University of North Carolina Asheville
Journal of Undergraduate Research
Asheville, North Carolina
May 2015

Computational Study of Substituent Effect on the Threshold Energy for the 1,2-Interchange of Halogens, Pseudohalogens, and Various R Groups

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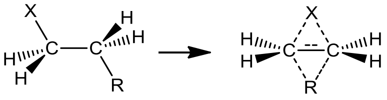
Abstract

The possibility of gaseous halocarbons undergoing a 1,2-interchange reaction in competition with typical 1,2-HF or HCl eliminations offers an interesting explanation for their reactivity in the atmosphere. In order to determine the most energetically feasible interchanges, the threshold energies for the interchange of various halogens (F, Cl, Br), pseudohalogens (SH, CH_3, NH_2, CN, OH, OCH_3), and other groups (OCF_3, OCH_3, CH=CH_2, CH_2CH_3, CH_3, CH_2OH, C≡CH, CH_2CF_3, CCl_3, CF_3) were calculated using computational methods. Ground state and transition state geometries were optimized with the B3PW91 level of theory and 6-311+G(2d,p) basis set. The Br-Br interchange had the lowest E_0 (33.8 kcal/mol), and CH_3-CH_3 had the highest (134.8 kcal/mol). In general, larger atoms/groups with lone pairs of electrons such as halogens, SH, OH, OCH_3, and NH_2 tend to lower the E_0 barrier for interchange, making them the most likely to undergo rearrangement, as their E_0 barriers were under 70 kcal/mol. Those groups can be considered for further experimental observation, but CH_3 is unlikely to interchange due to its high E_0 barriers. C-C≡N bond lengths were considered too long to represent accurate transition states for CN interchange.



1. Introduction

In previous studies we have demonstrated the existence of a series of unimolecular reactions involving the interchange of two halogen atoms on adjacent carbons.[1-5] This interchange mechanism has been supported by experimental and computational evidence for $CF_2ClCF_2CH_3$ ($CF_2ClCF_2CD_3$),[1-2] CHF_2CH_2Cl,[6-7] $CF_2ClCHFCH_3$ ($CF_2ClCHFCD_3$),[4] $CF_2ClCHFC_2H_5$ ($CF_2ClCHFC_2D_5$),[5] $CF_2ClCFClCH_2F$,[8] $CF_2BrCF_2CH_3$,[9] CF_3CHFCH_2Cl, CH_3CHFCH_2Cl,[10] CH_2FCH_2Cl (CH_2FCD_2Cl),[11] CH_2FCHCl_2,[12] CF_3CH_2Cl, and CF_2ClCH_2F[13] and is found to be in competition with unimolecular HX (X = F, Cl, or Br) eliminations. F-Cl, F-Br, and Cl-Br interchanges have all been observed.[1,2,4-13]

Cl-CH_3 and Br-CH_3 interchanges have been observed experimentally and computationally for $(CH_3)_3CCH_2Cl$ and $(CH_3)_3CCH_2Br$, providing an alternative mechanism for the formation of CH_2=$C(CH_3)C_2H_5$ and $(CH_3)_2C$=$CHCH_3$ from a Wagner-Meerwein rearrangement.[14] The interchange of Cl with CH_3 has been studied in $(CH_3)_3CCD_2Cl$[14] and 1,1-dichloroacetone and provided an energetically favorable reaction pathway for the acetone prior to a 1,2-HCl or 2,3-HCl elimination, as opposed to a 1,1-HCl or 1,3-HCl elimination with subsequent isomerization of a biradical or a carbene.[15] The existence of this halogen interchange leads to the question of whether it is only with halogens that this occurs or if pseudohalogens and univalent species, such as OH, SH, CN, NH_2, OCH_3, and CH_3, also undergo this reaction.

To examine these possibilities, we investigated the interchange between halogens (F, Cl, Br), pseudohalogens (SH, CH_3, NH_2, CN, OH, OCH_3), and other groups (OCF_3, OCH_3, $CH=CH_2$, CH_2CH_3, CH_3, CH_2OH, $C{\equiv}CH$, CH_2CF_3, CCl_3, CF_3) computationally. Electronic structure calculations were performed using density functional theory on molecules of the form CH_2XCH_2R, where X and R represent a halogen or one of the groups listed above. A diagram of the conversion from CH_2XCH_2R to its interchange transition state to CH_2RCH_2X can be found in Figure 1. The lowest energy conformation was used in all calculations; in each case this was the *anti* conformation, which is the conformation the molecule must be in to undergo the interchange reaction. The B3PW91 level of theory, and the 6-31G(d',p') and 6-311+G(2d,p) basis sets were used, which we have found to give energies close to those determined from experimental investigations for the halogen interchange**.** The main focus of this paper is on the threshold energy barriers and geometries of the transition state. It is hoped that this study will serve as a guide to whether these reactions are worth exploring experimentally and perhaps to help reevaluate results from previous experiments.

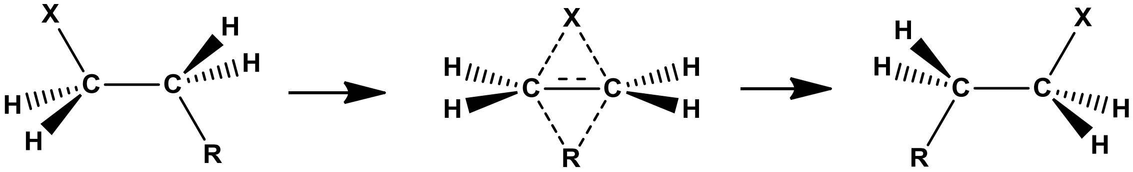


Figure 1. A general transition state for the interchange of substituents X and R, where CH_2XCH_2R converts into CH_2RCH_2X (e.g. CH_2FCH_2Br converts to CH_2BrCH_2F).

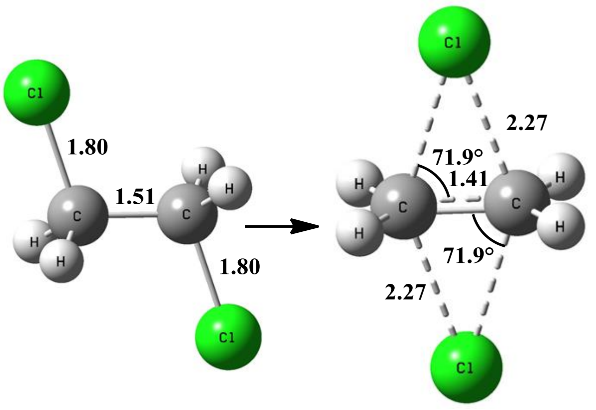
2. Computational Methods

Density functional theory (DFT) calculations were performed using the Gaussian 09 suite of programs.[16] Ground state and transition state geometries were optimized and vibrational frequencies and unscaled zero-point energies were calculated using Becke's three-parameter exchange functional[16] with Perdew and Wang's correlation functional,[18] B3PW91. The 6-31G(d',p') basis set was used initially to find the optimized geometries. Upon successful optimizations, the 6-311+G(2d,p) basis set was used and all values and geometries reported here were done with the latter basis set. Transition states were characterized by exactly one negative frequency. Intrinsic reaction coordinate (IRC) calculations were performed to verify that the transition state connected reactants and products. The threshold energy (E_0) for each interchange was calculated by multiplying the difference in zero-point energies (Hartrees) between the ground state and transition state by 627.5, thus converting to units of kcal/mol.

3. Transition State Geometry

The transition state geometries of Cl interchanging with each of the halogens, pseudohalogens, and R groups are shown in Figure 2. All geometries in Figure 2 have labeled bond lengths (Å) and angles (°).

