

CHEM 3418 005

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Completion of Unimolecular Substitution and Elimination Reactions

Abstract

Substitution reactions and elimination reactions are important when determining at which conditions and at which rate a reaction can proceed to completion. Through unimolecular substitution S_N1 reaction conditions, the molecule 2-chloro-2-methylbutane was established from the molecule 2-methyl-2-butanol. Hydrochloric acid was used as a protonating agent and a nucleophile and the reaction was washed using a separatory funnel. As a result, 2.506 g (68.73 mmol, 75.26%) of 2-chloro-2-methylbutane was recovered. Through the unimolecular elimination E_1 reaction conditions, the molecule cyclohexene was established from the molecule cyclohexanol. Heat was used to initiate the process of the elimination E_1 reaction, the methods of the reflux condenser were used to purify the product of the elimination E_1 reaction, sulfuric acid was used as a protonating agent and water was used as a base to complete the reaction. As a result, 0.282 g (3.43 mmol, 18.3%) of cyclohexene was recovered. Fourier transform infrared spectroscopy was used to confirm the completion of the unimolecular S_N1 and the occurrence of the E_1 reaction. In addition, 1H NMR was used to confirm the molecular structure of substitution S_N1 reaction and elimination E_1 reaction.

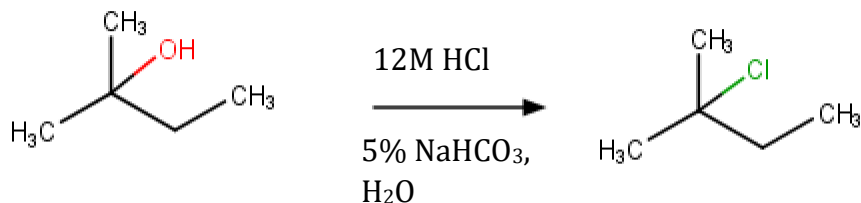
Introduction

The mechanism for the reaction of 2-methyl-2-butanol to 2-chloro-2-methylbutane is shown in Figure 1.



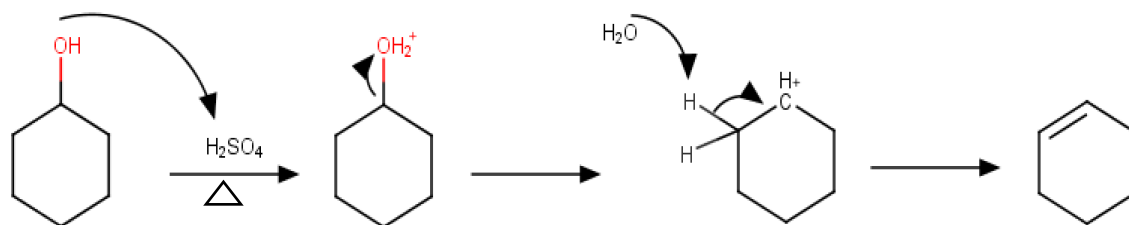
Figure 1: S_N1 2-methyl-2-butanol to 2-chloro-2-methylbutane Mechanism

Hydrochloric acid was used to proceed the completion of the S_N1 unimolecular substitution reaction as shown in Scheme 1.

