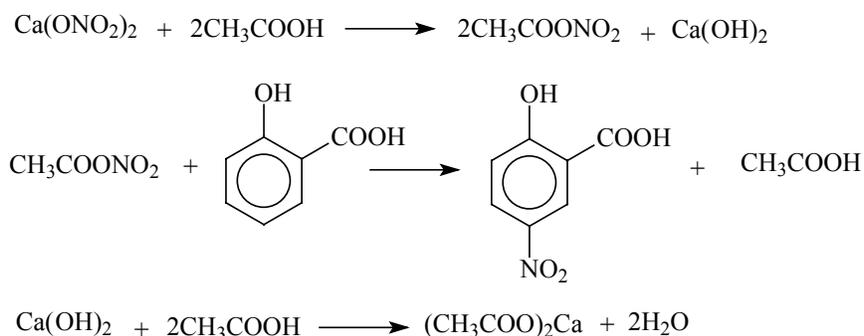
Green context:

- Nitration is rapid.
- Ecofriendly nitration of phenols and its derivatives without nitric acid
- Reagents and byproducts (calcium acetate) in this reaction are useful agrochemicals, environmentally benign and thus eco-friendly.
- Regioselective nitration is achieved.

Caution:

The yield of the reaction mainly depends on temperature of the reaction and solubility (since products are soluble in water). Very minimum amount of water should be used for washing of acetic acid as well as the byproducts like calcium acetate and calcium nitrate.

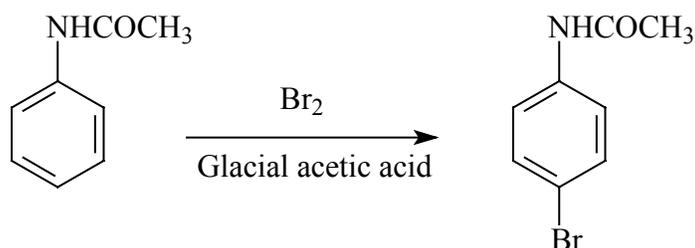
Mechanism:



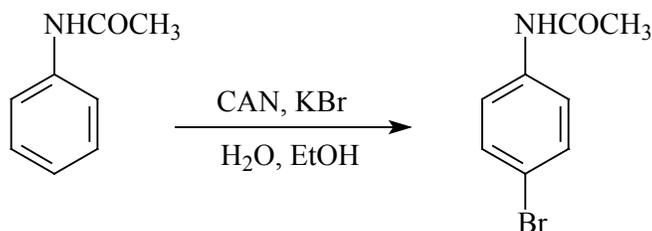
Note: This nitration procedure is very efficient with salicylic acid and thus may be used for making derivative of salicylic acid in identification of organic compounds for UG and PG level.

However, it may not give equally good results for nitration of all aromatic compounds and thus should not be treated as a general method of nitration..

A. K. Bose,* S. N. Ganguly, M. S. Manhas, S. Rao, J. Speck, U. Pekelny and E. Pombo-Villars, *Tetrahedron Lett.*, **2006**, 47,1885..

Experiment: PG-4**ELECTROPHILIC AROMATIC SUBSTITUTION REACTION-II
(Bromination of acetanilide)****Conventional Procedure:****Non-green Component:**

Liquid molecular bromine is used

Alternative Green Procedure:**Chemicals Required:**

- Acetanilide - 1 g
- Potassium bromide - 1 g
- Ceric ammonium nitrate - 6 g
- Ethanol - 15 mL
- Water - 15 mL

In a 250 ml conical flask acetanilide (1 g) was dissolved in ethanol (15 ml). Then potassium bromide (1 g) and ceric ammonium nitrate (6 g) were dissolved in water (15 ml). This solution was transferred into an addition funnel. This solution was added drop wise to the conical flask containing acetanilide solution. After the addition was over, the reaction mixture was stirred for 10 minutes in room temperature (white crystals appeared). Then this solution was poured into ice-cold

water. The white crystals were filtered through Buchner funnel and the solid was dried.

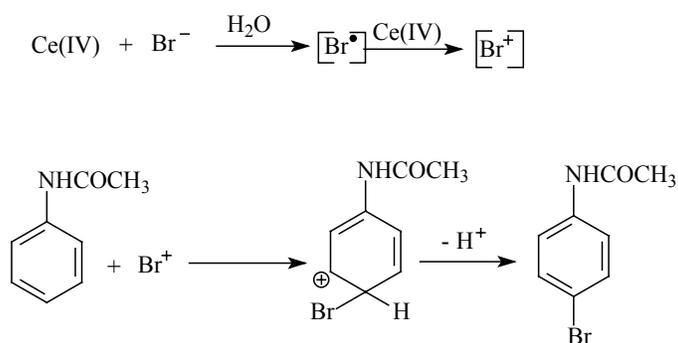
Yield: 1.34 g (85 %)

M.p. of *p*-bromoacetanilide = 165 °C

Green Context:

- Corrosive molecular bromine is replaced with a novel brominating agent.
- Bromination is carried out in aqueous medium.
- Chlorinated solvents are avoided.
- Use of acetic acid as solvent is avoided.
- Reaction is considerably fast.

Mechanism:

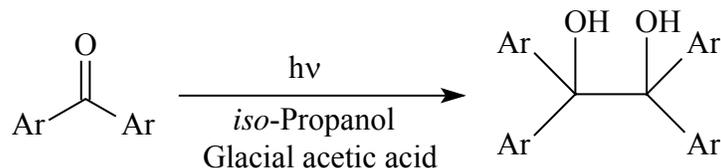


Note: This reaction can be used for making bromo-derivative of acetanilide in identification of organic compounds in UG as well as in PG level.

P. F.Schatz, *Journal of Chemical Education*. **1996**, 173, 267.

Experiment: PG-5**GREEN PHOTOCHEMICAL REACTION
(Photoreduction of benzophenone to benzopinacol)**

Benzopinacol can be prepared from benzophenone in presence of sun light (photochemically) using isopropanol as the reducing agent in presence of acetic acid. Acetic acid is added to prevent the cleavage of benzopinacol to benzophenone and benzhydrol by the alkali derived from the glass container used for the reaction.

**Chemicals Required:**

Benzophenone - 2.5 g

Iso-Propanol - 10 ml

Glacial Acetic Acid – one drop

Procedure:

Benzophenone (2.5 g) was placed in a test tube and dissolved in isopropanol ((10 ml). The test tube was then filled with isopropanol and to it was added a drop of glacial acetic acid. The test tube was stoppered and the reaction mixture was exposed to bright sun light. Colourless crystals of benzopinacol started appearing along the sides of the test tube after 5-6 hrs. The reaction mixture was allowed to stand in bright sun light for 4-5 days for the completion of the reaction. The solid was dried.

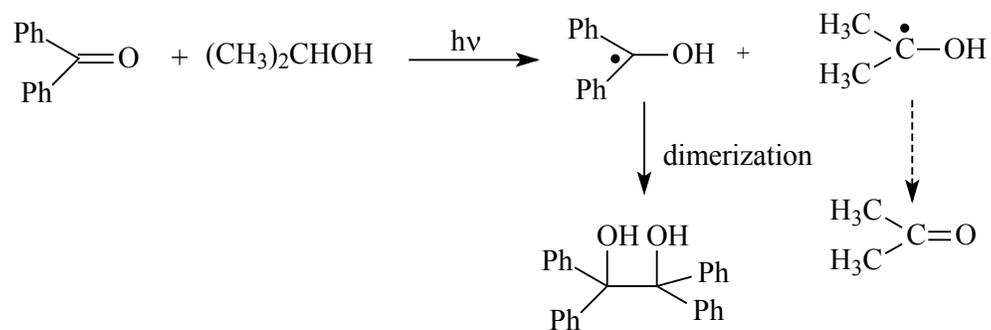
Report the yield and the m.p. (lit. m.p. 182 °C).

Green Context:

Use of safe chemicals and safer reaction conditions

Use of renewable source of energy (solar energy).

The product obtained above will be used in the next experiment (conversion of benzopinacol to benzopinacolone is pinacol-pinacolone rearrangement)

Mechanism:

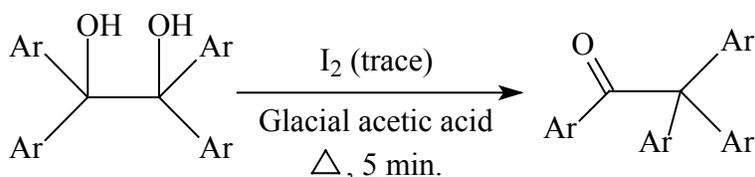
P.,D. L. Lampman and G.M.Chriz, *Introduction to Organic Lab Technique*; College Publishing, New York, 1982 exp. 47

Molecular Rearrangements

Experiment: PG-6

PINACOL PINACOLONE REARRANGEMENT REACTION-I (Preparation of benzopinacolone)

Benzopinacol obtained in the first experiment is converted to benzopinacolone by heating under reflux (5 minutes) with glacial acetic acid containing trace amount of iodine dissolved in it. This reaction is known as pinacol- pinacolone rearrangement.