The two interchanging atoms/groups are located halfway between the two carbons, and these four atoms/groups are nearly planar. The hydrogens are nearly planar with the two carbons, which takes on a trigonal planar geometry similar to an ethene. The C-C bond distance becomes shorter in the transition state compared to the ground state by about 0.10 Å.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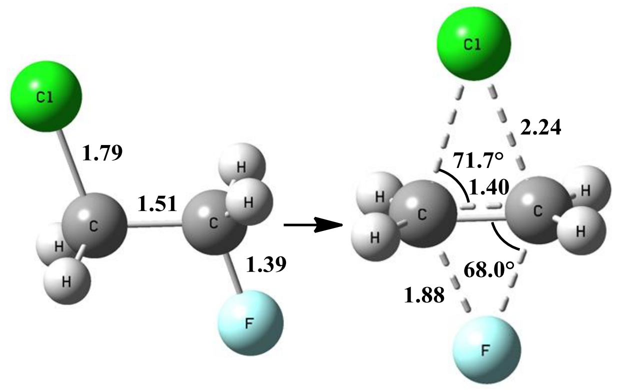
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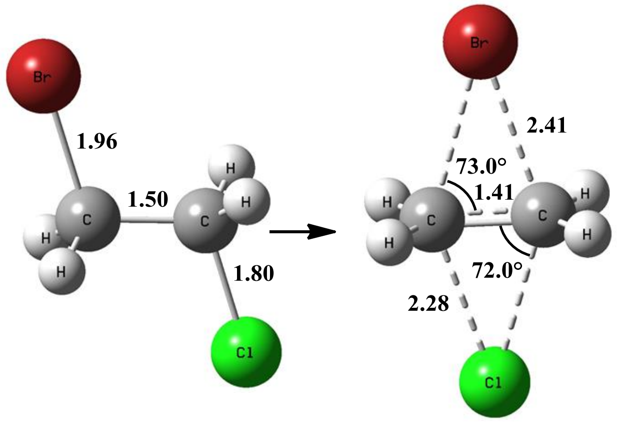
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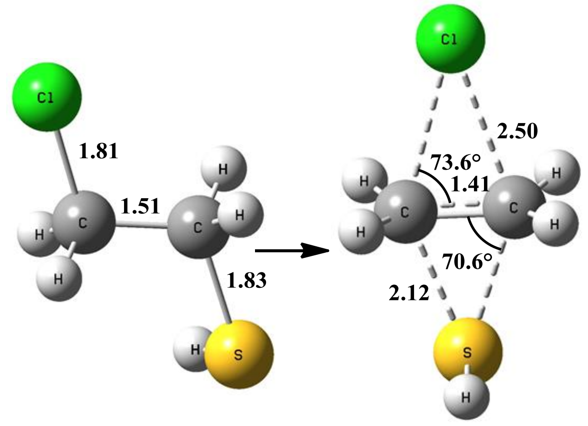
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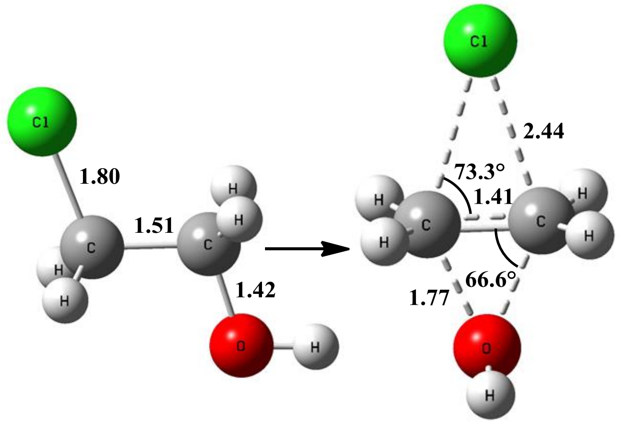
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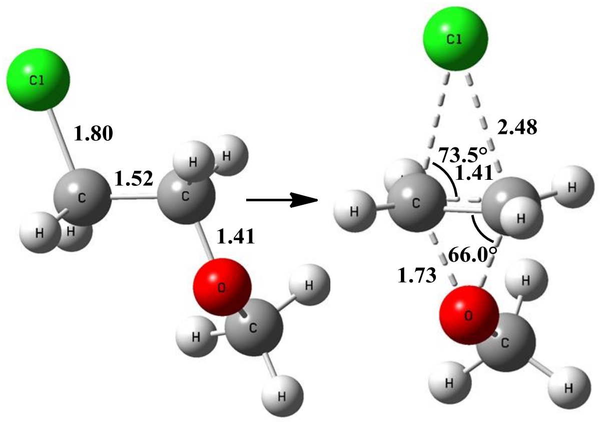
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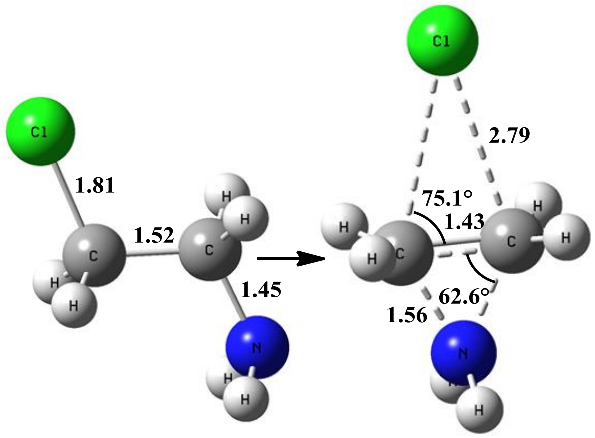
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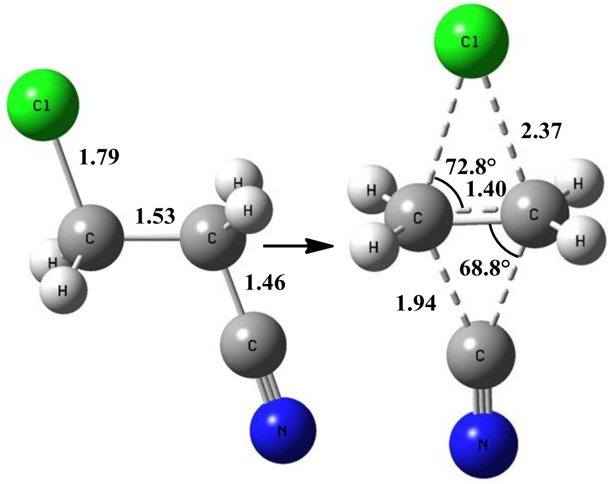
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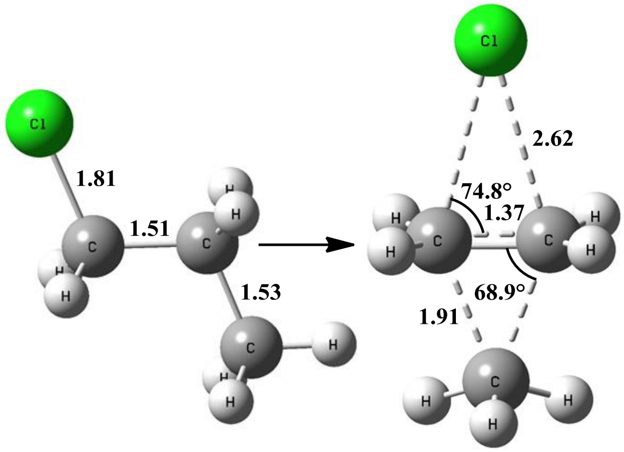
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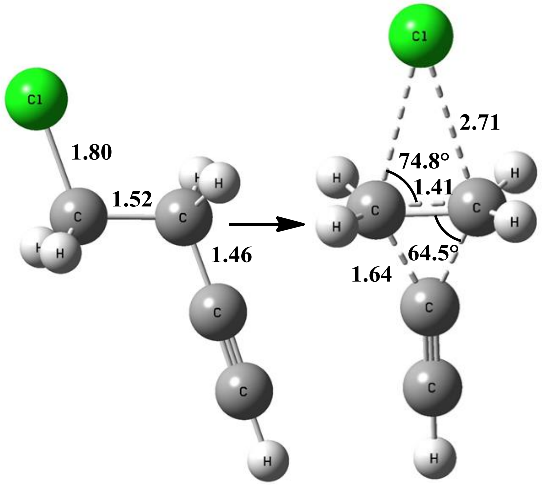
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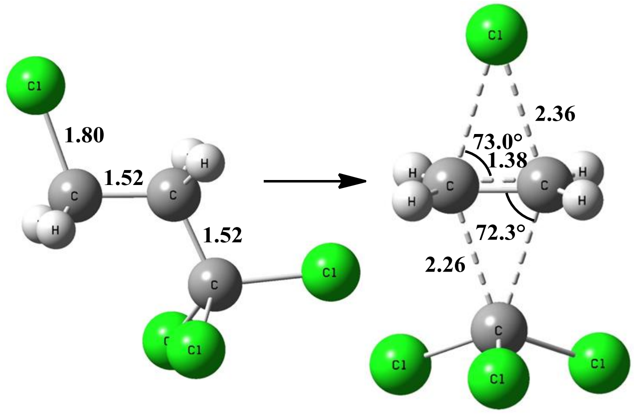
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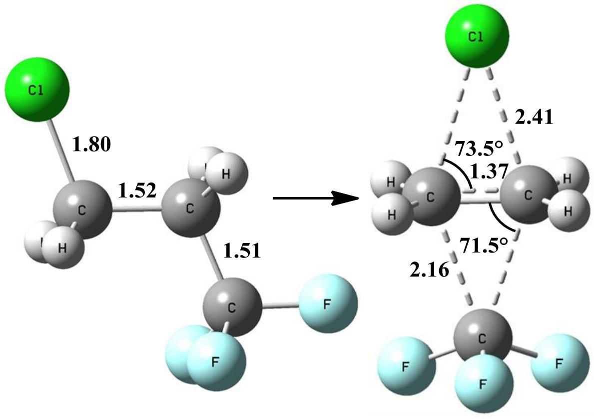
2.26
Cl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F
Cl
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2.16
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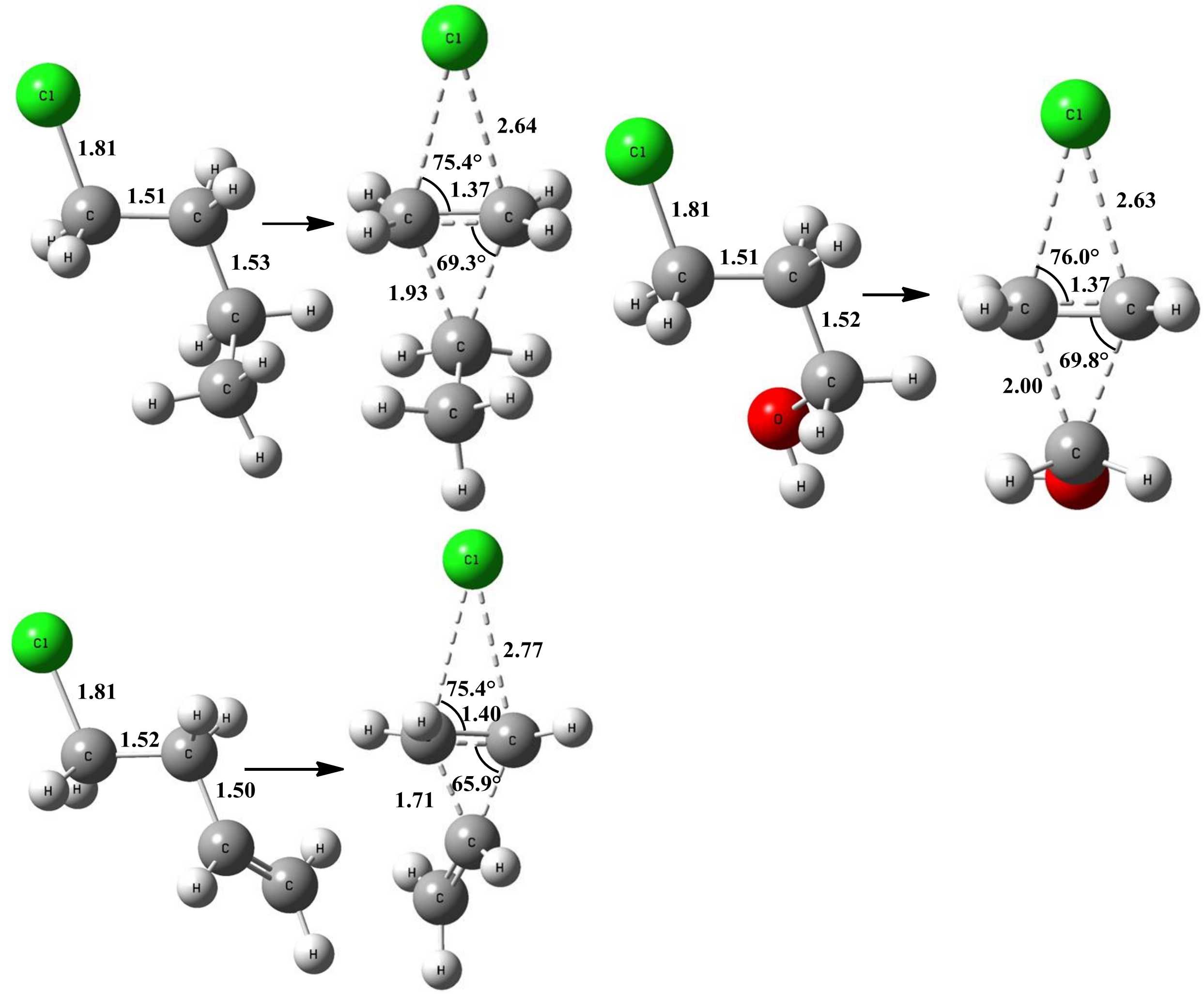