Scheme 1: S_N1 2-methyl-2-butenol to 2-chloro-2-methylbutane Scheme

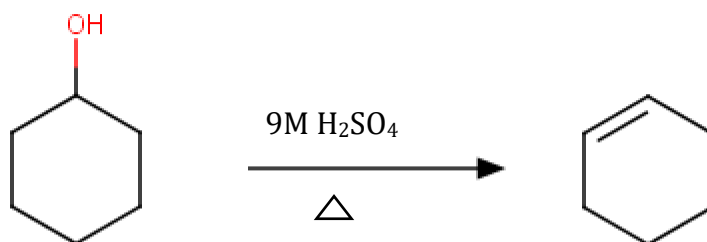
A substitution reaction is a process that involves the nucleophilic atom—an atom that contains high electron density—attacking an electrophile, an atom that contains a region of low electron density. There are two types of substitution reactions, one of which is the unimolecular S_N1 reaction which occurs through two steps. The first step involves the generation of a carbocation, which becomes the intermediate, via the leaving group—a group that can be expelled—leaving by itself, as indicated in Figure 1. It is followed by the second step in which the nucleophile donates an electron pair to the carbocation creating the product. Since S_N1 reaction is a nucleophilic substitution, the rate determining step is the formation of the carbocation intermediate which is independent of the concentration of the nucleophile and is more likely dependent on the concentration of the electrophile. The formation of the carbocation creates a sp² hybridized carbon which contains an empty p-orbital establishing a trigonal planar geometry, thus, allowing for the nucleophile to attack the carbocation from any direction. As result, the end-product will be a racemic mixture, as indicated in Figure 1. Additionally, the substitution S_N1 reaction proceeds faster in polar protic solvents. At any rate, the leaving group must be stable enough to leave and if it is not then it must be protonated first, or the reaction would not proceed, as indicated in Figure 1.

The mechanism for the reaction of cyclohexanol to cyclohexene is shown in Figure 2. The little triangle represents heat.

**Figure 1:** E₁ Cyclohexanol to Cyclohexene Mechanism

The use of heat and high concentration of sulfuric acid was used to proceed the reaction of unimolecular elimination E_1 reaction, as shown in Scheme 2. The little triangle represents heat.

Scheme 2: E_1 Cyclohexanol to Cyclohexene Scheme



An elimination reaction is a process that involves the nucleophilic atom acting as a base to attack the electrophile by deprotonating the electrophile. The deprotonation would then cause the formation of the double bond. There are two types of elimination reactions, one of which is the unimolecular elimination E_1 reaction, which (similarly to S_N1 reactions) occurs through two steps. The first step involves the generation of a carbocation, which becomes the intermediate, via the leaving group, as indicated in Figure 2. It is followed by the second step in which the nucleophile, acting as a base, removes a proton from carbon atoms adjacent to the carbocation to create the product. Since E_1 reaction is an elimination reaction, the formation of the carbocation is the rate determining step which is dependent on the concentration of the electrophile. The formation of the carbocation in both unimolecular S_N1 reactions and elimination E_1 reactions occur similarly, therefore, the use of heat and a polar protic solvent would help differentiate the E_1 reaction from the S_N1 reaction. Moreover, the leaving must be a stable anion and, in the case, that it is not (as indicated in Figure 2), the leaving group must be protonated, or the reaction cannot proceed.

Results and Discussion

S_N1 2-chloro-2-methylbutane

Upon the completion of the reaction S_N1 unimolecular substitution reaction, 2.506 g (68.73 mmol, 75.26%) of 2-chloro-2-methylbutane was recovered through the use of separatory funnel. As a result, 75.26% of 2-chloro-2-methylbutane was yielded close to the theoretical value, 3.329 g, with the limiting reagent being 2-methyl-2-butanol. In other words, the

leaving group, alcohol group, from 2-methyl-2-butanol was substituted with the nucleophile, chlorine.

The annotated spectra are in the Appendix 1 and all the wavenumbers are in cm^{-1} in which the number ranges do not have to have cm^{-1} . According to Appendix A (Figure 1A), a C-Cl $\text{sp}^3\text{-sp}^3$ hybridized stretch was detected at 801.91 cm^{-1} which is in between the literature range of 850 cm^{-1} - 550 cm^{-1} . The presence of the C-Cl stretch indicates that the $\text{S}_{\text{N}}1$ reaction did indeed progressed into completion. Additionally, a C-H hybridized $\text{sp}^3\text{-sp}^3$ stretch was detected around 2990.04 cm^{-1} - 2941.04 cm^{-1} , which is close to the literature range of 3000 cm^{-1} - 2850 cm^{-1} . As a result, the presence of C-H $\text{sp}^3\text{-sp}^3$ stretch indicates that only alkanes were present in the product and there was no indication of alkenes. Additionally, the lack of O-H $\text{sp}^3\text{-sp}^3$ stretch, which usually occurs around 3500 cm^{-1} - 3200 cm^{-1} , conveys that the reaction from 2-methyl-2-butanol to 2-chloro-2-methylbutane was successfully established.