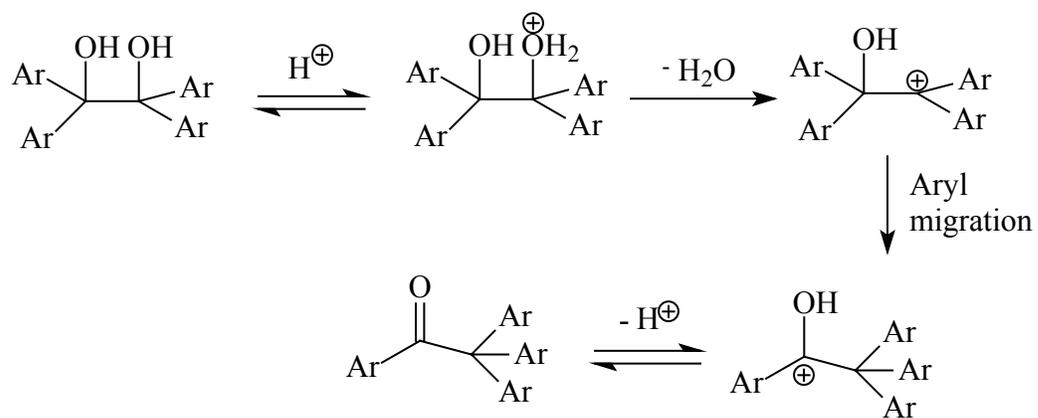
Chemicals Required:

Benzopinacol - 2.0 g
Glacial Acetic acid - 10 ml
Iodine – trace amount

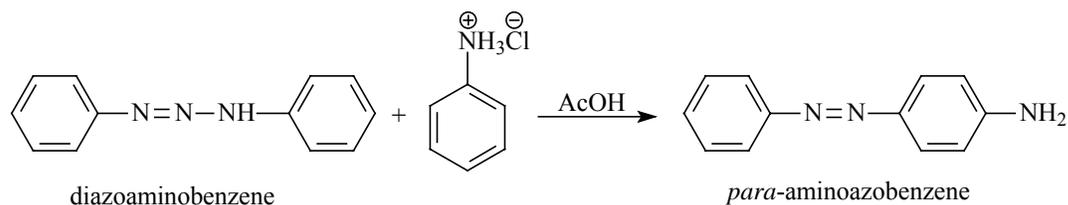
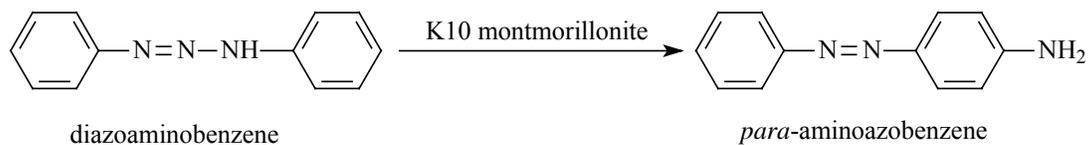
Procedure:

Benzopinacol (2.0 g) was placed in a round bottomed flask and to it was added a solution of iodine (trace) in glacial acetic acid (10 ml) and the reaction mixture was refluxed on a wire gauze by Bunsen burner for 5-7 minutes. The reaction mixture was allowed to cool down to room temperature and then kept in the refrigerator over night. The crystals of benzopinacolone were filtered, dried in air.

Report the yield and the m.p. (lit. m.p. 182 °C).

Mechanism:

W. E. Bachmann, *J. Am. Chem. Soc.* **1927**, 49, 246 (*Org. Synth.*, **1943**, Coll. Vol 2, p. 73)

Experiment: PG-7**REARRANGEMENT REACTION - II**
(Rearrangement of diazoaminobenzene to *p*-aminoazobenzene)**Conventional Procedure:****Alternative Green Procedure:****Chemicals Required:**

Diazoaminobenzene – 2 g

K10 montmorillonite – 2 g

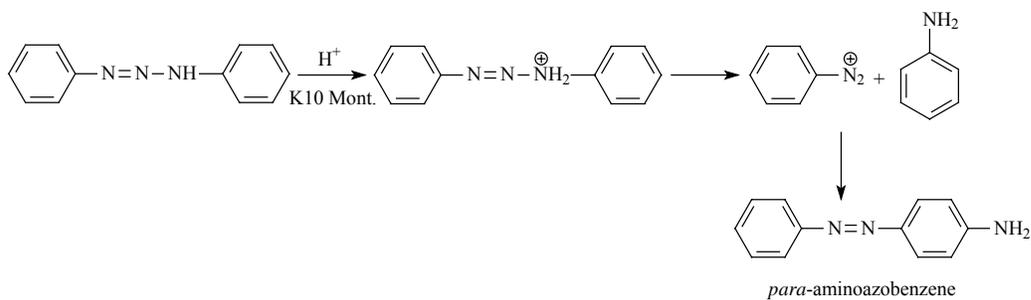
Diazoaminobenzene (2 g) was thoroughly mixed with K10 montmorillonite clay (2 g). The mixture was taken in a round bottom flask and heated in a water bath for 3 hours with periodical shaking after every 15 min. The mixture was then extracted with ether. The ether layer was evaporated and the residue was recrystallized from aqueous ethanol, m.p. 127-128 °C.

Yield : 1.7 g (85 %)**Green Context:**

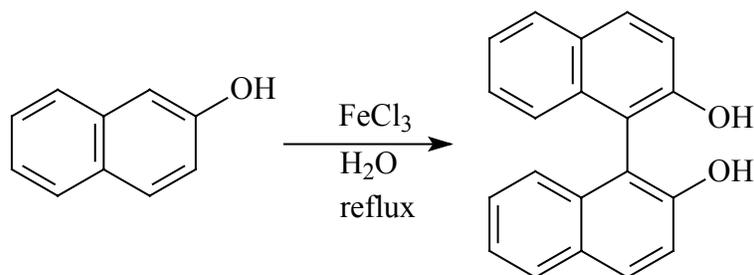
- Eco-friendly method
- Simple reaction procedure.

- No need for excess aniline and acetic acid

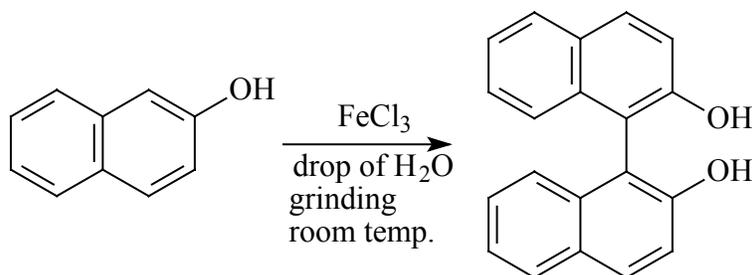
Mechanism:



K. Pitchumani, C. Venkatachalapathi and S. Sivasubramanian, *Indian J. Chem.*, **1997**, *36B*, 187.

Experiment: PG-8**RADICAL COUPLING REACTION
(Preparation of 1, 1-bis-2-naphthol)****Conventional Procedure:****Non-green Component:**

Use of more energy (reflux)

Green Procedure:**Chemicals Required:**

2-Naphthol - 2.88 g
 Iron(III) chloride - 0.7 g
 Water - 2 drops
 Toluene (for recrystallization)

A mixture of 2-naphthol (2.88 g) and iron(III) chloride (0.7 g) with 2 drops of water in an agate (or porcelain) mortar and pestle was ground for about 20

minutes. The mixture was allowed to stand for about 2 hrs with a little grinding now and then. The mixture was transferred with water (40 ml) into a 100 ml beaker and boiled for 10-15 minutes. The mixture was cooled and the solid was filtered, washed with boiling water (10 ml), dried and recrystallized from toluene., m.p. 214-217 °C.

Yield 3.9 g (90%)

Green Context:

Efficient method

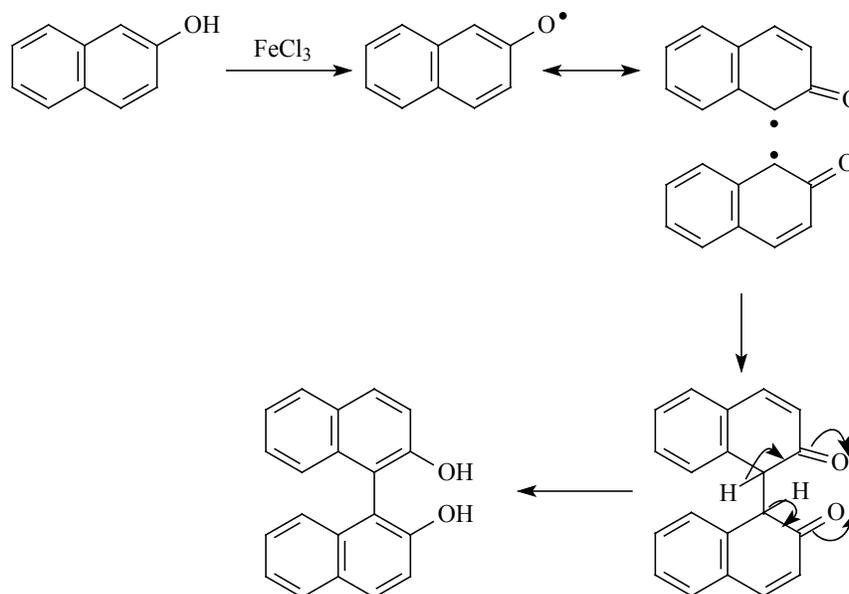
Easily available catalyst

Reaction is performed with simple grinding at room temperature without any solvent

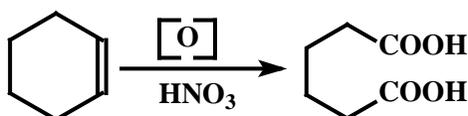
Work up of the reaction involves aqueous medium.

This demonstrates the concepts of oxidative coupling, free radical and C-C bond formations.

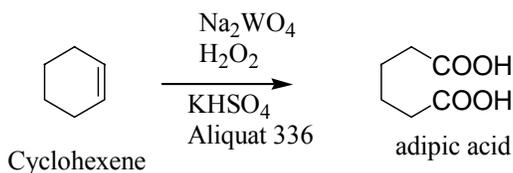
Mechanism:



A. I. Vogel, *Textbook of Practical Organic Chemistry*, Fifth Edition, 1989

Experiment: PG-9**GREEN OXIDATION REACTION
(Synthesis of adipic acid)****Conventional Procedure:****Non-green Component:**

This procedure involves corrosive conc. nitric acid. This causes evolution of oxides of nitrogen. The reaction has to be carried out in fume cupboard and oxides of nitrogen need to be absorbed in water.

Green Procedure:**Chemicals Required:**

Cyclohexene	- 2 g
Sodium Tungstate	- 0.5 g
Potassium hydrogen sulphate	- 0.37 g
Aliquat 336	- 0.5 g
Hydrogen peroxide (30%)	- 12 ml

To a 50 ml round- bottom flask fitted with a condenser sodium tungstate dihydrate (0.50 g) was added. This was followed by addition of aliquat 336 (0.5 g), 30% hydrogen peroxide (12 ml) and potassium hydrogen sulphate (0.37 g). The mixture was shaken and then cyclohexene (2 g) was added. The reaction mixture was heated on a sand bath to reflux for 2 hrs. The progress of the reaction was monitored by observing whether the layers are separated. As the liquid cyclohexene was converted to the water soluble adipic acid, the organic layer will eventually disappear. After two hours of reflux, the round-bottom flask was removed from the sand bath. Upon cooling, the crude adipic acid was precipitated. The crude sample was recrystallized from water to get pure adipic acid, m.p. 151-153 °C.

