

COMPLETION OF UNIMOLECULAR SUBSTITUTION AND ELIMINATION REACTIONS

Name:

School:

Subject:

Date

Abstract.

Substitution reactions is one where a single atom or a group is taken over and replaced by another one while substitution reaction is the one where components in an organic reaction is removed in either a mechanism with either one or two steps. These reactions are useful when establishing which situations can continue until they are completed and which ones cannot. By unimolecular substitution S_N1 the molecule 2-methyl-2-butanol was used to obtain 2-chloro-2-methylbutane molecule, during this process hydrochloric acid was utilized as an agent of protonating and a nucleophile and the reaction was purified using a separatory funnel. this resulted to recovery 2.507g(69.73 mmol, 76.26%) of 2-chloro-2-methylbutane. through unimolecular elimination $E1$, the cyclohexene was obtained from cyclohexanol molecule, the process of the reaction was initiated through heating, the protonating substance here use d was sulphuric acid, the base used to complete the reaction was water. this resulted to 0.342g(3.33mmol,19.4%) of cyclohexene being obtained. as a way of determining completion of the unimolecular substitution and the process of the $E1$ reaction. to confirm the molecular structure of both substitution and elimination reactions 1H NMR was used.

Introduction

The substantial reaction is the activity whereby it includes the nucleophilic atom, an atom that has more electron density, attacking an electrophile, atom, one which is an atom that is comprised of an area of low density reaction. The two types of substitution reaction that includes, unimolecular S_N1 which takes place in two stages; the first stage obtaining of carbocation, which is the intermediate through a group that can be removed. The second step is where the nucleophile gives two electrons to the carbocation thereby creating the final product. Because S_N1 reaction is a nucleophilic substitution, it is seen that the rate of determining stage is process of forming carbocation intermediate and it is not dependent on the concentration of electrophile. Following the formation of carbocation the sp^2 which is a higher hybrid carbon and it is comprised of an empty porbital that creates a trigonometric planar geometry and this makes it possible for it to be attacked by the nucleophile from any direction. Resultantly, the final product becomes racemic mixture. In addition the substitution S_N1 continues with a high speed in a polar protic solvents. At any given rate, the group that is leaving is mandatory for it to be

stable for it to leave for if it is not then it has to be protonated first, otherwise the reaction will not proceed.

Elimination reaction is where an atom that is nucleophilic acting as a base in order to attack an electrophile through deprotonating it. This then results to forming of a double bond. Elimination reactions are of two types, one of them is unimolecular elimination E1 and it is similar to S_N1 reactions. It takes place in two steps, the first one is formation of carbocation that serves as the intermediate through the leaving group. The step that follows is where the nucleophile, get rid of the proton from carbon that are next to the carbocation creating the product. Because it is an elimination reaction, carbocation rate is the determining stage and it is also independent of on what is the concentration of the electrophile. In both unimolecular S_N1 and Elimination E1 formation of carbocation takes place in a similar way. This therefore shows that the use of heat would help in distinguishing between the two reactions. In addition, the process of leaving should be the needs a stable anion or else it has to be protonated.

Results and Discussion.

S_N1 2 Chloro- 2- methyl butane.

When the S_N1 reaction was completed, 2.507g (69.73 mmol, 76.26%) of 2-chloro-methylbutane was gained back through the use of a separatory funnel. This resulted to 76.26% of 2 chloro-2-methylbutane having been obtained is near the theoretical figure, 3.329 g, where 2-methyl-2-butanol as the limiting reagent. This shows that the leaving group which is the alcohol group, got replaced with the nucleophile chlorine in the 2-methyl -2-butanol.

