

## Note

## Synthesis of cyclohexadienylstannanes – Novel example of vinylic $S_{RN}1$ mechanism: A theoretical and experimental study

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## ABSTRACT

The reaction of trimethyltinsodium (**1**) with 1-(diethoxyphosphoryl)oxy-1,3-cyclohexadienes in liquid ammonia under irradiation affords the corresponding 1-trimethylstannylcyclohexadienes. We suggest that these reactions occur by an  $S_{RN}1$  mechanism. On the other hand, 2-(diethoxyphosphoryl)oxy-1,3-cyclohexadiene reacts very slowly towards **1** and the substitution product decomposes under the reaction conditions employed. Thus, structurally similar compounds do not behave in the same way under ET conditions. We suggest that this behavior is mainly due to differences in spin density of their radical anions, which affect their fragmentation rates. Our results are supported by computational calculations.

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### 1. Introduction

Although vinyl substrates are very unreactive toward nucleophilic substitution [1], multiple mechanisms for nucleophilic substitution reactions with vinylic systems ( $S_NV$ ) are known [1,2]. Mainly, the mechanistic route depends on structural features.

In contrast with the various examples reported in the literature related with ionic nucleophilic vinylic substitutions, there have been reported only few examples associated with vinylic radical nucleophilic substitutions ( $S_{RN}1$ ). It should be mentioned that not only the substrate structure but also the nature of the anion are essential factors for the prevalence of an  $S_{RN}1$  vinylic route over ionic pathways and it is necessary an appropriate combination of both [3–6]. Thus, only vinyl systems supporting, at least, a phenyl group afforded the substitution product by  $S_{RN}1$ . Moreover, when the anion basicity prevails over its reducing character the presence of both vinylic and allylic hydrogen(s) should be avoided. Recently, we have demonstrated that the diethoxyphosphoryloxy group can act as an excellent nucleofuge in the reaction of aryl phosphate esters [7] as well as vinyl diethyl phosphate esters (vinyIDEP) [4], with trimethyl- and triphenyltin anions in liquid ammonia under irradiation, and that these reactions take place through an  $S_{RN}1$  mechanism. Because of the reducing character of organotin anions

[8] the  $S_{RN}1$  mechanism prevails over ionic routes even with substrates containing vinylic and allylic hydrogen(s).

The synthesis of vinylstannanes from vinyIDEP is of interest not only from a mechanistic point of view but also as an alternative route [9] for the synthesis of vinylstannanes starting from carbonylic substrates.

We now report the experimental results and a theoretical study of the reaction of cyclohexadienylDEPs with **1** in liquid ammonia. As far as we know this reaction represents the first example of a vinylic  $S_{RN}1$  route without the presence of aryl groups attached to the vinylic system.

The proposed mechanism is a chain process in which radicals and radical anions are involved as intermediates, as it is illustrated in Scheme 1 [10].

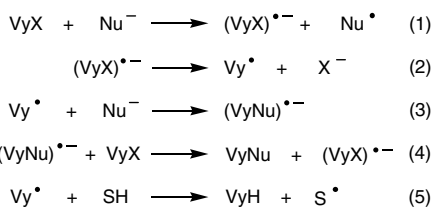
In few systems this chain process is initiated by spontaneous ET from the nucleophile to the substrate forming the vinylic radical anion (Eq. (1)) [10]. Stimulation by UV light or by  $Fe^{2+}$  has been recently applied in vinylic  $S_{RN}1$  reactions [3–5]. It should be noted that the coupling with the nucleophile (Eq. (3)) is not the only reaction that vinyl radicals can undergo: hydrogen atom transfer from the solvent is one of the most important side reactions (Eq. (5)). This competitive reaction is diminished by using liquid ammonia as solvent [10].