Yield 2.5 g (70%)

Green Context:

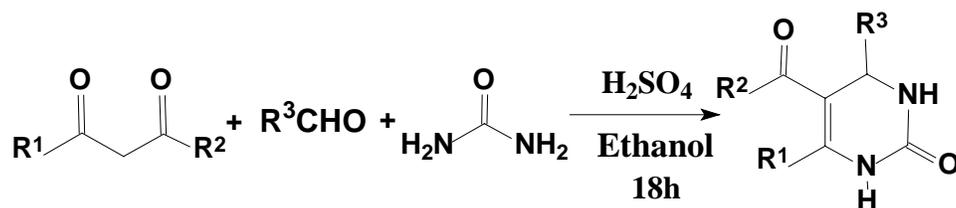
Eliminates the use of nitric acid

Atom economy: Waste by-products are minimized, better yield

Use of hydrogen peroxide as oxidizing agent in place of KMnO_4 or HNO_3

Phase transfer catalysis

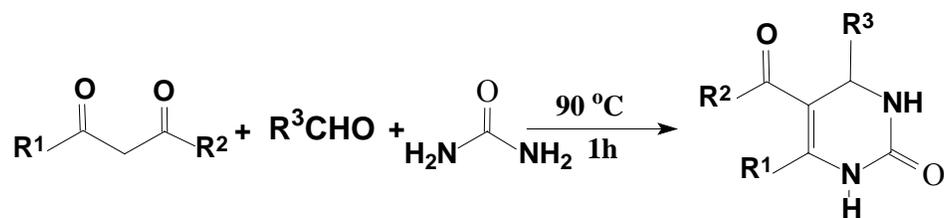
S. M. Reed and J. E. Hutchison, *Journal of Chemical Education*, **2000**, 77, 1627.

Experiment: PG-10**THREE COMPONENT COUPLING
(Synthesis of dihydropyrimidinone)****Conventional Procedure:****Non-green component:**

Use of sulphuric acid

Solvent workup

Long reaction time

Green Procedure:**Chemicals Required:**

Ethyl acetoacetate – 1.3 g

Benzaldehyde – 1.1 g

Urea – 0.7 g

Procedure:

A mixture of benzaldehyde (1.1 g), ethyl acetoacetate (1.3 g) and urea (0.7 g), taken in a round bottom flask was shaken by hand for 2 minutes. The reaction mixture was then heated in a water bath at 90 °C for one hour. With progress of the reaction a solid started to deposit and after one hour the flask is full of solid. The solid was taken out carefully with a spatula or spoon in a conical flask. The yellow solid was washed with cold water (1 ml) and then recrystallized from rectified spirit to give a colourless solid, mp 201-202 ° C.

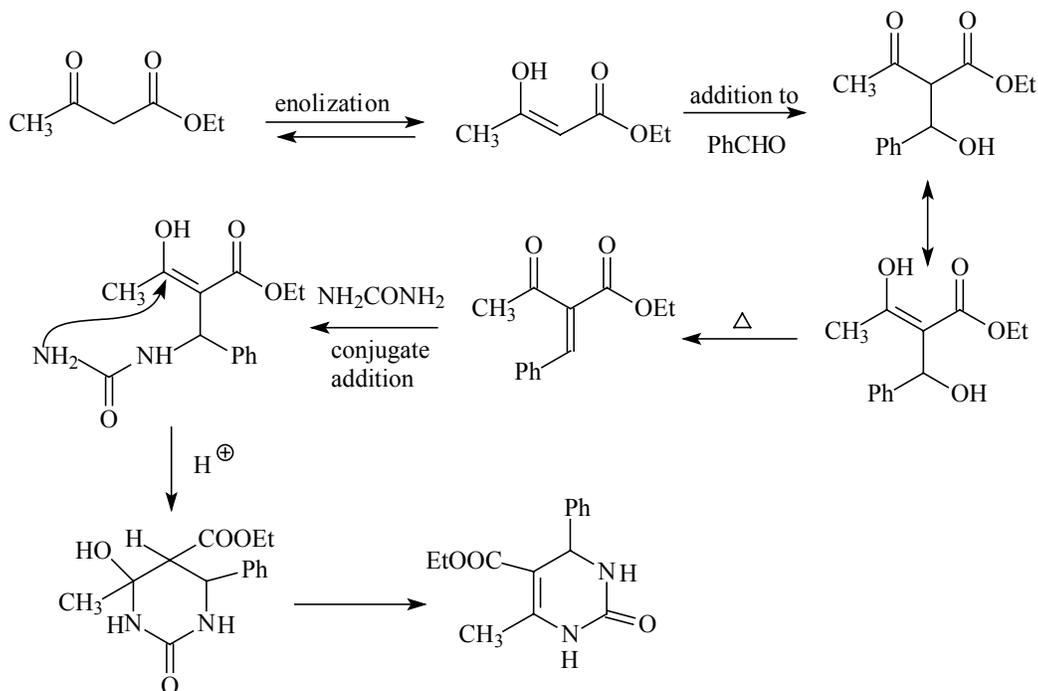
Yield: 2 g (79%)

Green context:

Use of no hazardous organic solvents

No requirement of catalyst

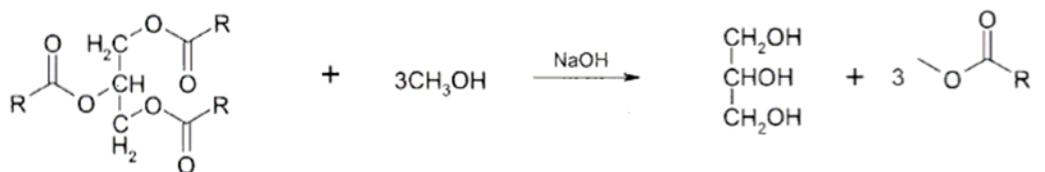
Faster reaction

Mechanism:

B. C. Ranu, A. Hajra and S. S. Dey, *Org. Proc. Res. Dev.* **2002**, 6, 817

Experiment: PG-11**TRANSESTERIFICATION REACTION
(Synthesis of biodiesel)****Introduction:**

This experiment focuses on synthesis of diesel fuel from vegetable oil. The mechanism involves a transesterification reaction, the process of transforming one type of ester into another type of ester.

Green Reaction:

Vegetable oil

Glycerol

Biodiesel

Chemicals Required:

Vegetable oil - 100 ml
Methanol - 20 ml
Sodium hydroxide - 3 pellets

Green Procedure:

The finely ground anhydrous NaOH was added into pure (99% or higher purity) methanol (20 ml) in a 250 ml Erlenmeyer flask and stirred vigorously until all the NaOH was dissolved. The pure vegetable oil (100 ml) was warmed to about 40 °C in a 250 ml beaker. The warmed up oil was poured into the methoxide solution with continuous stirring. At first the mixture would become cloudy, but should soon two layers would separate. This was stirred for 15-20 minutes. The contents of the flask were transferred into a 250 ml separatory funnel. The mixture will separate into two different layers. The glycerol will fall to the bottom, and the methyl ester (biodiesel) will float to the top. Allow the experiment to sit for an hour. The stopcock of the separatory funnel was opened and the glycerol was allowed to drain into a small beaker.

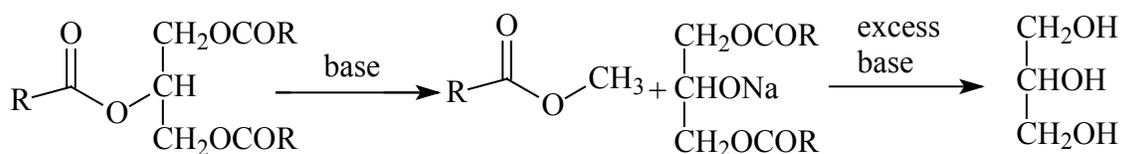
Green Context:

This lab experiment demonstrates three key green principles: the use of renewable feedstock, catalysis and design for degradation. Vegetable oil is a renewable starting material as it is derived from growing plants, rather than irreplaceable material like the earth's petroleum and natural gas supplies. The reaction is catalyzed by NaOH making this process economically viable for the industrial scale production of biodiesel. Biodiesel is an excellent product as it is environmentally friendly.

Safety:

- ❖ **Methanol:** Flammable and poisonous. Dispose excess by allowing it to evaporate in the fume hood.
- ❖ **NaOH:** Very corrosive. Causes severe burns. May cause permanent eye damage. Very harmful by ingestion.

Mechanism:



J. E. Thompson. *Greener Education Material for Chemists*
<http://greenchem.uoregon.edu/gems.html>

Experiment: PG-12**SOLVENT-FREE REACTION
(Microwave-assisted ammonium formate-mediated Knoevenagel reaction)****Chemicals Required:**

1. *p*-Anisaldehyde : 1.32 g
2. Ethyl cyanoacetate : 1.13 g
3. Ammonium formate : 630 mg
4. Domestic Microwave Oven

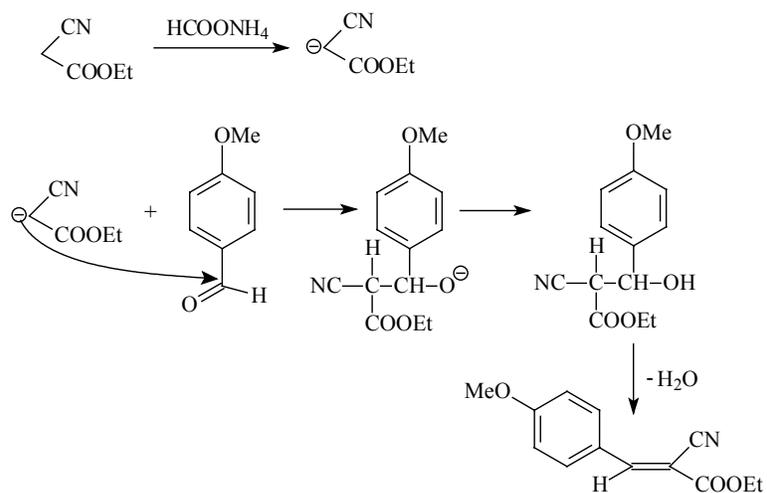
Procedure:

p-Anisaldehyde (1.32 g), ethyl cyanoacetate (1.13 g) and ammonium formate (630 mg, 1) were intimately mixed in a round bottomed flask fitted with CaCl₂ drying tube and placed on a bed of alumina taken in a beaker. This was then subjected to microwave irradiation for 90 seconds (with an installment of 30 sec each at a power level of 300 watts followed by intermittent cooling). After completion of reaction it was taken out, cooled to room temperature and crushed ice (20 gm) was added to the reaction mixture and shaken well. The solid product, precipitated in a granular form, was filtered, washed well with water and dried to furnish ethyl 2-cyano-3-(4'-methoxyphenyl)-propenoate (1.84 g, 80%) in practically pure form. The product can be further purified by recrystallization from ethyl acetate-petroleum ether (60°-80 °C), m.p. 88 °C.