Figure 2. Pictures of the reactant and transition state structures for various Cl interchanges with labeled C-C, C-Cl, and C-R bond lengths (Å), and Cl-C-C and R-C-C bond angles (°).

4. Results and Discussion

Ground state and transition state geometries were found computationally for the 1,2-XR interchanges on a two carbon system. E_0 was calculated for the interchange of each combination of two groups from the following list: F, Cl, Br, OH, OCH_3, SH, NH_2, CN, and CH_3. The E_0's (kcal/mol) are given in Table 1. All reported values were calculated using the B3PW91 level of theory and 6-311+G(2d,p) basis set.

The Br-Br interchange has the lowest E_0 (33.8 kcal/mol), while the CH_3-CH_3 interchange has the highest E_0 (134.8 kcal/mol). Systems involving Br have the lowest E_0's (33.8 – 67.5 kcal/mol), which is likely due to the large size of Br and its subsequently weaker bonds to carbon. The E_0 for interchanges involving Cl are about 5 kcal/mol higher than those involving Br, while the E_0 for F systems are 13-17 kcal/mol higher than Cl systems.

The barrier for CH_3 interchanges ranges from 67.5 kcal/mol (Br-CH_3) to 134.8 kcal/mol (CH_3-CH_3), which is due to the strong C-C bonds. CN systems also have high E_0's (76.1 – 124 kcal/mol), but the C-CN bond lengths in the calculated geometries are too long to be considered accurate representations of a transition state for a concerted interchange.

A general periodic trend can be seen in these E_0 values. There tends to be a decrease in E_0 going across the periodic table from C to F and from S to Cl. There is also a decrease in E_0 going down the periodic table from F to Br and from O to S. The pseudohalogens that have the same atom bonded to the carbon atoms in the ground state, such as OH and OCH_3 or CH_3 and CN, tend to have similar E_0 values. Interchanges involving CN and CH_3 generally have the highest E_0 values, and the only interchanges involving either of these groups that have a low enough E_0 to occur before decomposition are Cl with CN or CH_3 and OCH_3 with CH_3. As seen previously with halogen interchanges, several of the halide-pseudohalide interchanges have a low enough E_0 that they may be in competition with elimination reactions.

Groups with a lone pair of electrons had the lowest E_0 barriers, such as the halogens, SH, OCH_3, OH, and NH_2. Having lone pairs likely helps the groups to break and form new bonds as they interchange. If those bonds are considered coordination bonds, then a possible explanation for the lower E_0 for groups with lone pairs is that, as the electrons in the starting bond go to the interchanging group and form a new lone pair, the existing lone pair donates both of its electrons to form the new bond with the adjacent carbon. The equidistant position of the group with both carbons, along with the positions of the lone pairs further supports this theory.

Table 1. Threshold energy barriers for interchange reactions (kcal/mol) calculated at the B3PW91/6-311+G(2d,p) level of theory and basis set. * Transition state not found.

	Br	Cl	F	SH	OCH_3	OH	NH_2	CN	CH_3
Br	33.8	38.8	51.6	39.6	53.6	53.7	44.0	76.1	67.5
Cl		43.8	56.4	44.4	58.4	58.5	48.8	80.7	72.3
F			69.0	57.9	71.6	71.5	65.2	92.2	86.4
SH				53.8	66.7	67.4	67.8	84.0	86.6
OCH_3					78.3	79.4	80.2	96.4	98.2
OH						80.5	82.4	98.0	106.8
NH_2							98.6	*	112.6
CN								124.0	*
CH_3									134.8

Calculated E_0's (kcal/mol) for the interchange of a halogen with $-OCF_3$, $-CH=CH_2$, $-CH_2CH_3$, $-CH_2OH$, $-C\equiv CH$, $-CH_2CF_3$, $-CCl_3$, and $-CF_3$ are provided in Table 2. Several of these interchanges have low enough threshold energy barriers that they can be reasonably believed to occur, especially those involving Cl (58.4-72.5 kcal/mol) and Br (52.5-74.6 kcal/mol).

Among the halogens, Br lowers the E_0 barriers by 5-6 kcal/mol compared to Cl, while Cl lowers the E_0 barriers by 13-16 kcal/mol compared to F. This trend can be explained by the larger atomic size and lower charge density of Br and Cl compared to F, which leads to weaker C-Br and C-Cl bonds, and therefore, Br and Cl undergo interchange more readily than F. Interchanges involving CF_3 and CCl_3 are the least likely to occur, as they have the highest E_0 values. The F-OCF_3 and all OCH_3 interchanges have the lowest E_0 values.

The C-C bond lengths are approximately the same for F (1.36-1.40 Å), Cl (1.37-1.41 Å), and Br (1.37-1.42 Å) transition states. However, the C-Br bonds (2.51-2.95 Å) are about 0.16 Å longer than the C-Cl bonds (2.36-2.77 Å), and the C-Cl bonds are about 0.56 Å longer than the C-F bonds (1.82-2.19 Å). The longer carbon-halogen bond lengths support a correlation between longer bond lengths and lower E_0's for interchange involving a halogen.

Table 2. Threshold energy barriers for halogen (F, Cl, Br) interchanges (kcal/mol) with various R groups calculated at the B3PW91/6-311+G(2d,p) level of theory and basis set. E_0 is arranged in ascending order based on F systems. * Transition state not found.

R =	X = F	X = Cl	X = Br
OCF_3	67.7	*	*
OCH_3	71.6	58.4	53.6
$CH{=}CH_2$	82.8	66.1	60.6
CH_2CH_3	85.3	70.9	*
CH_3	86.4	72.3	67.5
CH_2OH	87.1	72.8	67.8
$C{\equiv}CH$	88.0	72.5	66.7
CH_2CF_3	89.4	*	*
CCl_3	93.9	80.2	74.6
CF_3	100.7	87.9	82.9

5. Conclusions

The optimized ground state and transition state for several interchange reactions involving halogens, pseudohalogens, and other groups were found computationally. Zero-point energies were used to calculate the threshold energy barrier for interchange. In general, larger atoms/groups with lone pairs such as Br, Cl, SH, and OCH_3 tend to lower the E_0 barrier for interchange, making them the most likely to undergo rearrangement. Systems with an E_0 around 70 kcal/mol and lower can be considered for experimental observation.

Transition states for CN-NH_2 and CN-CH_3 interchanges were not optimized, but the long C-CN bond lengths in the optimized transition states for other CN systems indicate that they are not accurate transition states. The Cl-OCF_3, Br-OCF_3, Cl-CH_2CF_3, Br-CH_2CF_3, and Br-CH_2CH_3 transition states were also not optimized. Based on the trend of increasing E_0 from OCH_3 to CF_3, it is reasonable to assume that Cl-OCF_3 and Br-OCF_3 would have lower E_0 barriers than Cl-OCH_3 (58.4 kcal/mol) and Br-OCH_3 (52.5 kcal/mol).

