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SYNTHESIS OF POLY ARYL HYDROCARBONS VIA ULLMANN HOMOCOUPLING OF 1,4-DIBROMOBENZENE

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Aryl-aryl coupled polymers are a class of conjugated polymers that possess useful chemical, electrochemical and photochemical properties. Transition metal-catalysed C-C cross-coupling reactions employed in the synthesis of aryl-aryl coupled polymers require sophisticated reaction conditions and expensive catalysts. Therefore, this research project focused on the synthesis and characterisation of linear open-chain 4,4′-dibromo aromatic oligomers of 1,4-dibromobenzene using the Ullmann homocoupling reaction, which is feasible in the Sri Lankan context. Several synthetic attempts for the condensation of 1,4-dibromobenzene were carried out using Ullmann coupling in the presence of an activated Cu bronze catalyst, Cs_2CO_3 base in N-methyl-2-pyrrolidone (NMP) / dimethyl sulfoxide / dimethyl formamide solvent at refluxing conditions under normal atmospheric conditions / N_2 over 3.5 h to 36 h of varying periods. The reaction progress of nine different reaction conditions investigated was monitored using thin-layer chromatography (TLC). Among them, the synthetic attempts that indicated the new product formation in TLC analysis were purified using column chromatography. The purified products were characterised using UV-visible spectroscopy and gas chromatography-mass spectrometry. Among the four out of nine reaction mixtures that demonstrated new product formation, the coupling of 1,4-dibromobenzene in NMP at 190 ^oC over 24 h in a normal atmosphere demonstrated the most intense peak in the TLC analysis. The column chromatography of the crude mixture yielded a clear, pale yellow colour liquid product with a relatively low yield, which was caused by the sublimation followed by the deposition of the starting material at temperatures above 130 ^oC. The UV-visible spectra of the obtained liquid demonstrated the highest absorption at a wavelength of 287 nm in n-hexane. This absorption peak can be attributed to the π to π^* transition of the conjugated aryls. Observation of a light blue fluorescence of the product under the UV light at 366 nm indicated the presence of an extended π system. In summary, condensation attempts of 1,4-dibromobenzene using the Ullmann coupling reaction yielded a fluorescence-active pale yellow colour liquid. Further characterisation of the product using ^1H and ^{13}C NMR spectroscopy is needed to confirm the product formation.

Keywords: aryl-aryl coupled polymers, 1,4-dibromobenzene, Ullmann coupling

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INTRODUCTION

Aryl-aryl coupled conjugate polymers are an interesting class of organic compounds with unique chemical, electrochemical and photochemical properties which make them promising candidates in various applications, including molecular electronics and host-guest chemistry (Nakabayashi, 2018; Perveen et al., 2025). Transition metal-catalysed C-C cross-coupling reactions are widely employed in the condensation of aryl compounds. Most of the C-C cross-coupling reactions require sophisticated reaction conditions and expensive catalysts, and generate toxic byproducts (Luo et al., 2023; Todd D. Nelson, 2004). However, Cu-catalysed Ullmann homocoupling reactions (Figure 1) can be carried out using a relatively inexpensive Cu catalyst and feasible reaction conditions under the Sri Lankan context (Hassan et al., 2002; Mastalir & Molnár, 2023; Perveen et al., 2025; Thapa et al., 2015). Therefore, this research project focused on the synthesis and characterisation of linear open-chain 4,4′-dibromo aryl oligomers of 1,4-dibromobenzene and eventually cyclic compounds, [n]paracyclophanes, using the Ullmann coupling reaction, which is feasible in the Sri Lankan context.

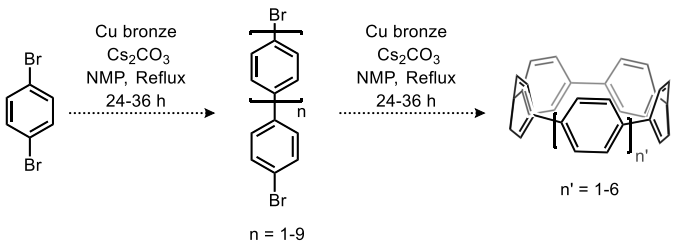

Figure 1: Synthesis of a series of linear open-chain 4,4′-dihalo aromatic oligomers of 1,4-dihalobenzenes and [n]paracyclophanes using Ullmann coupling reaction.

