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Original research

Designing green and sustainable experiments for undergraduate organic chemistry labs

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Abstract:

Four synthesis experiments were redesigned for university chemistry laboratories via green and sustainable methodology: synthesis of acetanilide; synthesis of dibromopropanone; synthesis of stilbene di-bromide; and synthesis of nitro salicylic acid. The structure of the resulted compounds was confirmed via elemental analysis, ^{1}HNMR, and ^{13}CNMR spectral data. The green framework of the experiments was assessed by matching the new design with the conventional ones. In each planned synthesis, the twelve principles of green chemistry were pronounced through; preventing waste, accidents, and pollution; maximizing atom economy and energy efficiency; minimizing hazardous and derivatives; designing for safer chemicals and degradation; using safer solvent and catalysis; and employing renewable feedstock. Group discussions were arranged among the targeted undergraduate students to ensure the green and sustainable context of green methodologies as well as the non-green components of traditional ones. The project opened a research frame for applying successive green and progressive sustainable practices in academic study plans. Our mission in this research is to design and implement green chemistry and sustainable experiments, practices, and methodologies in academic curricula, also, continuing encouraging such practices in our university core courses describing the green and sustainable context of these practices side by side the non-green components of the traditional ones.

Keywords: Green chemistry, sustainability, chemical education, green synthesis, organic chemistry.

1- Introduction

Creation, proposal, improvement and apply chemical yields and progressions to decrease or remove the usage and building of substances dangerous to humans' wellbeing and the surroundings, are all among the learning objectives and academic values recommended for building qualified green and sustainable study strategies, (**Warner et al, 2004)**.

In chemistry practices, preventing waste before it is formed is better than treating or cleaning up, designing chemical roots to exploit the integration of all ingredients used in the process into the ending products that reserve efficiency of function while plummeting toxicity to humanity and the surroundings, and minimizing supplementary substances as well as recognizing energy requirements for its ecological and economical influence are a must for a synthetic method that should be maintained at suitable reaction conditions employing renewable rather than depleting raw material feedstock, **(Caldeira, 2022; Eissa, 2018)**.

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Likewise, avoiding unnecessary derivatives and catalysis, that should be as selective as possible, and developing chemical products, that do not remain wasted in the environment and break down into inoffensive degradable at the end of their function, and analytical methodologies, that allow for immediate in-process checking and control prior to the origination of risky substances, is a must for green and sustainable chemical practices, **(Fahrenkamp-Uppenbrink, J, 2002)**. In addition, substances and the forms of the substance used in chemical reaction should be selected so as to minimize the potential of chemical accidents, including releases, explosions, and fires, **(Eissa & Abdelhameed, 2006; Eissa et al, 2019; Eissa & Mohamed, 2018)**.

The concepts green chemistry and sustainability are essential parts of chemistry teaching curricula, hence, green education must be taught in the classroom and laboratory in parallel, hand in hand, to promote the real practice of these concepts in academia, industrial application, economy, and then the surrounding as a whole, **(Abdelsadek et al, 2024; Alshammre, 2024)**. Unfortunately, in undergraduate education, green chemistry and sustainability are still taught in a limited extent in few academic institutions and laboratories, thus, experimental methodologies remain as traditional as they were fifty years ago, **(Ranu et al, 2004; Namboodiri & Varma, 2002; Chaudhuri, 2001)**.

Great efforts were made to prove a green research for a reaction already showed theory class. The conventional technique for a specific reaction is stated throughout trials that highlight the dangerous constituent of it, and then there is a more ecological procedure designated. In a specific trial, if the designated procedure is not totally green, can be enhanced at a later stage, **(Thompson, 2020; Ranu et al, 2002; ACS, 2002; Bose et al, 2006)**.

The aim of the current research is to design and implement green chemistry and sustainable experiments, practices, and methodologies in academic curricula, also, continuing encouraging such practices in our university core courses describing the green view and sustainable setting of these practices side by side the non-green constituents of the traditional ones..

2. Material and Methods

All chemicals were purchased; Merck Co, Egypt dealer. Melting points were estimated in open glass capillaries on a Gallenkamp melting point apparatus and were uncorrected. Elemental analysis was achieved on a Thermo Finnigan Flash EA 1112 Element Analyzer (Italy). ^{1}H NMR and ^{13}CNMR spectra were checked on a Varian Mercury 400 MHz spectrometer using TMS, Tetramethylsilane, as an internal standard and DMSO-d6 as solvent and compared with those obtained by simulation, (ChemDraw 22.00 64 bit). Mass spectra were recorded at 70 eV on a Shimadzu GCMS-QP1000EX using an inlet type injector. All reactions were monitored by TLC (silica gel, aluminum sheets 60 F254, Merck). All schemes were sketched via ChemDraw 22.00 64 bit.