The systems studied here were done with four hydrogens on a two-carbon backbone. For further research, the hydrogens could be replaced with various electron donating and withdrawing groups to determine their effect on the E_0 for interchange. The carbon backbone could also be elongated or changed to a C-Si or Si-Si backbone. Replacing C with larger Si atoms could further lower the E_0 barrier for interchange since Si would form weaker bonds to its substituents. There is also a possibility that the greater bulk of Si could alter the geometry of the transition state.

The systems studied here involve the interchange of various groups on a small, two carbon backbone, where the rearrangement yields the same product as the reactant. However, when the backbone is expanded and larger molecules undergo interchange, the rearranged product will be different from the reactant, and the interchange can then be compared to other reaction pathways such as 1,2-eliminations.

6. Acknowledgements

The author expresses gratitude to professors Dr. Bert E. Holmes and Dr. George L. Heard for their instruction, guidance, and support over the course of his undergraduate experience and research. He thanks fellow student members of the research group, both past and current, for their advice and companionship. He also thanks the University of North Carolina at Asheville and the Department of Chemistry for providing an incredible learning environment. Financial support from the National Science Foundation grants NSF-1111546 and NSF-1229406 is gratefully acknowledged for funding this research.

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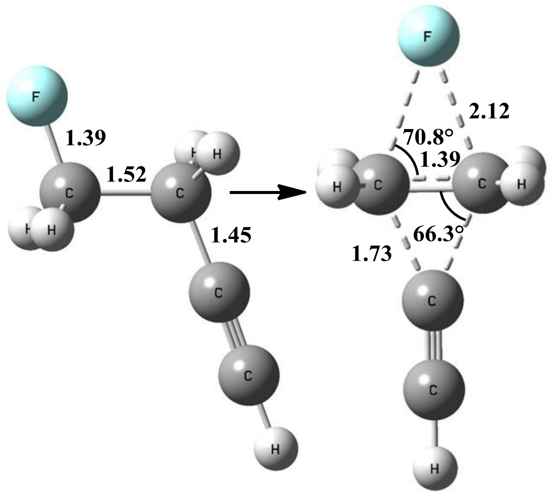
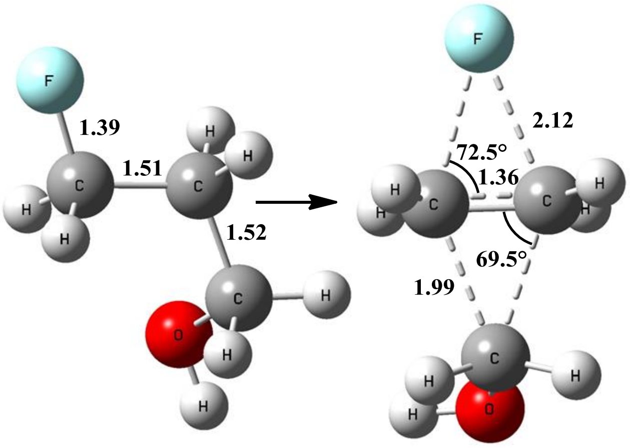
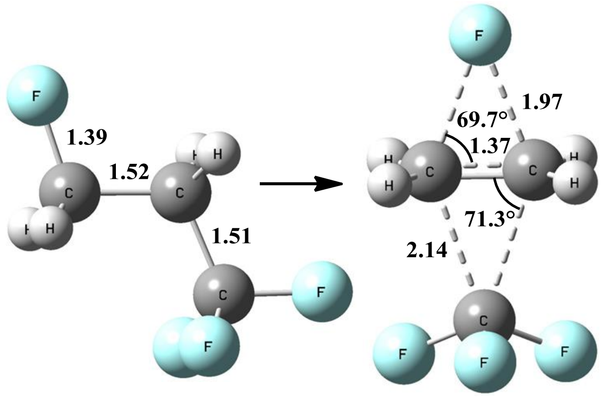
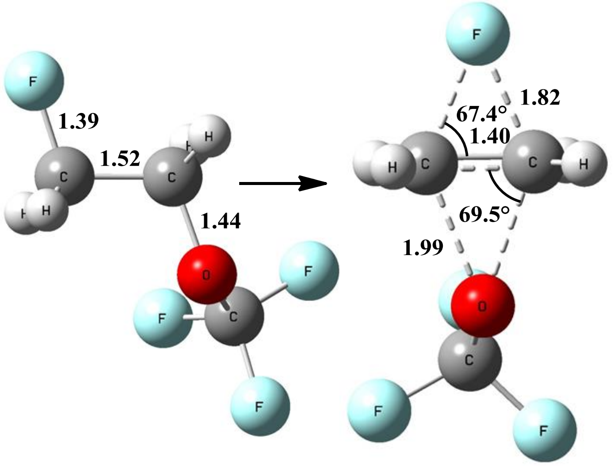
8. Supporting Information

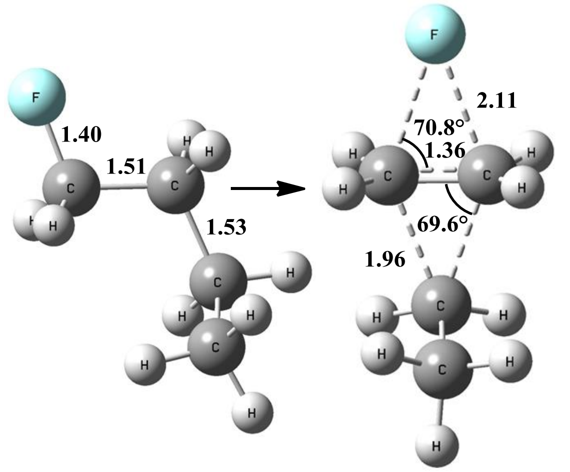
Pictures of the ground state and interchange transition state geometries, with labeled bond lengths and angles, for the rest of the systems that are not shown in Figure 2 are provided below.



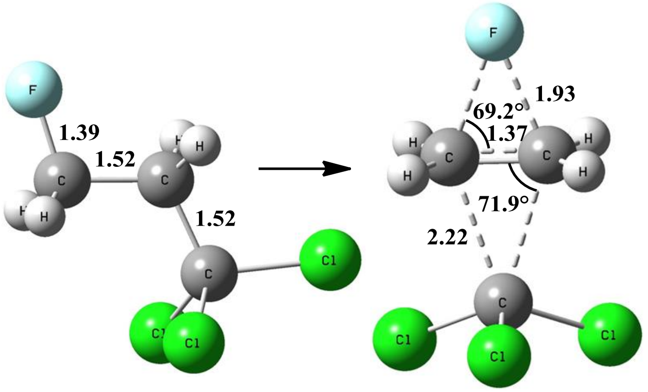




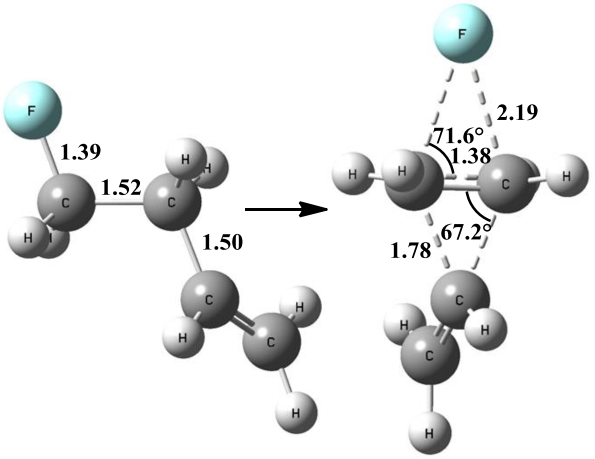




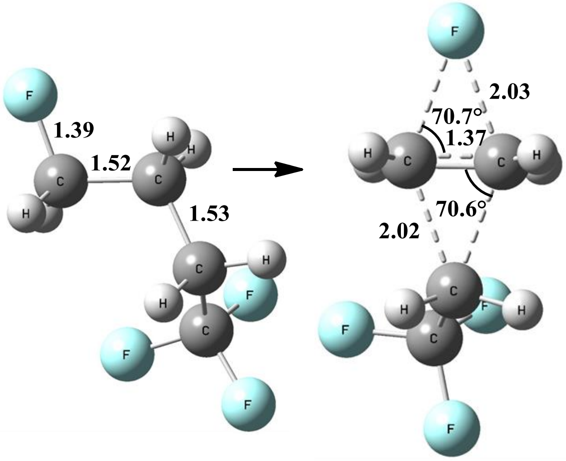
F
C
H
1.40
1.51
1.53
2.11
70.8°
1.36
69.6°
1.96



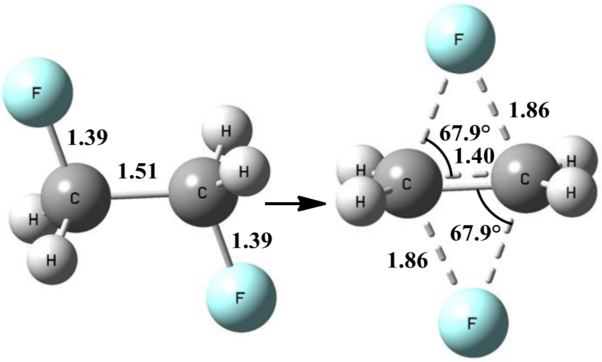
F
C
H
Cl
1.39
1.52
1.52
1.93
69.2°
1.37
71.9°
2.22