Yield : 1.8 g (80 %)

Green Context:

- Solvent-free reaction procedure
- Simple workup and rapid conversion (within 90 sec)
- Use of microwave energy for activation

Mechanism:

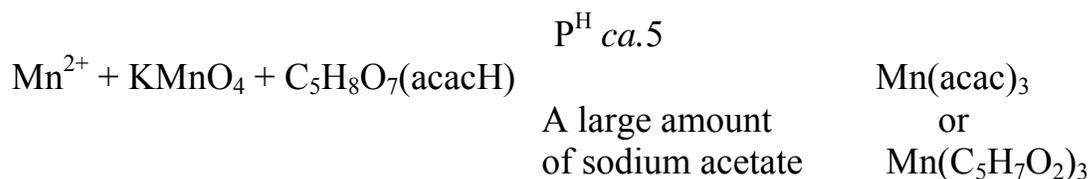
S. Bhar, Unpublished results

INORGANIC PREPARATION

Experiment: PG-13

Preparation of Manganese(III) acetylacetonate, $\text{Mn}(\text{acac})_3$ or $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3$

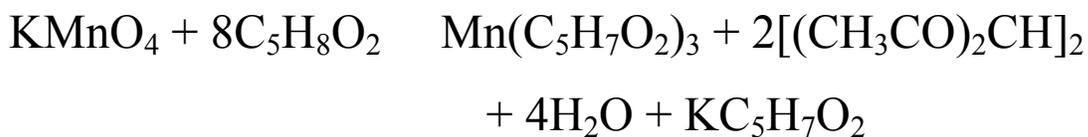
Conventional Procedure:



Non-green Component:

- Use of an excess of acetylacetonate
- Use of large amount of sodium acetate as buffer

Green Procedure:



Chemicals Required:

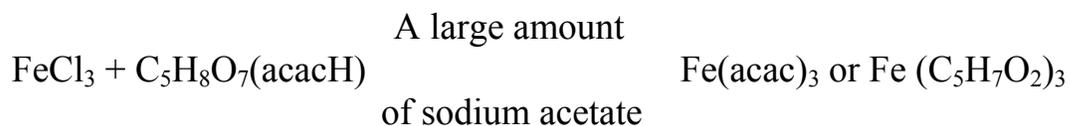
KMnO_4 : 5.0 g
 Acetylacetonate ($\text{C}_5\text{H}_8\text{O}_2$): 29 ml

Powdered KMnO_4 (5.0 g) was dissolved in a minimum amount of water by slight warming over a steam bath and the solution then filtered. Distilled acetylacetone (23.19 ml) was added to the solution with continuous stirring. A white crystalline compound was precipitated. The whole mixture was stirred for 15 min over steam bath and then allowed to cool for 10 min. The dark brown shiny crystals of Manganese(III) acetylacetonate, $\text{Mn}(\text{acac})_3$ was filtered and finally dried *in vacuo* over fused CaCl_2 .

Yield: 9.7g (87.03%)

The compound does not have sharp melting point but decomposes at *ca.* 155 °C (dec.).

M.N. Bhattacharjee, M.K. Chaudhuri and D.T. Khathing, *J. Chem. Soc., Dalton Trans.*, **1982**, 669.

Experiment: PG-14**Preparation of Iron(III) acetylacetonate, Fe(acac)₃ or Fe (C₅H₇O₂)₃****Conventional Procedure:****Non-green Component:**

- Use of a large excess of sodium acetate as buffer
- Use of an excess of acetylacetone

Green Procedure:**Chemicals Required:**

Ferric Chloride: 15 g

Aqueous KOH (20%): 83 ml

Procedure:

Iron(III) chloride (15 g) was dissolved in water (200 ml) in a 500 ml beaker followed by addition of 20% aqueous solution of KOH (83 ml) in parts with constant stirring to precipitate the metal as its hydroxide. The suspended precipitate was allowed to settle with the supernatant liquid becoming colourless. The flocculent was washed several times with water by decantation, finally by filtration through Whatman No. 42 filter paper and again washing twice with cold water. Then the precipitate was quantitatively transferred into a 250 ml beaker and the whole was kept on ice-water bath for 15min.. Distilled acetylacetone (30.55 ml) was added to the slurry and mixed thoroughly with a glass rod. The whole mixture was continued to stand on ice-water bath for 30 min and then at room temperature for 30 min with occasional stirring. An exothermic reaction sets in leading to the formation of deep red shiny crystals of Iron(III) acetylacetonate, $\text{Fe}(\text{acac})_3$. The reaction container was then placed in an ice-water bath for 15 min. The compound was filtered through Whatman No.42 filter paper and dried *in vacuo* over fused CaCl_2 .

Yield: 28.6g (87.56%)

Mp 180-181°C.

M. K. Chaudhuri and S.K. Ghosh, *J. Chem. Soc. Dalton Trans.*, **1983**, 839.

4. Synthesis of Green Reagents

i) Synthesis of tetrabutylammonium tribromide (TBATB)

A sample of molybdic acid monohydrate, $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ (0.16 mmol, 0.029 g) was taken in a 250 mL glass beaker and 30% hydrogen peroxide, H_2O_2 (15.52 mmol, 1.76 mL) was added to it. The mixture was stirred for 30 min. at room temperature. The solution, which was slightly turbid, was filtered through Whatman No.1 filter paper on a glass funnel. The clear filtrate was collected in a 250 mL glass beaker and kept in the ice-water bath. Tetrabutylammonium bromide, TBAB (15.51 mmol, 5 g) and potassium bromide, KBr (31.01 mmol, 3.69 g) dissolved in (0.3M) H_2SO_4 (15.52 mmol, 51.70 mL) was added to this solution slowly with continuous stirring leading to the formation of a yellow precipitate. The mixture was continued to stir in ice-water bath for another ~1h and then kept standing in ice-water bath for 2 h to get an orange yellow compound of Tetrabutylammonium tribromide, TBATB. The compound was separated by filtration under suction using Whatman No.1 filter paper. It was dried *in vacuo* over fused CaCl_2 and was recrystallized from acetonitrile.

Yield: 7.2 g (96%)

Melting Point: 76-77 $^{\circ}\text{C}$. The chemical analyses, IR and conductance of the compound match very well with those reported in literature.

Application

Bromination of Chalcone by TBATB

Crystals of tetrabutylammonium tribromide, **TBATB**, (0.524 g, 1 mmol) were finely powdered by grinding with a pestle in a mortar for a few minutes. To it chalcone (0.416 g, 1 mmol) and 0.5 mL of water were added. The whole was mixed thoroughly and left at room temperature with occasional agitation or grinding for 15 min. The progress of the reaction was monitored by dissolving a small amount of the sample in ethyl acetate followed by TLC of the ethyl acetate solution over silica gel. Upon

completion of the reaction, 20 mL of water was added to the reaction mixture and stirred for 10 min. The reaction mixture was filtered, washed with water and air-dried to afford the compounds.

Yield: 0.7 g (95%).

Green Context:

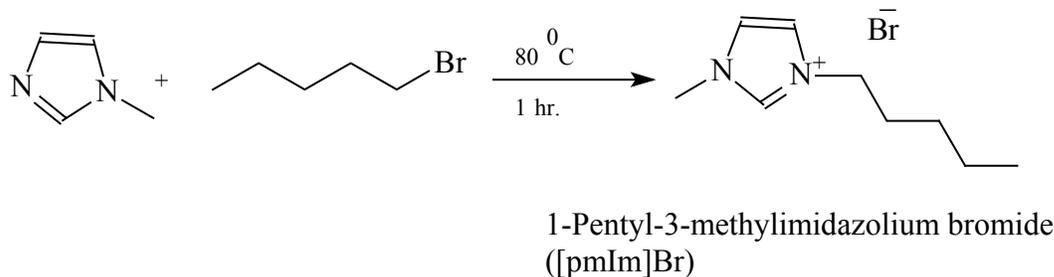
This reagent is a green brominating agent and avoids the use of highly toxic and hazardous liquid bromine.

M. K. Chaudhuri, A.T. Khan, B. K. Patel, D. Dey, W. Kharmawphlang, T. R. Lakshmiprapha and G.C. Mandal, *Tetrahedron Lett*, **1998**, 39, 8163;

M.K. Chaudhuri et al., *Pure Appl. Chem.*, **2001**, 73, 93;

US Patent No. 7005548, February 28, 2006.

ii) Preparation of ionic liquid, [pmlm]Br



Chemicals required:

- i) *N*-Methyl imidazole
- ii) *n*-Pentyl bromide

Experimental procedure:

N-Methyl imidazole (1.2 g, 15 mmol) and *n*-pentyl bromide (2.71 g, 18 mmol) were taken in a small round bottom flask. Then the mixture was heated in water bath at 80 °C for an hour, keeping a guard tube at the mouth of the round bottom flask. A clear yellow viscous liquid was formed. It was then cooled and washed with a small amount of ether (1 ml) twice with ether to remove any unreacted bromide and remaining viscous liquid was dried by a vacuum pump.

Yield - 3.42 g (88%)

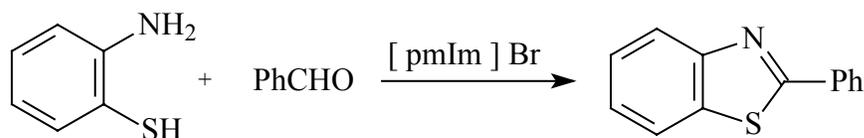
Spectroscopic Data:

¹HNMR (300MHz, CDCl₃): δ 0.8 (t, *J* = 6.9 Hz, 3H), 1.23 (m, 4H), 1.78 (m, 2H), 3.9 (s, 3H), 4.17 (t, *J* = 7.28 Hz, 2H), 7.65 (d, *J* = 11.0 Hz, 2H), 9.5 (s, 1H).

V. Namboodiri and R.S. Varma, *Org. Lett.* **2002**, *4*, 3161

Application of ionic liquid:

Preparation of 2- phenylbenzothiazoles catalyzed by ionic liquid, [pmlm]Br.



Chemical Required:

- i) Benzaldehyde – 1.0 g
- ii) 2-Amino-thiophenol – 11.25 g
- iii) Ionic liquid [pmlm]Br – 0.5 g

Experimental Procedure:

A mixture of benzaldehyde (1.0 g) and 2-amino-thiophenol (1.25 g,) was heated in microwave oven (10% power, 120 W) in presence of ionic liquid [pmlm]Br (500 mg) for 3 mins. After being cooled the reaction mixture was extracted with ether and the ether extract was evaporated to leave the crude product which was recrystallized from ethanol-water (4:1) to give a white solid.