The confirmation of the structure of the molecules that underwent $\text{S}_{\text{N}}1$ and E_1 unimolecular reactions were conveyed via ^1H NMR proton spectroscopy. According to Appendix B, Figure 1B conveys that 2-chloro-2-methylbutane conveyed three proton signals, Hb at 1.7962 ppm, quartet, 2H; Ha at 1.5609 ppm, singlet, 6H; Hc at 1.033 ppm, triplet, 3H. The splitting pattern—quartet, singlet, and triplet—conveyed the number of hydrogens in each adjacent carbon and the number of protons—2,6, and 3—indicated the number of hydrogens that generated the signal. As a result, Hb was detected more downfield which conveys that it the proton that is attached to the carbon holding the chlorine and the carbon holding this proton is less shielded, and Ha was detected a little upfield than Hb because the proton is more shielded. Similarly, Hc was detected upfield, which conveys that this proton is located away from the most electronegative atom, chlorine, and is more shielded. Consequently, the three signals and the splitting patterns along with the number of protons that have generated the signals convey that reaction from 2-methyl-2-butanol proceeded and was completed into 2-cholor-2-methylbutane.

E₁ Cyclohexene

Upon the completion of the elimination E_1 reaction and the use of heat to initiate the reaction, 0.283 g (3.43 mmol, 18.3%) of cyclohexene was recovered. With the limiting reagent being sulfuric acid, 18.3% of cyclohexene was yielded from the value of theoretical yield, 1.54 g. Even though, 18.3% yield is not a big value, the reaction can be said to have completed, meaning that the leaving group, the alcohol group, was eliminated and the carbocation was stabilized through the nucleophile, water, deprotonating adjacent hydrogens and creating an alkene.

The annotated spectra are in the Appendix 1 and all the wavenumbers are in cm^{-1} in which the number ranges do not have to have cm^{-1} . According to Appendix A (Figure 2A), a C-H $\text{sp}^3\text{-sp}^3$ hybridized stretch was detected at 2933.84 cm^{-1} - 2837.54 cm^{-1} which is in between the literature range of 2830 cm^{-1} - 2695 cm^{-1} . The presence of the C-H stretch indicates that the E_1 reaction did indeed progressed into completion and not all of the carbons were sp^2

hybridized. Additionally, a C-H hybridized sp^2 - sp^3 stretch was detected around 3022.84 cm^{-1} , which is close to the literature range of 3100 cm^{-1} - 3000 cm^{-1} . As a result, the presence of C-H sp^2 - sp^3 stretch indicates that an alkene was present and that the deprotonation step of the E_1 reaction did occur. A C=C sp^2 - sp^2 stretch was detected at 1652 cm^{-1} , which also confirms the presence of an alkene. Consequently, the lack of O-H sp^3 - sp^3 stretch, which usually occurs around 3500 cm^{-1} - 3200 cm^{-1} , conveys that the reaction from cyclohexanol to cyclohexene was successfully completed.

According to Appendix B, Figure 2B conveys that cyclohexene conveyed three proton signals, Ha at 5.67 ppm, triplet, 2H; Hb at 2.00 ppm, quartet, 4H; Hc at 1.63 ppm, triplet, 4H. The splitting pattern—triplet, quartet, and triplet—conveyed the number of hydrogens in each adjacent carbon and the number of protons—2, 4, and 4—indicated the number of hydrogens that generated the signal. As a result, Ha was detected more downfield which conveys that it is a proton that is attached to the carbon involved in the alkene, and Hb was detected a little upfield than Ha, in which this detection conveys that this proton is attached to the carbon adjacent to the alkene. Similarly, Hc was detected upfield, which conveys that this proton is located away from the alkene and is more shielded from the alkene. Consequently, the presence of three signals and the splitting patterns along with the number of protons that have generated the signals all convey that reaction from cyclohexanol to cyclohexene was established.

