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Theoretical Investigation of Stevens Rearrangement of P and As Ylides. Migration of H, CH_3, $CH{=}CH_2$, SiH_3, and GeH_3 Groups on P and As Atoms

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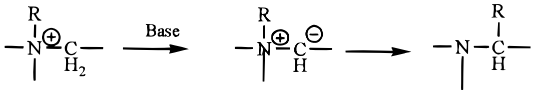
Abstract: Ylides are considered as intermediates of the well-known Stevens rearrangement. To investigate the mechanism of this rearrangement, theoretical calculations for the rearrangements of monosubstituted ylides, $ZH_2MCH_2 \rightarrow H_2MCH_2Z$ ($Z = H$, CH_3, $CH{=}CH_2$, SiH_3, and GeH_3; $M = P$ and As), were performed with the Møller−Plesset perturbation theory up to the fourth order. The IRC calculations at the RMP2 level show that the reaction mechanism is strongly dependent on the migrating group. While the methyl and vinyl migrations are antarafacial with large activation energies of 37−47 kcal/mol, the IRC of the SiH_3 migration along with that of GeH_3 migration displays that it is a suprafacial process. While the migration of the groups with the heavier elements of Si and Ge utilizes their hypervalency to have a small activation energy of 13 kcal/mol, the transition states for the migrations of the methyl and vinyl groups as well as the hydrogen atom are higher in energy. The RMP2 transition state for the methyl migration is less stable than the radical dissociation limit, $H_2MCH_2 + Z$, the radical dissociation−recombination path being more favorable, and it may not exist as real. On the other hand, the transition state for the vinyl migration as well as that for the hydrogen migration is slightly more stable than the dissociation limit. If the entropy effect is properly taken into account, the radical dissociation−recombination path would be more favorable than the concerted mechanism for these migrations as well.

Introduction

The Stevens rearrangement originally discovered on nitrogen ylides[1] (eq 1) has also been shown to occur in certain sulfur ylides[2−5] (eq 2). Both nitrogen and sulfur ylides readily undergo thermally induced rearrangement to give amines and sulfides, respectively. The plausible mechanism of these rearrangements has been a topic of investigation and discussion for many years. The mechanism proposed first by Stevens based on the substituent effects is a dissociation−recombination ion-pair mechanism following initial ylide formation.[6,7]



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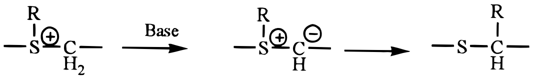

(2)

Since then, many important experimental facts have been reported especially regarding stereospecificity[8−11] and intramolecularity[12−14] of the rearrangement. In the migration of a chiral group, the product is formed with almost complete retention of configuration of the migrating group, suggesting that the rearrangement is intramolecular. The stereospecificity was found to be dependent on solvent and temperature, and it was demonstrated that intramolecularity and stereospecificity decrease as solvent viscosity decreases.[12] These facts imply the possibility of involving an intimate radical pair or an ion pair in a solvent cage. Since no solvation occurs to stabilize ionic species in the solvent cage, the dissociation energy to an ion pair in the solvent cage would be on the same order as in the gas phase, and therefore the dissociation to a radical pair is expected to be easier than that to an ion pair. As a matter of fact, Ollis, Rey, and Sutherland observed CIDNP spectra in the

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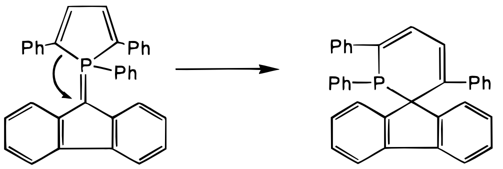
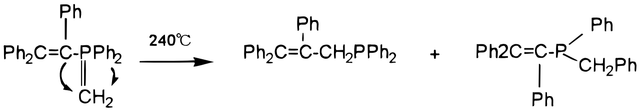
Stevens rearrangement of nitrogen ylides,[12] supporting the radical dissociation−recombination path.[16] Furthermore, it has been reported that the thermal benzyl group migration of α-benzylmethylthiophenacylide showed CIDNP effects.[5] Since concerted suprafacial 1,2-migration with retention of configuration of a migrating group is symmetry-forbidden according to the Woodward−Hoffmann[15] rule, the radical-pair mechanism looks reasonable.

Phosphorus ylides, in general, undergo the Stevens rearrangement only under forcing conditions. The thermal phospha-Stevens rearrangement of heterocyclic ylide which expands the ring upon refluxing in toluene (eq 3) is the first authentic example of this rearrangement.[17]



(3)

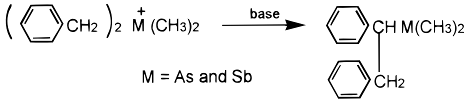
The second phospha-Stevens rearrangement[18] was found in 1-phenyl-(2,2-diphenylvinyl)diphenylmethylenephosphorane, which gave the products by vinyl or phenyl group migration (eq 4), with the temperature being higher than 200 °C. The



(4)

observed 1,2-migrations of vinyl and phenyl groups were proposed to proceed through an ionic or radical elimination−addition mechanism.[6,7] The rearrangement of an isolated bisylide[19] into a carbodiphosphorane has also been reported.

