

Synthesis of 7.7 –  
dichlorobicyclo  
heptane – phase  
transfer catalysis  
essay



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## Abstract

The preparation of 7,7-dichlorobicyclo heptane which is also known as 7,7-dichloronorcaradiene was done by reacting cyclohexene, chloroform and a base (50% aqueous sodium hydroxide) with benzyl triethylammonium chloride. The latter being a water soluble phase transfer catalyst (PTC). The reaction was performed at room temperature and was distilled at atmospheric pressure. The mechanism of action of the above mentioned PTC is described in the text along with the mechanism for the addition of a dichlorocarbene. The percentage yield obtained was 38.

0%. This is considerably low due to an unfortunate spillage of the product at the stage of semi-micro distillation. Introduction Phase transfer catalysts (PTC) are used to catalyze reactions involving chemical species which are present in different phases. These types of reactions are known as heterogeneous two phase reactions and are usually very slow because the two primary reactants (in this case  $\text{CHCl}_3$  and  $\text{NaOH}$ ) are in different phases.

The reaction catalyzed in this experiment is the addition of a dichlorocarbene to cyclohexene. The dichlorocarbene must first be generated in solution and this is done using the strong base, 50% aqueous sodium hydroxide, with the aid of the PTC. The benzyl triethylammonium chloride (PTC in this experiment) serves as a transporter of  $\text{OH}^-$  ions which dissociate from sodium, from the aqueous phase to the organic phase where chloroform is present. The reaction between  $\text{OH}^-$  ions and chloroform can then proceed to

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generate the dichlorocarbene which then reacts with cyclohexene to produce the desired product. The dissociation of NaOH and the subsequent transporting reaction between the PTC and OH ion is illustrated below. Previously, literature reports describing the generation of a dichlorocarbene often have low yields due to the reaction been conducted under strict anhydrous conditions.

The reason for these conditions is because once a dichlorocarbene is generated in an aqueous solution, it readily undergoes hydrolysis to yield undesired products (see reactions a and b below). These side reactions are avoided when the reaction is carried out in a biphasic system in the presence of concentrated NaOH and a quaternary ammonium PTC. The effectiveness of this procedure was first demonstrated by Makosza and resulted in high yields of 7.7-dichlorobicyclo heptane. Results Preparation of 7.7-

7-dichlorobicyclo heptane Cyclohexene Chloroform Mass: Grams Volume: 10 ml. Molecular Weight: 82.08 g/mol. Density: 1.49g/ml. Melting point: 104 °C. Molecular Weight: Amount: 0.0249 mol.

Amount: 0.13 mol. Cyclohexene and Chloroform react in a 1:1 stoichiometric ratio therefore cyclohexene is clearly the limiting reagent in this reaction. Therefore the maximum amount of 7.7-

7-dichlorobicyclo heptane that can be formed is 0.0249 mol. 7.7-dichlorobicyclo heptane. Mass: 1.58 g.

Molecular Weight: 163.04 g/mol. Boiling point: 180-190 degrees. Celsius

Amount: 0.

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0096 mol. Percentage Yield = actual amount of product / theoretical amount of product =  $1.58 \text{ g} / 4.072 \text{ g} \times 100 = 38.80\%$

### **Discussion**

The synthesis of the desired product (7.7-dichlorobicyclo heptane) was obtained by following the experimental procedure very carefully but due to unfortunate circumstances during the actual practical, some of the product was lost by spillage at the stage of semi-micro distillation.

Therefore the actual yield of product recovered was quite low which resulted in a final percentage yield of only 38.80%. Nevertheless the rest of the experiment was carried out with as much precision as possible. After the addition of all the reactants, the reaction flask was placed under reflux, warmed and stirred vigorously for 40 minutes. It was necessary to stir the reaction intensely to ensure that the organic and aqueous layer in the reaction flask is well mixed, hence promoting mass transfer of the OH ion to the Chloroform molecule at the phase interface. The vigorous stirring also increases the turbulence in the reaction flask which facilitates collisions between the primary reactants.