Yield – 1.9 g (90%).

M.P. 112-115 °C

IR (Kbr) : 1645, 1510, 1477, 962, 765 cm^{-1}

^1H NMR (300 MHz, CDCl_3): δ 7.39 (t, $J = 7.3$ Hz, 1H), 7.48-7.55 (m, 4H), 7.90 (d, $J = 7.9$ Hz, 1H), 8.09-8.12 (m, 3 H).

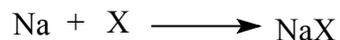
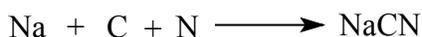
Green Context:

This ionic liquid, [pmlm]Br is benign and works here as catalyst as well as reaction medium and thus no other solvent is required in this reaction. The reaction is also atom efficient.

B. C. Ranu, R. Jana and S. S. Dey, *Chem. Lett.* **2004**, 33, 274

5. Alternative Green Procedures for Organic Qualitative Analysis - Detection of N, S, Cl, Br, I

In the present practice, the use of metallic sodium for fusion with organic compound is terribly hazardous and is a cause of great worry and concern in a student laboratory. The idea of fusion with sodium metal is to convert the water insoluble organically bound extra elements to water-soluble sodium salts which can be easily detected by various tests.



(X = Cl/Br/I)

A non hazardous and safe procedure:

i) Use of zinc and sodium carbonate instead of metallic sodium

Organic sample (about 50 mg) is thoroughly mixed with an intimate mixture of Zn dust (200 mg) and Na_2CO_3 (300 mg) powder in a fusion tube, heated first gently and then strongly in the flame till it becomes red hot and kept at red-hot condition for two minutes. The bottom part of the fusion tube is plunged into 5 ml of distilled water taken in a mortar, ground well with the pestle and filtered. With the filtrate tests for S, N and Cl / Br / I are carried out as usual as in the case of Lassaigne's Test.

1. The fusion tube must be heated VERY STRONGLY, KEEPING AT RED HOT CONDITION THROUGHOUT FOR AT LEAST TWO MINUTES. If not properly heated, fusion is not properly done (as in case of sodium also), and thus expected observation (colour change) may not be made. In that case, it is advised to repeat the fusion.

2. The amount of water taken in the mortar must be within 5 ml.; otherwise, the solution will be too dilute to respond to tests, described below.
3. While carrying out the test for nitrogen, ferrous sulphate crystals are to be added; not the solution. This is to avoid excessive dilution.
4. Acidification must be carried out with dilute sulfuric acid, not with HCl.
5. No ferric chloride should be added.

S. No.	Experiment	Observation	Inference
1.	0.5 ml filtrate + FeSO ₄ crystal heat + dil. H ₂ SO ₄	Prussian blue color	N present
2.	a) 0.5 ml filtrate + Sodium nitroprusside	Violet color	S present
	b) filtrate + dil acetic acid + Lead acetate	Black ppt	S present
3.	filtrate + FeCl ₃	Blood red	N+S both present
4.	filtrate + 2 drops Conc HNO ₃ boil cool + AgNO ₃	Curdy white ppt (Soluble in NH ₄ OH)	Chlorine present
		Pale yellow ppt (Partly soluble in NH ₄ OH)	Bromine present
		Yellow ppt (Insoluble in NH ₄ OH)	Iodine present

Green context:

- This experiment totally eliminates the risk of explosion and fire hazard which are often met while carrying out the same experiments using metallic sodium.
- The aforesaid zinc-alkali mixture (prepared by intimately mixing 2 parts by weight of zinc dust and 3 parts by weight of sodium carbonate can be stored in a stoppered bottle for more than a month.

II) Novel Use of Salts of Some Organic Acids in the Detection of Extra Elements Present in Organic Compounds

In an ignition tube fuse a few milligrams of compound with twice the quantity of sodium or potassium salts of any of the following organic acids, acetic /oxalic/succinic/benzoic or phthalic. To have enough concentration of the material, repeat the process of fusion in 2-3 ignition tubes. Plunge the red hot tubes in 5-8 ml of distilled water taken in a china dish. Boil for a minute. Filter and test a few drops as follows to infer result.

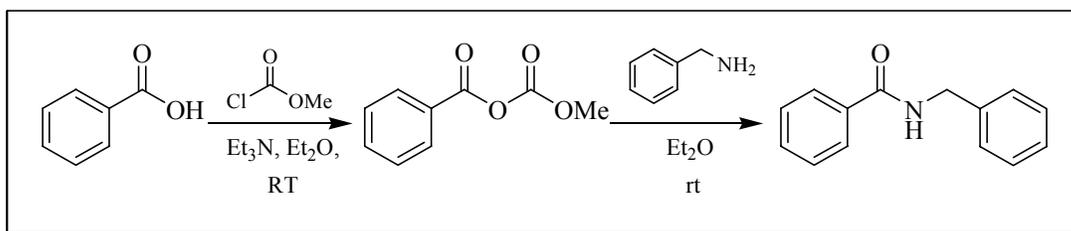
S.No	COMPOUND	REAGENT	OBSERVATION (COLOR)	REMARK
1	SULPHUR	Sodium Nitroprusside	Violet Color	S present
2	NITROGEN	Ferrous Sulphate Crystals, heat +dil.H ₂ SO ₄	Prussian Blue	N present
3	HALOGENS (Cl ⁻ , Br ⁻ , I ⁻) Boil with dil.HNO ₃ and cool	AgNO ₃	1. Curdy white ppt 2. Pale yellow ppt 3. Yellow ppt	1. Cl 2. Br 3. I

NOTE: This method works well with covalently bound nitrogen of aromatic compounds (except p-nitrophenol and p-aminophenol)

6. Alternative Green Procedure for Preparation of a Derivative for Carboxylic Acid

In qualitative organic analysis the preparation of a derivative of the identified organic compound is required for confirmation of its identity. For carboxylic acids the most common derivative is amide and acetanilide which are prepared through acid chlorides by treatment with phosphorus pentachloride or thionyl chloride which are highly toxic. Thus, an alternative method for preparation of a solid derivative of carboxylic acids avoiding these toxic chemicals is highly desirable. The *N*-benzyl benzamide can be a good alternative and it can be prepared in a greener way.

Preparation of *N*-Benzyl Benzamide from Benzoic acid



To a solution of benzoic acid (1.2 g) and triethylamine (1.5 ml) in diethyl ether (50 ml) at room temperature was added methyl chloroformate (0.8 ml) dropwise with vigorous mixing. After two minutes, the mixture was filtered through a Buchner funnel and the precipitate was washed with diethyl ether (10 ml). The combined ether layer was treated with benzylamine (1.1 ml) at room temperature and then the diethyl ether was allowed to evaporate over water bath. The viscous residue was treated with crushed ice and the

resultant white precipitate was filtered through a Buchner funnel. The white precipitate was air-dried (0.9 gm, 44%). M.p: 104-106 °C (recrystallized from ethyl acetate/hexane mixture).

Spectral data for *N*-benzyl benzamide: IR (Neat): 3321, 3059, 1640, 1543, 1418 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.8-7.98 (d, $J = 7.5$ Hz, 2H), 7.48-7.516(t, $J = 7.4$ Hz, 1H), 7.404-7.441 (t, $J = 7.4$ Hz, 2H) 7.348-7.359 (d, $J=7.8$ Hz, 3H), 7.294-7.315 (t, $J=7.2$ Hz, 1H), 6.47(bs,1H) 4.637-4.651(d, 2 H) ; ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 138.1, 134.3, 131.5, 128.8, 128.6, 127.9, 127.6, 126.9, 44.1.

Note: This procedure can be used for making derivative of other carboxylic acids and is suitable for both UG and PG levels.

7. Inorganic Analysis

Background

Inorganic mixture analysis involves the isolation and identification of anions (acidic radicals) and the cations (basic radicals). It is advised that anions are analysed first and then the cations.

For the systematic analysis of anions, the usual practice is to prepare a sodium carbonate extract. 0.5-1g of the mixture is boiled with 1.5–3g (4 to 5 times) of sodium carbonate in 20 ml-distilled water. When the volume reduces to $\frac{2}{3}$ rd it is cooled and filtered. The filtrate known as sodium carbonate extract contains various anions as their sodium salts and is analysed in detail.

Discussion:

In the classical procedures the fate of the residue of this extract is completely omitted. Consequently the residue is rejected and thrown away.

Since fifty percent of the original mixture comprises of anions, it is logical to expect that the residue left after filtering off the sodium carbonate extract should contain the cations (50% of the mixture) as their carbonates.

In the absence of this sample reasoning a lot of wastage of the mixture and consequently time, energy and resource are resulted.

Present Proposal:

It is strongly recommended that cation analysis be carried out with the residue of sodium carbonate extract.

The procedure can be slightly modified when Cu^{+2} , As^{+3} or Sb^{+3} are present as cations. Since these form soluble salt with Na_2CO_3 these may escape from the residue into the filtrate. To overcome this problem do as follows:

Take $\frac{1}{4}$ th of the Na_2CO_3 extract and neutralize with a slight excess of dil HCl, heat and pass H_2S into it. If coloured precipitates are obtained (Cu_2S –

Brown-black, As_2S_3 yellow, $\text{Sb}_2\text{S}_3 + \text{Sb}_2\text{S}_5$ – orange) proceed for their confirmatory tests.

In the absence of any precipitate the possibility of the presence of these three cations may be ruled out.

Novel use of Some Organic Acids in Inorganic Mixture Analysis

In an ignition tube fuse a few milligrams of mixture with twice the quantity of sodium or potassium salts of any of the following organic acids, acetic/oxalic/succinic/ benzoic or phthalic. To have enough concentration of the material, repeat the process of fusion in 2-3 ignition tubes. Plunge the red hot tubes in 5-8 ml of distilled water taken in a china dish. Boil for a minute, filter and test a few drops as follows to infer result.