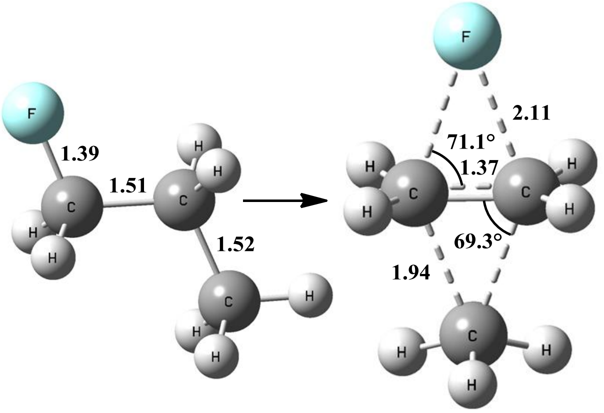
F
C
H
1.39
1.52
1.50
2.19
71.6°
1.38
67.2°
1.78



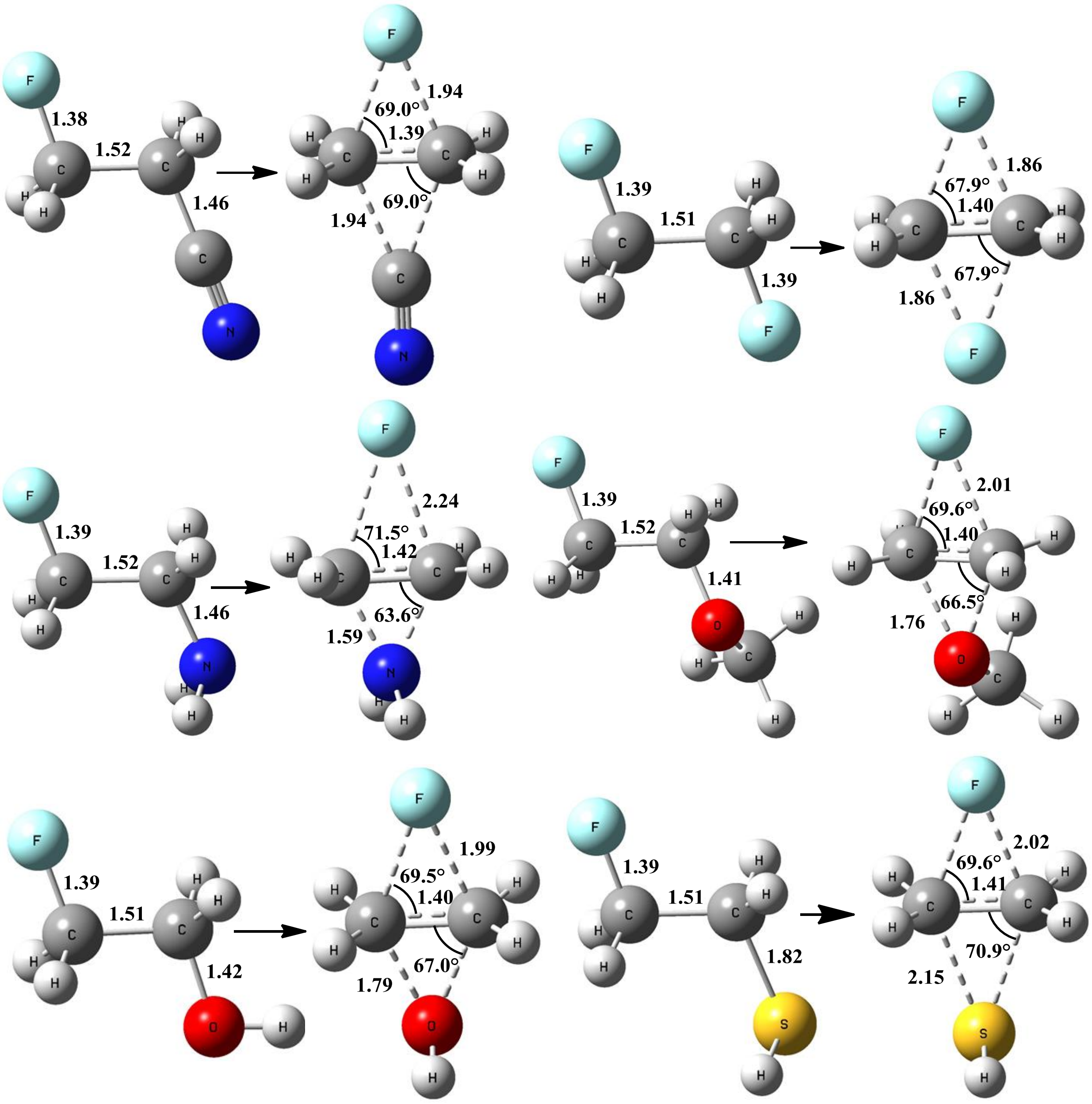
F
C
H
1.39
1.52
1.53
2.03
70.7°
1.37
70.6°
2.02



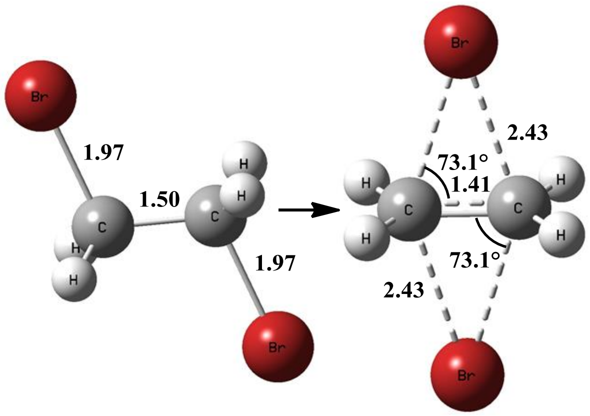
F
C
H
1.39
1.51
1.39
1.86
67.9°
1.40
67.9°
1.86

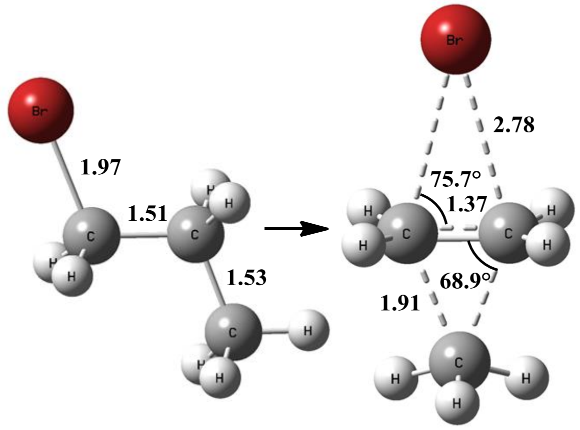


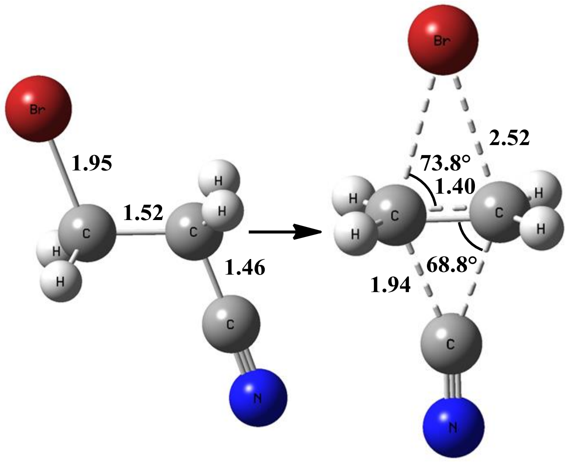
F
C
H
1.39
1.51
1.52
2.11
71.1°
1.37
69.3°
1.94

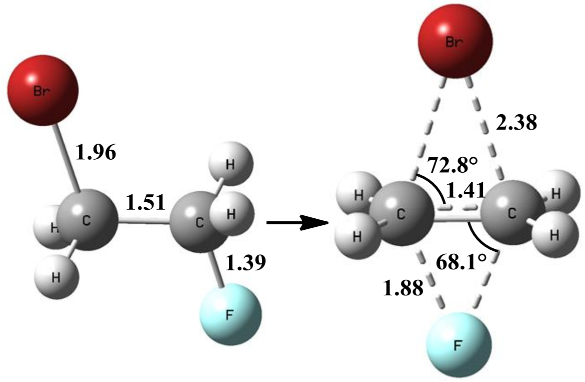


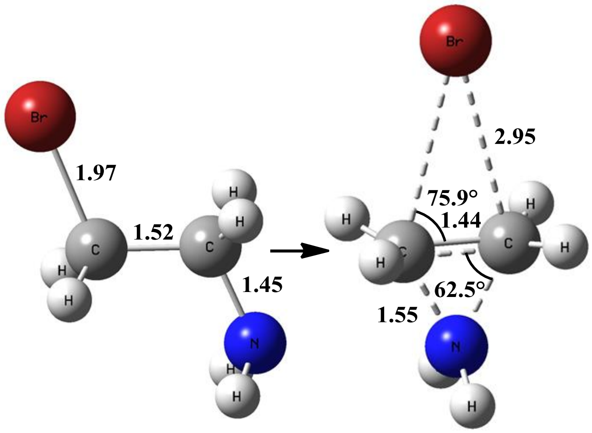
S1. Pictures of the reactant and transition state structures for various F interchanges with labeled C-C, C-F, and C-R bond lengths (Å), and F-C-C and R-C-C bond angles (°).