METHODOLOGY

Chemicals, analytical grade 1,4-dibromobenzene, N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), reagent grade caesium carbonate and copper bronze were used as received without further purification unless otherwise mentioned. Synthetic attempts 1-9, dimerisation of 1,4-bromobenzene, were carried out using an activated copper bronze catalyst, 2 mol equivalent of base Cs_2CO_3 in the given solvent at the specified temperature over the given reaction time

under normal atmospheric conditions / N_2 (Table 1). The reaction progression of all C-C coupling synthetic attempts was monitored using thin layer chromatography (TLC). The workup procedure was carried out as follows for the crude reaction mixtures, which indicated new product formation in the TLC analysis. The crude reaction mixture was filtered after dilution with hexane (~50 mL) and washed with cool water. The organic phase was concentrated under reduced pressure and purified using preparative or / and column chromatographic techniques with a silica gel stationary phase, and ethyl acetate, hexane mixtures as mobile phases. The purified products were characterised using Fourier transform infrared (FTIR), UV-visible spectroscopy and gas chromatography-mass spectrometry (GC-MS).

Table 1: Synthetic attempts to synthesise linear open-chain 4,4′-dibromo aromatic dimers or oligomers of 1,4-dibromobenzenes using C-C Ullmann coupling.

Attempt	Solvent	Temperature / ºC	Time / h	Atmosphere
1	NMP	140	3.5	Normal
2	DMF	153	3.5	Normal
3	DMF	153	5	N_2
4	NMP	202	4.5	N_2
5	NMP	202	10	N_2
6	NMP	202	36	N_2
7	NMP	190	24	Normal
8	DMSO	180	36	Normal
9	DMF	145	36	Normal

RESULTS AND DISCUSSION

Several synthetic attempts were made to dimerise 1,4-dibromobenzene via Ullmann C-C coupling. The reaction conditions, including solvent, catalyst, reaction temperature, reaction time, and atmospheric conditions, play an important role in obtaining the desired dimerisation product of 1,4-dibromobenzene via C-C Ullmann coupling. Activated copper bronze was used as the catalyst and prepared immediately prior to the synthesis (Todd D. Nelson, 2004) to prevent the deactivation of the catalyst by air and moisture. The dimerisation of 1,4-dibromobenzene may proceed through an oxidative addition of 1,4-dibromobenzene to Cu(0), generating Br-Ar–Cu(II)–Br. This intermediate is then reduced by another Cu(0) atom to yield Br–Ar–Cu(I), which can subsequently undergo an oxidative addition with another 1,4-dibromobenzene, followed by the reduction, yielding Br-Ar–Cu(III)(Br)–Ar-Br. This step may lead to a reductive elimination, generating the 4,4′-dibromobiaryl and Cu(I)Br. A subset of synthetic attempts was carried out under N_2 to avoid the interferences caused by atmospheric oxygen, carbon dioxide, or water vapour, leading to a low yield and formation of byproducts. In order to successfully carry out the Ullmann coupling reaction, high-boiling solvents that can provide sufficient reaction temperatures and good solubility of the starting material in the solvent are important. Therefore, high-boiling polar aprotic solvents such as NMP, boiling point (b.p.) 202

°C, DMSO, b.p. 189 °C and DMF, b.p. 153 °C are the most frequently used solvents in Ullmann coupling reactions (Hassan et al., 2002; Perveen et al., 2025; Todd D. Nelson, 2004).

Among the crude products of the nine reaction mixtures (Table 1), four of them demonstrated an additional spot in the TLC analysis. The appearance of an additional spot may be responsible for the desired product, 4,4′-dibromobiphenyl formation. Among them, the crude mixture of synthetic attempt 7, the coupling of 1,4-dibromobenzene in NMP at 190 °C over 24 h demonstrated a relatively intense spot in the TLC analysis (Figure 2(a) and (b)). Therefore, the column chromatography was carried out to separate the compounds in the crude mixture of synthetic attempt 7. Among the eluted fractions from the column, fractions E10 and E11 yielded a clear light yellow colour liquid product with an R_f value of 0.52 (Figure 2(c)). The relatively low yield of a clear, pale yellow colour liquid product may be caused by the sublimation followed by the deposition of the starting material at temperatures above 130 °C. When the clear light yellow color liquid eluate (Figure 2(d)), E11 was observed under the UV light at 254 and 366 nm, it indicated light green and light blue fluorescence (Figure 2(e)-(f)).

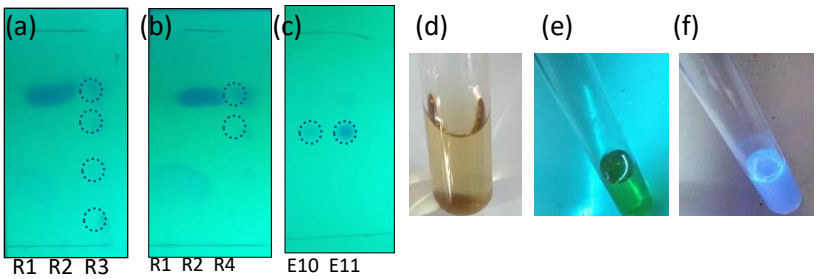

Figure 2: Thin-layer chromatograms of synthetic attempt 7 (Table 1) observed under UV light of 254 nm. (a) crude mixture with solvents and starting materials, R1 = NMP, R2 = 1,4-dibromobenzene, R3 = crude mixture and (b) hexane extract with solvents and starting materials, R4 = hexane extract, (c) fractions E10 and E11 eluted from column chromatography (Mobile phase: ethyl acetate, stationary phase: silica). Images of hexane extract observed (d) under visible light, (e) at 254 nm and (f) 366 nm UV light.