S.No	SALT	REAGENT	OBSERVATION (COLOR)	REMARK
1.	Sulphides Sulphites Thiosulphate	Sodium Nitroprusside	Violet Color	S present
2.	Sulphates	-do-	Transient Violet (Fleeting)	S present
3.	Nitrites	Ferrous Sulphate Crystals, heat + dil. H_2SO_4	Prussian Blue	N present
4.	Halogens (Cl^- , Br^- , I^-) Boil with dil. HNO_3 and cool	AgNO_3	1. Curdy white ppt 2. Pale yellow ppt 3. Yellow ppt	1. Cl 2. Br 3. I

1. Soluble in NH_4OH
2. Partly soluble in NH_4OH
3. Insoluble in NH_4OH

Qualitative Inorganic Analysis

As the conventional wet analysis of basic and acidic radicals involve a large amount of strong mineral acids such as sulfuric, nitric and hydrochloric acids the whole laboratory is often filled with all these acid vapour, which is not at all a healthy atmosphere. Thus to minimize this problem Spot test might be a good alternative.

Spot test may be carried out in a number of ways. (a) on “filter paper” (ordinary or sometimes Whatman No. 42 or preferably, the hardened variety No.542. The paper should be cut into strips and stored in petri dishes) (b) on a “spot plate” (c) in a “micro crucible” or (d) in “test tube”. For convenience every analysis may be divided into certain categories :

1. Preliminary test (both for cations and anions)
2. Test for basic radicals (in solution).
3. Test for acid radicals (in solution).

Preliminary Test (Dry Tests for Basic Radicals)

In this category details have been outlined in standard text books. Borax bead test (for coloured salts) and flame test (for basic radicals) should be carried out extensively.

Direct vision spectroscopy should be introduced for routine tests in qualitative analysis. Atomic absorption spectroscopy may be used, if fund is permitted.

IN THE FOLLOWING TABLE FLAME COLOURS AND THE CORRESPONDING WAVE LENGTHS OF SOME METALS ARE GIVEN.

<i>ELEMENT</i>	COLOUR	WAVE LENGTH IN nm
(a) Sodium	(a) Golden Yellow (colourless through double blue glass)	a) 589.0 , 589.6

(b) Potassium	(b) (i) Bluish violet (ii) Crimson red (with double blue glass)	b) (i) 404.4 , 404.7 (ii) 766.5, 769.9
(c) Calcium	(c) (i) Transient brick red (ii) Light green (with double blue glass)	618 – 620 , 554.4, 422.7
(d) Strontium	(d) (i) Persistent crimson (ii) Purple (with double blue glass).	(d) 674.4, 662.8, 606.0, 460.7
(e) Barium	(e) (i) Persistent apple green (ii) Blush green	(e) 553.6, 534.7, 524.3, 513.7, 487.4
(f) Copper	(f) Bluish green	
(g) Borate	(g) Blue flame with green edge	
(h) Pb, As, Sb, Bi, Sn	(h) Lumbent blue	
(i) CaF ₂	(i) Transient deep red (ii) Crimson red (with double blue glass)	

Separation of Cu²⁺ and Cd²⁺

Conventional Procedure: Highly poisonous KCN (aq.) is used.

Suggestion: A Green Procedure, described below.

Solution A: An ammoniacal solution of a mixture of Cu²⁺ and Cd²⁺ is prepared by diluting and ammoniating equal volumes of Cu²⁺ and Cd²⁺ solutions.

Solution B: Prepared from Solution A by evaporating off ammonia, followed by acidification with *ca.* 5% AcOH or *ca.* 0.1 (N) HCl.

Procedure: Hydrochloric acid-sulphide method: Soln. A or Soln. B is diluted with water. To the hot solution is added H₂S-water till CuS and CdS precipitate completely. The slurry is either filtered and the residue is taken up with *ca.* 1 M HCl, or directly acidified with HCl to *ca.* 1 M, boiled for a few minutes. CuS remains insoluble but CdS dissolves. It is filtered and a few ml of the filtrate is neutralized (NH₄OH) and H₂S-water is added –

yellow CdS appears. The residual CuS is dissolved in HNO₃ and tests for Cu²⁺ are performed.

SPOT TESTS FOR BASIC RADICALS

Spot tests utilize a very little amount of the salt solution. The great advantage of spot test is economy of materials, time, space and labour. The sensitivity of such tests is expressed in micrograms

(1 μg = 10⁻⁶ g).

Since spot tests are interfered by presence of other radicals, these should be carried out in the respective groups.

Apparatus needed in spot analysis :

- (a) Spot plate (b) Filter paper (c) Micro Test tubes (d) Droppers (e) Electrical centrifuge (f) Dropping bottle (g) Silica watch glass (h) Micro burner.

GROUP – I Ag⁺, Pb⁺⁺, Hg₂⁺⁺

1. Test for Ag ⁺	Experiment	Observation
Reagent: 1% K ₂ CrO ₄ solution in neutral or slightly acetic acid medium	Two or three drops of the test solution are taken in a spot plate, a few drops of ammonium carbonate solution are added, stirred and allowed to settle for some time. A drop of the clear solution is taken out from the top and placed on a filter paper. A drop of potassium chromate solution is added on the filter paper.	A red ring is formed $2 \text{Ag}^+ + \text{CrO}_4^{=}$ Ag ₂ CrO ₄
2. Test for Hg ₂ ⁺⁺ (a) With Diphenyl Carbazide	A piece of filter paper is impregnated with freshly prepared reagent. A drop of the test solution	A blue ring is developed [Hg (II) ion may

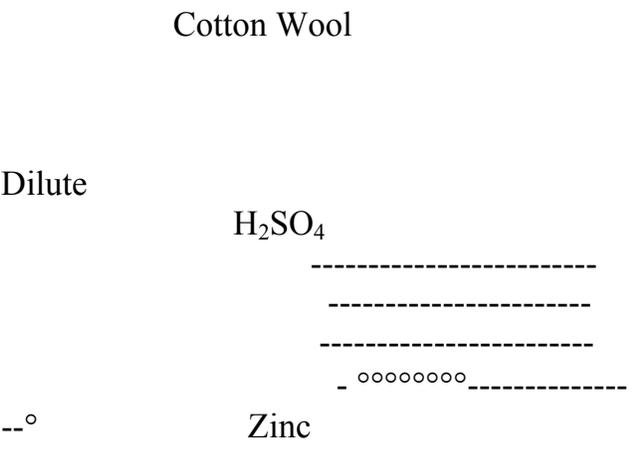
Reagent : 1% alcoholic solution.	is added on the reagent and allowed to dry at room temperature.	interfere]
(b) With Potassium nitrite Reagent : Concentrated aqueous solution of potassium nitrite	A drop of the faintly acidic test solution of the sample is placed on a filter paper and a drop of potassium nitrite solution is added. It is then washed with distilled water.	A black or dark grey spot is produced $\text{Hg}_2^{++} + \text{NO}_2^- + \text{H}_2\text{O} = 2\text{Hg} + \text{NO}_3^- + 2\text{H}^+$
3. Test for Pb⁺⁺ a) Reagents : I) Dilute HCl (ii) KI	(a) A little of the test solution is taken in a test tube, dilute hydrochloric acid is added.	$\text{Pb}^{++} + 2\text{Cl}^- \rightarrow \text{PbCl}_2$ A white ppt is obtained which dissolves on heating but reappears as needle shaped crystals on cooling.
(b) Cinchonine– Potassium iodide Reagent test: 0.1 g of Cinchonine is dissolved in 10 ml of boiling water acidified with a little HNO ₃ The solution is cooled and 0.2 g of KI is added to it.	A filter paper is moistened with the reagent and then a drop of faintly acidic solution containing Pb ⁺⁺ ion is placed on it.	A deep yellow ring confirms Pb ⁺⁺

Gr . II A (Cu²⁺, Hg²⁺, Cd²⁺, Pb²⁺ Bi³⁺)

4. Test for Cu²⁺ (a) With ammonia solution : Reagent : Liquor ammonia :	Expt. A little of cupric (II) salt solution is taken in a test tube, excess of liquor ammonia is added.	Obs. A deep blue solution is obtained (nickel salt may interfere)
(b) With Rubaenic acid .	A drop of the neutral or	A greenish – black (olive green) spot is obtained.

<p>Reagent: (0.5% rubaenic acid solution in ethanol.</p>	<p>acidic test solution is placed on What man paper, a drop of the reagent is added or sprayed. The paper is exposed to ammonia vapour and then air dried.</p>	
<p>5. <u>Test for Cd²⁺</u> (a) With ammonia solution and Na₂S or (NH₄)₂ S. Reagent: (i) Liquor ammonia. (ii) (NH₄)₂ S or Na₂S aqueous solution.</p>	<p>The test solution is taken in a test tube, treated with excess ammonia, centrifuged, and the centrifugate is preserved. A What man filter paper is impregnated with white ZnS ppt. A little of the centrifugate is taken in a capillary & touched the, ZnS ppt. It is then acidified by HCl/ CH₃ COOH.</p>	<p>A bright yellow ring will gradually develop.</p>
<p>(b) Diphenyl carbazide test (Feigl's test): Reagent : 3%</p>	<p>A drop of the previously made diphenyl carbazide</p>	<p>Red-violet ring or spot develops.</p>

alcoholic solution of diphenyl carbazide saturated with KSCN and a few crystals of KI	solution is added on a filter paper, dried and one drop of the test solution is added and dried over ammonia.	
<p>6. Tests for Hg²⁺ (a) with diphenyl carbazide:</p> <p>Reagent : 1% alcoholic solution of diphenylcarbazine.</p>	One drop of the test solution (neutral or in acetic acid) is placed on the filter paper. The drop on the filter is moistened with the reagent followed by a drop of 0.2M HNO ₃	A violet or a blue colour appears.
(b) With ammonium thiocyanate and cobalt (II) acetate:	A drop of the test solution is taken on a spot plate. A small crystal of each of ammonium thiocyanate and cobalt (II) acetate are added. It is stirred with a glass rod.	<p>A blue or violet colouration is developed.</p> $\text{Hg}^{2+} + \text{Co}^{2+} + 4\text{SCN}^-$ $\text{Co}[\text{Hg}(\text{SCN})_4]$
<p>7. Test for Bi³⁺ Cinchonine - potassium iodide reagent test: Reagent: 1 g. of Cinchonine is dissolved in 100 mL. hot water in</p>	A filter paper is moistened with one drop of the reagent. A drop of the faintly acidic test solution is added on it.	An orange spot with Cinchonine is obtained.

