

# Hydrogen Migration and Lithium Iodide $\alpha$ -Elimination in 1-Iodo-1-lithioethene. Concerted vs Stepwise Mechanism

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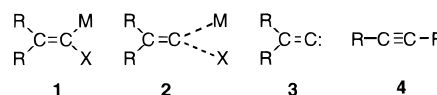
1-Iodo-1-lithioethene is prepared from 1-iodoethene and LDA in THF. The lithiated derivative can be trapped by electrophiles, but it readily decomposes to acetylene; the decomposition process cannot be analyzed by experimental techniques. Ab initio calculations indicate that 1-iodo-1-lithioethene should be a monomer in a THF solution. Furthermore, hydrogen migration and lithium iodide  $\alpha$ -elimination procedures should occur through a concerted mechanism. The activation barrier for the cis and trans hydrogen migration should be almost identical.

## Introduction

It has been concluded that vinyl halides are adequate substrates for the preparation of alkylidene carbenes since they can undergo halogen–metal interconversion and hydrogen–metal interconversion with ease.<sup>1</sup> Regarding the nature of alkylidene carbenes, one must consider three major species: organometallic reagents such as **1**, carbenoids such as **2**, and “free” carbenes such as **3** (Chart 1).<sup>1b</sup> Intermediate **1** may convert to **2** and **3** by  $\alpha$ -elimination of MX. Furthermore, alkylidene carbenes may suffer intramolecular rearrangement with the formation of acetylene **4** (Chart 1).<sup>1</sup>

However, despite the theoretical interest devoted to the intramolecular rearrangement from **3** to **4**,<sup>2</sup> as far as we know, no extensive theoretical study has been carried out on the  $\alpha$ -elimination process. We have recently described the ab initio calculations for stereoselective lithiations of 2-alkoxy-1,1-diiido-1-alkenes.<sup>3</sup> The agreement between our experimental<sup>4</sup> and theoretical results<sup>3</sup> prompted us to study the parent 1-iodo-1-lithioethene, **5**. For a better understanding of the behavior of this substrate, we carried out a parallel research study at both levels, experimental and theoretical. In the Experimental Section, we test its capability to react as an organometallic reagent or as a carbenoid. On the theoretical side, we address the following questions in this paper: (i) Is the lithiated vinyl iodide a monomer or a dimer? (ii) Does  $\alpha$ -elimination of LiI occur prior to hydrogen migration? To answer these questions fully, electron correlation and

Chart 1



solvation (coordination with the solvent and solute–continuum interaction) should be taken into account.<sup>3,5</sup>

## Experimental Results

We started from the idea that a solution of 1-iodo-1-lithioethene, **5**, could have been obtained from 1-iodoethene (by lithium–hydrogen exchange reaction) or 1,1-diiidoethene (by lithium–iodine exchange reaction). 1-Iodoethene can be easily prepared by reaction of vinylmagnesium bromide with iodine in tetrahydrofuran at 0 °C. A solution containing this iodoolefin was cooled to –100 °C, filtered under an inert atmosphere (to eliminate the magnesium salts), and treated with an organolithium system to give 1-iodo-1-lithioethene, **5**. The reaction of **5** with different electrophiles at this temperature yielded the corresponding products **6–11** (Scheme 1). The best results were obtained when we added 3 equiv of lithium diisopropylamide (relative to the starting vinylmagnesium bromide) as the organolithium system. We also tested the lithium–iodine exchange reaction from 1,1-diiidoethene, **8**, but it always gave large amounts of acetylenic compounds resulting from lithium–hydrogen exchange followed by  $\beta$ -elimination (Scheme 2).

The solution of 1-iodo-1-lithioethene readily begins to decompose after 5 min at –100 °C, yielding lithium acetylide that can be trapped by different electrophiles (Scheme 3). The formation of lithium acetylide can be explained by interconversion from **5** to acetylene and the reaction of acetylene with the remaining LDA. This transformation to give acetylene can occur through a mechanism involving simultaneous  $\alpha$ -elimination and