There is only one report[20] on the Stevens rearrangement of arsenic and antimony ylides (eq 5). Dibenzyldimethylarsonium

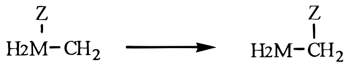


(5)

and -stibonium bromides were treated with phenyllithium to yield the ylide, in which the migration of a benzyl group occurred easily, indicating that the arsenic and antimony ylides undergo the Stevens rearrangement more easily than the phosphorus ylides.

The heavier elements in group 14 such as silicon and germanium often show chemistry different from that of carbon, though they belong to the same group. One of the examples is observed in the Wittig rearrangement which has been thought to involve an intramolecular radical pair cleavage−recombination process. In the ordinal Wittig rearrangement, i.e., 1,2-anionic rearrangement of an ether to its isomeric alcohol, the migration of a carbon atom from oxygen to an α-carbanion takes place. However, the alkyl migration takes place rather slowly, and yields are reduced significantly by the side reactions.[21,22] On the other hand, the silyl or germyl counterparts of the Wittig rearrangements[23−28] were reported to occur very easily because silicon and germanium can become pentacoordinate in the transition state (TS), removing the symmetry restrictions to the rearrangements.[29] The same reasons are considered to facilitate the rearrangements of silylcarbinols to silyl ethers, well-known as the Brook or anti-Wittig rearrangements.[30] Also, the migratory ability of silicon in 1,2-anionic rearrangements of silylhydrazines[31] and silylhydroxyamines[32] was reported to be remarkable.

In this paper, we report the results of the theoretical calculations for reaction 6, model Stevens rearrangement of phosphorus and arsenic ylides, to clarify the reaction mechanisms by following intrinsic reaction coordinates (IRCs) and to analyze factors determining reaction mechanisms which are dependent on the migrating groups. To our knowledge, six theoretical studies on the Stevens rearrangement have been published,[16] in which the rearrangement of a nitrogen ylide has been investigated by a semiempirical method[16a] or ab initio method.[16b−f] While the semiempirical method prefers the concerted mechanism, the ab initio calculations showed that the radical dissociation is more favorable.



(6)

M=P, As

Z= H, CH_3, $CH{=}CH_2$, SiH_3, GeH_3

The most common migrating groups in the [1,2] sigmatropic rearrangement of carbanions have an sp^2 carbon center such as acyl, phenyl, and vinyl groups.[33] The $CH{=}CH_2$ group was chosen as a model of such migrating groups. Also, it has been observed that the alkyl group such as the benzyl group migrates to a sufficiently negative center in the Stevens rearrangement, and thus we will compare the migrating aptitude between $CH{=}CH_2$ and CH_3. Similar to the difference in the Wittig rearrangement, the SiH_3 and GeH_3 migrations are expected to

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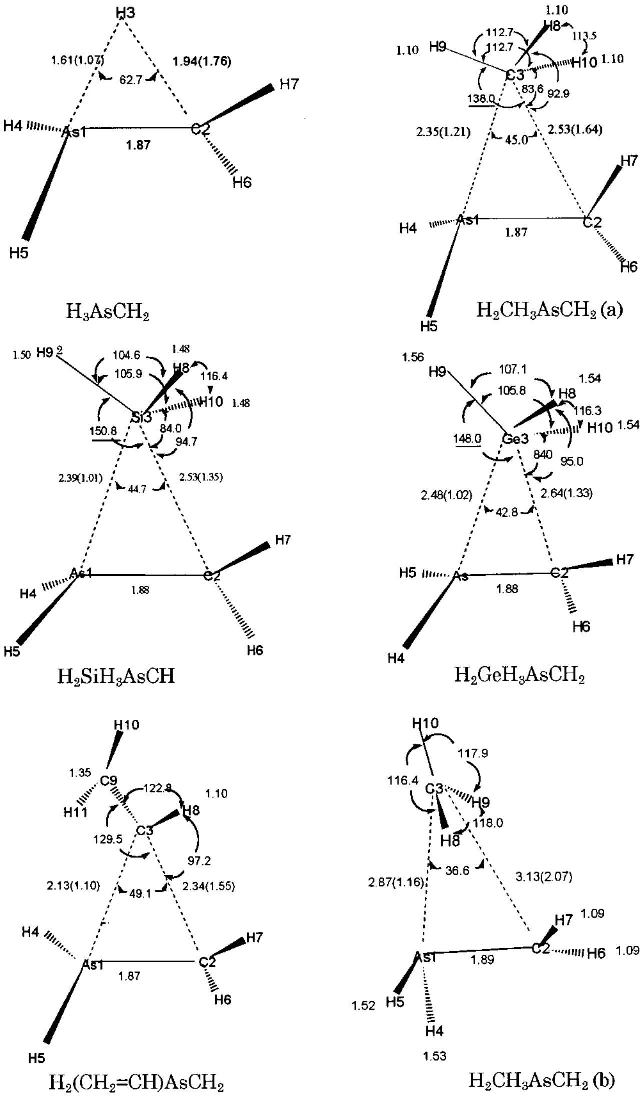