<p>presence of a few drops of HNO_3. It is cooled and then added 2 g. of KI</p>		
<p>8. Test for As^{3+} (a) <u>Gutzeit's test</u> : Reagent : a) Granulated zinc (As free) (b) Pure dil H_2SO_4 . (c) cuprous chloride.</p>	<p>In a test tube 2-3 drops of test solution, a few pieces of arsenic free granulated zinc and 5-6 ml dilute H_2SO_4 are added. The test tube is plugged with cotton impregnated with cuprous chloride and dried. A filter paper moistened with a solution of (1:1) AgNO_3 is placed on the mouth of the test tube. After a few minutes, the filter paper is removed. A drop of water is then added in the centre of the spot. Zn or Al and sodium hydroxide solution may replace zinc and dil . H_2SO_4. In that case the solution is to be warmed.</p>	<p>A grey (black) ring will be observed.</p> <p>Filter paper with AgNO_3 Soln</p> <p>Cotton Wool</p> <p>Dilute H_2SO_4</p> <p>--° Zinc</p> 

<p>(c) Test with silver nitrate solution: Reagent: (i) Ammonia (ii) 10% H₂O₂ (iii) Acetic acid (iv) 1% AgNO₃ Solution.</p>	<p>2 or 3 drops of the test solution, a few drops of ammonia and 10% H₂O₂ solution are taken in a semimicro test tube and then warmed. The mixture is then acidified with dilute acetic acid. One or 2 drops of 1% AgNO₃ solution are added.</p>	<p>A red brown ppt. or coloration appears.</p>
<p>9. <u>Test for Sb³⁺</u>: a) Test with Rhodamine B Reagent : 0.01% aqueous solution of Rhodamine B</p>	<p>One drop of the test solution is taken on a spot plate. A few drops of conc. HCl are added to make the solution strongly acidic. A few crystals of NaNO₂ are added and stirred with a glass rod. One drop of the Rhodamine – B solution is added.</p>	<p>Bright red Solution changes to violet.</p>
<p>(b) Test with H₂S or (NH₄)₂S solution Reagent (i) H₂S – water (ii) Aqueous solution of</p>	<p>A few drops of the test solution (dilute HCl) are taken in a Semi-micro test tube.</p>	<p>Orange ppt.</p>

(NH ₄) ₂ S	A few drops of H ₂ S – water or (NH ₄) ₂ S Solution are added.	
10. <u>Test for Sn²⁺</u> (a) Cacotheline test: Reagent : 0.25% aqueous solution of Cacotheline. Sn (II) solution must be used. HCl solution of tin salt is to be reduced with metallic iron / aluminium . The test solution should be 2(M) HCl.	(a) A filter paper is impregnated with a drop of the reagent followed by a drop of the test solution.	A violet spot is obtained.
(b) Methylene blue test: Reagent: 1% methylene blue in (M) HCl	(b) One or two drops of methylene blue are taken on a spot plate. One drop of the test solution (in HCl) is added.	Blue colour of the indicator is discharged.

Gr. IIB (Co²⁺, Ni²⁺, Mn²⁺, Zn²⁺)

15. <u>Test for Co²⁺</u> <u>Ammonium thiocyanate test:</u> Reagent: 10% aqueous or acetone solution of NH ₄ CNS	In a semi micro test tube one or two drops of the slightly acidic test solution, a few mg. of NaF or NH ₄ HF ₂ and 5-6 drops of acetone solution of NH ₄ CNS and amyl alcohol are added and shaken.	A green to blue colour appears.
16. <u>Test for Ni²⁺</u> Dimethyl glyoxime test:	In a semi-micro test tube one or two drops of the test solution (acidic or neutral), a little of NaF, one or two drops of saturated sodium tartarate	A rose-red ppt. will be formed.

	solution and two or three drops of dimethyl glyoxime solution are added. This mixture is then made ammonical with NH_4OH solution.	
17. Test for Mn^{2+} Reagent: NaBiO_3	One drop of the test solution is taken in a semimicro test tube ; One or two drops of conc. HNO_3 are added. Now a pinch of NaBiO_3 (sodium bismuthate) is added and then shaken.	A purple colour develops.
18. Test for Zn^{2+} a) Test with H_2S or $(\text{NH}_4)_2\text{S}$:	a) One or two drops of the test solution are taken in a semimicro test tube, dilute acetic acid are added just to acidity & then added H_2S water or $(\text{NH}_4)_2\text{S}$.	A white ppt. will be formed.
b) Ammonium mercurithiocyanate test. Reagents: (i) 0.1% CuSO_4 in aqueous solution (ii) 4.25 g. of mercuric chloride and 4.5 g. of ammonium thiocyanate are dissolved in 50 ml. Water (stock solution)	On a spot plate one drop of zinc or zincate solution, one drop of CuSO_4 solution, one drop of acetic acid and one drop of ammonium mercuric thiocyanate solution are added. The mixture is stirred with a glass rod. [If $\text{Co}(\text{NO}_3)_2$ solution is used in place of copper sulphate solution then a deep blue ppt. will be obtained] .	Violet colouration or precipitate is obtained.
	GrIV : Ba^{2+}, Ca^{2+}, Sr^{2+}	
19. Test for Ba^{2+} a) Barium chromate test: Reagents: (i) 10% solution disodium salt of EDTA (ii) 20% solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (iii) 30% $\text{CH}_3\text{COONH}_4$ solution. (iv) 30% K_2CrO_4 soln.	In a semi-micro test tube one drop of the test solution and two drops of Na_2EDTA are added & kept on a water bath for 15-20 seconds. One drop of MgCl_2 solution, four drops of ammonium acetate and two drops of K_2CrO_4 solution are added and placed on the water bath for 1-2 minutes	Yellow ppt. will be formed . (may also be confirmed by Flame test).
(b) Sodium Rhodizonate test.	One drop of the neutral or faintly acidic test solution is placed on a drop reaction paper.	A reddish brown spot is developed.

<p>Reagent: 0.5% aqueous solution of sodium Rhodizonate.</p>	<p>One drop of the sodium Rhodizonate soln. is added. Now one or two drops of 0.5M HCl are added on the brown spot.</p>	<p>Formation of bright red spot confirms Ba^{2+}. In absence of Ba^{2+} the reddish brown spot disappears (Ca^{2+} and Mg^{2+} do not interfere).</p>
<p>20. Test for Ca^{2+} :</p> <p>a) Calcium oxalate test: Reagents : 40% $(NH_4)_2SO_4$ solution.</p> <p>b) Sodium rhodizonate test: Reagent : i) 0.5% aqueous solution of rhodizonate (ii) Solid $(NH_4)_2SO_4$</p>	<p>a) Two drops of the dilute test solution, one drop of 2(M) HCl and 2-3 drops of 40% $(NH_4)_2SO_4$ solution are taken in a test tube. The mixture is kept on the water bath for 5 minutes and then centrifuged.</p> <p>b) Gr. IV carbonates are dissolved in dilute HCl. One or two drops of this solution are taken in a micro crucible, evaporate nearly to dryness, 0.5g. of solid $(NH_4)_2SO_4$ are added, heated gently and finally strongly heated until no more white fumes are obtained. It is then cooled. Now one drop of sodium rhodizonate solution and one drop of dilute alkali (NaOH) are added.</p>	<p>White ppt, confirms Sr^{2+} To the centrifugate acetate buffer solution (pH = 4) and ammonium or potassium oxalate solution are added. It is again kept on the water bath, if required, for a few minutes. White crystalline ppt. confirms Ca^{2+}</p> <p>Violet ppt. is obtained. This confirms Ca^{2+}</p>
<p>21. Test for Sr^{2+}</p> <p>(i) Test with sodium Rhodizonate solution. Reagent : 0.5% aqueous solution.</p> <p>(ii) In presence of Ba^{2+} Reagent: saturated solution of potassium chromate</p>	<p>(i) One drop of neutral test solution is taken on a spot plate and one drop of the reagent is added.</p> <p>(ii) One drop of saturated solution of potassium chromate is placed on a Whatman paper. It is dried. One drop of the test solution is added to the paper; After one or two minutes one drop of the reagent is added on the moist spot.</p>	<p>(i) A reddish brown ppt. or colouration confirms Sr^{2+}</p> <p>(ii) A brownish red spot or ring confirms Sr^{2+}</p>

	Gr. V Radicals	
<p>22. <u>Test for Mg²⁺</u> Titan Yellow test: Reagent : 0.1% aqueous solution of Titan yellow: [Note : This test is easily carried out in absence of radicals from Gr I to IV] Reagents :</p> <p>(i) 10 g of disodium salt of EDTA, 15 ml conc, NaOH solution and 45 ml water are mixed to give a solution. (ii) Saturated solution of Ba(NO₃)₂</p>	<p>(i) <u>In absence of Gr I to IV radicals.</u> To one drop of the test solution on a spot plate one drop of the reagent and one drop of 2M sodium hydroxide solution are added. [This test can also be performed in a test tube]</p> <p>One drop of test solution, 8 drops of EDTA solution (i) are mixed and kept on water bath for 1 minute . In case of any turbidity, it is centrifuged . The centrifugate is taken. To this are added 1-2 drops of Titan yellow and 10 drops of Ba(NO₃)₂ solution. [Blank test must be performed]</p>	<p>A red ppt. or colour confirms Mg²⁺ [Blank test must be performed side by side]</p> <p>Red colouration or ppt. confirms Mg²⁺</p>
<p>23. <u>Tests for Na⁺</u> <u>Zinc Uranyl acetate test:</u> Reagent:</p> <p>(a) 10 g. uranyl acetate dihydrate is dissolved in a mixture of 5ml glacial acetic acid and 20 ml water. The solution is diluted to 50 ml. (b) 30 g zinc acetate dihydrate is dissolved in a mixture of 5ml glacial acetic acid and 20 ml water. It is diluted to 50 ml with water. Solutions a and b are mixed together. 0.5 g sodium chloride is then added . The mixture is allowed to stand for 24 hours and</p>	<p>One drop of the neutral aqueous solution of the test solution is taken on a black watch glass and stirred with 8 drops of the reagent .</p> <p>[Note: the sensitivity of the test is increased in dilute alcoholic solution]</p>	<p>Formation of yellow ppt or turbidity confirms Na⁺</p>

then filtered. The filtrate is used.		
<p>24. Tests for K^+ Reagent: Sodium cobaltinitrite solution.</p>	<p>In a centrifuge tube (semi-micro tube) a few drops of the neutral or acetic acid test solution and a few drops of sodium cobaltinitrite solution (freshly prepared) are added. It is shaken.</p> <p>[Note: The sensitivity of the test may be increased by adding a little of 0.05% $AgNO_3$ solution.</p> <p>Ammonium salts, iodides and other reducing agents must be absent.</p> <p>If $AgNO_3$ solution is added then the test solution must be halide free.]</p>	Yellow ppt. confirms K^+
<p>25. Test for NH_4^+ Nessler's Reagent test: <u>Reagent:</u> 11.5 g of HgI_2 and 8 g of KI are dissolved in 50ml ammonia free water, 50 ml of 6M KOH solution is added, allowed to stand for 24 hours. The clear liquid is decanted & kept in the dark</p>	<p>i) A few drops of the test solution are taken on a watch glass and mixed with a few drops conc. KOH solution. One drop of this solution is taken on filter paper and one drop of Nessler's solution is added.</p> <p>(ii) The above test can also be carried out in a t,t, In that case test solution and KOH solution are taken in a test tube It is heated. A filter paper soaked with Nessler's solution is held over the mouth of the test tube</p>	<p>(i) A yellow or brown spot confirms NH_4^+</p> <p>(ii) The filter paper becomes yellow or brown.</p>