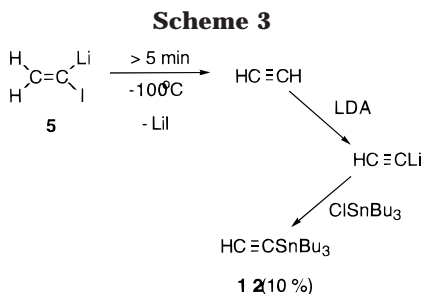
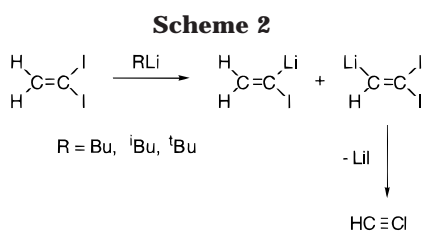
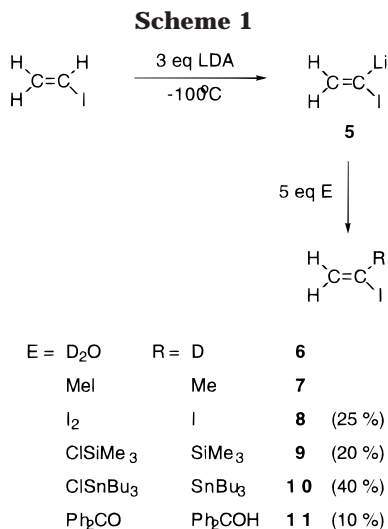
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hydrogen migration or a stepwise procedure, with formation of the vinylidene H<sub>2</sub>C=C: as the intermediate. Vinylidene should have an extremely short lifetime because of its low barrier for isomerization to acetylene,<sup>2</sup> and as a result, it has been very elusive.<sup>6</sup> It has therefore been supposed that the experimental elucidation between the two alternative mechanisms would have serious limitations. Indeed, we tried to trap the possible intermediate by adding an unsaturated system instead of an electrophile to the above-mentioned solution of **5** at -100 °C; but we did not obtain a successful result either with alkenes (cyclohexene, cyclooctene, norbornene, butyl vinyl ether, phenyl vinyl sulfide, and methyl vinyl ketone) or with alkynes (3-hexyne and diphenylacetylene). This fact could indicate not only a concerted reaction but also a stepwise mechanism with a very elusive intermediate. On the other hand, it was felt that the theoretical methods could provide a useful tool to investigate the reaction mechanism.

### Computational Details

All the calculations on 1-iodo-1-lithioethene, **5**, solvated with water molecules were carried out by using

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the Gaussian94 program package.<sup>7</sup> The molecular geometries were first optimized without any molecular symmetry constraints at the Hartree–Fock self-consistent-field (HF) level of theory and reoptimized by the Møller–Plesset perturbation theory<sup>8,9</sup> with second-order corrections (MP2) using Schlegel’s analytical gradient procedure.<sup>10</sup> Regarding the atomic basis set, the pseudorelativistic effective core potential (ECP) by Hay and Wadt<sup>11</sup> augmented by one set of six d functions ( $\zeta_d = 0.266$ )<sup>12</sup> for I (21/21/1) and the standard split-valence 6-31G(d) or 6-31G(d,p) basis sets<sup>13,14</sup> for C, Li, O, and H appeared to be a good choice. These basis sets, hereafter referred to as DZV(d) and DZV(d,p), respectively, were felt to be well balanced for all the atoms involved and included relativistic corrections by using ECP for I. The optimized structures were characterized as minima or saddle points (representing transition structures) by numerical evaluation of force constants.

To assess the importance of higher level correlated methods, additional single-point calculations on the optimized geometries were performed with incorporation of correlation energy using the Møller–Plesset perturbation theory with third-order (MP3)<sup>15</sup> or fourth-order (MP4SDTQ)<sup>16</sup> corrections.

Furthermore, the existence of ionic species may require functions of higher angular momentum. We therefore carried out single-point calculations at the MP2 level using the uncontracted pseudorelativistic ECP by Hay and Wadt<sup>11</sup> augmented by two sets of d functions ( $\zeta_d = 0.105$  and  $0.334$ )<sup>12</sup> and one set of f functions ( $\zeta_f = 0.433$ )<sup>17</sup> for I (111/111/11/1) in conjunction with a 6-311G(2df) or 6-311+G(2df,2p)<sup>18</sup> basis set for C, Li, O, and H. These basis sets will be hereafter referred to as TZV(2df) and TZV(2df+,2p), respectively.

For a complementary modeling of the solvation effect,<sup>5</sup> single-point calculations were carried out using the Onsager model, as implemented within a self-consistent reaction field (SCRFF) method in Gaussian94,<sup>7</sup> using the dielectric constant of THF ( $\epsilon = 7.58$ ). The Onsager model at the MP2 level predicts energy differences of solvated systems that were in good agreement with the experimental results.<sup>19</sup> Finally, to obtain reliable rela-