The spectra that has been annotated are in the Appendix 1, the wavenumbers are in cm⁻¹, the number ranges doesn't have to have cm¹. As per Appendix A (Figure 1A), a C-Cl sp³-sp³ that is a hybridized stretch was identified at 801.91 cm⁻¹ which is in between the range of 840 cm⁻¹-560 cm⁻¹. The availability of C-Cl stretch means that the S_N1 reaction indeed progressed up to completion. In addition to that, a C-H hybridized sp³-sp³ stretch got identified along 2890.04 cm⁻¹-2841.04 cm⁻¹, which is close to the range of 3000 cm⁻¹-2850 cm⁻¹. Hence, C-H sp³-sp³ stretch presence shows that it is only alkanes that were there in the product, there wasn't a sign of alkenes. Additionally, the lack of O-H sp³-sp³ stretch, which normally takes place at around 3500 cm⁻¹- 3200 cm⁻¹, concludes that reaction from 2-methyl-2-butanol to 2-chloro-2-methylbutane was successfully set up.

The confirming of the structure of the molecules that had gone through S_N1 and E₁ unimolecular reactions were shown via ¹H NMR proton spectroscopy. According to Appendix B, Figure 1B shows that 2-chloro-2-methylbutane took three proton signs ,H_b at 1.8321ppm, also quarter, 2H; H_a at 1.5612ppm,singlet, 6H;H_c at 1.034ppm,triplet, 3H. The parting sequence –quarter, singlet and triplet–showed the number of hydrogens in every carbon that is adjacent and the amount of protons – 2, 6, and 3– indicates the amount of hydrogens that produced the sign. Due to this H_b was identified more downfield and this shows that the proton onto the carbon is the one holding that chlorine and the carbon holding that proton is less protected , and H_a being detected up field shows that this proton is found far from the atom that is the most electromagnetic , chlorine, and is more protected . Resultantly, the three signals and the pattern of splitting along the amount of

protons that had produced the signs shows that the reaction of 2-methyl-2-butanol took place up to completion into 2-chloro 2-methylbutane.

E₁ Cyclohexene.

After completing the process of elimination E₁ where heat was used in initiation of the reaction, 0.342g (3.33mmol, 19.4%) of cyclohexene was obtained. Here the limiting reagent was sulphuric acid, 19.4% of cyclohexene was obtained from the theoretical figure of 1.54g. Although 19.4% is not a large value, it can still be said that the reaction was completed, this means that the leaving group which is the alcohol group was eliminated and the carbocation got stabilized through the nucleophile, water, the deprotonating next to the hydrogen and formation of an alkene.

Spectra annotated are in the Appendix 1, the wavenumbers are in cm^{-1} in which the number ranges do not have to have cm^{-1} . As in Appendix A (Figure 2A), a C-H $\text{sp}^3\text{-sp}^3$ which is a hybridized stretch got identified at 2933.84 cm^{-1} - 2837.54 cm^{-1} and it is in between the range of 2830 cm^{-1} - 2695 cm^{-1} . The identification of the C-H stretch indicates that the E₁ reaction did indeed continued up to completion, not all of the carbons were sp^2 hybridized. Additionally, a C-H hybridized $\text{sp}^2\text{-sp}^3$ stretch was identified around 3022.84 cm^{-1} , which is close to the range of 3100 cm^{-1} - 3000 cm^{-1} . Consequently, the presence of C-H $\text{sp}^2\text{-sp}^3$ stretch shows that an alkene was there and that deprotonation stage of the E₁ reaction did occur. the C=C $\text{sp}^2\text{-sp}^2$ stretch was detected at 1652 cm^{-1} , which also confirms the alkene presence as well as that the deprotonation stage didn't occur. This therefore results to lack of 1652 cm^{-1} and normally happens around 3500 cm^{-1} - 3200 cm^{-1} conveying that the reaction of cyclohexanol to cyclohexene finished successfully.

Appendix B, figure 2B shows that three proton signs are transferred by cyclohexene, Ha at 5.67ppm, triplet, 2H; Hb at 2.00ppm, quartet, 4H; Hc at 1.63ppm, triplet, 4H. the pattern of in which they break is -triplet, quartet, and triplet- communicates that number of hydrogen in each next carbon and the number of protons-2, 4, and 4- shows that the amount of hydrogen that produced the sign. Thus, Ha was identified more downfield and this means that it is a positive ion that is held onto the carbon that is involved in the alkene. Hb was identified a bit up field than Ha, meaning that it is away from the alkene and it is more protected from the alkene. This therefore results Hc being found up field means that it is found away from the alkene and is more protected from the alkene. Presence of three signs and the breaking patterns together with the number of protons which generates the signal, all mean that the reaction of cyclohexanol to cyclohexene was successfully set up.

