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Theoretical Confirmation of the Stereoselectivity in the Reverse Brook Rearrangement

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Abstract: Quantum chemical ab initio calculations on the systems $RCHM(OSiH_3)$(M=-,Li,Na; R=H,CH_3,CH_2=CH) and their silyl group migrations confirm the following facts: The methyl group favors the retention while the vinyl group with its delocalizing ability favors the reversion of the configuration of the central carbon. The migration of the silyl group is very facile and retains the configuration at the silicon center. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Brook and reverse Brook rearrangements have a fascinating stereoselectivity. The configuration of the carbon is retained when there are only alkyl substitutents on carbon[1], whereas aryl substitutents lead to the inversion of the configuration[2,3]. These reactions have become key steps in many very useful organic reactions[4-6]. Therefore, it is highly desirable to gain some insight into the reaction mechanisms of these rearrangements. Till now, there are only a few papers[6,7,8] trying to give explanations for the stereoselectivity or the reactivity, among which Boche et al[7]. made an important contribution with the analysis of their crystal structures. In this paper, using the methods of ab initio electronic structure theory, we want to show that the relative energy of different transition states is influenced by different substituents on the carbon, and that this leads to the high stereoselectivity of the reverse Brook rearrangement.

COMPUTATIONAL DETAILS

All local minima and transition states (TS) reported here were optimized at MP2/6-31+G* level

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of theory with the GAUSSIAN 98 program package[9]. A frequency analysis at the same level of theory did confirm the local minima (without imaginary frequency) and TS (with a single imaginary frequency). At the same time, zero point energies (ZPE) were estimated. We also did optimizations for $RCHM(OSiH_3)$ (R=H, M=-) with 6-31+G(d, p), 6-311+G(d, p), 6-311+G(2d,p) and 6-311++G(d, p) basis sets. The differences between them and 6-31+G* are within 0.015Å and 0.8° for bond lengths and bond angles, respectively. We employed the MP2/6-311++G(3df,2pd) level of theory to estimate the energies, in which three d- and one f-polarization functions are added to the heavy atoms while two p- and one d-polarization function are added to hydrogen. Diffuse functions are also added to both heavy atoms and hydrogen in order to get reliable results for anionic species. For the sake of comparing all the species at the same level of theory, we choose the MP2/6-311++G(3df,2pd)//MP2/6-31+G* calculational model.

RESULTS AND DISCUSSION

We did calculations on the systems $RCHM(OSiH_3)$ (M=-,Li,Na; R=H,CH_3, CH_2=CH). Anions and lithium salts are related to the free anions and isolated lithium salts, respectively. Since in solution the species may neither be free nor be completely isolated lithium salts, sodium salts are also investigated to give some hints about the role of the metal. R = CH_3 is the simplest alkyl substituent on the carbon, and R = CH_2=CH is intended to model groups which have a delocalizing ability for negative charges. In the latter case, we restrict all H and C to a plane during the calculations, because in this way CH_2=CH has more similarity to the conditions in a phenyl group. This limitation is also true when CH_2=CH is a part of strained systems[10] or is involved in some tandem reactions for the synthesis of different types of compounds (cyclic silyl enol ethers and seven-membered ring compounds to name a few)[4,11,12].

The Local Minima

The potential energy surface for systems involving a silyl group may have numerous local minima[13]. For all species investigated here, we obtained three types of local minima **1**, **2** and **3**. Like in our previous calculations on some related systems[14], α-metallated silyl ethers may exist in the form of three-membered rings **1** in which the metal interacts with both the negative charge on carbon and the lone pair on oxygen, but structure **2** is ideal for carbanion type reactions. The product of the reverse Brook rearrangement has the structure **3**.

It is very interesting that for anionic species the three-membered ring structure **2** is much lower in energy than structure **1** (when R is CH_2=CH, structure **1** even can not be located any longer). This is not very surprising, because pentacoordinated silicon anions have been synthesized in gas phase and have been proven to be stable[15,16]. Our calculations show that this tendency is transferred to lithium and sodium salts, i.e., the three-membered ring structures **2** of lithium and sodium salts species also exist. We attribute structure **2** to the relatively small electronegativity of silicon. The

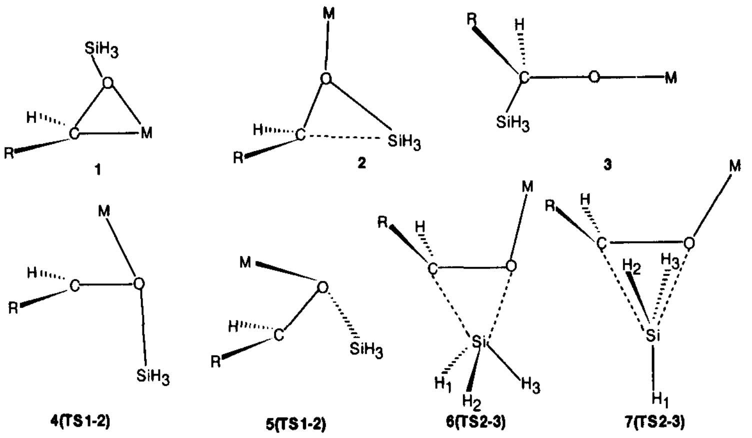

Figure. Structures of RCHM(OSiH$_3$) (R= H, CH$_3$,CH$_2$=CH; M=-,Li,Na)