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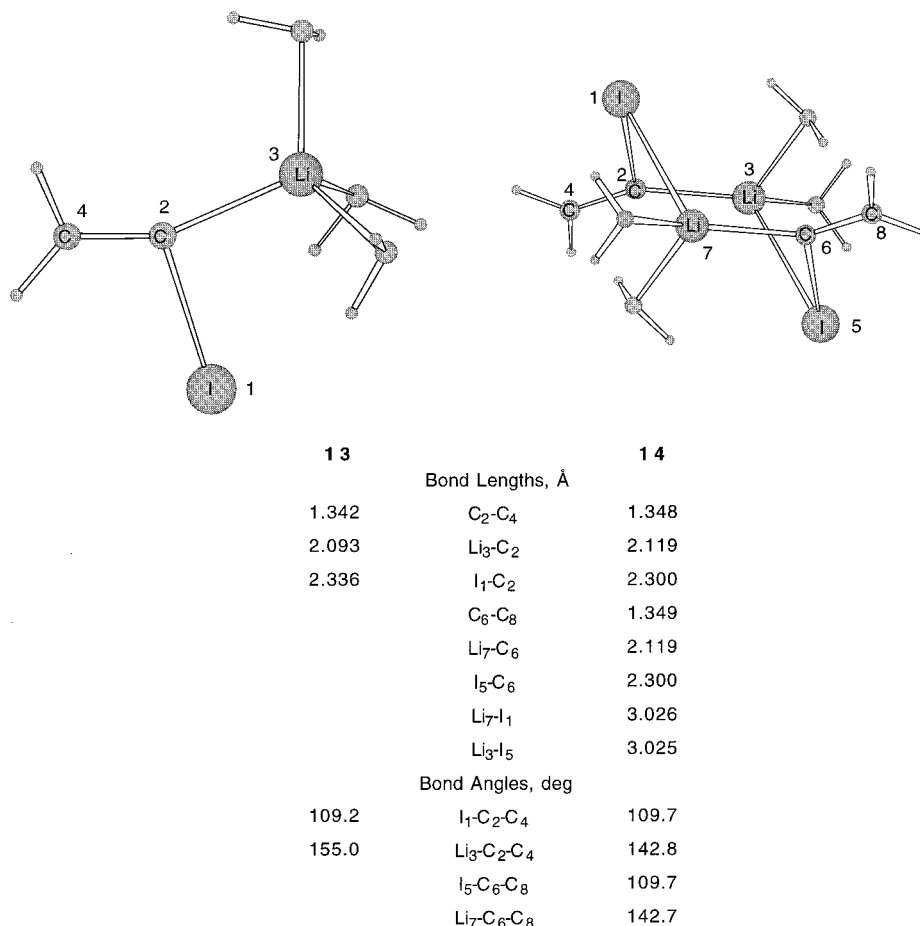
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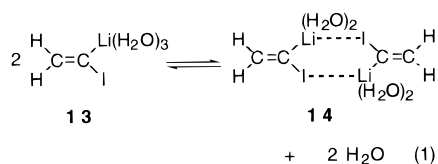


**Figure 1.** Computer plot and selected geometrical parameters of the MP2/DZV(d)-optimized structures for water-solvated 1-iodo-1-lithioethene monomer (**13**) and dimer (**14**).

tive energies for the investigated species, we indicate the MP3/TZV(2df)+SCRFF [based on the MP3/DZV(d) energies and modified by additive corrections obtained from the MP2/TZV(2df) and MP2/DZV(d)+SCRFF energies] and MP4/TZV(2df+,2p)+SCRFF [based on the MP4/DZV(d,p) and modified by additive corrections obtained from the MP2/TZV(2df+,2p) and MP2/DZV(d,p)+SCRFF] energies.

### Theoretical Results

**CH<sub>2</sub>=CILI. Monomer vs Dimer.** Previously to the theoretical study of  $\alpha$ -elimination of LiI and the hydrogen migration reactions, it was essential to determine the monomeric or dimeric nature of the lithiated vinyl iodide. A monomer-dimer equilibrium also had to be analyzed. Equation 1 shows this equilibrium, where the lithium tetracoordination has been completed with water molecules.<sup>20</sup>



The relevant geometrical parameters of the optimized structures of **13** and **14** with the MP2/DZV(d) wave function are given in Figure 1. The Li<sub>3</sub>-C<sub>2</sub> (2.093 Å), I<sub>1</sub>-C<sub>2</sub> (2.336 Å), and C<sub>2</sub>-C<sub>4</sub> (1.342 Å) distances and the

Li<sub>3</sub>-C<sub>2</sub>-C<sub>4</sub> (155.0°) and I<sub>1</sub>-C<sub>2</sub>-C<sub>4</sub> (109.2°) bond angles in monomer **13** are related to those obtained experimentally<sup>21</sup> or calculated<sup>22</sup> for similar vinylidenecarbenoid systems with a chlorine instead of an iodine atom. Dimer **14** shows a chair conformation of C<sub>i</sub> type symmetry (although no geometry constraints were imposed) with a smaller Li<sub>3</sub>-C<sub>2</sub>-C<sub>4</sub> bond angle (142.8°), larger Li<sub>3</sub>-C<sub>2</sub> distance (2.119 Å), and a Li<sub>3</sub>-I<sub>5</sub> distance of 3.025 Å.

To evaluate the monomer-dimer preference, Table 1 shows the absolute energies calculated for the trisolvated 1-iodo-1-lithioethene monomer, **13**, disolvated dimer **14**, and water molecules and the energy differences according to eq 1. We found that, at the MP2/DZV(d)/MP2/DZV(d) level of theory, the equilibrium should favor the monomer by 7.0 kcal/mol. Table 1 also gives the additional single-point calculations on the MP2/DZV(d) geometries at the MP3/DZV(d), MP2/TZV(2df), and MP2/DZV(d) + SCRFF levels of theory. The higher correlated level method increases the energy difference and also predicts that monomer **13** should be more favored [MP3/DZV(d),  $\Delta H = 7.9$  kcal/mol]. The same tendency is predicted with the improved basis set