Conclusion

The resulting products of both, S_N1 and E₁, reaction transfer were achieved and the use of FTIR; that showed the lack of the availability of the O-H $\text{sp}^3\text{-sp}^3$ stretch; and the positive ions in their respective environments, confirmed the necessary properties of 2-chloro-2-methylbutane and cyclohexene. Even though S_N1 and E₁ occur through similar steps, the presence of heat distinguished the competition between S_N1 and E₁, favoring E₁,

Use of hydrochloric acid, S_N1 reaction, 2.507g (69.73 mmol, 76.26%) of 2,2-chloro-2-methylbutane was generated. however, E₁ process resulted to 0.342g (3.33mmol, 19.4%) of

cyclohexene after using sulphuric acid, H_2SO_4 . the experiment was successful and even the results that were being investigated were achieved.

Experimental.

The reactants for all the reactions above were provided by the University of Colorado Denver Chemistry Department. FTIR spectra was gotten with a Nicolet iS5 ATR FTIR spectrometer and the measurements were in cm^{-1} . The ^1H NMR spectra were gotten using a Bruker 400 MHz spectrometer by use of CDCl_3 as the solvent. All measurements were in ppm and the following short forms have been used, s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet)

Synthesis of 2-chloro-2-methylbutane

A separatory funnel of capacity 12mL was added 10mL of 2-methyl-2-butanol (91.3 mmol) and 25 mL of concentrated 12 M HCl (697mmol). The separating funnel was then shaken inverted and vented to make an organic layer, the hydrochloric acid layer which is denser. The organic layer of the product was washed with deionized water (10mL*3) and 5% NaHCO_3 (10mL*2). The product was dried using anhydrous magnesium sulfate and was gravity filtered into a tared 50mL beaker. As a result, 2.506g (68.73mmol, 75.26%) of 2 chloro-2 -methylbutanol. FTIR was obtained and produced an 801.91 cm^{-1} , C-Cl $\text{sp}^3\text{-sp}^3$ hybridized stretch; 2990.04 cm^{-1} - 2941.04 cm^{-1} , C-H hybridized $\text{sp}^3\text{-sp}^3$ stretch. ^1H NMR was obtained and produced three signals—Hb at 1.7962 ppm, q, 2H; Ha at 1.5609 ppm, s, 6H; Hc at 1.033 ppm, t, 3H.

Synthesis of cyclohexene

a 25 mL round bottomed flask was charged with 2mL of (9.46 mmol) and 1 mL of sulfuric acid, H_2SO_4 (18.8 mmol) with a magnetic bar. The round bottomed flask was attached to a reflux condenser and placed on bird's nest heater to initiate the reaction. The process was heated for around 15 minutes. the reflux condenser was placed with a three way adapter to complete simple distillation and a the zoetrope, 0.606g (18.8mmol, 39.3%), was collected in a scintillation vial. the product was then dried through anhydrous magnesium sulfate and the product and the product collected in a scintillation vial. as a result, 0.283 g (3.43 mmol, 18.3%) of cyclohexene was recovered from cyclohexanol. FTIR was obtained and produced a 2933.84 cm^{-1} - 2837.54 cm^{-1} , C-H $\text{sp}^3\text{-sp}^3$ hybridized stretch; 3022.84 cm^{-1} , C-H hybridized $\text{sp}^2\text{-sp}^3$ stretch; 1652 cm^{-1} , C=C $\text{sp}^2\text{-sp}^2$ stretch. ^1H NMR was obtained and produced three signals, Ha at 5.67 ppm, t, 2H; Hb at 2.00 ppm, q, 4H; Hc at 1.63 ppm, t, 4H.

References

Sarda, V., Farooqi, J. A., & Malhotra, S. (2017). Unit-16 Alkyl Halides: Substitution and Elimination Reactions