A phenyl group attached to a vinylic carbon increases the stability of the  $\pi$ -system and, particularly, lowers its LUMO, being this beneficial to the  $S_{RN}1$  substitution since this increases the electron affinity of the substrate [11]. Taking into account the energy of the LUMO MO in cyclohexadienyl systems [12] and the excellent nucleofuge character of a diethoxyphosphoryloxy group, we

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Scheme 1. Vinylic  $S_{RN}1$  mechanism.

considered that cyclohexadienylDEPs may possibly be adequate substrates for the predominance of an  $S_{RN}1$  mechanism. Thus, we started the study of the reaction of 1- (**2a**) and 2-(diethoxyphosphoryl)oxy-1,3-cyclohexadiene (**2e**) with **1** in liquid ammonia. The results obtained are summarized in Table 1. The results presented are average yields of three to four runs.

Significant differences were found in both reactions. Thus, **2a** reacted with **1**, by a photostimulated reaction, rendering 1-trimethylstannyl-1,3-cyclohexadiene (**3a**, 27%) together with starting material, not quantified (entry 1). We found that no substitution product was formed when the reaction was carried out in the dark, recovering almost quantitatively the starting substrate. These results indicate the occurrence of a photo electron-induced substitution route. In order to improve the yield of **3a**, we carried out a reaction using an excess of **1**. An increase in the **1/2a** ratio (5/1) produced a complex reaction mixture from which neither **3a** nor **2a** could be detected.

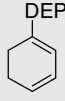
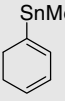


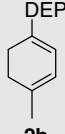
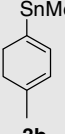
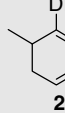
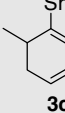
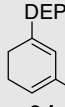
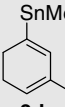
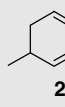
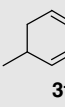
Otherwise, in the reaction of isomer **2e** and **1** (1/1.2 ratio), even after 8 h under irradiation, no substitution product, i.e., 2-trimethylstannyl-1,3-cyclohexadiene (**3e**) was detected and the starting substrate was recovered in 85% (entry 2). It should be mentioned that some unidentified stannylated products were detected (CG/MS). When the reaction was carried out in the presence of an excess of **1** (**1/2e**, 5/1 ratio), once more a complex mixture of unidentified products was obtained without the presence of **2e**.

We also found that there is no reaction between either 1-(diethoxyphosphoryl)oxy-4-methyl-1,3-cyclohexadiene (**2b**) or 1-(diethoxyphosphoryl)oxy-6-methyl-1,3-cyclohexadiene (**2c**) and **1** in the dark (6 h) and the unreacted precursors were recovered in each case. Nevertheless, under irradiation in the same time period, the substitution products 1-trimethylstannyl-4-methyl-1,3-cyclohexadiene (**3b**) and 1-trimethylstannyl-6-methyl-1,3-cyclohexadiene (**3c**) were obtained in 44% and 46% yields, respectively (entries 3 and 5). It should be mentioned that both photostimulated reactions were largely inhibited by addition of *p*-dinitrobenzene (*p*-DNB) (10%), a well-known radical anion trap and inhibitor of the  $S_{RN}1$  propagation cycle (entries 4 and 6) [3,10]. These results clearly indicate that these substrates also react with **1** by the  $S_{RN}1$  mechanism.

In addition, we have carried out the synthesis of 1-(diethoxyphosphoryl)oxy-3-methyl-1,3-cyclohexadiene (**2d**). Unfortunately, **2d** was difficult to purify because it decomposed either on column chromatography or by distillation. Anyway, we carried out the reaction of **2d**, without previous purification, with **1**. Meanwhile, the reaction carried out in the dark (6 h) was negative recovering the starting material, under irradiation the corresponding 1-trimethylstannyl-3-methyl-1,3-cyclohexadiene (**3d**) was detected as principal product, as characterized by GC/MS (entry 7). When we carried out the reaction of 2-(diethoxyphosphoryl)oxy-5-methyl-1,3-cyclohexadiene (**2f**) with **1**, no substitution product was detected even after 8 h under irradiation and the starting substrate was almost completely recovered (88%) together with small amounts of unidentified stannylated compounds (entry 8).