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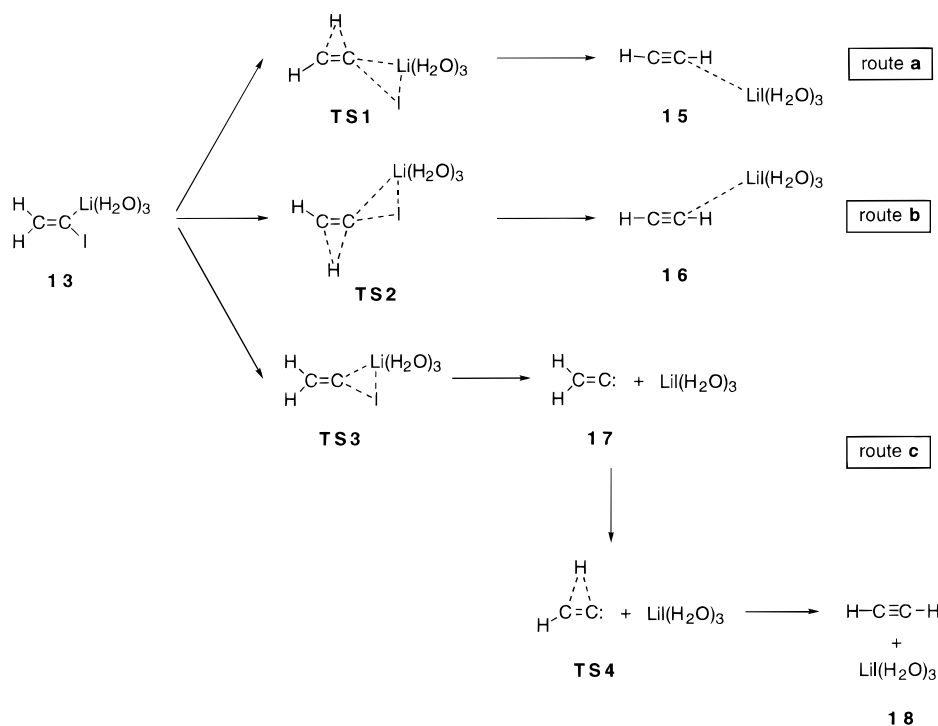
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**Table 1. Calculated Absolute Energies (Hartrees) for H<sub>2</sub>O and Water-Solvated 1-Iodo-1-lithioethene Monomer (13) and Dimer (14) and Energy Differences ( $\Delta H$ , kcal/mol) for Monomer/Dimer Equilibrium (eq 1)<sup>a</sup>**

	13	14	H <sub>2</sub> O	$\Delta H$
MP2/DZV (d)	-324.543 827	-496.682 818	-76.196 847	7.0
MP3/DZV(d)	-324.577 802	-496.737 679	-76.202 697	7.9
MP2/TZV(2df)	-324.934 848	-497.286 578	-76.285 101	8.1
MP2/DZV(d) + SCRF	-324.546 165	-496.682 818	-76.201 052	4.6
MP3/TZV(2df) + SCRF <sup>b</sup>	-324.971 161	-497.341 438	-76.295 156	6.6

<sup>a</sup> All calculations at the MP2/DZV(d)-optimized geometries. <sup>b</sup> Based on MP3/DZV(d) energies and modified by additive corrections obtained from MP2/TZV(2df) and MP2/DZV(d) + SCRF.

**Scheme 4**

TZV(2df) at the MP2 level ( $\Delta H = 8.1$  kcal/mol). On the other hand, the inclusion of solvation by the SCRF method decreased the energy difference, but it did not reverse the relative stability [MP2/DZV(d) + SCRF,  $\Delta H = 4.6$  kcal/mol]. To obtain an improved energy difference, we considered that all corrections to the MP2/DZV(d) energies should be additive; given this consideration, our best level of calculation also indicated a preference for the monomeric species [MP3/TZV(2df) + SCRF,  $\Delta H = 6.6$  kcal/mol]. Last, taking into account that Li may attract another solvent molecule in 14, because the dimeric form enforces a distortion from tetrahedral symmetry (see Figure 1), we carried out the optimization of the dimer considering that each lithium atom is solvated with three water molecules, but we found that, at the MP2/DZV(d) level, the dimer is dissociated in the course of optimization.

Summarizing the results of this section, we specify the monomer that appears to be the most stable structure for 1-iodo-1-lithioethene in the polar medium. Consequently, we consider a monomer system in the calculation of  $\alpha$ -elimination and hydrogen migration reactions.