H_3AsCH_2

$H_2CH_3AsCH_2$ (a)

H_2SiH_3AsCH

$H_2GeH_3AsCH_2$

$H_2(CH_2{=}CH)AsCH_2$

$H_2CH_3AsCH_2$ (b)

Figure 1. RMP2 optimized structures, in angstroms and degrees, of TSs for Z migration of H_2ZAsCH_2 (Z = H, CH_3, SiH_3, GeH_3, and $CH_2{=}CH$).

be different from the CH_3 migration. To confirm this, we studied the SiH_3 and GeH_3 migrations.

Method of Calculations

The basis set used was LANL2DZ stored in the Gaussian series of programs, which was modified by adding a set of five d-type polarization functions for heavy atoms (d exponents 0.600 (C), 0.262 (Si), 0.246 (Ge), 0.340 (P), and 0.293 (As)). The LANL2DZ set is composed of the Huzinage−Dunning split valence basis functions, called D95V, for first-row atoms[34] and effective core potentials (ECP) plus valence double-ζ (DZ) basis functions for P, As, Si, and Ge developed by Wadt and Hay[35] at the Los Alamos National Laboratory.

The structures of all the reactants, products, and TSs were optimized using Gaussian92[36] and Gaussian94[37] at the restricted second-order Møller−Plesset perturbation (RMP2) level.[38] Those of radicals such as H_2MCH_2 (M = P and As), and Z (Z = H, CH_3, $CH{=}CH_2$, SiH_3, and GeH_3), i.e., the radical dissociation products, were optimized by the unrestricted (UMP2) method. The optimizations were performed without any constraints; i.e., all the $3N - 6$ internal coordinates were relaxed. Vibrational analysis was carried out at the MP2 level to characterize all the stationary points.

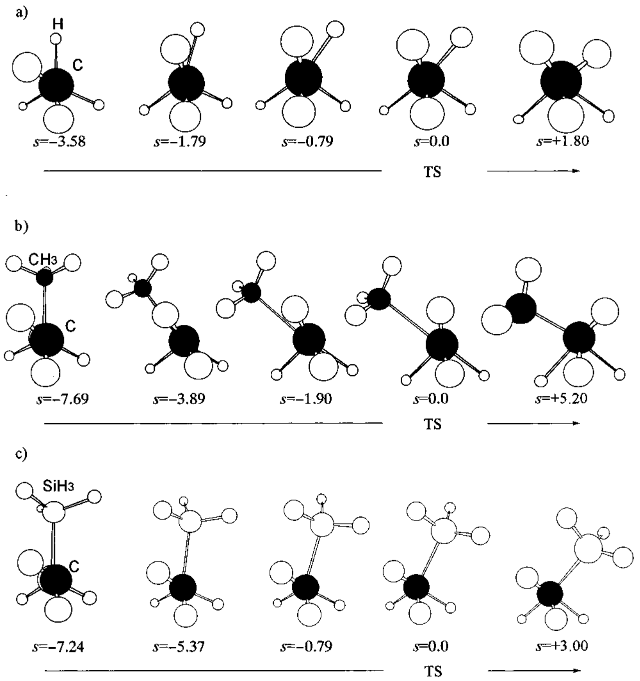

Figure 2. Structure change along the IRC for (a) H, (b) CH_3, and (c) SiH_3 migrations.

To obtain reliable energetics, the energy calculations at the MP2 optimized structures were performed at the full fourth-order Møller−Plesset perturbation (MP4) level. When the RHF wave functions for the TSs were unstable, we carried out the projected unrestricted MP4 energy calculations (PMP4) as discussed later. This is the case for Z = H, CH_3, and $CH{=}CH_2$. The energies of the radicals were also calculated at the PMP4 level. In addition, we carried out the geometry determination of the TS structures for the H and CH_3 migrations with M = As, the RHF wave functions of which are unstable, using the theory of UMP2, restricted quadratic configuration interaction with single and double substitutions (RQCISD), and unrestricted quadratic configuration interaction with single and double substitutions (UQCISD) as well as restricted B3LYP (RB3LYP) and unrestricted B3LYP-(UB3LYP) hybrid density functional.