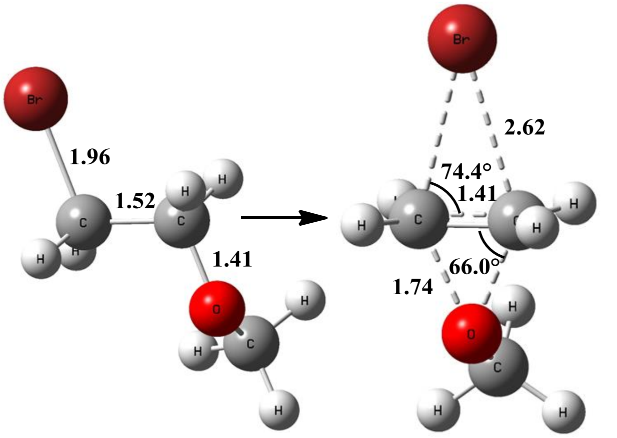

Br
1.97
1.50
1.97
2.43
73.1°
1.41
73.1°
2.43

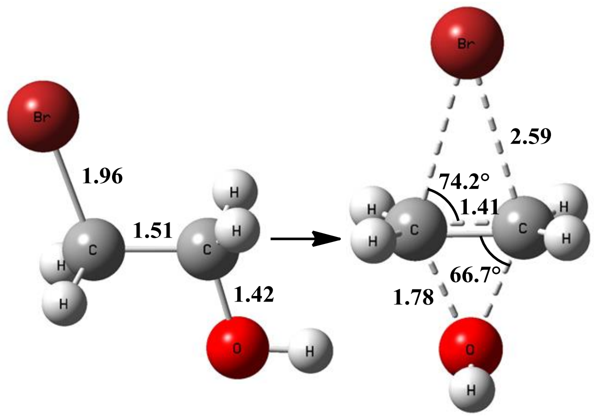

Br
1.97
1.51
1.53
2.78
75.7°
1.37
68.9°
1.91

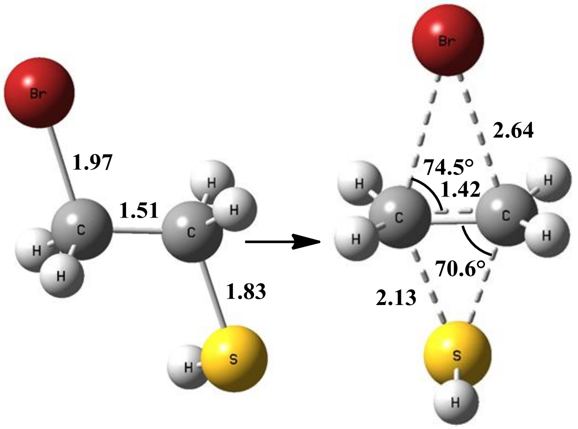

Br
1.95
1.52
1.46
2.52
73.8°
1.40
68.8°
1.94

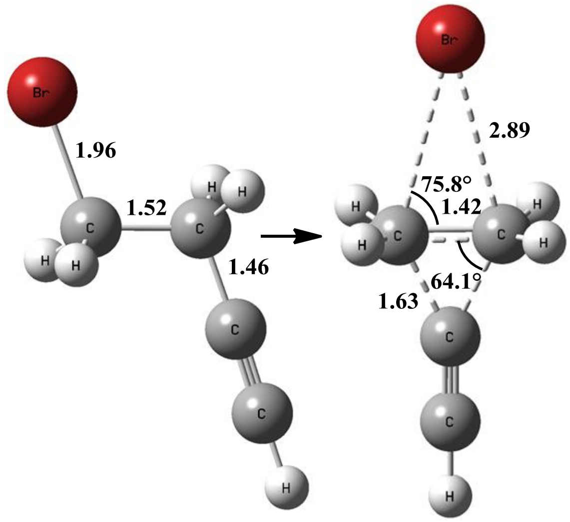

Br
1.96
1.51
1.39
F
2.38
72.8°
1.41
68.1°
1.88

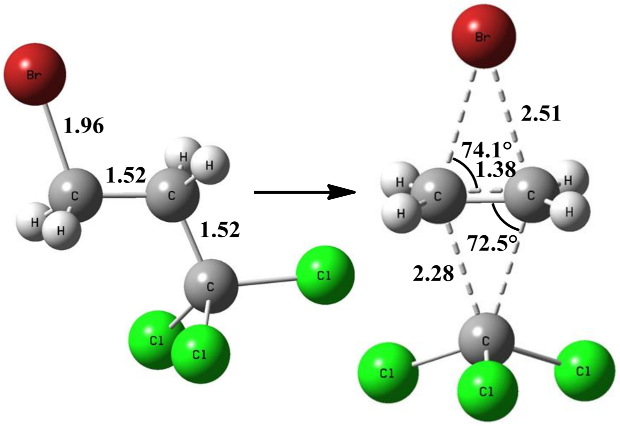

Br
1.97
1.52
1.45
N
2.95
75.9°
1.44
62.5°
1.55

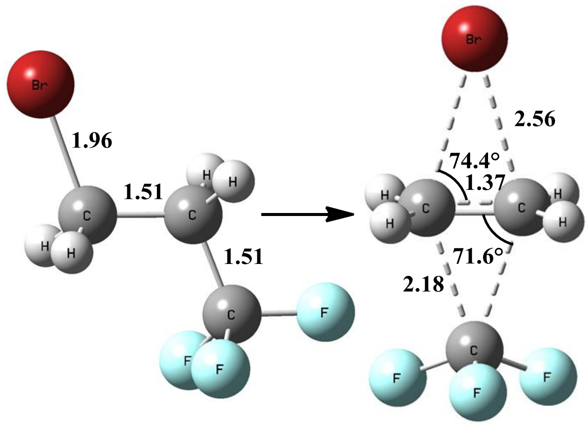

Br
1.96
1.52
1.41
O
2.62
74.4°
1.41
66.0°
1.74


Br
1.96
1.51
1.42
C
H
O
2.59
74.2°
1.41
66.7°
1.78


Br
1.97
1.51
1.83
C
H
S
2.64
74.5°
1.42
70.6°
2.13


Br
1.96
1.52
1.46
C
H
2.89
75.8°
1.42
64.1°
1.63


Br
1.96
1.52
1.52
C
H
Cl
2.51
74.1°
1.38
72.5°
2.28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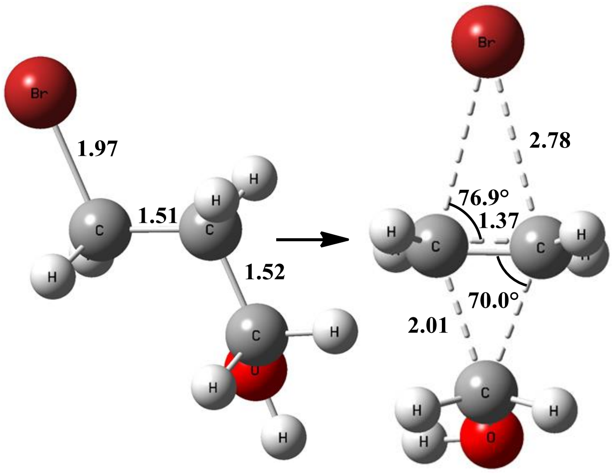