**CH<sub>2</sub>=CILI → HC≡CH + LiI. Concerted vs Stepwise Mechanism.** 1-Iodo-1-lithioethene could evolve to acetylene by different procedures, as shown in Scheme 4. Thus, one concerted pathway involves

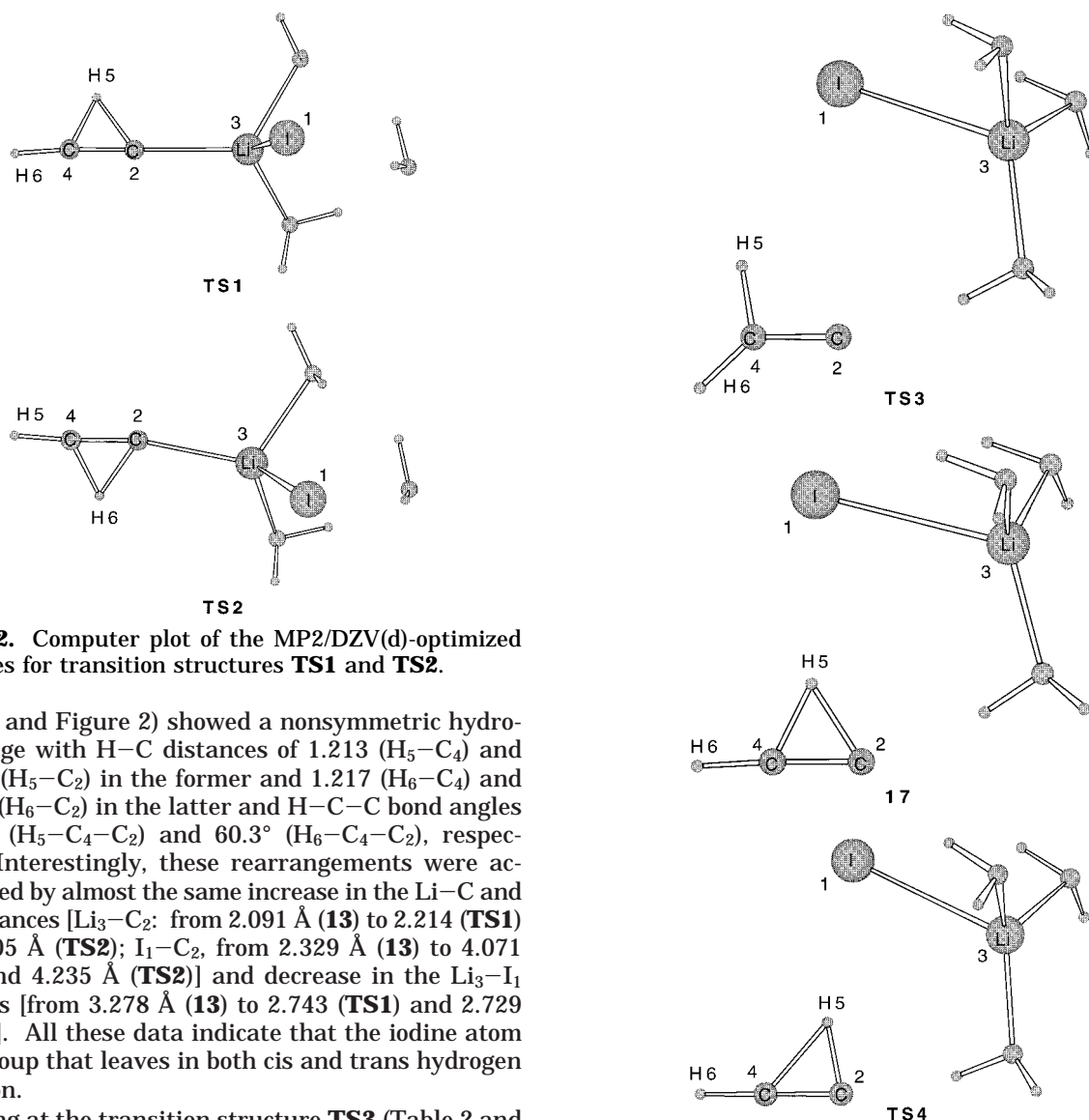
migration of the hydrogen with a cis relationship to the lithium atom together with a simultaneous loss of lithium iodide (Scheme 4, route a), through the transition state TS1, to yield the acetylene 15. In the second concerted pathway, the hydrogen with a trans relationship to the lithium atom migrates (route b). In this case, the transition state TS2 gives the acetylene 16. Last, in the stepwise procedure (Scheme 4, route c), the formation of carbene 17 supposes the initial loss of lithium iodide through the transition state TS3. From the intermediate 17, hydrogen migration leads to the transition state TS4 and, finally, acetylene 18.

The existence of hydrogen-bridged structures may require polarization functions on the hydrogen atoms. We therefore carried out the optimization at the MP2/DZV(d,p) level. Selected optimized structural parameters for minima 13, 15, 16, 17, and 18 and transition structures TS1, TS2, TS3, and TS4 are listed in Table 2. Searches for these transition states were carried out by the synchronous transit-guided quasi-Newton (STQN) method.<sup>23</sup> Several features may be emphasized. Apart from the logical evolution from the alkene 13 to the alkynes 15, 16, and 18, reflected in the parameters, it is interesting to look at the hydrogen migration. The geometries of the transition structures TS1 and TS2



**Table 2.** Selected MP2/DZV(d,p)-Optimized Structural Parameters for Minima **13**, **15**, **16**, **17**, and **18** and Transition Structures **TS1**, **TS2**, **TS3**, and **TS4** (Lengths in Å, Angles in deg)<sup>a</sup>