Table 1

Photostimulated reactions of (diethoxyphosphoryl)oxy-1,3-cyclohexadienes with  $\text{Me}_3\text{SnNa}$  (**1**) in liquid ammonia<sup>a</sup>

Entry	Substrate	Time (h)	Product	Yield (%) <sup>b</sup>
1	 <b>2a</b>	6	 <b>3a</b>	27
2	 <b>2e</b>	8	 <b>3e</b>	0 <sup>c</sup>
3	 <b>2b</b>	6	 <b>3b</b>	44 <sup>d</sup>
4	<b>2b<sup>e</sup></b>	6	<b>3b</b>	12
5	 <b>2c</b>	6	 <b>3c</b>	46 <sup>d</sup>
6	<b>2c<sup>e</sup></b>	6	<b>3c</b>	15
7	 <b>2d</b>	6	 <b>3d</b>	49 <sup>d,f</sup>
8	 <b>2f</b>	8	 <b>3f</b>	0 <sup>g</sup>

<sup>a</sup> Substrate/**1** molar ratio 1/1.2; [Substrate] = 5.45 mM. No substitution products were detected without irradiation.

<sup>b</sup> Isolated yield unless otherwise stated.

<sup>c</sup> 85% of substrate recovered.

<sup>d</sup> 2–4% of the reduced cyclohexadiene parent compound.

<sup>e</sup> 10% *p*-DNB added.

<sup>f</sup> GC/MS, relative percentage in the crude product.

<sup>g</sup> 88% of substrate recovered.

It should be mentioned that in experiments 3, 5 and 7, together with the corresponding substitution products **3b**, **3c** and **3d** there were detected the related reduction products, i.e., 1-methyl-1,3-cyclohexadiene (**4b**), 5-methyl-1,3-cyclohexadiene (**4c**) and 2-methyl-1,3-cyclohexadiene (**4d**) in ca. 2–4%. When these reactions were carried out in the dark no reduction products were detected. We inferred that their presence may be due to the competitive hydrogen abstraction reaction by the radical intermediate from ammonia (Scheme 1, Eq. (5)).

Taking into account the possibility that the 2-trimethylstannyl-1,3-cyclohexadienes are being formed but are not isolable under the reaction conditions employed, as suggested but one referee, we carried out a series of reactions, at shorter times, employing **2e** as starting material. The products mixtures were analyzed by GC/MS and we informed the relative percentages obtained. When the photostimulated reaction between **2e** and **1** was quenched at

30 min, compound **3e** was detected in 6% yield, together with starting material (92%) and traces of unidentified stannylated compounds (2%). The mixtures obtained under similar conditions but at longer reaction times (1 h and 2 h, respectively) showed that meanwhile the yield of compound **3e** decreased (1.5% and none, respectively) the yield of the unidentified stannylated compounds increased (11.5% and 13%, respectively); in both cases the starting material was recovered in about 87%. It should be mentioned that the reaction of **2e** and **1** in the dark, after 1 h, showed the absence of **3e** as well as of the unidentified stannylated compounds, recovering the starting substrate. These results indicate that there is a photostimulated electron transfer (PET) between **2e** and **1** rendering product **3e**, which decomposed under the reaction conditions employed. Moreover, the results point out that this PET reaction is inhibited with time (perhaps due to the presence of the decomposition products?) and similar mixtures were obtained after either 2h or 8 h of reaction.

In order to compare the reactivity of both **2a** and **2e** towards **1** we carried out the photostimulated reaction (30 min) of a mixture of **2a** (1 mmol) and **2e** (1 mmol) with **1** (1.2 mmol). This competition reaction showed, as expected, that the relative reactivity of **2a** is higher than **2e** towards **1**. Thus, by CG/MS we detected **3a** and **3e** in a ratio of 5/1, together with large amounts of both starting substrates and traces of unidentified stannylated compounds.

