# Friedel-Crafts Acetylation of Bromobenzene

## Aims

This experiment aims to carry out the acylation of bromobenzene using the Lewis acid aluminium chloride and acetic anhydride to form the acylium ion necessary for electrophilic aromatic substitution.

## Introduction

In this experiment acetic anhydride is first reacted with aluminium chloride to yield CH3CO+, an acylium ion and primary carbocation. This ion is sufficiently reactive to attract and bond with delocalised electrons in the bromobenzene, temporarily giving the ring a net positive charge. This charge is quenched when the ring is deprotonated by aluminium chloride, yielding hydrogen chloride gas and 4-bromoacetophenone.

## Experimental Procedure

Aluminium Chloride (7.5g, 0.0562 moles), dry dichloromethane (10ml, 13.3 g) and bromobenzene (2.5ml, 3.74g, 0.0238moles) were added to a dry 100ml round bottomed flask, along with a magnetic stirrer bar.

The flask containing the solution was placed on an aluminium heating block on hotplate/magnetic stirrer. The flask was connected to a condensation tube. This was connected via a multiple adapter to a dropping funnel containing acetic anhydride (7.5g, 0.0735moles) and to a funnel which was submerged in water.

The acetic anhydride was added dropwise over a 5 minute period. This was accompanied by the evolution of HCl gas from the solution in the flask and a colour change to dark red/brown. The HCl gas was absorbed through the funnel submerged in water. The hot plate was turned on to 100oC and the solution was refluxed with continued stirring for 30 minutes.

30g ice and 10ml water were placed in a 600ml beaker. The contents of the reaction flask were slowly poured into the beaker in the fume cupboard while stirring the ice solution continuously. Heat and HCl gas were observed to evolve. The mixture was observed to change yellow/green during pouring before becoming dark red. The remaining contents of the reaction flask were rinsed into the beaker using 6ml dichloromethane. The contents of the beaker were placed in a separation funnel and two phases (an upper aqueous phase and lower organic phase) formed. The dropping funnel used previously for the condensation setup was rinsed with Dichloromethane and the organic phase was collected in it. The aqueous phase was discarded.

The dichloromethane solution was washed with water (2x 10mL), with 2m NaOH (10mL), and with half saturated NaCL solution (2x10mL). The dichloromethane solution was collected in a dry conical flask and dried over solid calcium chloride. The solution was then filtered into a dry 100mL round bottomed flask. The solvent was removed using the rotary evaporator. The product obtained was a light brown liquid, of mass 1.36g.

## Results

The synthesis was carried out successfully. However due to time constraints the product was not purified using the vacuum distillation technique. Also, crystallisation of the product was not achieved on cooling so the melting point of the product was not tested. The percentage yield of the product was calculated to be 28.73%.

## Discussion and Conclusions

The Product obtained failed to crystallise due to time constraints. The inability to test the melting point of the product resulted in uncertainty as to the overall purity of the product. The percentage yield was low, at 28.73%. However on repetition of the experiment the yield may have been improved with by allowing the condensation procedure to continue for a greater period of time.

## Post Practical Questions

1. Bromine is an ortho, para director because like all halogens it possesses a pair of unshared electrons. Therefore Bromine donates electron density to the *pi* system in the benzene ring, creating resonance structures that stabilize the ring. At the same time, it has an inductive electron withdrawing effect which causes it to be a para (and to a lesser extent, ortho) director. Therefore acetyl group is orientated primarily to the 4 position on the benzene ring.
2. The products formed were 4-bromoacetophone and 2-bromoacetophenone. Only a small amount of 2-bromoacetophenonewas formed due to the electron withdrawing induction effect of the bromine atom on the aromatic ring. Also the bulky Bromine atom hinders the ortho-isomer forming because is not favoured sterically.
3. AlCl3 is used to create the carbocation by reacting with the acetic anhydride. It is later used to deprotonate the bromoacetophene. Since 1 molar equivalent is used in two steps of the reaction and it is necessary in excess, a molar ratio of 2.2 to 1 of the other reactants is necessary.