	<b>13</b>	<b>TS1</b>	<b>TS2</b>	<b>TS3</b>	<b>17</b>	<b>TS4</b>	<b>15</b>	<b>16</b>	<b>18</b>
H <sub>5</sub> -C <sub>4</sub>	1.089	1.213	1.070	1.100	1.283	1.532	1.065	1.067	1.071
H <sub>5</sub> -C <sub>2</sub>	2.054	1.304	2.333	1.881	1.314	1.180	2.287	2.289	2.292
H <sub>6</sub> -C <sub>4</sub>	1.082	1.071	1.217	1.076	1.070	1.071	1.067	1.065	1.064
H <sub>6</sub> -C <sub>2</sub>	2.190	2.333	1.300	2.191	2.331	2.319	2.289	2.287	2.284
Li <sub>3</sub> -C <sub>2</sub>	2.091	2.214	2.205	3.805	3.750	3.726	2.488	2.489	4.000
I <sub>1</sub> -C <sub>2</sub>	2.329	4.071	4.235	3.846	3.836	3.751	4.609	4.609	3.929
C <sub>4</sub> -C <sub>2</sub>	1.342	1.265	1.265	1.293	1.262	1.248	1.222	1.223	1.222
Li <sub>3</sub> -I <sub>1</sub>	3.278	2.743	2.729	2.804	2.843	2.841	2.689	2.689	2.766
H <sub>5</sub> -C <sub>4</sub> -C <sub>2</sub>	115.0	60.2	175.0	103.2	59.2	52.9	0.8	177.7	1.9
H <sub>6</sub> -C <sub>4</sub> -C <sub>2</sub>	128.9	174.5	60.3	135.0	176.8	179.6	177.8	0.8	176.0
Li <sub>3</sub> -C <sub>2</sub> -C <sub>4</sub>	155.2	172.0	168.7	128.9	124.2	136.8	74.0	74.0	116.0
I <sub>1</sub> -C <sub>2</sub> -C <sub>4</sub>	109.2	132.8	139.5	86.0	80.2	92.2	45.8	45.8	156.8

<sup>a</sup> See Scheme 4.**Figure 2.** Computer plot of the MP2/DZV(d)-optimized structures for transition structures **TS1** and **TS2**.

(Table 2 and Figure 2) showed a nonsymmetric hydrogen bridge with H-C distances of 1.213 (H<sub>5</sub>-C<sub>4</sub>) and 1.304 Å (H<sub>5</sub>-C<sub>2</sub>) in the former and 1.217 (H<sub>6</sub>-C<sub>4</sub>) and 1.300 Å (H<sub>6</sub>-C<sub>2</sub>) in the latter and H-C bond angles of 60.2° (H<sub>5</sub>-C<sub>4</sub>-C<sub>2</sub>) and 60.3° (H<sub>6</sub>-C<sub>4</sub>-C<sub>2</sub>), respectively. Interestingly, these rearrangements were accompanied by almost the same increase in the Li-C and I-C distances [Li<sub>3</sub>-C<sub>2</sub>: from 2.091 Å (**13**) to 2.214 (**TS1**) and 2.205 Å (**TS2**); I<sub>1</sub>-C<sub>2</sub>, from 2.329 Å (**13**) to 4.071 (**TS1**) and 4.235 Å (**TS2**)] and decrease in the Li<sub>3</sub>-I<sub>1</sub> distances [from 3.278 Å (**13**) to 2.743 (**TS1**) and 2.729 Å (**TS2**)]. All these data indicate that the iodine atom is the group that leaves in both cis and trans hydrogen migration.

Looking at the transition structure **TS3** (Table 2 and Figure 3), a slight increase in the H<sub>5</sub>-C<sub>4</sub> bond length was observed [from 1.089 Å (**13**) to 1.100 Å (**TS3**)] together with a small decrease in the H<sub>5</sub>-C<sub>2</sub> distance

**Figure 3.** Computer plot of the MP2/DZV(d)-optimized structures for minimum **17** and transition structures **TS3** and **TS4**.

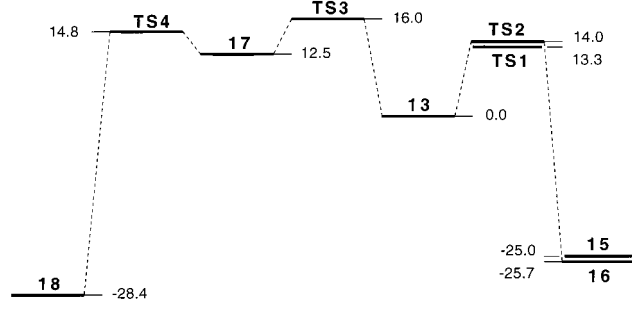
**Table 3. Calculated Absolute Energies (Hartrees) and Relative Energies (in parentheses, kcal/mol) for Minima 13, 15, 16, 17, and 18 and Transition Structures TS1, TS2, TS3, and TS4<sup>a</sup>**