2.1 Experiment 1:

Aminobenzene (10 ml, 0.01mol), zinc powder (0.5 g, 0.01mol), and acetic acid (30 ml) were refluxed via means of sun light reflector for 1/2 hrs. The reaction mixture was then transferred into ice (100 gm.) with continuous stirring. The precipitated crystals were collected by filtration, washed over the Buchner funnel with water and dried (yield, 10 gm.). The product was recrystallized in boiling water, m.p. 114^{0}C. **Yield:** 10 g (91%).

Chemical Formula: C_8H_9NO, **Molecular Weight:** 135.17, m/z: 135.07 (100.0%), 136.07 (9.2%), **Element Analys. (cld):** C, 71.09; H, 6.71; N, 10.36; **Element Analys. (fnd):** C, 71.13; H, 6.69; N, 10.34; **^{1}HNMR:** 2.06(s, 3H-CH_3); 7.07(t, 1H-Ar); 7.30(t, 2H-Ar); 7.49(d, 2H-Ar) ; 9.84(s, 1H-NH)**; ^{13}CNMR:** 24(CH_3); 121(2CH-Ar); 128(CH); 129(2CH-Ar); 138(C-Ar); 168(CO).

2.2 Experiment 2:

In a well fitted conical flask, Benzaldehyde (1 ml, 0.01mol), acetone (3.8 ml, 0.01mol) and ethanol (15 ml) were mixed with vigorous stirring 2 minutes and 10% sodium hydroxide solution was added drop wisely with continuous stirring for 12 minutes with real-time pressure relief. The reaction mixture was poured in ice till the pale yellow solid was precipitated, filtered off, washed, dried, collected, and recrystallized from ethanol, m. p. (120-122^{0}C). **Yield:** 3 g (90%)

Chemical Formula: $C_{17}H_{14}O$, **Molecular Weight:** 234.30, m/z: 234.10 (100.0%), 235.11 (18.6%), 236.11(1.8%); **Element Analys. (cld):** C, 87.15; H, 6.02; **Element Analys. (fnd):** C, 87.14; H, 6.09; **^{1}HNMR:** 7.03(d, 2H-2CHCO); 7.09-7.43(m, 6H-Ar); 7.61(d, 4H-Ar); 7.92(d, 2H, 2CH-Ar)**; ^{13}CNMR:** 122(2CH, CHCO); 129(10CH-Ar); 136(2C, Ar); 143(2CH, 2CH-Ar); 188(CO).

2.3. Experiment 3:

A solution of trans-stilbene (1.80 g, 0.01 mol) dissolved in ethanol (15 ml) was refluxed via sun light reflector. A mixture of HBr (33%) (5.2 ml) and hydrogen peroxide (H_2O_2, 30%) (7 ml) were drop wisely added to the refluxing solution of stilbene. The disappearance of the deep orange color indicated the bromination of stilbene. The reaction mixture was allowed to cool down and the precipitated stilbene dibromide was filtered, recrystallized and dried. (m.p.): 237^{0}C. **Yield:** 2.4 g (70%).

Chemical Formula: $C_{14}H_{12}Br_2$, **Molecular Weight:** 340.06, m/z: 339.93 (100.0%), 337.93 (51.4%), 341.93(48.6%); **Element Analys. (cld):** C, 49.45; H, 3.56; Br, 46.99; **Element Analys. (fnd):** C, 49.43; H, 3.60; Br, 46.98; **^{1}HNMR:** 5.87(s, 2H-2CHBr); 7.19-7.93(m, 10H, Ar); **^{13}CNMR:** 53(2CH, 2CHBr); 131(10CH, Ar); 140(2C, Ar).

2.4. Experiment 4:

A mixture of Calcium nitrate (1.5 g, 0.01mol), acetic acid (5 ml, 0.01 mol) and salicylic acid (1 g) was refluxed via means of sun light reflector at > 80 ^{o}C. Till the solution turned dark red, it was instantly poured into a 10 gm. of ice. The resulting deep red mix was placed in ice and the resulted yellow were washed, filtered off, and then dried. (m.p.) of 4-nitrosalicylic acid = 234^{0}C. **Yield:** 0.66 g (60 %).