Conclusion

Using hydrochloric acid, the substitution S_N1 reaction produced 2.506 g (68.73 mmol, 75.26%) of 2-chloro-2-methylbutane. On the contrary, elimination E_1 reaction produced 0.283 g (3.43 mmol, 18.3%) of cyclohexene using sulfuric acid, H_2SO_4 . The products of both, S_N1 and E_1 , reaction conveyed were achieved and the use of FTIR—which conveyed the lack of the presence of the O-H sp^3 - sp^3 stretch—and the use of 1H NMR—which conveyed the presence of three signals generated by the protons in their respective environments—confirmed the necessary characteristics of 2-chloro-2-methylbutane and cyclohexene. Even though S_N1 and E_1 occur through similar steps, the presence of heat distinguished the competition between S_N1 and E_1 , favoring E_1 . The experiment worked as expected and the products were achieved as expected.

Experimental

All reactants were reagent grade and provided by the University of Colorado Denver Chemistry Department. FTIR spectra were obtained with a Nicolet iS5 ATR FTIR spectrometer and all measurements were in cm^{-1} . The 1H NMR spectra were obtained using a Bruker 400 MHz spectrometer using $CDCl_3$ as the solvent. All measurements were in ppm and the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

Synthesis of 2-chloro-2-methylbutane

A 125 mL separatory funnel was charged with 10 mL of 2-methyl-2-butanol (91.3 mmol) and 25 mL of concentrated 12 M HCl (697 mmol). The separatory funnel was then shaken, inverted, and vented to create organic layer which is the layer containing 2-methyl-2-butanol and is less dense, and the aqueous layer which is the hydrochloric acid layer and is denser. Next, the organic layer of the product was washed with deionized water (10 mL x 3) and 5% NaHCO₃ (10 mL x 2). The product was then dried via anhydrous magnesium sulfate and was gravity filtered into a tared 50 mL beaker. Consequently, 2.506 g (68.73 mmol, 75.26%) of 2-chloro-2-methylbutane was obtained from 2-methyl-2-butanol. FTIR was obtained and produced a 801.91 cm⁻¹, C-Cl sp³-sp³ hybridized stretch; 2990.04 cm⁻¹-2941.04 cm⁻¹, C-H hybridized sp³-sp³ 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 bottom flask was charged with 2 mL of cyclohexanol (9.46 mmol) and 1 mL of sulfuric acid, H₂SO₄ (18.8 mmol) along with a magnetic stir bar. The round bottom flask was attached to a reflux condenser and placed on bird's nest heater to initiate the reaction. The process was heated for 15 minutes. The reflux condenser was replaced with a three-way adapter to complete simple distillation and the azeotrope, 0.606 g (18.8 mmol, 39.3 %), was collected in a scintillation vial. The product was then dried through anhydrous magnesium sulfate and the product was collected via a disposable pipette into 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 sp³-sp³ hybridized stretch; 3022.84 cm⁻¹, C-H hybridized sp²-sp³ stretch; 1652 cm⁻¹, C=C sp²-sp² 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

1. PubChem, *Open Chemistry Database*. <https://pubchem.ncbi.nlm.nih.gov/compound/2-Chloro-2-methylbutane>

Appendix A. Fourier Transform Infrared Spectroscopy (FTIR)