species	MP2/DZV(d,p)	MP4/DZV(d,p)	MP2/TZV(2df+,2p)	MP2/DZV(d,p) + SCRFF	MP4/TZV(2df+2p) + SCRFF <sup>b</sup>
<b>13</b>	-324.626 200 (0.0)	-324.703 079 (0.0)	-325.017 392 (0.0)	-324.628 803 (0.0)	-325.096 874 (0.0)
<b>TS1</b>	-324.602 798 (14.7)	-324.676 754 (16.5)	-324.989 455 (17.5)	-324.615 079 (8.6)	-325.075 692 (13.3)
<b>TS2</b>	-324.604 131 (13.8)	-324.678 060 (15.7)	-324.989 750 (17.3)	-324.615 033 (8.6)	-325.074 581 (14.0)
<b>TS3</b>	-324.604 085 (13.9)	-324.682 595 (12.9)	-324.988 039 (18.4)	-324.608 914 (12.5)	-325.071 377 (16.0)
<b>17</b>	-324.612 805 (8.4)	-324.685 662 (10.9)	-324.999 940 (11.0)	-324.617 002 (7.4)	-325.076 994 (12.5)
<b>TS4</b>	-324.608 080 (11.4)	-324.681 455 (13.6)	-324.996 836 (12.9)	-324.611 175 (11.1)	-325.073 306 (14.8)
<b>15</b>	-324.674 992 (-30.6)	-324.745 243 (-26.5)	-325.061 916 (-27.9)	-324.679 494 (-31.8)	-325.136 669 (-25.0)
<b>16</b>	-324.674 992 (-30.6)	-324.745 243 (-26.5)	-325.061 908 (-27.9)	-324.680 585 (-32.5)	-325.137 752 (-25.7)
<b>18</b>	-324.674 853 (-30.5)	-324.745 412 (-26.6)	-325.062 863 (-28.5)	-324.683 565 (-34.4)	-325.142 134 (-28.4)

<sup>a</sup> See Scheme 4. All calculations at the MP2/DZV(d,p)-optimized geometries. <sup>b</sup> Based on MP4/DZV(d,p) energies and modified by additive corrections obtained from MP2/TZV(2df+,2p) and MP2/DZV(d,p) + SCRFF.

[from 2.054 Å (**13**) to 1.881 Å (**TS3**)] and in the H<sub>5</sub>-C<sub>4</sub>-C<sub>2</sub> bond angle [from 115.0° (**13**) to 103.2° (**TS3**)]; these indicate a tendency to carry out the rearrangement in the course of the carbene formation reaction. Indeed, only a hydrogen-bridged structure could be located for intermediate **17** (Table 2 and Figure 3. H<sub>5</sub>-C<sub>4</sub>, 1.283 Å; H<sub>5</sub>-C<sub>2</sub>, 1.314 Å; H<sub>5</sub>-C<sub>4</sub>-C<sub>2</sub>, 59.2°). This minimum would evolve to the transition state **TS4** (Table 2 and Figure 3), which also presents a highly nonsymmetric hydrogen-bridged structure that is closer to the acetylene **18** than to the starting structure **13** (H<sub>5</sub>-C<sub>4</sub>, 1.532 Å; H<sub>5</sub>-C<sub>2</sub>, 1.180 Å; H<sub>5</sub>-C<sub>4</sub>-C<sub>2</sub>, 52.9°).

Total and relative energies from the optimized MP2/DZV(d,p) calculations for minima **13**, **15**, **16**, **17**, and **18** and transition structures **TS1**, **TS2**, **TS3**, and **TS4** are shown in Table 3. As expected, at all levels of theory, the acetylenic structures **15**, **16**, and **18** are the most stable species (energies: from 25.0 to 34.4 kcal/mol, relative to **13**). Regarding the transition structures, **TS1**, **TS2**, and **TS3** should be 14.7, 13.8, and 13.9 kcal/mol, respectively, less stable than **13** at the MP2/DZV(d,p) level. The inclusion of electron correlation [MP4/DZV(d,p)] lowers the activation barrier of **TS3** (12.9 kcal/mol) but increases that of **TS1** and **TS2** (16.5 and 15.7 kcal/mol, respectively). On the other hand, the extension of the basis set [MP2/TZV(2df+,2p)] increases all the barriers, and this effect is higher in **TS3** (18.4 kcal/mol) than in **TS1** and **TS2** (17.5 and 17.3 kcal/mol, respectively). Since electron correlation favors the stepwise procedure and the extension of the basis set favors the concerted mechanisms, it is quite possible that further improvements to the theory would almost equalize these barriers. However, continuum solvation effects could modify the activation energies. Thus, single-point calculations were carried out at the [MP2/DZV(d,p) + SCRFF] level. As shown in Table 3, the barriers of both concerted pathways are highly reduced (**TS1**, from 14.7 to 8.6 kcal/mol; **TS2**, from 13.8 to 8.6 kcal/mol), while that of the stepwise mechanism is only slightly reduced (**TS3**, from 13.9 to 12.5 kcal/mol). Thus, considering additive corrections to the MP2/DZV(d) energies, our best level of calculation indicates a preference for the concerted hydrogen migration and lithium iodide loss procedure [MP4/TZV(2df+,2p) +



**Figure 4.** MP4/TZV(2df+,2p) + SCRFF/MP2/DZV(d,p) relative energies (kcal/mol) for minima **13**, **15**, **16**, **17**, and **18** and transition structures **TS1**, **TS2**, **TS3**, and **TS4** (see Scheme 4).