SPOT TESTS FOR ACID RADICALS

<p>1. Tests for F^- (a) Zirconium-Alizarin- S tests : Reagents : (i) 0.1% aqueous solution of Alizarin-S (ii) (ii) 0.1 g solid zirconyl chloride or $Zr(NO_3)_2$ is</p>	<p>(a) 2 drops each of Alizarin-S and Zirconyl nitrate (chloride) solution are taken an a spot plate. One or two drops of the fluoride solution</p>	<p>(a) Reddish-violet colour changes to yellow</p>
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<p>dissolved in 20 ml conc. HCl and diluted to 100 ml with water.</p> <p>(b) Ferric thiocyanate-fluoride test :</p>	<p>(aqueous) are added.</p> <p>[Note : Interference : SO_4^{2-}, $\text{S}_2\text{O}_3^{2-}$, PO_4^{3-}, ASO_4^{3-}, Al(III), SI(iv)]</p> <p>(b) [Ferric chloride forms red solution with thiocyanate. The red colour disappears in presence of F^- ion]. One drop of ferric chloride solution is taken in a test tube. 2-3 drops of NH_4SCN solution are added. A red solution is obtained. Now test solution is added.</p>	<p>Disappearance of red colour confirms F^- ion.</p>
<p>2. Test for Cl^- Diphenylcarbazide Test :</p> <p>Reagent : 1% alcoholic solution of diphenylcarbazide</p>	<p>A little of the test sample is taken in a semimicro test tube. A little of powdered $\text{K}_2\text{Cr}_2\text{O}_7$ and a few drops of conc. H_2SO_4 are added. The test tube is corked and a dropper having one drop of NaOH solution is introduced into the test tube without touching the contents inside. The apparatus is heated for a few minutes. The alkali solution becomes yellow. After cooling the yellow</p>	<p>Formation of a violet colour confirms Cl^-</p>

	<p>solution is added to diphenyl carbazide solution, acidified with sulphuric acid.</p> <p><u>Alternatively:</u> The yellow solution of the dropper is taken in a semimicro test tube, acidified with dil H_2SO_4, 1-2 ml of amyl alcohol and little hydrogen peroxide solution are added and the mixture is shaken.</p> <p>[covalent chlorides like Hg_2Cl_2, AgCl do not respond to chromyl chloride test. For such salts, sodium carbonate extract may be prepared. The extract on evaporation to dryness will give residue of NaCl. The solid residue may be used for the test.</p>	
<p>3) <u>Test for Br^-</u> a) Fuchsin (or magenta) test : Reagent : 0.1% Fuchsin solution decolorised by saturating with SO_2 gas.</p>	<p>(a) A few milligrams of the test solid is taken in a microtube. A little solid $\text{K}_2\text{Cr}_2\text{O}_7$ and a few drops of conc. H_2SO_4 are added and heated slowly. A piece of filter paper impregnated with the fuchsin-sulphur dioxide reagent is held over the liberated bromine (reddish-brown vapour).</p>	<p>(a) A blue or violet colour confirms Br^- (Cl^-, F^-, I^- don't interfere)</p>

<p>b) Chlorine water test : test : Reagent (i) chlorine water. (ii) carbon disulphide or carbon tetrachloride. (iii) H₂SO₄</p>	<p>(b) A little of the test sample is taken in a test tube, dil. H₂SO₄ and 2 ml of CCl₄ are added now, dropwise added chlorine water to this mixture and shaken.</p>	<p>(b) Reddish brown colour or the organic layer confirms Br⁻</p>
<p>4. <u>Tests for I</u> a) Starch Test : Reagent : 1% starch solution in hot water. b) <u>Chlorine water Test</u> :</p>	<p>(a) One drop of the acidic test solution is placed on a spot plate. One drop of starch solution and one drop of NaNO₂ solution are added. (b) Similar to that of Bromide. In this case iodide salt is to be taken.</p>	<p>(a) Blue colouration confirms I⁻ (b) Violet colour of the organic layer confirms I⁻</p>

Note : Iodide is recognised by its violet vapour on heating.

<p>5. <u>Test for NO₂⁻</u> a) AZO-dye test: Reagents : (i) Sulphanilic acid : 0.5 g of sulphanilic acid dissolved in 30 ml of glacial acetic acid and 75 ml of water. It is filtered and the clear filtrate is used. (ii) α - Naphthyl amine: 0.1 g of - α - naphthyl amine is heated with 70 ml. of water. It is cooled 30 ml of acetic acid is added, filtered & the clear filtrate is used. b) <u>Starch-iodide Test:</u></p>	<p>(a) One drop of the dilute acetic acid solution of the nitrite salt is taken on a spot plate, one drop of sulphanilic acid reagent is added. It is mixed with a glass rod. Then one drop of α-naphthyl amine reagent is added. b) In a semi-micro test tube a little of the</p>	<p>(a) A red colour indicates Nitrite.</p>
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<p>Reagent: 2.5 percent aqueous solution of starch containing a little of potassium iodide.</p>	<p>solid sample, few drops of very dilute (less than 2N) acetic acid and one or two drops of starch-potassium iodide solution are added.</p>	<p>b) Blue solution confirms Nitrite.</p>
<p>6. Test for Nitrate (NO_3^-) a) (In absence of Nitrite) Reagent: i) Sulphanilic acid . ii) α – Naphthyl amine. iii) Zinc dust. b) In presence of Nitrite : Test for nitrate in presence of nitrite may be carried out by decomposing nitrite by boiling with sulphuric acid.</p>	<p>a) One drop of acetic acid test solution of the sample is taken on a spot plate, a little of zinc dust added. One drop each of sulphanilic acid and α-naphthylamine are added.</p>	<p>a) A red colouration confirms Nitrate.</p>
<p>7. Test for Sulphide, thiosulphate and thiocyanate ($\text{S}^{=}$, $\text{S}_2\text{O}_3^{=}$, SCN^-) (Raschig's test): Iodine Azide test: Reagent: 2.5 g of NaN_3, 12.7 g. of iodine and 10 g. of KI are dissolved in 100 ml water.</p>	<p>One drop of the test solution and one drop of the iodine-azide reagent are mixed on a watch glass.</p>	<p>Brown colour of iodine solution is discharged immediately. A gas (N_2) is also evolved slowly.. $\text{S}^{=}$, $\text{S}_2\text{O}_3^{=}$, SCN^- is present.</p>
<p>8. a) Test for sulphide ($\text{S}^{=}$) : (In absence) of $\text{SO}_3^{=}$, $\text{S}_2\text{O}_3^{=}$, SCN^-): Sodium nitro prusside test: Reagent : 1% aqueous solution of sodium nitro prusside. (b) Iodine-Azide Test: (In presence of $\text{SO}_3^{=}$,</p>	<p>a) The test sample is taken in a test tube, fitted with a bent tube. A few drops dil H_2SO_4 are added, the liberated gas is passed through sodium hydroxide solution in another test tube. One drop of this alkali solution is added to sodium nitroprusside solution on a spot plate. b) Na_2CO_3 extract of the test sample is</p>	<p>a) A violet colour confirms sulphide ($\text{S}^{=}$).</p>

<p>$S_2O_3^{2-}$ and SCN^-) Reagent : Solid $CdCO_3$</p>	<p>prepared. An excess of solid $CdCO_3$ is added & shaken vigorously. A yellow ppt. is obtained. It is collected. With this yellow ppt. iodine- azide test is performed.</p>	<p>b) Discharge of brown colour of the solution & evolution of colour less gas confirms S^{2-}</p>
<p>9. Test for Sulphite (SO_3^{2-}). Sodium nitro -prusside test: Reagent: a) 1% nitroprusside solution. b) Saturated Zinc sulphate solution.</p>	<p>A few drops of an alkaline solution of the test sample are taken in a semi-micro test tube., 1 or 2 drops of sodium nitroprusside solution and 1 or 2 drops of $ZnSO_4$ solution are added. [Note; In presence of S^{2-} ion, this test may be carried out by removing S^{2-} ion with $CdCO_3$ as described above.]</p>	<p>Intense red solution confirms SO_3^{2-} [The colour may be intensified by adding one drop of $K_4[Fe(CN)_6]$.</p>

<p>10. Test for Sulphate (SO_4^{2-}). a) <u>Barium sulphate-potassium permanganate Test:</u> <u>Reagent:</u> a) 1% $BaCl_2$ Solution b) 1% MnO_4 Solution c) H_2O_2 or Oxalic acid solution (1N) b) <u>Test for insoluble sulphate:</u> A little amount of the insoluble sulphate is reduced in the reducing zone of the Bunsen flame on a platinum wire. The mass on the platinum wire is then introduced in alkaline sodium nitro prusside solution on a</p>	<p>Two or three drops of the test solution are taken in a centrifuge tube. Two drops of $KMnO_4$ and two drops of $BaCl_2$ solution are added. The pink colour of supernatant solution is discharged by adding a few drops of H_2O_2 or oxalic acid.</p> <p>A violet colouration is obtained</p>	<p>Violet colour of the ppt. Confirms (SO_4^{2-}).</p> <p>(SO_4^{2-}) is confirmed.</p>
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<p>spot plate.</p> <p>The mass on the platinum , wire may also be dipped in iodine-azide solution</p>	<p>The azide solution gradually becomes colourless with the evolution of a gas (nitrogen).</p>	<p>(SO₄⁼) is confirmed.</p>
<p>11. <u>Test for Thiocyanate (SCN⁻)</u> <u>Reagent : 10% FeCl₃ solution.</u> A filter paper is impregnated with a drop of FeCl₃ solution, it is dried over the flame. One drop of neutral test solution and one drop of HCl are added. It is allowed to stand.</p>	<p>A red ring is formed.</p>	<p>SCN⁻ is confirmed</p>