Results and Discussion

We determined the structures of the TSs as well as the reactants, ylides, and products for the migrations at the RMP2 level and calculated the IRCs to investigate the reaction mechanism. The TS structures for M = As are shown in Figure 1, and the corresponding structure changes along the IRCs are shown in Figure 2 for Z = H, CH_3, and SiH_3, respectively. The structure changes for M = P (not shown) are qualitatively similar. The potential energy changes are summarized in Table 1.

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Table 1. Activation Energies ($\Delta E^{\ddagger}$) and Energies of Reactions (ΔE_r) for $H_2ZMCH_2 \rightarrow H_2MCH_2Z$, the Expectation Values of s^2 at the Corresponding TSs, Radical Dissociation Energies (ΔE_d) for $H_2ZMCH_2 \rightarrow H_2MCH_2 + Z$,[a] and Migration Mode

	$\Delta E^{\ddagger}$						
	RMP2	PMP2	PMP4	ΔE_r	$\langle s^2 \rangle$	ΔE_d	reaction mechanism
			M = P				
H	35.1	36.3	33.6	−56.7	0.6121	39.6	suprafacial
CH_3	52.5	51.7	47.1	−47.7	0.8889	40.1	antarafacial
$CH{=}CH_2$	44.7	47.8	43.8	−50.6	1.0183	49.8	antarafacial
SiH_3	13.2	13.2	13.1	−52.5	0.0	29.0	suprafacial
GeH_3	12.8	12.8	12.5	−49.7	0.0	23.5	suprafacial
			M = As				
H	325	33.0	30.4	−68.2	0.7803	31.3	suprafacial
CH_3	45.2	42.4	38.1	−58.0	0.9489	31.0	antarafacial
$CH{=}CH_2$	39.7	41.5	37.1	−61.3	1.1201	40.5	antarafacial
SiH_3	12.9	12.9	12.8	−60.4	0.0	22.8	suprafacial
GeH_3	12.2	12.2	12.0	−56.8	0.0	18.0	suprafacial

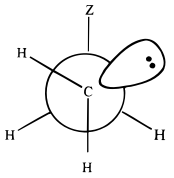
[a] All the energies are in kcal/mol.

Table 2. Dihedral Angles, in degrees, of the Reactants and Transition States for $H_2ZAsCH_2 \rightarrow H_2AsCH_2Z$[a]

Z	α	β	γ	δ	θ
H					
R	114.8	122.6	58.8	173.9	52.6
TS	86.0	166.9	56.4	143.8	84.2
CH_3					
R	116.1	122.5	62.7	168.7	53.0
TS	181.2	79.9	−51.9	216.4	94.8
SiH_3					
R	114.5	126.6	57.2	175.3	59.1
TS	96.3	151.6	80.2	146.4	60.8
GeH_3					
R	114.6	126.5	57.0	176.3	59.7
TS	95.0	154.6	77.9	148.8	65.3
$CH{=}CH_2$					
R	117.9	120.9	64.3	164.9	50.3
TS	172.5	84.1	−58.1	222.2	84.0

[a] For the definition of α, β, γ, δ, and θ see **3** and **9** in the text.

Ylides and Products of 1,2-Migration. This is the starting point in investigating the mechanisms of the migration to elucidate the conformation of the ylides. That of parent ylides, H_3MCH_2,[39,40] has been previously reported (**1** with Z = H below). In the most stable conformation the ylides have the substituent on the pnictogen atom in the gauche position with respect to the lone pair on the methylene carbon as shown in **1**, and anti-form **2** is slightly less stable by 2−3 kcal/mol for all Z's. The dihedral angles specifying the conformation of the ylides defined in **3**, α, β, γ, and δ, are summarized in Table 2, which will be compared with those in the TSs later. Those for M = P are not shown, since the changes in the dihedral angles for M = P are similar.



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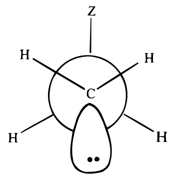

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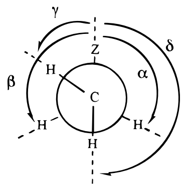

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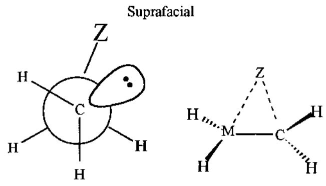
The products of the rearrangements are phosphine and arsine. The rearrangement stretches the $M{-}C^{CH_2}$ bond by 0.17−0.22 Å for M = P and by 0.16−0.19 Å for M = As, because the $M{-}C^{CH_2}$ bonds of the reactants have double bond character due to the electron donation from the lone pair to the M−H σ* orbital[41] and the $M{-}C^{CH_2Z}$ bonds of the products are a single bond.