From the above mentioned results it is evident that, in the systems studied, the substitution products were formed through an  $S_{RN}1$  mechanism: the reactions did not take place in the dark and their rates were significantly reduced when *p*-DNB was added. It is also evident that the incidence of the  $S_{RN}1$  mechanism appears to be dependent on some structural features of the starting substrate. Meanwhile compounds supporting the DEP group on carbon-2 react very slowly towards **1** and the substitution product decomposes under the reaction conditions employed, substrates supporting the nucleofuge on carbon-1, did afford the substitution products in rather low to good yields.

These results were unexpected since as the  $\pi^*$  MO energy is not likely to be affected by the position of the DEP group in the ring, all the substrates would have similar electron affinities making feasible their single-electron reduction (Scheme 1, Eq. 1)). Thus, we inferred that the dissimilar reactivity observed would be probably due to differences in the fragmentation rates of the radical anions formed (Scheme 1, Eq. 2). Moreover, we considered that the fact that no reduction products (coming from the abstraction of hydrogen from ammonia by the vinyl radical) were found in the reaction of either **2e** or **2f** with **1**, was a signal that step 2 did not take place.

In order to obtain information on this matter we theoretically study the neutrals and the radical anions of compounds **2a'** and **2e'**, the dimethoxyphosphoryloxy (DMP) analogs of **2a** and **2e**. The calculations were performed with the B3LYP [13] DFT [14] functional and the 6-31+G<sup>\*</sup> basis set known to be an appropriate methodology for the theoretical study of the electronic and geometric properties of radical anions [15]. Some of the relevant parameters calculated for the system are presented in Table 2. The LUMO MOs of the neutrals have  $\pi$  symmetry and they are, as expected, similar in energy (−1.049 eV and −1.081 eV for **2a'** and **2e'**, respectively) [16]. The unpaired electron of both radical anions locates in the butadienyl  $\pi$  system. In going from the neutrals to the radical anions elongation of both C=C double bonds and shortening of the C<sub>sp2</sub>–C<sub>sp2</sub> single bond are the main geometric modifications of the  $\pi$  system (Table 2). Also C–O elongation and O–P(O) shortening occur along the electron capture.

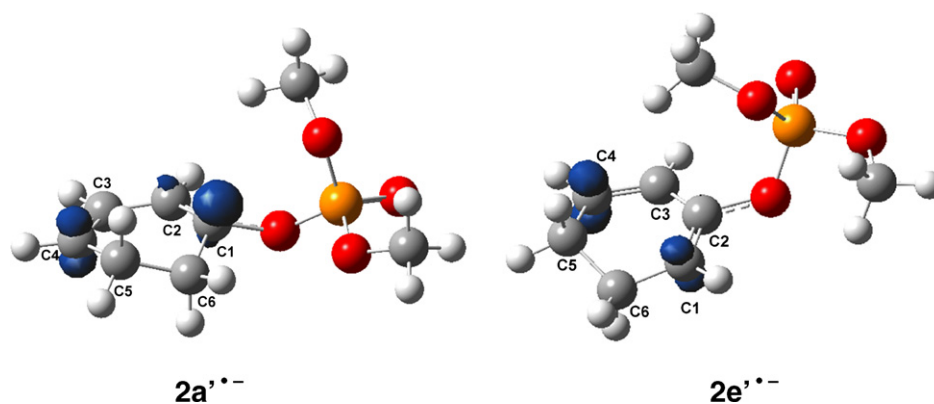
The C–C bond distances of the butadienyl systems of these intermediates correlate with the localization of the unpaired electron mainly at the terminal carbons of the butadienyl  $\pi$  system of both radical anions with a considerably low density at the C<sub>ipso</sub> to the DMP group in **2e'**<sup>•−</sup>. The unpaired spin distribution of both intermediates is shown in Fig. 1. This spin density does not modified when methanol is included in the calculation of both species to model a polar protic solvent within a continuum model.