Chemical Formula: $C_7H_5NO_5$, **Molecular Weight:** 183.12, m/z: 183.02 (100.0%), 184.02 (7.8%), 185.02(1.3%); **Element Analys. (cld):** C, 45.91; H, 2.75; N, 7.65; **Element Analys. (fnd):** C, 45.88; H, 2.76; N, 7.66; **^{1}HNMR:** 7.33(d, 1H, Ar); 8.20(d, 1H, Ar); 8.61(s, 1H, Ar); 11.91(s, 1H, COOH); 12.66(s, 1H, OH); **^{13}CNMR:** 116.1(1C, Ar); 116.5(1CH, Ar); 125.3(1CH, Ar); 131.3(1CH, Ar); 140.5(1C, C-NO_2); 163.5(1C, C-OH); 169.8(1C, COOH).

3. Results & Discussion

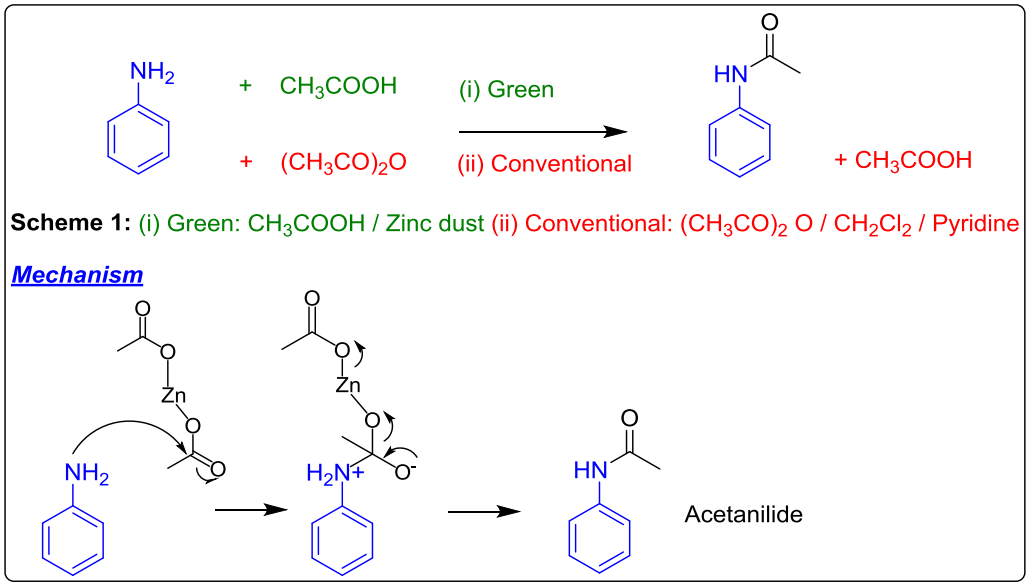
Due to the shortage of raw materials and non-renewable energy sources and the need for safe practices that are less risky, higher safety and production performance, and less risk to the

ecosystem, green practices and sustainable operations are of utmost importance in today's world and every day for the prosperity of humanity and the preservation of the universe's environment and its capabilities, **(Sethi et al, 2023)**.

In Academia, green chemistry experiment is familiarized not to significantly substitute the traditional, fairly; they are reflected harmonizing to the present procedures. This not only delivering a broader view of various practices but also pioneering minds for future development and progress of the theme in general with due importance to the concepts of green and sustainability, **(Zimmerman et al, 2020)**. The lecturers may take periodic tests to evaluate appreciative of the students about the experiment practiced. Wherever conceivable and viable, the traditional practice should be switched to greener and sustainable ones to convey the meaning of this methodology whenever practicable.

3.1 Experiment 1: *Synthesis of acetanilide*

Primary amine, phenols, and phenolic acid, were conventionally acetylated via acetic anhydride as acetylating agent. In CH_2Cl_2 in presence of pyridine catalyst, aniline was converted to acetanilide whereas use of chlorine containing solvent like CH_2Cl_2 and pyridine is not ecological, moreover, acetic anhydride leaves wasted molecule of acetic acid, (not atom-economy). In the alternative green procedure acetic acid with Zinc powder were employed as acetylating agent instead, avoiding both usage of acetic anhydride, (banned due to its utility in narcotics) and hazardous chlorinated solvent, minimizing waste by-products; Scheme 1.