As shown in Table 1 the reactions are exothermic by 48−57 kcal/mol for M = P and by 57−68 kcal/mol for M = As. The energy of reaction can be expressed by eq 7 in terms of the

$$\Delta E = D(M{-}Z) + D(M{-}C^{CH_2}) - D(C{-}Z) - D(M{-}C^{CH_2Z}) \qquad (7)$$

bond energies, where the M−Z and $M{-}C^{CH_2}$ bonds are those of the reactant and the $M{-}C^{CH_2Z}$ and C−Z bonds are those of the product. The large exothermicity means that, although the $M{-}C^{CH_2}$ bond has a double bond character, it is not much stronger than the $M{-}C^{CH_2Z}$ bond and that the C−Z bond in the product is much stronger compared with the M−Z bond in the reactant. If we reasonably assume that $D(M{-}C^{CH_2}) - D(M{-}C^{CH_2Z})$ is independent of the migrating group, the narrow range of about 10 kcal/mol in the exothermicity suggests that the difference in the dissociation energies between the M−Z and C−Z bonds is not so dependent on the migrating group.

Possible Mechanism of 1,2-Migration. During the course of the reactions, Z migrates from M to the lone pair orbital on the methylene carbon, and thus we can expect that the three-centered TS **4** is passed through. The Woodward−Hoffmann[15] rule has, however, shown that this process, suprafacial migration, is a forbidden process and that the antarafacial migration is allowed as shown in **5**. Nevertheless, during the allowed antarafacial migration the overlap among the atomic orbitals would become so small that dissociation leading to a radical pair ((i) in Scheme 1) would be an alternative favorable reaction path. In addition we have the other possible reaction paths if a specific orbital is available in the migration. The three-centered TS is allowed, if an asymmetric orbital of the migrating group such as a 2p atomic orbital would participate in the bond



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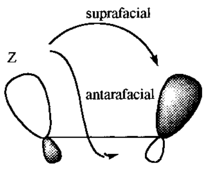

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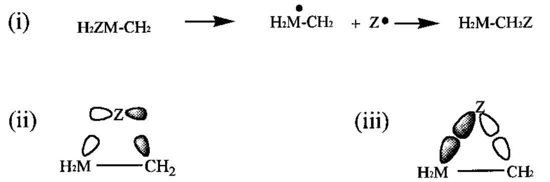
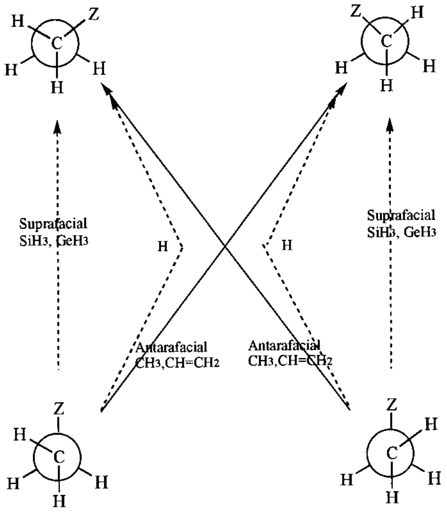
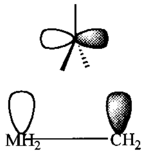
Scheme 1



Scheme 2



exchange as shown in (ii) in Scheme 1. In the present reaction this would lead to the inversion of a migrating group (**6**). Recent theoretical calculations on [1,3] sigmatropic shift in allylsilane[42,43] have shown that such an inversion path is less favorable than a retention path. Also, participation of two different orbitals on a migrating group would make the three-centered TS allowed ((iii) in Scheme 1). This is expected in the migration of the SiH_3 and GeH_3 groups, because the Si and Ge atoms could be hypervalent as discussed in the Introduction.



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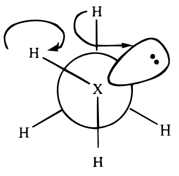
RMP2 Reaction Coordinates. The RMP2 calculations gave the three-centered TSs as shown in Figure 1, demonstrating that they are the TSs for the concerted mechanism in which the bond breaking and formation take place simultaneously without passing through an intermediate. However, the IRCs show that the detailed reaction mechanism is strongly dependent on the migrating group. As shown in Figure 2b for the case of $H_2CH_3AsCH_2$, the methyl migration is antarafacial where the methyl group attacks the lone pair on the methylene carbon from the backside accompanied by rotation of the methylene plane and inversion of the $AsCH_2$ moiety. The sum of the dihedral angles of γ and δ at the TS shown in Table 2 is about 160°, indicating that the $AsCH_2$ moiety is almost planar and in the course of inversion. The vinyl migration adopts the same mechanism, and thus the dihedral angles γ and δ are similar to those for the methyl migration. These antarafacial migrations are as expected, since they are allowed.