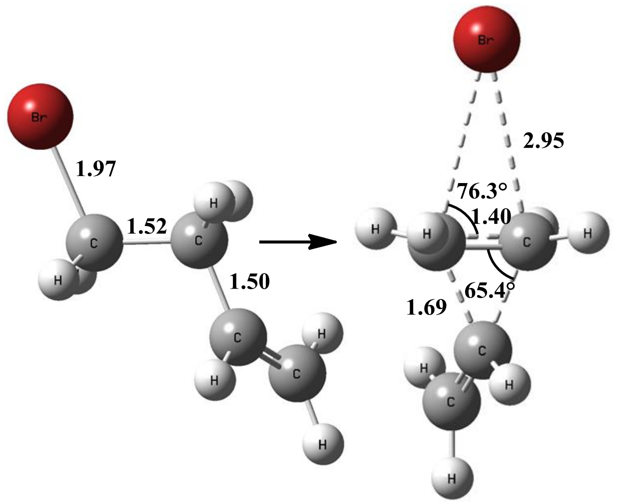
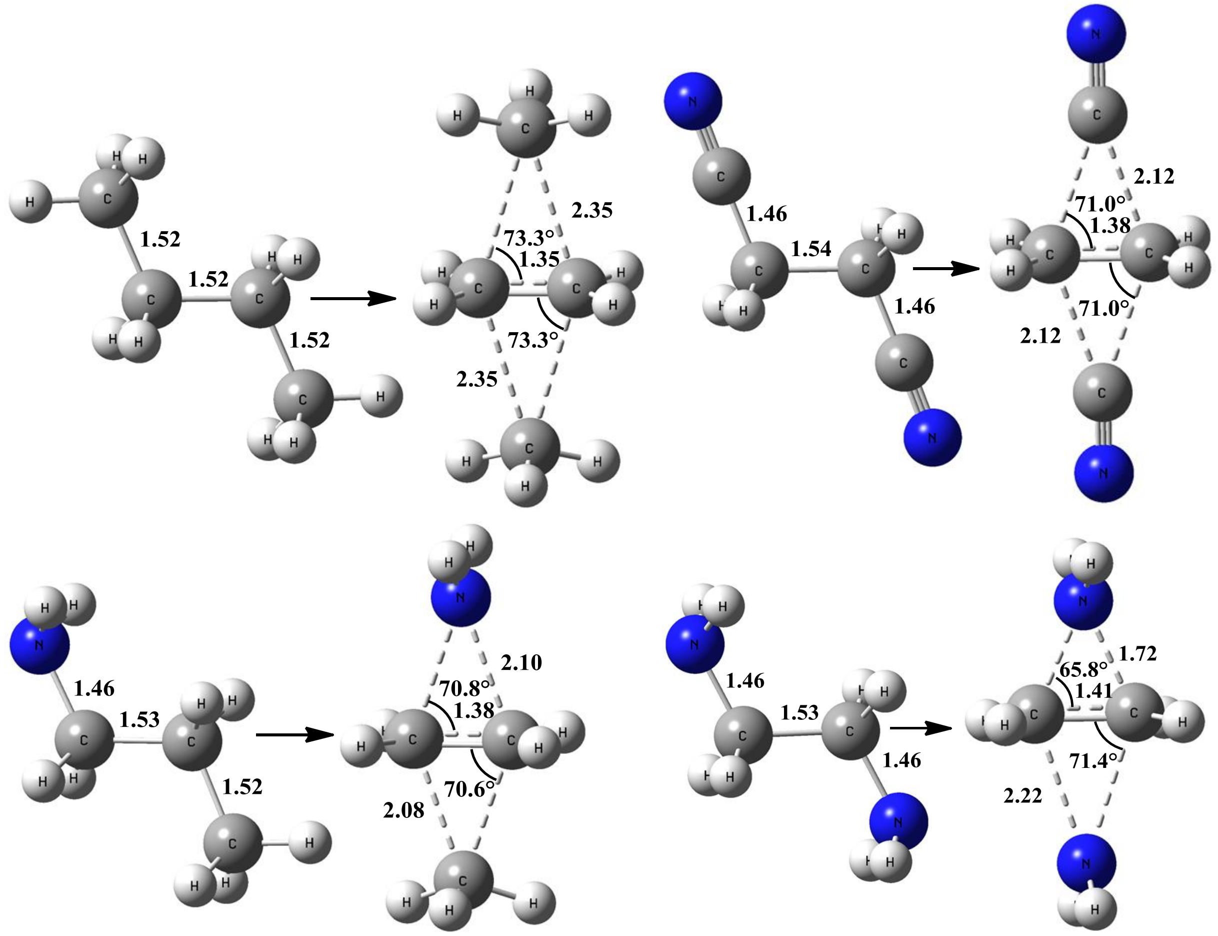
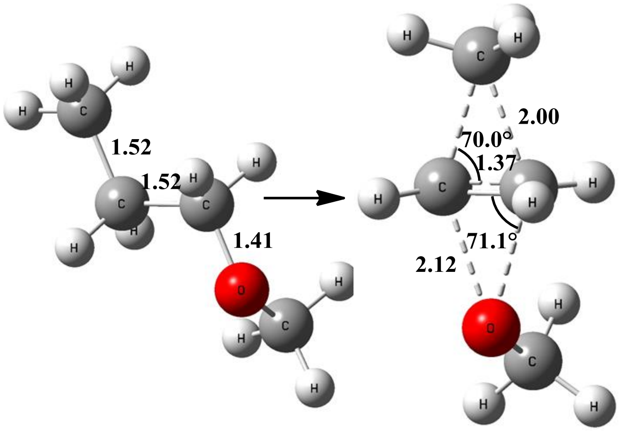
1.51
1.51
C
H
F
2.56
74.4°
1.37
71.6°
2.18


Br
1.97
1.51
1.52
C
H
O
2.78
76.9°
1.37
70.0°
2.01



S2. Pictures of the reactant and transition state structures for various Br interchanges with labeled C-C, C-Br, and C-R bond lengths (Å), and Br-C-C and R-C-C bond angles (°).

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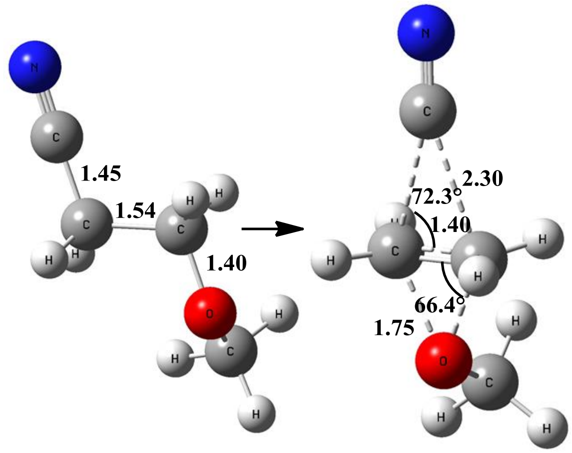
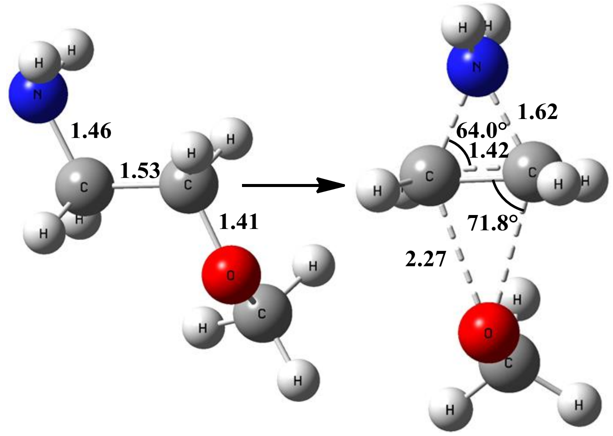
1.52
1.41
2.00
70.0°
1.37
71.1°
2.12


1.45
1.54
1.40
2.30
72.3°
1.40
66.4°
1.75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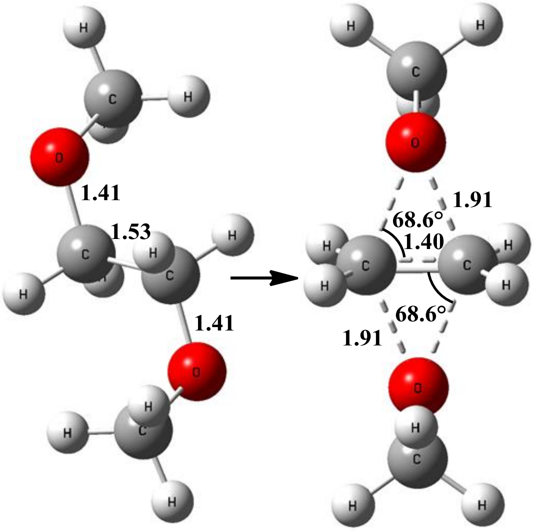
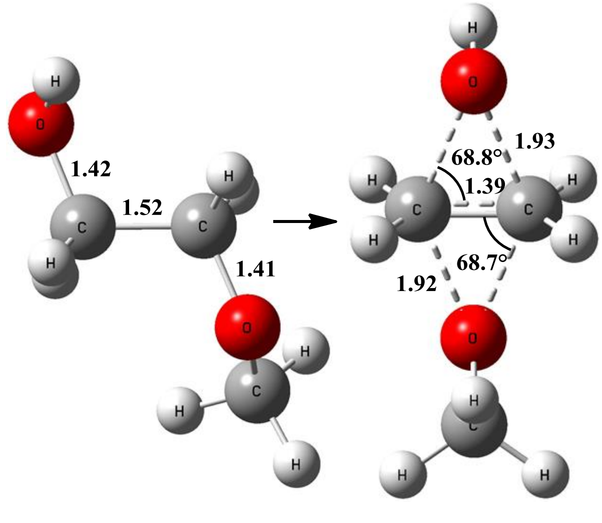
1.53
1.41
1.62
64.0°
1.42
71.8°
2.27