Table 1. Relative Energies (kJ/mol) for Different Isomers and Transition States (with ZPE correction*)

R	M	1	2	3	4(TS1-2)	5(TS1-2)	6(TS2-3)	7(TS2-3)
H	-	0	-70.4	-69.5	10.9	15.9	-61.5	39.9
	Li	0	4.7(4.3)	-44.1	53.2	57.4	3.3(6.3)	165.5
	Na	0	-12.0	-35.2	49.3	38.7	-6.0	149.8
CH$_3$	-	0	-93.3	-84.1	5.3(6.8)	6.0(6.4)	-82.1	16.2
	Li	0	-13.7	-59.4	59.9	44.6	-11.3	102.5
	Na	0	-28.2	-52.4	56.4	27.0	-20.8	89.6
CH$_2$=CH-	-		0	17.0			17.2	118.2
	Li	0	-15.5	-58.0	-2.0	38.7	-11.5	115.4
	Na	0	-5.3	-24.3	5.7	44.1	3.7	122.3

* Values in parentheses are without ZPE correction

Table 2. Results of NPA Analysis for Negative Charges on the Central Carbon

structure	R = H			R = CH$_3$			R = CH$_2$=CH		
	-	Li	Na	-	Li	Na	-	Li	Na
1	-0.666	-0.737	-0.723	-0.388	-0.479	-0.453		-0.420	-0.387
4(TS)	-0.784	-0.861	-0.834	-0.514	-0.634	-0.602		-0.452	-0.403
5(TS)	-0.657	-0.738	-0.722	-0.382	-0.509	-0.488		-0.493	-0.472

electronegativity for H, C, O and Si is 2.2, 2.5, 3.5, and 1.7, respectively[17]. Thus, silicon will possess a positive charge, and it prefers to form a three-membered ring with O and the anionic carbon center.

Reaction Mechanism

Cross-over experiments have shown that the reverse Brook rearrangement is an intramolecular process while incorporation of a radical trap revealed that the rearrangement does not involve radical intermediate[1-3]. We propose that the reverse Brook rearrangement undergoes through two steps. First, we get a metallated species with structure **1** after α-metallation of the silyl ethers, which then changes into the more stable structure **2**. There are two possible paths for structure **1** to change into structure **2**. The path through inversion transition state (TS) **4** will invert the configuration of the central carbon, whereas the way through rotation transition state (TS) **5** will retain it. Second, the silyl group migrates to carbon. In the process of migration, the silyl group can move from oxgen to carbon either through TS **6** in which the silyl group retains its configuration, or through TS **7** where inversion is observed (the sum of the bond angles around silicon in all species in TS **7** is nearly 360°). In species with R = H and M=Li, the relative energy of **2** is a little higher than **1** and the ZPE makes the barrier of TS **8** negative, thus it is also appropriate to conclude that **2** is not an intermediate. However, the barriers through rotation or inversion of the central carbon can not be avoided for the whole process of silyl group migration.

The barriers in the first step depend on the substituents on the carbon. When R is H, the energy differences between TS **4** and TS **5** are of variable sign, thus, the isomerizations have no obvious preference. When R is CH_3, it is clear that TS **5** is always lower in energy than TS **4** (except in the free anion), i.e., the configuration of the central carbon in salts will most likely be retained. When R is $CH_2{=}CH$, TS **5** is much higher in energy than TS **4**, and without doubt inversion will occur.

The barriers in the second step are -1.4 - 17.2kJ/mol via TS **6** or 110 - 162 kJ/mol via TS **7**. Apparently, the configuration of the silyl group will be retained via TS **6** both in free anions and in salts, for both lithium and sodium compounds.

Natural Population Analysis (NPA)

The results of a natural population analysis (NPA) (see Table 2) also show some interesting hints regarding the negative charges on the central carbon. Compared to the values for structure **1**, the net charges increase a little in TS **4**, and remain almost unchanged in TS **5** for both R=H and $R{=}CH_3$. However, the negative charge on central carbon in TS **5** is increased but almost unchanged in TS **4** when R is $CH_2{=}CH$. Furthermore, carbon is much less negative when R is $CH_2{=}CH$. This indicates that the relative energies of different TS have a clear relation to the negative charge on the central carbon.

Summary

Considering the whole reaction, in the salts the isomerization is the rate-determining step, but in the anions the isomerization and the silyl group migration are of comparable speed and both undergo rapidly. The results of the sodium salts indicate a reasonable compromise on the rapidity and the stereoselectivity for the whole reaction. Another interesting finding is the remarkable decrease in energy of TS **4** when CH_2=CH is introduced to the carbon. This may give hints to explain the fact that electron withdrawing groups on the carbon facilitate the Brook rearrangement[18]. The latter was the crucial basis for the experiments of Takeda et al. who determined the stability of different carbanions[8].

CONCLUSION

The systems $RCHM(OSiH_3)$(M=-,Li,Na; R=H,CH_3,CH_2=CH) and their silyl group migrations have been investigated at MP2/6-311++G(3df,2pd)//MP2/6-31+G* level of theory. We confirm the following facts in the reverse Brook rearrangement: The methyl group favors the rotation transition state **5**, while the vinyl group with its delocalizing ability dramatically reduces the relative energies of the inversion transition state **4**. The migration of the silyl group is very facile and retains the configuration at the silicon center. In a few words, the relative energy of different transition states is influenced significantly by different substituents on the carbon, and this leads to the high stereoselectivity of the reverse Brook rearrangement.

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