On the contrary, the IRC of the SiH_3 migration in Figure 2c as well as that of the GeH_3 migration displays that it is a suprafacial process. The migrating group stays in the same side of the methylene plane throughout the migration, the configuration of the $AsCH_2$ moiety being retained. Also, H migration was exhibited to be a forbidden, suprafacial process as shown in Figure 2a. However, the careful investigation of the conformation change along the IRC showed that the migrating H atom tries to move to the backside of the lone pair in the initial stage of the reaction, a process expected for the antarafacial migration, but it cannot pass through the barrier to the conformation change. As a result the suprafacial migration takes place (**7**). Scheme 2 summarizes the reaction profiles starting from the two enantiomers of the reactants. The vinyl group adopts the antarafacial migration, being the same as the methyl migration, whereas the GeH_3 migration is suprafacial, the same as the SiH_3 group. This is reasonable if one considers the atomic orbitals of the vinyl carbon and germanium atoms.



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The potential energy changes in Table 1 demonstrate that for both M = P and M = As the forbidden suprafacial migrations of the SiH_3 and GeH_3 groups require the smallest activation energies of about 13 kcal/mol. On the other hand, the allowed, antarafacial processes with Z = CH_3 and $CH{=}CH_2$ require much larger activation energies of 37−47 kcal/mol. The activation barrier to the suprafacial H migration is in between. So, with the RMP2 transition structures it is shown that the migrating aptitude through the concerted mechanism is in the order SiH_3, $GeH_3 \gg H > CH{=}CH_2 > CH_3$.

We also determined the TS for reaction path (ii) in Scheme 1 as shown in Figure 1 ($H_2CH_3AsCH_2$ (b)). At the PMP4 level the activation energy was calculated to be 36.4 kcal/mol. Although this path is symmetry-allowed, the large activation energy is required. Presumably, the structure is not appropriate for obtaining sufficient overlap among the atomic orbitals responsible for the bond exchange. Since the activation energy is comparable to that for the concerted mechanism, this path cannot be excluded as a candidate of the concerted mechanism for the alkyl group migration. However, substituents on the migrating group would make this structure overcrowded, and thus the alkyl migration is not likely to pass through this reaction path.

Comparison of RMP2 Transition States among the Migrating Groups. The differences in the reaction mechanism and activation energies do not come from those in exothermicity, which are relatively small. Thus, to investigate the origin of the differences, the TS structures with M = As will be compared among the migrating groups. While the following discussions will be limited to the TSs with M = As, the TS structures and reaction mechanisms for M = P are qualitatively similar as seen in Tables 1 and 2.

First, we compare the TS structures for the CH_3 and SiH_3 migrations shown in Figure 1 in detail, i.e., $H_2CH_3AsCH_2$ (a) and $H_2SiH_3AsCH_2$. All three CH bonds of the methyl group are 1.10 Å long, and the HCH bond angles are close to 110°,

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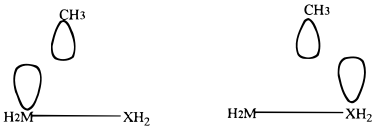
[42] Yamabe, T.; Nakamura, K.; Shiota, Y.; Yoshizawa, K.; Kawauchi, S.; Ishikawa, M. *J. Am. Chem. Soc.* **1997**, *119*, 807.

[43] Takahashi, M.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 1948.

indicating that the methyl group is tetrahedral and that sp^3 hybridization is kept during the reaction. On the other hand, one can see the significant differences in the SiH bonds; the SiH9 bond is 0.02 Å longer than the others, the H8SiH9 and H8SiH10 bond angles are smaller than the H8SiH10 angle by more than 10°, and also the H9SiC2 angle of 150.8° is 12.2° larger than the H8C3C2 angle of the TS for the CH_3 migration. These structural features show that the $As-H_3Si-C$ moiety has a deformed trigonal bipyramidal structure, indicating that the Si atom is hypervalent. Accordingly, the two isolated As−Si and Si−C bonds are formed at the TS as shown in (iii) in Scheme 1. This bonding nature is different from that in the TS for the CH_3 migration, in which one sp^3 hybrid orbital of the carbon atom is shared by the As−C and C−C bonds schematically shown in **8**. Although the SiH_3 migration is apparently forbidden, it is in fact not because of hypervalency of the Si atom, and the quite small activation energies for the SiH_3 and GeH_3 migrations are the results of hypervalency of the Si and Ge atoms.



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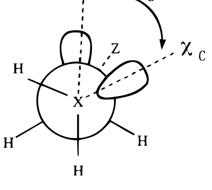
The structure with three atomic orbitals forming a triangle and being occupied by four electrons is electronically unstable. A simple example is H_3^- of a regular triangle which suffers from the Jahn−Teller[44] deformation. This holds true for the TS for the CH_3 migration. One can observe large deformations to relieve the TS from instability. The CH_3 group at the TS is located further from the H_2MCH_2 moiety than the SiH_3 group as shown in Figure 1 and Table 2; the $As-CH_3$ bond distance of 2.35 Å at the TS is 1.21 times longer than that of the reactant, and the partially formed CH_3-CH_2 bond of 2.53 Å is still 1.64 times longer than that of the product. Compared with them, the $As-SiH_3$ bond (2.39 Å) at the TS is only 1% stretched relative to that of the reactant (2.36 Å), indicating that the As−Si bond remains at the TS utilizing the hypervalency of the Si atom, and the Si−C bond partially formed is only 35% longer than that in the product. Similar trends were found in the TS for the GeH_3 migration.