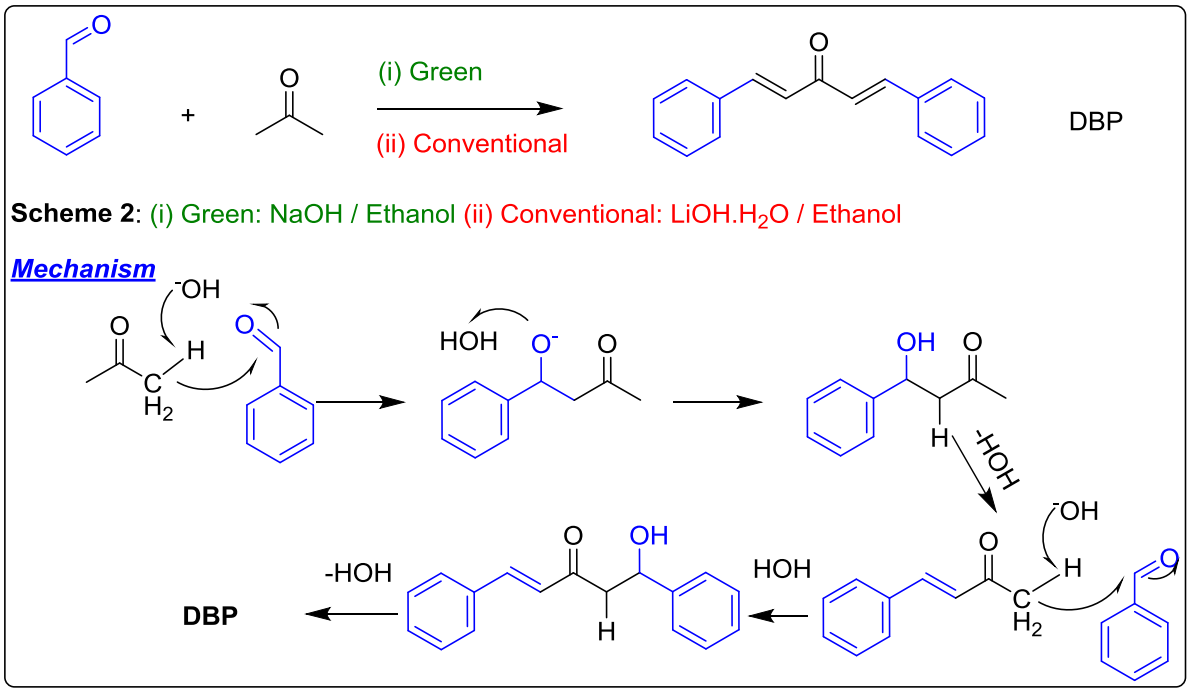


Scheme 1: (i) Green: CH_3COOH / Zinc dust (ii) Conventional: $(CH_3CO)_2O$ / CH_2Cl_2 / Pyridine

Mechanism

3.2 Experiment 2: *Synthesis of dibenzalpropanone, DBP*

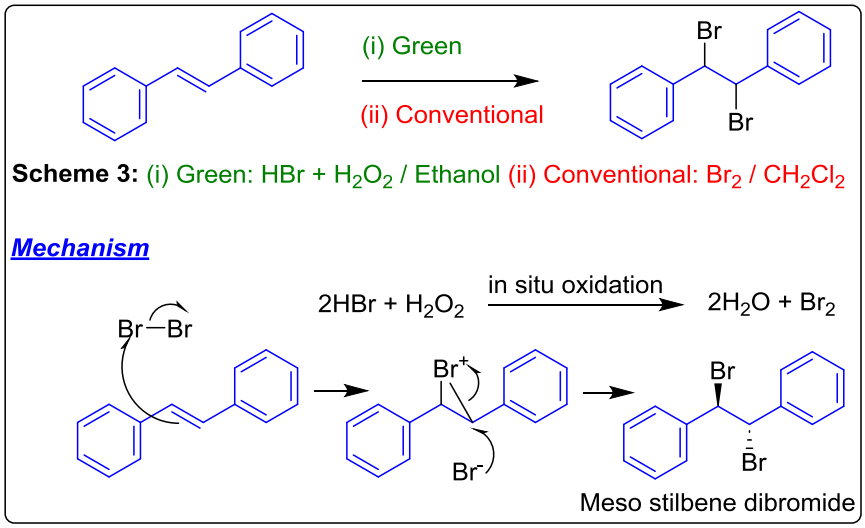
DBP was traditionally achieved via reacting benzaldehyde with acetone in ethanol and sodium hydroxide as catalyst. In the green procedure, the hazardous organic solvent was minimized and the employed substances are non-toxic, LiOH is safe, as it is comparatively less hygroscopic than other alkali hydroxide, and the catalytic amount of the alkali was stoichiometric; Scheme 2.