**Table 2**  
B3LYP/6-31+G<sup>\*</sup> main geometric and electronic properties of **2a'**, **2e'** and their radical anions

Compound	Bond distances (Å)						LUMO (eV)	AEA <sup>a</sup> (eV)	Spin density <sup>b</sup>
	C <sub>4</sub> –C <sub>3</sub>	C <sub>3</sub> –C <sub>2</sub>	C <sub>2</sub> –C <sub>1</sub>	C–O	O–P(O)	P=O			
<b>2a'</b>	1.345	1.466	1.341	1.399	1.612	1.478	−1.0495	−0.135	
<b>2a'</b> <sup>•−</sup>	1.388	1.419	1.409	1.489	1.572	1.491			0.46 (0.40)
<b>2e'</b>	1.345	1.465	1.341	1.402	1.617	1.478	−1.0816	−0.082	
<b>2e'</b> <sup>•−</sup>	1.405	1.410	1.385	1.450	1.596	1.484			0.04 (0.09)

<sup>a</sup> Adiabatic electron affinity [AEA =  $E_{RDMP} - E_{RDMP^{\bullet-}}$  (zero-point energy corrected)].

<sup>b</sup> Mulliken spin density at C<sub>ipso</sub> to the DMP leaving group. NBO spin density within parentheses.



**Fig. 1.** Gas phase B3LYP/6-31 + G<sup>\*</sup> spin density of **2a'**<sup>•−</sup> and **2e'**<sup>•−</sup>.

**Table 3**

B3LYP/6-31+G\* energetic and main geometric properties of transition states for dissociation of  $2a'^-$  and  $2e'^-$

	$2a'^-$	$2e'^-$
$\Delta E$ (RDMP $^- \rightarrow R + DMP^-$ ) <sup>a</sup>	-3.22	-1.88
$E_a$ <sup>a</sup>	3.9	7.2
Transition state		
Bond distances (Å)		
C–O	1.807	1.768
O–P(O)	1.545	1.560
P(O)	1.500	1.492
C <sub>1</sub> –C <sub>2</sub>	1.383	1.369
C <sub>2</sub> –C <sub>3</sub>	1.441	1.433
C <sub>3</sub> –C <sub>4</sub>	1.367	1.365
Charges <sup>b</sup>		
at oxygen: C <sub>olefinic</sub> –OP	-0.69	-0.68
Me–OP	(-0.98)	(-0.97)
(O)P	-0.62	-0.63
	(-0.86)	(-0.86)
At phosphorous	-0.85	-0.81
	(-1.15)	(-1.11)
	2.13	2.18
	(2.60)	(2.61)
Spin density <sup>b</sup>	0.57	0.41
at C (C–OP)	(0.54)	(0.41)

<sup>a</sup> kcal/mol.

<sup>b</sup> Mulliken analysis. NBO analysis within parentheses.

The spin distribution calculated can *a priori* be taken as an indication of a more facile dissociation for type  $2a'^-$  intermediates. It has been shown that the nodal properties of the MO that hosts the unpaired electron and the unpaired spin density distribution are relevant factors for the cleavage of radical anions [17]. This reaction is possible through an intramolecular dissociative ET (intra-DET) from the  $\pi$  system to the  $\sigma^*$  C–O bond. The potential energy surfaces (PES) evaluated for the dissociation show this intra-DET taking place adiabatically for both intermediates. The energetic and main geometric properties of the transition states (TS) evaluated are presented in Table 3. As shown in Table 3, and as expected from the low spin density at the C<sub>ipso</sub> to its leaving group, radical anion  $2e'^-$  is the one that dissociates with higher activation energy (7.2 kcal/mol vs 3.9 kcal/mol for  $2a'^-$ ). Moreover, similar activation energy is obtained by evaluation of the intra-DET under a continuum model solvent (It has to be kept in mind that the reactions occur in liquid NH<sub>3</sub> at -33 °C). Also, despite both radical anions dissociate exothermically, the cleavage of  $2e'^-$  occurs with lower exothermicity (see Table 3). A schematic profile of both PES is presented in Fig. 9 of the Supplementary Information.