Also, the large deformation at the TS for the CH_3 migration is observed in the conformation. In Table 2 we show the estimated dihedral angle, θ, between the atomic orbital of M (χ_M) responsible for the M−Z bond and the lone pair orbital (χ_C) on the methylene carbon at the TSs (**9**). In this estimation we approximated this angle by the dihedral angle between the bisector of the H−C−H angle and that of the H−M−H angle. As shown in Table 2 θ values in the reactants are approximately 60°. While θ at TS for the SiH_3 migration is close to 60°, that of 94.8° for the CH_3 migration is much larger. χ_M and χ_C in the latter TS is almost orthogonal, a structure in which electronic instability is diminished. The angle θ for the H and $CH=CH_2$ migrations is slightly smaller than that for the methyl migration but much larger than that for the SiH_3 and GeH_3 migration. Since the mechanism of the $CH=CH_2$ migration is similar to that of the CH_3 migration, large θ is reasonable. As discussed before, the mechanism in the initial stage of the H migration is in fact antarafacial and then the reaction coordinate turns to the antarafacial path from the enantiomeric reactant as shown in Scheme 2. Thus, although the migration is apparently suprafacial, the TS is similar to that for the antarafacial migration. Consequently, the dihedral angle θ for the H migration is similar to that for the CH_3 migration.



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At the TS for the $CH=CH_2$ migration $As-C^{CH=CH_2}$ distance is 10% stretched relative to that in the reactant, and the partially formed $Z-C^{CH_2}$ distance is 55% longer than that in the product, the TS for the migration of the $CH=CH_2$ group is closer to the H_2AsCH_2 moiety than that for the migration of the CH_3 group. Also, the activation energies are smaller than those for the CH_3 migration by 3.3 and 1.0 kcal/mol for M = P and M = As, respectively, consistent with the experimental facts in various rearrangements discussed in the Introduction that the migrations of phenyl and vinyl groups are observed more than those of the alkyl groups. These results suggest that the π and/or π^* orbital(s) of the $CH=CH_2$ group participate in the bond exchange.

Path through Radical Dissociation. There is a possibility of the radical cleavage and the recombination of a resultant radical pair ((i) of Scheme 1). The activation energies for the concerted mechanism calculated using the RMP2 transition structures should be compared with the radical dissociation energies also listed in Table 1.

As for the CH_3 migration the activation energies for the concerted mechanism through the RMP2 transition states were calculated at the PMP4 level to be 47.1 and 38.1 kcal/mol for M = P and M = As, respectively. They are 7 kcal/mol larger than the dissociation energies to the radicals. This fact as well as electronically unfavorable three-centered interaction suggests the possibility of triplet instability of the RHF wave function of the TS. As shown in Table 1 we actually found that the RHF wave functions of the RMP2 TSs for the H, CH_3, and $CH=CH_2$ migrations are unstable with respect to becoming UHF wave functions. The UHF calculations at these RMP2 TSs gave the expectation values of s^2 significantly deviated from zero, and especially those for the CH_3 and $CH=CH_2$ migrations are close to 1.0, indicating large biradical character. Spin projection, however, did not change the energetics very much; the RMP2 activation energy for Z = CH_3 and M = As, for instance, is 45.2 kcal/mol, and the PMP2 activation energy is 42.4 kcal/mol. Presumably, a triplet state is close to the singlet state in energy.

Though the RHF wave functions of the TSs for the H migrations are similarly unstable, the expectation value of s^2 is smaller. Presumably, the spherical 1s orbital of hydrogen would facilitate the three-centered M−H−C interaction more than the directional carbon sp^3 or sp^2 hybrid orbital. This is further supported by the smaller activation energies of 33.6 and 30.4 kcal/mol for M = P and As, respectively, and the smaller changes in the conformation required to reach the TSs.

The unstable TSs and significant instability of the RHF wave functions suggest that the RMP2 TSs for the concerted mechanism could be an artifact of the RHF-based methods and might not exist. Thus, we located the TS for the CH_3 migration with

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(44) Jahn, H. A.; Teller, E. *Proc. R. Soc. London* **1937**, *A164*, 220.

M = As by the UMP2 and UB3LYP methods, to find that the radical dissociation takes place, the CH_3 group weakly binding to the H_2AsCH_2 fragment at the TS; the As−CH_3 distance of 3.822 and 4.306 Å was obtained at the UMP2 and UB3LYP levels, respectively. Similarly, the CASSCF calculations in which the three orbitals and four electrons were included in the active space gave the longer distance of 4.481 Å. On the other hand, the RQCISD, UQCISD, and RB3LYP methods gave the shorter distance of 2.392, 2.510, and 2.353 Å, respectively. These results suggest that the dissociation limit and the TSs for the concerted migration are close to each other in energy, and their relative stability is strongly dependent on the computational levels. However, the dissociation would be definitely favorable, if the entropy effect is taken into account. Although we did not determine the TS with these methods, similar results are reasonably expected for the $CH{=}CH_2$ migration. Therefore, it is safe to conclude that the radical mechanism could play an important role in the alkyl and vinyl group migrations in the Stevens rearrangement, in agreement with the experimental facts reported by Ollis et al.[12] Even if the concerted mechanism is operating, TSs would have large biradical character.