Scheme 2: (i) Green: NaOH / Ethanol (ii) Conventional: $LiOH.H_2O$ / Ethanol

3.3 Experiment 3: *Synthesis of meso stilbene dibromide*

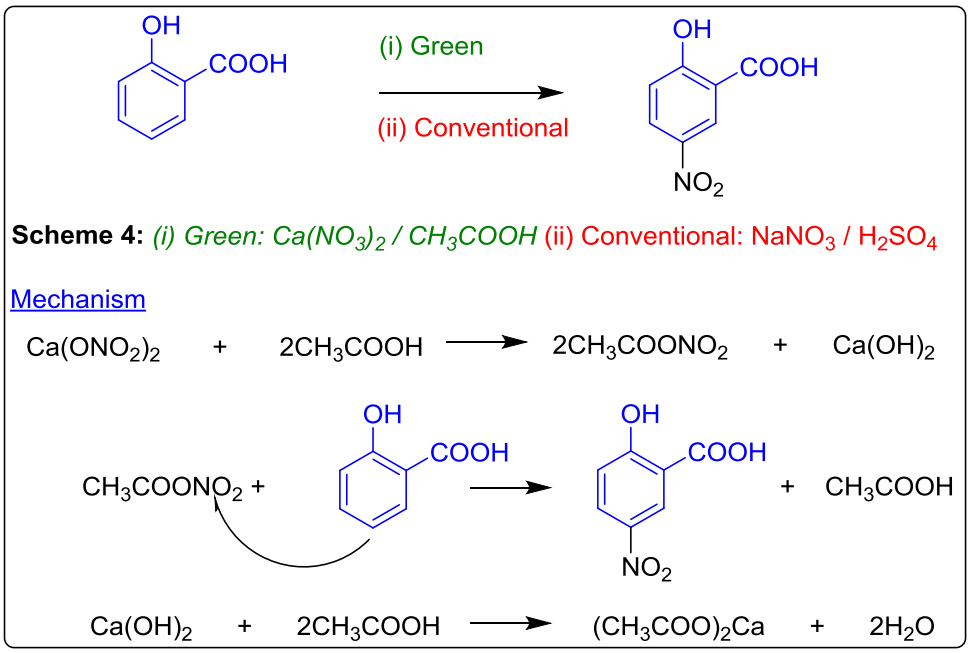
Stilbene dibromide was prepared through reacting trans-stilbene with corrosive liquid bromine in the highly toxic chlorinated solvent CH_2Cl_2, both are non-green reagents. Alternative green and sustainable procedure was designed to avoid both the highly corrosive liquid bromine and the highly toxic chlorinated solvent, through a highly atom efficient procedure; Scheme 3.



Scheme 3: (i) Green: HBr + H_2O_2 / Ethanol (ii) Conventional: Br_2 / CH_2Cl_2

3.4 Experiment 4: *Synthesis of nitro-salicylic acid*

The traditional nitration of aromatic compound is a terrible procedure due to the use of concentrated sulfuric acid. A green and sustainable procedure was designed to allow rapid and ecofriendly nitration without nitric acid. Also, a regioselective nitration was achieved with derivatives (calcium acetate) in this reaction are valuable agro-chemicals, and thus eco-friendly; Scheme 4.



Scheme 4: *(i) Green: $Ca(NO_3)_2$ / CH_3COOH* (ii) Conventional: $NaNO_3$ / H_2SO_4

4. Conclusion

The green and sustainable framework of these experiments were highly pronounced compared with the traditional practices through its high yield and excellent conversion, atom economy, solvent less practice, easiness, ecofriendly, and integrity of green chemistry and sustainability performances. A group discussion between undergraduate students, who carried out these three experiments, and the findings were highly marked. They were had excellent vision about the concept of green chemistry and sustainability as well as strict recognition about the non-green constituents of the traditional practices, side by side the green and sustainable setting.

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