We thought that these theoretical results support, without doubts, the experimental results. This system is an interesting example of isomers whose radical anions dissociate with similar thermochemistry but different activation energy due to differences in their SOMOs composition despite they have similar energy difference between the  $\pi$  and  $\sigma^*$  MOs involved in the intra-DET [17].

In general, the scope for a vinylic S<sub>RN</sub>1 route is rather limited due to severe competitions by ionic routes. We informed now the first example of vinylic S<sub>RN</sub>1 mechanism without the incidence of an aryl moiety attached to the vinylic system. We also informed another example that shows that structurally similar compounds do not behave in the same way under ET conditions and that this behavior is mainly due to differences in spin density of their radical anions.

## 2. Experimental

### 2.1. General

<sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectra were recorded on a Bruker ARX 300 spectrometer (300 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C, 112 MHz

for <sup>119</sup>Sn) using CDCl<sub>3</sub> as solvent. Chemical shifts ( $\delta$ ) are reported in ppm from TMS with solvent resonance as the internal standard (<sup>1</sup>H:  $\delta$  7.27 ppm and <sup>13</sup>C:  $\delta$  77.0 ppm), or Me<sub>4</sub>Sn (<sup>119</sup>Sn). Coupling constants (*J*) are given in Hz. NMR spectra were recorded at 25 °C. Mass spectra were obtained with a GC/MS instrument (HP5-MS capillary column, 30 m, 0.25 mm i.d.  $\times$  0.25  $\mu$ m) equipped with 5972 mass selective detector operating at 70 eV (EI). GC analyses were carried out on a Shimadzu GC-9A chromatograph, equipped with a flame-ionization detector and a 2 m packed column (1.5% OV17 9A SUS Chrom 103 80/1000). Heating program: initial temperature: 50 °C, initial time: 5 min, speed of heating: 5 °C/min and final temperature: 250 °C. Retention times (*t<sub>R</sub>*) are given in minutes.

### 2.2. Photostimulated reaction in liquid ammonia

Irradiation was conducted in a reactor equipped with four 250 W UV lamps emitting maximally at 350 nm water-cooled. The following procedure of the reaction of 1-(diethoxyphosphoryl)oxy-1,3-cyclohexadiene (**2a**) with **1** is representative of all. 90 mL of sodium-dried ammonia were condensed into a three-necked, round-bottomed Pyrex flask equipped with a cold finger condenser, a nitrogen inlet and a magnetic stirrer. Me<sub>3</sub>SnCl (0.120 g, 0.6 mmol) and sodium metal (0.033 g, 1.44 mg atom) were added. When the blue color disappeared, **2a** (0.116 g, 0.50 mmol) was added and then the mixture irradiated with stirring for 6 h. The reaction was quenched by adding ammonium chloride, and ammonia was allowed to evaporate. The residue was treated with water and then extracted three times with ether (25 mL). Ether extracts were washed with brine and dried over anhydrous MgSO<sub>4</sub>. Ether removal under reduced pressure followed by column chromatography over silica gel 60-120 employing *n*-hexane as eluent, afforded cyclohexadienylstannane **3a** as a colourless oil (0.033 g, 27%).

Cyclohexadienylstannanes were difficult to isolate due to protonolysis and can be isolated by chromatography only if the silica-gel is pretreated with triethylamine and/or the eluent contains triethylamine (1%).