This is needed for the reaction to occur at an optimum rate. Hence, the rate constants of the reaction increase as stirring speed increases. If the reaction mixture was not stirred at high speeds, the reaction will not proceed to yield maximum product in the given time and will result in low percentage yields. It was during this stirring time that the action of the PTC is significant. The mechanism of action of the PTC is illustrated and explained below.

The base used in this reaction is a strong one (NaOH) which dissociated completely in the aqueous phase to give an excess of OH ions which is needed for the generation of the dichlorocarbene in the organic phase. As seen above, benzyl triethylammonium chloride undergoes a nucleophilic substitution with NaOH. The hydroxyl group from the base displaces the chloride group on the PTC which results in the formation of a quaternary ammonium hydroxide. The PTC is now able to transport the OH ion to the organic phase where it can react with chloroform.

The three step mechanism describing the formation of 7.7-dichlorobicyclo heptane is illustrated and explained below. In step one, the hydroxyl group transported into the organic layer via the PTC deprotonates the chloroform molecule to form water. The water subsequently moves into the aqueous layer keeping the water content in the organic layer low.

This is important since an accumulation of water can result in undesired reactions between chloroform or carbene with water. These reactions (a and b) are illustrated below. 3 Deprotonation of chloroform results in the formation of a trichloromethide anion. It follows that this anion then slowly releases a chloride group to form the dichlorocarbene (mechanism 2). Here the PTC can also transport the chloride ions back to the aqueous phase via a base-induced  $\beta$ -elimination.

The carbene then attacks the double bond of cyclohexene to finally produce 7.7-dichlorobicyclo heptane. An Infrared and Gas chromatography analysis was done on the product for identification purposes. The IR spectra were

analyzed and the C-Cl bond was identified in the region 580-785  $\text{cm}^{-1}$ . The  $\text{sp}^3$  hybridized C-H bonds were identified in the region just below 3000  $\text{cm}^{-1}$ .

$\text{CH}_2$  bending and stretching peaks were identified in the region 1250-1465  $\text{cm}^{-1}$ . The gas chromatogram had two peaks and this could be due to the possibility of obtaining an impure product. These spectra are attached at the end of this report. Conclusion The synthesis of 7,7-dichlorobicyclo heptane achieved in a reasonable duration of time with the aid of the phase transfer catalyst, benzyl triethylammonium chloride which facilitated the generation of the dichlorocabene which reacted with hexane to produce the desired product.

The percentage yield however was low (38.80%) due to a loss of product at the final distillation step. Experimental Synthesis of 7,7-dichlorobicyclo heptane Cyclohexene (2.

5g), chloroform (10.00ml) and benzyl triethylammonium chloride (0.26g) was placed in a 100ml quick fit conical flask. To the flask, 10ml of 50% aqueous NaOH was added using an addition funnel. A reflux condenser and a dropping funnel were then set up over the flask.

1ml of 50% aqueous NaOH was poured into the addition funnel and was added to the reaction mixture. The reaction flask was then gently heated and vigorously stirred over a heater/stirrer unit with the aid of a magnetic stirrer. The remainder 9ml of aqueous NaOH solution was then added drop wise over the next 20 minutes while the reaction mixture was to refluxing. After the addition was complete the mixture was left to reflux for a further 40minutes. When the waiting period had elapsed, 15 ml of saturated sodium  
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chloride and 15ml of hexane was slowly added to the reaction mixture. The mixture was then transferred to a separating funnel and the lower aqueous layer was separated and discarded.

The organic layer was washed with two portions 25 ml of deionised water and was dried with anhydrous magnesium sulphate. A distillation apparatus was set up and the solvents from the dried organic layer were distilled off using a steam bath. The distillate was then discarded and the remaining liquid was transferred to semi micro distillation apparatus where the product was distilled using a Bunsen burner. The product was then weighed and the % yield was calculated.

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