SCRFF energy barriers, 13.3 (**TS1**), 14.0 (**TS2**), and 16.0 kcal/mol (**TS3**); see Table 3 and Figure 4]. In addition, **TS3** would be the limiting step in the nonconcerted mechanism since the relative energy calculated for **TS4** is lower [14.8 kcal/mol at the MP4/TZV(2df+,2p) + SCRFF level]. Finally, the calculated activation barrier from intermediate **17** to **TS4** is 2.3 kcal/mol [MP4/TZV(2df+,2p) + SCRFF level; from 12.5 to 14.8 kcal/mol], in good agreement with the previously described vinylidene-acetylene isomerization barrier in the gas phase.<sup>2</sup>

## Conclusions

1-Iodo-1-lithioethene was prepared from 1-iodoethene and LDA in THF. The lithiated derivative can be trapped by electrophiles, but it readily decomposes to acetylene. Since the decomposition process cannot be analyzed by experimental techniques, we carried out ab initio calculations. Three important conclusions can be derived from high-level calculations with inclusion of solvation [MP4/TZV(2df+,2p) + SCRFF level]. The first of these is that 1-iodo-1-lithioethene should be a monomer in a THF solution. Second, the concerted reaction pathway for hydrogen migration and lithium iodide  $\alpha$ -elimination procedures is energetically more favorable than the stepwise mechanism. Third, our calculations

indicate that the iodine atom is the group that leaves in both cis and trans hydrogen migration.

### Experimental Section

**General Methods.**  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on a Bruker ARX-300 spectrometer in  $\text{CDCl}_3$  with TMS as internal standard. Gas chromatography mass spectra were obtained on an HP G1800A apparatus. All solvents were purified and dried by standard procedures and freshly distilled prior to use.

**General Procedure.** To a solution of vinylmagnesium bromide (1 mmol, 1.0 mL of a commercial 1.0 M solution, Aldrich) in anhydrous THF (10 mL) was added 1.0 mmol of iodine (0.254 g), at 0 °C under an Ar atmosphere. After 5 min of stirring, the solution of 1-iodoethene was cooled at  $-100$  °C and filtered under an Ar atmosphere to eliminate the magnesium salts. The resulting solution was treated with 3 equiv of LDA (1.5 mL of a commercial 2.0 M solution, Aldrich), and after 2 min the corresponding electrophile was added to the reaction flask. The reaction was hydrolyzed and extracted with  $\text{Et}_2\text{O}$  ( $3 \times 25$  mL). The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and filtered, and the solvent removed under reduced pressure. The resulting products were purified by column chromatography (silica gel, hexane/ $\text{Et}_2\text{O}$ , 2:1).

**1-Iodo-1-deuterioethene (6).** The product was not isolated but was detected by GC-MS. GC-MS:  $m/z$  155 ( $\text{M}^+$ ).

**2-Iodo-1-propene (7).** The product was not isolated but was detected by GC-MS. GC-MS:  $m/z$  168 ( $\text{M}^+$ ).

**1,1-Diiodoethene (8):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.4 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  143.0, 51.3; GC-MS  $m/z$  280 ( $\text{M}^+$ , 35), 254 (15), 153 (65), 127 (100).

**1-Iodo-1-trimethylsilylethene (9):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.7 (d,  $J = 1.7$  Hz, 1H), 6.6 (d,  $J = 1.7$  Hz, 1H), 0.2 (s, 9H); GC-MS  $m/z$  226 ( $\text{M}^+$ , 14), 185 (73), 153 (13), 127 (35), 99 (18), 73 (100), 43 (59).

**1-Iodo-1-(tributylstannyl)ethene (10):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.0 (d,  $J = 1.8$  Hz, 1H), 6.8 (d,  $J = 1.8$  Hz, 1H), 1.5 (m, 6H), 1.3 (m, 6H), 1.1 (m, 6H), 0.9 (t, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  139.9, 112.5, 28.6, 26.8, 13.7 11.2; GC-MS  $m/z$  361 ( $\text{M}^+$ , 65), 247 (100), 177 (47), 121 (94), 57 (67).

**2-Iodo-1,1-diphenyl-2-propen-1-ol (11):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.8–7.3 (m, 10H), 6.1 (d,  $J = 2.1$  Hz, 1H), 5.7 (d,  $J = 2.1$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  142.0, 137.1, 127.8, 127.6, 127.4, 122.8, 83.7; GC-MS  $m/z$  336 ( $\text{M}^+$ , 2), 259 (1), 209 (5), 183 (60), 105 (82), 77 (100), 51 (40).

**(Tributylstannyl)ethyne (12):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.2 (s, 1H), 1.6 (m, 6H), 1.3 (m, 6H), 1.0 (m, 6H), 0.9 (t, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  96.8, 89.0, 28.9, 27.3, 13.5 11.0; GC-MS  $m/z$  259 ( $\text{M}^+$ , 95), 203 (57), 145 (100), 121 (26).

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