1.41
1.53
1.41
1.91
68.6°
1.40
68.6°
1.91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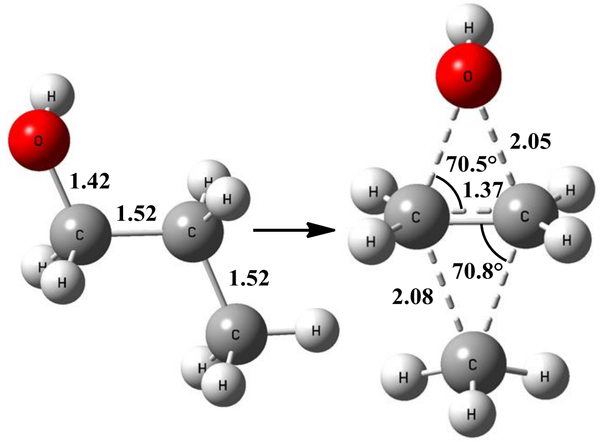
1.52
1.41
1.93
68.8°
1.39
68.7°
1.92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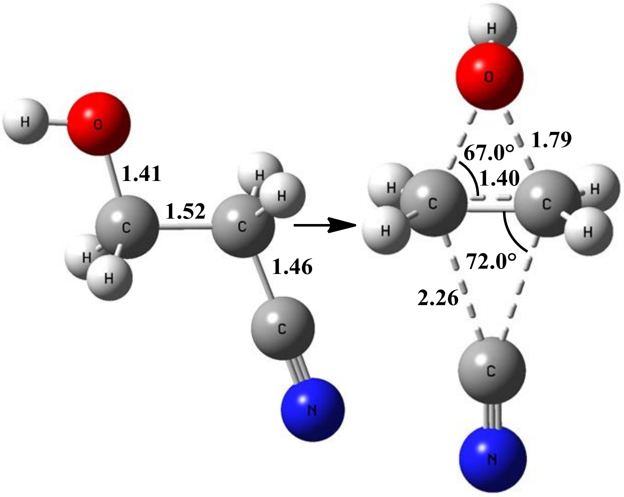
1.52
1.52
2.05
70.5°
1.37
70.8°
2.08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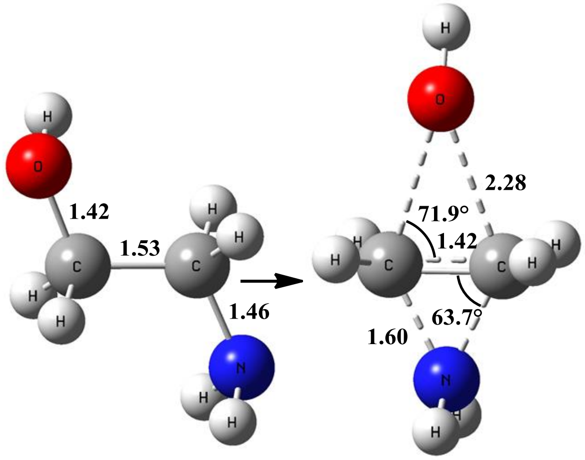
1.52
1.46
67.0°
1.79
1.40
72.0°
2.26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1.53
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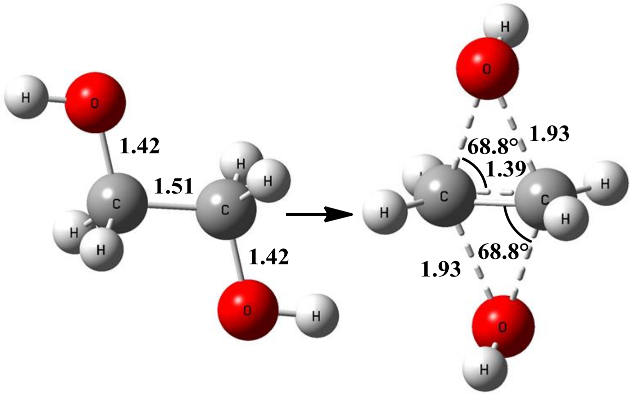
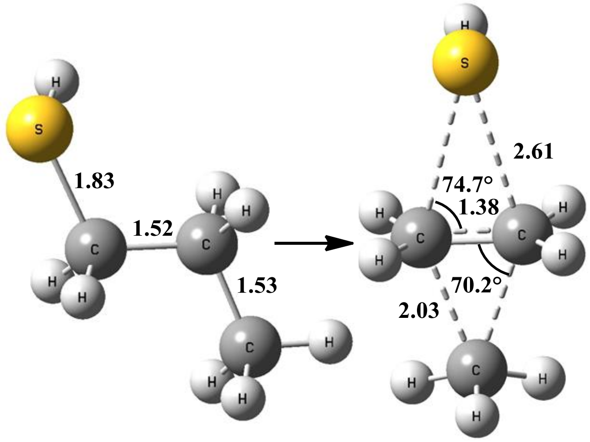
2.28
71.9°
1.42
63.7°
1.60


1.42
1.51
1.42
68.8°
1.93
1.39
68.8°
1.93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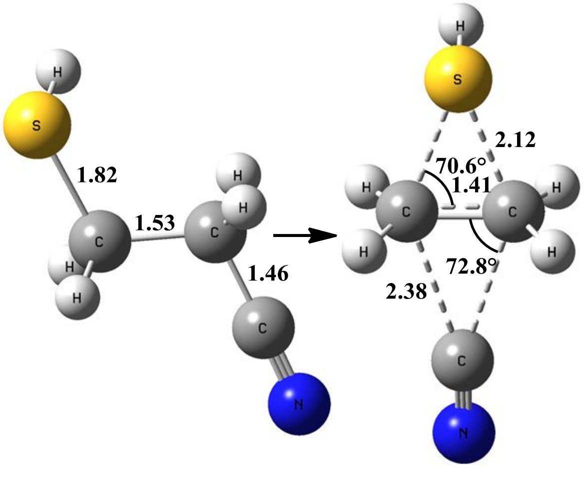
1.52
1.53
2.61
74.7°
1.38
70.2°
2.03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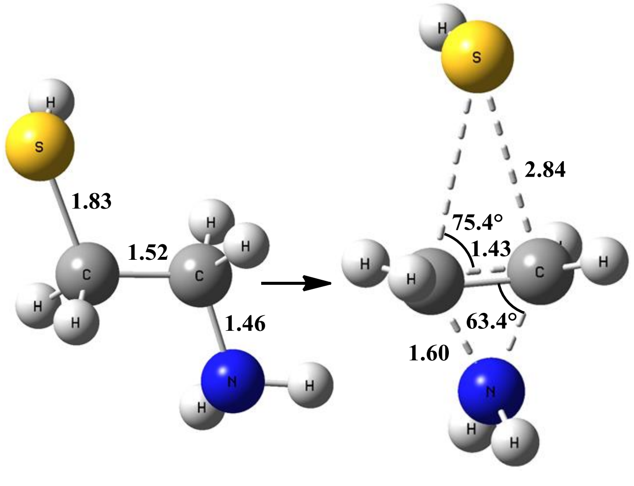
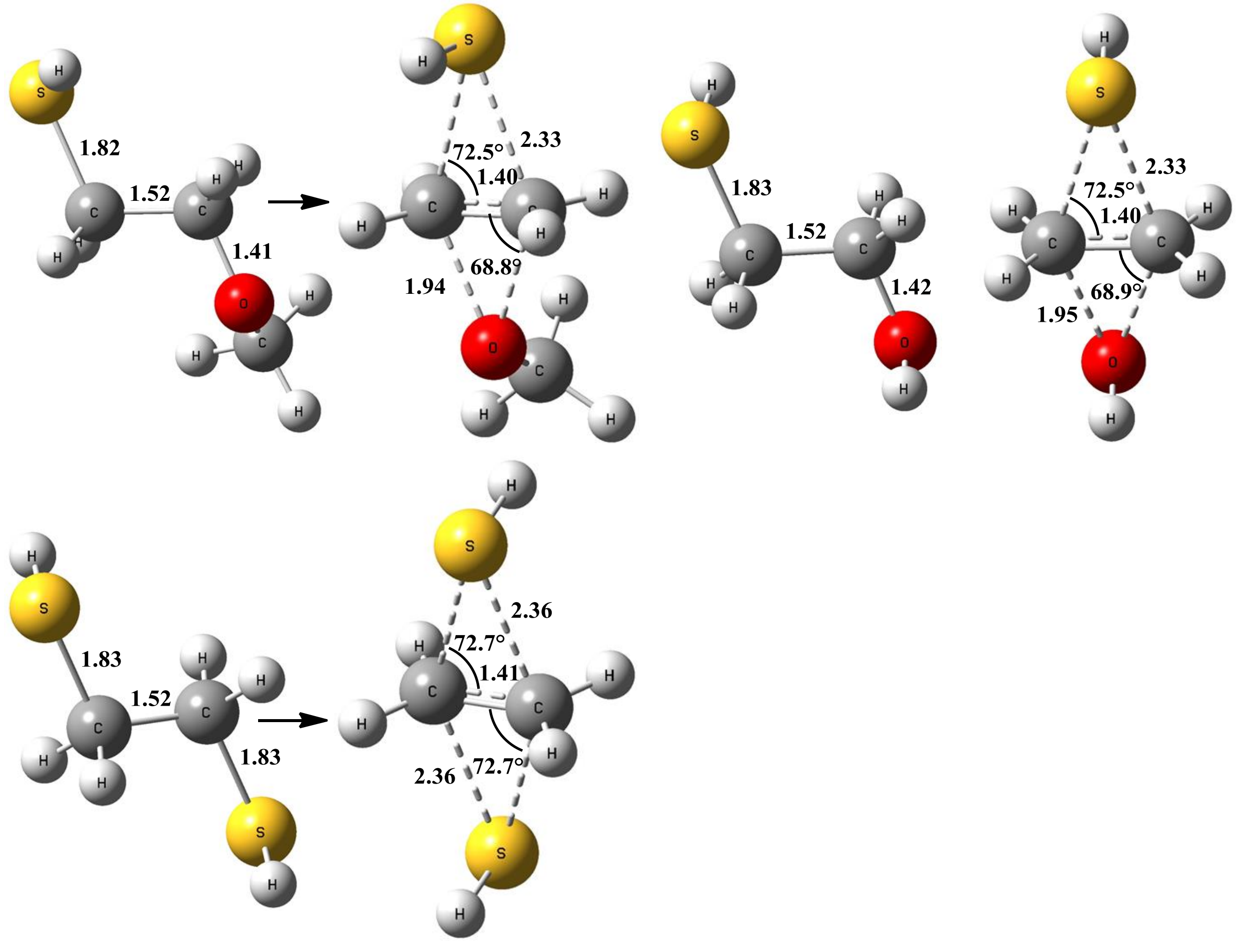
1.46
2.12
70.6°
1.41
72.8°
2.38


1.83
1.52
1.46
2.84
75.4°
1.43
63.4°
1.60



S3. Pictures of the ground and transition state structures for the interchanges between various R groups: SH, OCH_3, OH, NH_2, CN, and CH_3. The C-C, C-R_1, and C-R_2 bond lengths (Å), and R_1-C-C and R_2-C-C bond angles (°) are provided.