As discussed in the Introduction, the rearrangement of the As ylides takes place more easily than that of the P ylides. The energetics in Table 1 are in agreement with this since the As−C bond is weaker than the P−C bond, the activation energies for the CH_3 and $CH{=}CH_2$ migrations of M = As are smaller, and in addition the radical dissociation energies for M = As are smaller.

On the other hand, the TSs for H migration for M = P and for As are 6.0 and 0.9 kcal/mol, respectively, more stable than the dissociation limit, and therefore they are probably real. In fact, the UMP2, RQCISD, and UQCISD calculations gave the three-centered TS structure with the As−H distance of 1.713, 1.670, and 1.870 Å. Similarly, the TSs for $CH{=}CH_2$ migration are more stable than the dissociation limit by 6.0 and 3.4 kcal/mol for M = P and As, respectively, and therefore, the TSs for the concerted mechanism would exist. However, since the energy differences between the RMP2 TS and the dissociation limit for these migrations are so small, the concerted mechanism would be adopted only at low temperature and the radical mechanism would be more favorable at high temperature.

The activation energies for the SiH_3 and GeH_3 migrations shown in Table 1 are reasonably low and much smaller than those for the H, CH_3, and $CH{=}CH_2$ migration, and in addition much smaller than the dissociation energy to the radical pair. Consequently, in the migration of the groups of heavier elements which could be hypervalent the concerted mechanism should be adopted. Actually, on the basis of the present results, we experimentally found the novel silyl group migration in $Ph_2(Me_3Si)PCHPh$ which leads to $Ph_2PCH(SiMe_3)Ph$ under thermal conditions.[45] We believe the concerted suprafacial migration takes place. To our knowledge this is the first Stevens rearrangement of a silyl group. The experimental results will be published elsewhere in the near future.

Summary

In this paper we investigated the mechanism of the Stevens rearrangement of ylides, ZH_2MCH_2 (M = P and As, Z = H, CH_3, $CH{=}CH_2$, SiH_3, and GeH_3), comparing the mechanism of the concerted migration with the radical dissociation−recombination path. We determined the structures of the TSs at the RMP2 level and followed the IRCs to investigate the reaction mechanism.

The IRCs show that the migration mechanism is strongly dependent on the migrating group. The migration of the methyl and vinyl groups is antarafacial, in which the migrating group attacks the lone pair on the methylene carbon from the backside, as expected from the Woodward−Hoffmann rule. These allowed antarafacial processes require large activation energies of 37−47 kcal/mol, because at the TSs a single orbital of the methyl and vinyl groups is available in the bond exchange and sufficient overlaps for stabilization are not realized. On the other hand, the IRC of the silyl migration along with that of the germyl migration displays that it is a suprafacial process. These forbidden suprafacial migrations of the silyl and germyl groups require smaller activation energies of about 13 kcal/mol for both M = P and M = As. These small activation energies are ascribed to the hypervalent property of the Si and Ge atoms which can form the M−Si and M−Ge bonds and the Si−C^{CH_2} and Ge−C^{CH_2} bonds simultaneously at the TSs. Although the H migration adopts the suprafacial migration, the TS structure is similar to that for the antarafacial migration and in addition the activation energies of 30−34 kcal/mol are similarly large. This is ascribed to the fact that, since the barrier to the conformation change cannot be passed during the course of this migration, the reaction path turns to the antarafacial path from the enantiomeric ylide.

These activation energies for the concerted migration were compared with the energies required by the dissociation to radicals, H_2MCH_2 + Z. The dissociation energies for the silyl and germyl migrations are much larger than the activation energies, showing that the concerted migration mechanism should be adopted as a main reaction route. On the other hand, the dissociation energy for the methyl group is smaller than the activation energy, demonstrating that the rearrangement should take place through the radical dissociation−recombination path. Actually the RHF wave functions of the TSs for the methyl migration are unstable, and methods such as CASSCF and UMP2 gave TS structures with a long As−methyl distance; the RMP2 transition state may be an artifact of the RHF-based method. Although the RHF wave functions of the TSs for the H and vinyl migration are unstable, the TSs are more stable than the dissociation limit to the radicals. However, the energy difference between them is so small that the entropy term would definitely favor the radical dissociation reaction mechanism.

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(45) Makita, K.; Koketsu, J.; Koga, N. To be submitted.