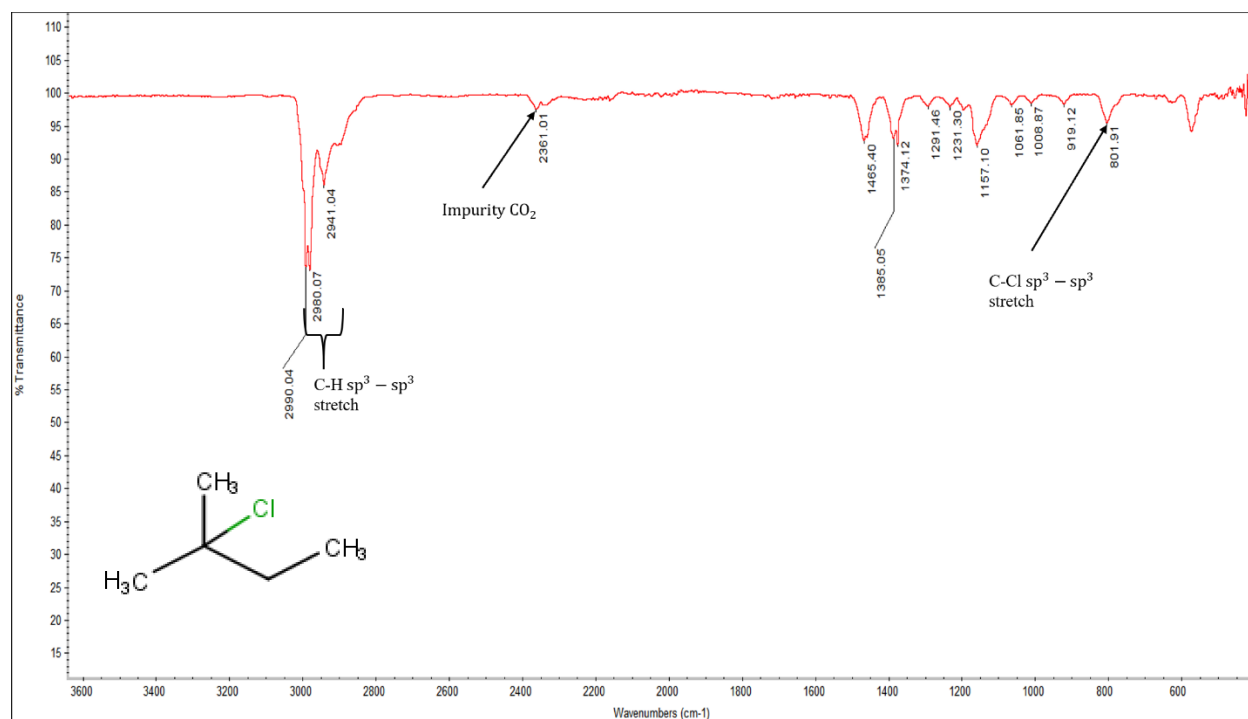


Figure 1A: Spectroscopy of 2-chloro-2-methylbutane

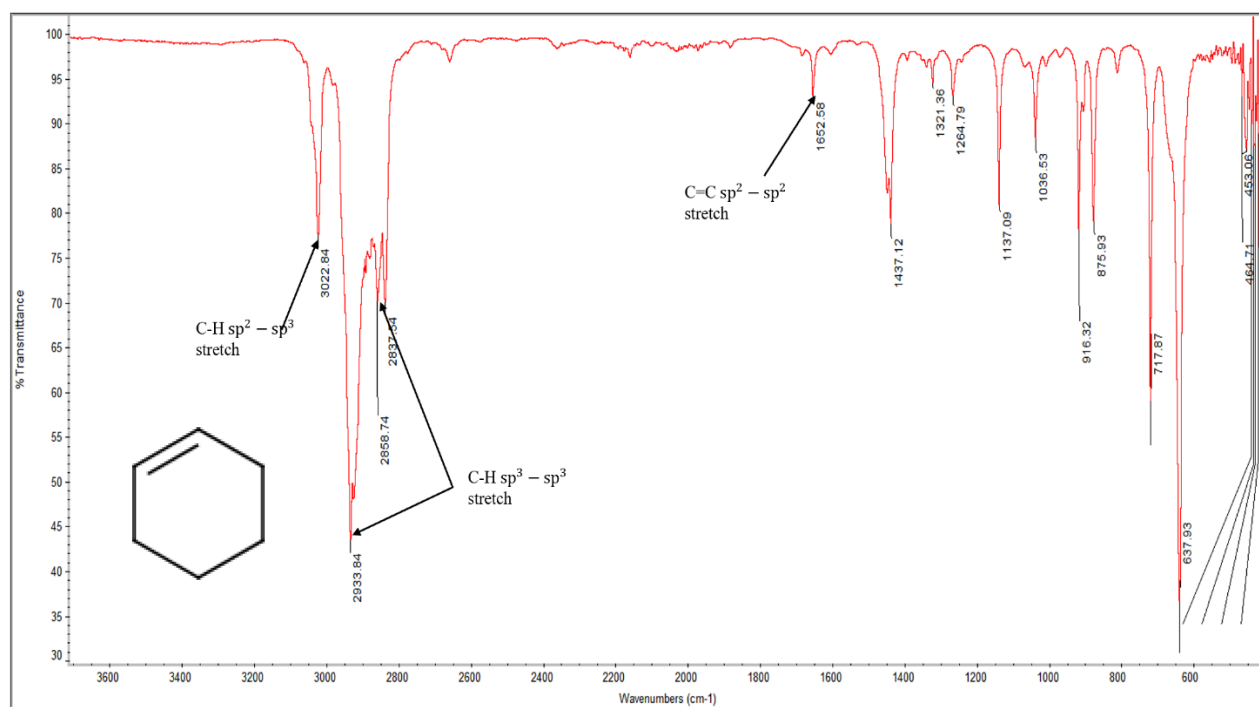


Figure 2A: Spectroscopy of Cyclohexene

Appendix B. ^1H NMR Spectra for $\text{S}_{\text{N}}1$ and E_{1} Unimolecular Reactions