## 3. Identification of the products

### 3.1. 1-Trimethylstannyl-1,3-cyclohexadiene (**3a**)

Colourless oil; *t<sub>R</sub>*: 10.9 min; <sup>1</sup>H NMR:  $\delta$  (ppm) 0.15 (9H, s, <sup>2</sup>J<sub>H<sub>Sn</sub></sub> = 52.0/54.4 Hz), 2.90–2.18 (4H, m), 5.77–5.64 (2H, m), 5.96 (1H, m, <sup>3</sup>J<sub>H<sub>Sn</sub></sub> = 67.4 Hz); <sup>13</sup>C NMR  $\delta$  (ppm) -9.9 (CH<sub>3</sub>Sn, <sup>1</sup>J<sub>C<sub>Sn</sub></sub> = 328.6/343.9 Hz), 22.7 (CH<sub>2</sub>, <sup>3</sup>J<sub>C<sub>Sn</sub></sub> = 27.6 Hz), 28.4 (CH<sub>2</sub>, <sup>2</sup>J<sub>C<sub>Sn</sub></sub> = 38.2 Hz), 125.0 (CH, <sup>2</sup>J<sub>C<sub>Sn</sub></sub> = 61.0 Hz), 127.1 (CH, <sup>4</sup>J<sub>C<sub>Sn</sub></sub> = 14.3 Hz), 134.2 (CH, <sup>3</sup>J<sub>C<sub>Sn</sub></sub> = 29.9 Hz), 142.5 (C, <sup>1</sup>J<sub>C<sub>Sn</sub></sub> = 452.5/473.0 Hz); <sup>119</sup>Sn NMR  $\delta$  (ppm) -33.6; **MS**: *m/z* = 244 (M<sup>+</sup>, 6%), 229 (47), 199 (4), 165 (36), 151 (18), 135 (34), 120 (17), 79 (100), 51 (8). Anal. Calc. for C<sub>9</sub>H<sub>16</sub>Sn: C, 44.52; H, 6.64. Found: C, 44.61; H, 6.53%.

### 3.2. 1-Trimethylstannyl-4-methyl-1,3-cyclohexadiene (**3b**)

Colourless oil; *t<sub>R</sub>*: 13.5 min; <sup>1</sup>H NMR:  $\delta$  (ppm) 0.12 (9H, s, <sup>2</sup>J<sub>H<sub>Sn</sub></sub> = 51.8/54.6 Hz), 1.79 (3H, s), 2.04 (2H, t, *J* = 9.5 Hz), 2.29 (2H, t, *J* = 9.5 Hz), 5.67 (1H, m), 6.04 (1H, m, <sup>3</sup>J<sub>H<sub>Sn</sub></sub> = 66.4 Hz); <sup>13</sup>C NMR:  $\delta$  (ppm) -9.9 (CH<sub>3</sub>Sn, <sup>1</sup>J<sub>C<sub>Sn</sub></sub> = 328.1/343.3 Hz), 23.7 (CH<sub>3</sub>), 28.5 (CH<sub>2</sub>, <sup>3</sup>J<sub>C<sub>Sn</sub></sub> = 28.8 Hz), 29.1 (CH<sub>2</sub>, <sup>2</sup>J<sub>C<sub>Sn</sub></sub> = 43.3 Hz), 119.9 (CH, <sup>2</sup>J<sub>C<sub>Sn</sub></sub> = 61.6 Hz), 134.7 (CH, <sup>3</sup>J<sub>C<sub>Sn</sub></sub> = 31.2 Hz), 136.9 (C, <sup>4</sup>J<sub>C<sub>Sn</sub></sub> = 12.4 Hz), 138.2 (C); <sup>119</sup>Sn NMR:  $\delta$  (ppm) -32.7; **MS**: *m/z* = 258 (M<sup>+</sup>, 4%), 243 (3), 213 (5), 165 (4), 151 (27), 135 (38), 120 (26), 93 (100), 77 (41), 65 (9), 51 (18); Anal. Calc. for C<sub>10</sub>H<sub>18</sub>Sn: C, 46.76; H, 7.06. Found: C, 46.63; H, 6.98%.



