Supplementary Material for Organic & Biomolecular Chemistry

Supplementary Information Section for

"Effect of cyclodextrin complexation in bromine addition to unsymmetrical olefins: Evidence for participation of cyclodextrin hydroxyl groups"

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a) Preparation and characterization of cyclodextrin complexes. 1:1 CD complexes were prepared[24] by mixing an equimolar amount of the substrates 1-4 and the appropriate CD, stirring for 12h, filtering and washing with small amount of ether to remove any uncomplexed substrate. This complex was dried in an air oven at 50°C for 6 h. The host-guest ratio was calculated by adopting the following procedure. A known amount of the solid complex was dissolved in a minimum amount of distilled water and the guest was extracted with warm chloroform. The amount of the recovered guest was estimated gravimetrically after the removal of chloroform. The values are closer to unity indicating that a 1:1 complex is formed in all the cases.

A stock solution of substrates **1-4** (1×10^{-3} M) was prepared by dissolving a known mass in 2% methanol-water mixture. 0.1 ml of this stock solution was transferred into 10mL volumetric flask, the respective cyclodextrin (from a 0.01M freshly prepared stock solution in water) was added, diluted to 10mL with water and stirred for 6h to ensure the equilibrium in complexation. The absorption spectrum was recorded at room temperature using a JASCO 7800 UV/Vis spectrophotometer and the absorption maximum for substrates **1-4** are 245, 258, 233 and 253nm respectively.

^{1}H- NMR Chemical shifts exhibit an upfield shift for H-3, H-5 protons of CD in all CD-olefin complexes. For example, the chemical shifts (in ppm) for uncomplexed α-CD are H1- 4.89, H2- 3.50, H3- 3.83, H4- 3.40, H5- 3.58, H6- 3.70 and for α-CD-styrene complex the corresponding values are H1-4.89, H2- 3.48, H3- 3.77, H4- 3.44, H5- 3.35, H6- 3.71. Such change in chemical shift values are known to be strong the consequence of diamagnetic anisotropic effect of the aromatic ring residing inside the cavity and are considered to be evidence for the formation of inclusion complex in aqueous CD solution.

b) Preparation of styrene dibromide 5 and styrene bromohydrin 7.

Styrene (2 g) was dissolved in 20 mL of CCl_4 taken in a conical flask. To this solution, 12 mL of a stock solution of bromine was added dropwise with constant stirring at 0^{o}C. After the reaction was over in about 30 min, the excess bromine was removed with sodium thiosulphate solution and the products were separated by column chromatography (silica gel 60-80 mesh; solvent-petroleum benzene 60-80^{o}C). A liquid sample of styrene bromohydrin was separated and its Bp 74^{o}C (lit.[17] 75^{o}C) and a solid sample of styrene dibromide was also separated Mp 72^{o}C (lit.[17] 74^{o}C). The products were confirmed by ^{1}H NMR (200 MHz) for 5: 6.65δ (s, 5H), 4.5δ (t, 1H), 3.0δ (d.2H) and for 7: 6.8δ (s, 5H), 5.5δ (s, 1H), 4.8δ (d, 1H), 4.5δ (d, 1H).

c) Preparation of dibromide 6 and bromohydrin 8 of methyl cinnamate. Methyl cinnamate (3 g) was added slowly to 18 mL of a stock solution of bromine with constant stirring and the temperature was maintained at 0^{o}C. After the reaction was over (about 30 min), the excess bromine was removed with sodium thiosulphate solution. The products were extracted with CCl_4 and the products are separated by chromatography (silica gel 60-120 mesh; solvent- hexane). The product (dibromide of methyl cinnamate) was confirmed by the Mp 115^{o}C (lit.[18]

117°C) and methyl cinnamate bromohydrin was separated and its Mp 61°C (lit. [18] 60°C). The products were confirmed by ^{1}H NMR (200 MHz) 6.6δ (s, 5H), 4.8δ (d, 1H), 5.2δ (d, 1H), 3.0δ (s, 3H); for **8**: M^{-+} 242, 209,181, 161, 129, 102.

d) Preparation of *trans*- and *cis*- phenylacetylene dibromide (9 and 10). Phenylacetylene (2 mL) was added dropwise to 13 mL of a stock solution[10] of bromine in a conical flask for about 30 min. After the reaction was over the excess bromine was removed by thio solution. Then the products were extracted with chloroform and were separated by chromatography (silica gel 60-120 mesh; solvent-hexane). The mixture of *trans*- and *cis*- isomers was identified by their Mps 132 (lit. [19] 133°C) and 135°C (lit. [19] 136°C) respectively and the ^{1}H NMR (200 MHz) spectra for **9:** 7.5δ (s, 5H), 5.8δ (S, 1H); for **10**: 7.6δ (s, 5H), 5.5δ (s, 1H).

e) Preparation of phenacyl bromide 12. A solution of 0.21 M of acetophenone in 25 mL of dry ether was placed in a dry three-necked flask fitted with a separating funnel, mechanical stirrer and reflux condenser. The solution was cooled in an ice bath, 0.25 g of anhydrous $AlCl_3$ was introduced and 35.5 g (0.21 M) of bromine was added gradually from a separating funnel with stirring. After all the bromine has been added, the ether and dissolved HBr were removed under reduced pressure. The solid mass obtained was washed several times with a 1:1 mixture of water and petroleum ether (40-60°C). The crystals of phenacyl bromide were filtered and recrystallised one to three times in ethanol and dried over vacuum for several hrs and their purity was confirmed by Mp 48°C (lit.[19] 49°C) and ^{1}H NMR (200 MHz) spectra for **12**: 6.9δ (s, 5H), 3δ (s, 2H)

f) Preparation of bromophenylacetylene 11. Thirty millilitre of 10 M aq. NaOH and 21.8 g (7.0 mL, 0.136 M) of bromine was added and stirred for 1 h. Then 13.0 g (14.0 mL, 0.127 M) of phenylacetylene was added and stirred vigorously for 5 h.

The products were extracted from the reaction mixture thrice with 50 mL portions of ether, washed with water and the ethereal layer was dried over anhydrous sodium sulphate. The solution was filtered and the ethereal layer was removed by rotary evaporation and the purity was confirmed by its Bp 96^{o}C (lit. [19] 97 ^{o}C) and ^{1}H-NMR (200 MHz) spectra for 11: 8.0δ (s, 5H); IR data for 11: 3200-3250 cm^{-1} (strong), 875 cm^{-1}.

g) Preparation of dibromide of allylbenzene 13. Allylbenzene (2 mL) was dissolved in 20 mL of CCl_4 in a conical flask. The solution was kept at 0^{o}C. To this solution 12 mL of a stock solution of bromine was added dropwise with constant stirring for 30 min. The products were extracted after removing the excess of bromine with thio solution. The products were separated by column chromatography (silica gel 60-120 mesh; solvent-hexane) and were identified by its Mp 131^{o}C (lit. [27] 130^{o}C).