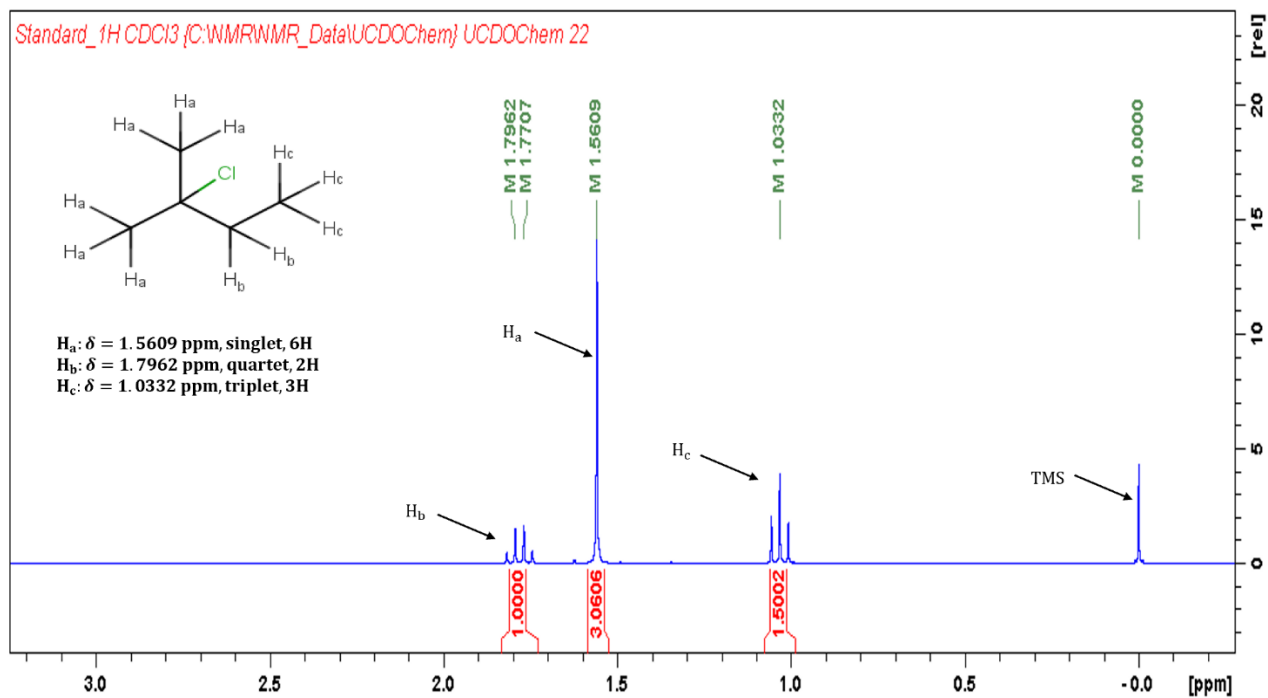


Figure 1B: ^1H NMR Spectroscopy of $\text{S}_{\text{N}}1$ Reaction 2-chloro-2-methylbutane