### 3.3. 1-Trimethylstannyl-6-methyl-1,3-cyclohexadiene (3c)

Colourless oil;  $t_R$ : 12.4 min;  $^1\text{H}$  NMR  $\delta$  (ppm) 0.16 (9H, s,  $^2J_{\text{HSn}} = 51.9/54.0$  Hz), 1.02 (3H, d,  $J = 7.1$  Hz), 1.98 (1H, m), 2.29 (1H, m), 2.41 (1H, m), 5.74 (1H, m), 5.85 (1H, m), 6.03 (1H, m,  $^3J_{\text{HSn}} = 66.1/69.2$  Hz);  $^{13}\text{C}$  NMR  $\delta$  (ppm)  $-8.8$  ( $\text{CH}_3\text{Sn}$ ,  $^1J_{\text{CSn}} = 325.3/341.9$  Hz), 20.4 ( $\text{CH}_3$ ,  $^3J_{\text{CSn}} = 16.0$  Hz), 30.9 ( $\text{CH}_2$ ,  $^3J_{\text{CSn}} = 24.6$  Hz), 33.1 (CH,  $^2J_{\text{CSn}} = 35.8$  Hz), 124.2 (CH,  $^2J_{\text{CSn}} = 59.2/62.4$  Hz), 126.2 (CH,  $^4J_{\text{CSn}} = 14.1$  Hz), 133.1 (CH,  $^3J_{\text{CSn}} = 29.9$  Hz), 149.1 (C);  $^{119}\text{Sn}$  NMR  $\delta$  (ppm)  $-32.1$ ; MS:  $m/z = 258$  ( $\text{M}^+$ , 2%), 243 (42), 213 (6), 165 (100), 151 (30), 135 (51), 120 (24), 93 (79), 77 (40), 65 (11), 51 (7); Anal. Calc. for  $\text{C}_{10}\text{H}_{18}\text{Sn}$ : C, 46.76; H, 7.06. Found: C, 46.69; H, 6.99%.

### 3.4. 1-Trimethylstannyl-3-methyl-1,3-cyclohexadiene (3d)

$t_R$ : 14.0 min; MS:  $m/z = 258$  ( $\text{M}^+$ , 9%), 243 (48), 213 (4), 165 (45), 151 (23), 135 (30), 120 (16), 93 (100), 77 (37), 65 (9), 51 (7).

### 3.5. General procedure for the synthesis of (diethoxyphosphoryloxy)-1,3-cyclohexadienes

The method used was essentially that described by Rubottom *et al* [18], trapping the enolate with diethylchlorophosphate.

### 3.6. Computational procedure

The calculations were performed with GAUSSIAN 03 [19] and the Jaguar programs [20]. The initial conformational analysis of compounds **2a'** and **2e'** was performed with the semiempirical AM1 method. The geometry of the most stable conformers thus obtained was used as starting point for the B3LYP studies of their radical anions. The exploration of the potential surface for the dissociation of the radical anions was carried out varying the selected coordinate ( $\text{C}_{\text{olefinic}}\text{-OP}$  bond distance) with full optimization for the remainder degrees of freedom. The characterization of all stationary points was done by Hessian matrix calculations of geometries obtained with full optimization for a minimum and by using the TS methodology for a transition state. The Berny analytical gradient optimization routines were used. The requested convergence on the density matrix was  $10^{-9}$  atomic units, the threshold value for maximum displacement was 0.0018 Å, and that for the maximum force was 0.00045 Hartree/Bohr. In all the cases, the spin contamination along the whole fragmentation paths was negligible. The zero point energy corrections were made at the 6-31+G\* level for the thermodynamic quantities. The energies in solution were obtained with full geometry optimization within the Tomasi's polarized continuum model (PCM) [21] as implemented in GAUSSIAN 03. Compounds **2a'** and **2e'** have negative electron affinities (EA); for these species the conventional valence anion state has been characterized as the radical anion. The basis sets and methodologies have been already tested and expected to yield the right anion state, reproducing EAs within few tenths of eV [15]. The natural bond orbital (NBO) analyses were performed using the NBO program as implemented in GAUSSIAN 03 [22]. The figures were built with the GAUSSVIEW program using a spin density isosurface of 0.02. The potential surfaces evaluated in the presence of methanol (dielectric constant = 33.62, probe radius ( $r_p$ ) = 2.00196 Å) to model a protic solvent were performed with the Jaguar program [20] and the continuum solvent model [23] therein implemented. The stationary points on this potential surface were located by following the procedure outlined for similar studies in the gas-phase.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.018.

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