This observation indicated the presence of fluorescence-active chemical species in the hexane extract. The UV-visible characterisation of the starting material and the light-yellow liquid obtained from the column exhibits the wavelength at the highest absorbance (λ_{max}) at 287 nm and 290 nm, respectively (Figure 3(a)), which can be attributed to π-π* transitions of conjugated π systems of the product and the starting material, respectively. Since the λ_{max} of 4,4′- dibromobiphenyl in methanol is 262 nm, λ_{max} changes based on the solvent (Xie et al., 2002). Further characterisation of the resulting clear light yellow colour liquid using GC-MS, selected ion monitoring (SIM) mode revealed two major peaks at 9.49 and 34.82 min (Figure 3(b)). The peak

at 9.49 min goes along with the retention time of 1,4-dibromobenzene, supporting its assignment as the unreacted starting material. Notably, the GC-MS database misidentified this reference sample peak as 1,3-benzenediol, 5-iodo, highlighting limitations in spectral matching. Although the database suggested the peak at 34.82 min as 2-fluoro-4-iodotoluene, it is tentatively assigned to the expected product, 4,4′-dibromobiphenyl with a molecular mass of 312 $gmol^{-1}$. These discrepancies could reflect known challenges in automated identification of halogenated aromatics with similar fragmentation patterns. Therefore, confirmation of the product formation requires characterisation by ^{1}H and ^{13}C NMR spectroscopy.

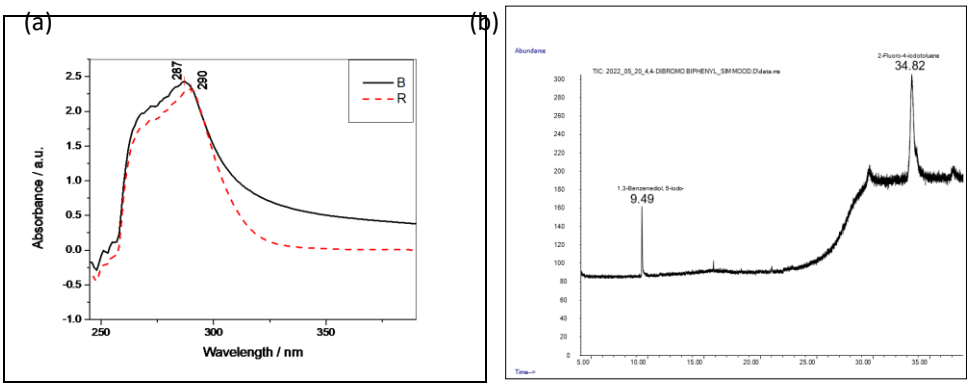

Figure 3: (a) UV-Visible spectra of 1,4-dibromobenzene (R) and the light-yellow liquid product eluted from the column (B) in hexane and (b) gas chromatogram of the light-yellow liquid obtained from the column.

The relatively low yield observed for the successful synthetic attempts could be due to sublimation of 1,4-dibromobenzene around 90 – 100 ºC and condensation of the sublimed compound around the neck of the round-bottom flask while carrying out the reaction. Since the Ullmann reaction required relatively long reaction times and high reaction temperatures, sublimation of the starting material at the initial stage restricted the product formation. Additionally, since the new product formation gave an exceptionally low yield, scaling up and further studies of this synthetic attempt are not practical and economical.

CONCLUSIONS / RECOMMENDATIONS

Synthesis of di / oligo / poly aryls via C-C Ullmann homocoupling of 1,4-dibromobenzene is limited by the sublimation of the starting material, 1,4-dibromobenzene, around 90-100 ºC. In order to obtain the desired product of aryl-aryl coupled compounds using the Ullmann coupling reaction, it may require a relatively long reaction time and moderately high temperatures. In order to avoid the sublimation of 1,4-dibromobenzene in the C-C coupling, the possibility of dimerisation of 1,4-dibromobenzene under the reduced pressure conditions can be carried out. Also, the possibility of replacing the starting material, 1,4-

dibromobenzene, with other 1,4-dihalocompounds, such as 1,4-diiodobenzene and 1,4-dichlorobenzene can be carried out.

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