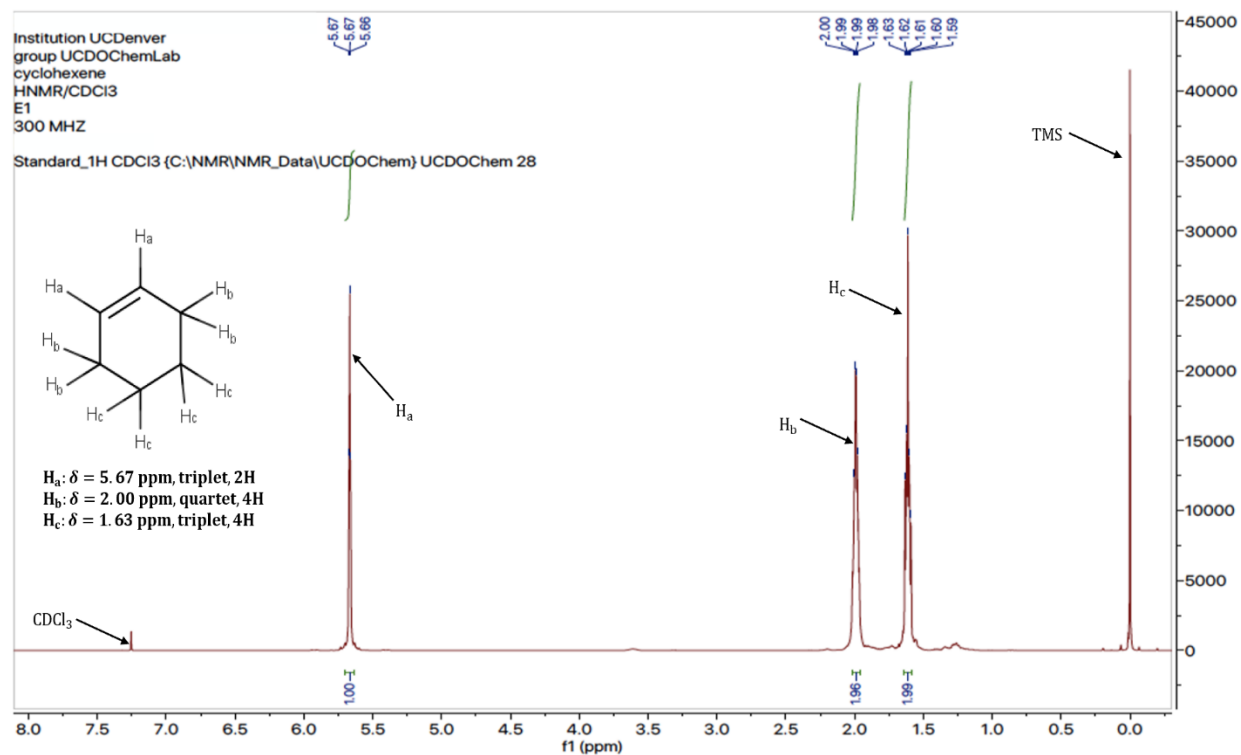


Figure 2B: ^1H NMR Spectroscopy of E_{1} Reaction Cyclohexene

