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THE STRUCTURE OF THE INTERMEDIATE RADICAL IN THE HYDROSTANNATION OF PHENYLACETYLENE

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ABSTRACT

Hydrostannation of phenylacetylene, both thermal and free radical catalyzed, results in a Z/E mixture of β-(trialkylstannyl)styrenes with the Z isomer the kinetic product and the E isomer the thermodynamic product. The stereoselectivity of the kinetic product is a result of the structure of the intermediate vinyl radical. Semi-empirical calculations using the PM3 Hamiltonian indicate the radical species formed in the

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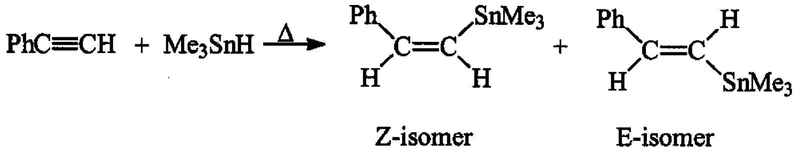
addition of trisubstituted tin hydride across the triple bond of phenylacetylene leads to an intermediate with an sp-geometry at the radical carbon. The reaction proceeds to form the Z product for a number of reasons. First, there is a small barrier to tin group rotations hindering hydrogen abstraction *syn* to tin. There is a nearly unhindered reaction plane *anti* to tin. A trialkyltin hydride is quite sizable and does not readily fit in the reaction plane necessary to form the E product. Finally, the value of the Singly Occupied Molecular Orbital (SOMO) is highest where radical attack occurs. The value of the SOMO is highest *anti* to the tin group in the sp-structures. Experimentally, the kinetic product isomerizes and the thermodynamically more stable E isomer is isolated.

INTRODUCTION

Organostannanes are an increasingly indispensable component of the synthetic organic chemist's repertoire of reagents. Vinylstannanes in particular have proven to be useful synthons[1], thus an understanding of their structure is necessary for the reliable prediction of regioselectivity and stereoselectivity in their synthesis. Hydrostannation, a common method by which vinylstannanes may be efficiently prepared, involves addition of a trisubstituted tin hydride across a carbon-carbon triple bond[2]. In 1960, Fulton[3] observed that hydrostannation of phenylacetylene by trimethylstannane resulted in two isomeric products: (Z)-β-(trimethylstannyl)styrene, the product of *anti* addition, and (E)-β-(trimethylstannyl)styrene, the product of *syn* addition (Eq. 1).



(1)

Subsequent studies confirmed that free radical catalyzed hydrostannation of terminal triple bonds involves *anti* addition to give the Z isomer as the kinetic product, followed by isomerization, induced by tin radicals, to the more stable E isomer[2,4–7]. In the above example, with phenylacetylane and trimethylstannane, the thermodynamic equilibrium E/Z ratio is about 14 as determined by gas chromatography[2]. The accepted mechanism for a free-radical initiated hydrostannation involves attack of the trisubstituted tin radical at the unsubstituted position of a terminal alkyne to yield a potentially resonance stabilized vinyl radical. H-atom abstraction from the stannane results in predominantly the Z product. As expected, the reaction is accelerated by free radical catalysts such as AlBN and retarded by free radical inhibitors such as galvinoxyl.

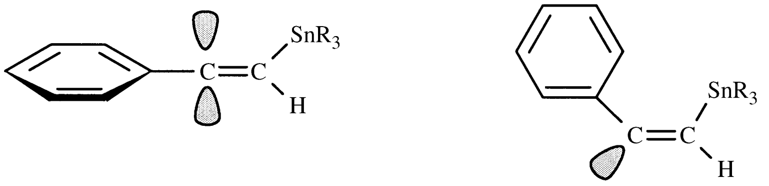
We wish to interpret the stereoselectivity of this reaction, and report here semi-empirical calculations performed on the intermediate vinyl radical formed from free radical initiated hydrostannation.

Theoretical Methodology

Equilibrium geometries were computed at the SCF level using the PM3 Hamiltonian implemented in the semi-empirical[8–10] portion of Spartan[11], using an Unrestricted Hartree-Fock (UHF) wavefunction. Two geometries were considered as possible intermediates in the radical reaction (Figure 1).

Structure (**1**) has sp-hybridization at the radical carbon, with the p-orbital on the radical carbon conjugated with the aryl group. The second structure (**2**) is sp^2-hybridized at the radical carbon and allows conjugation between the aryl and vinyl π systems. Both the E and Z form of (**2**) were considered. In each case, optimizations were begun from starting geometries having the phenyl group coplanar with, and perpendicular to, the vinyl system. The dihedral angle (τ) is denoted by 0.0° and 90° (Figure 2), respectively. Vibrational analyses were performed on all optimized structures to ensure their position as minima on the potential energy surface.

An initial geometry optimization was carried out on (**1**) and (**2**). In these calculations the dihedral angle, τ, formed by the phenyl carbon,



(1) **(2)**

Figure 1. Possible intermediate radical structures formed in the reaction of phenylacetylene with the trialkyltin radical.

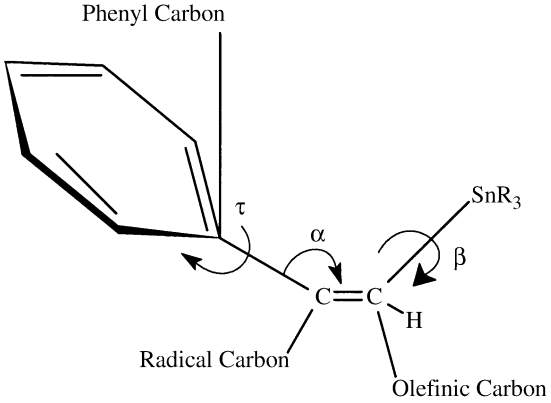
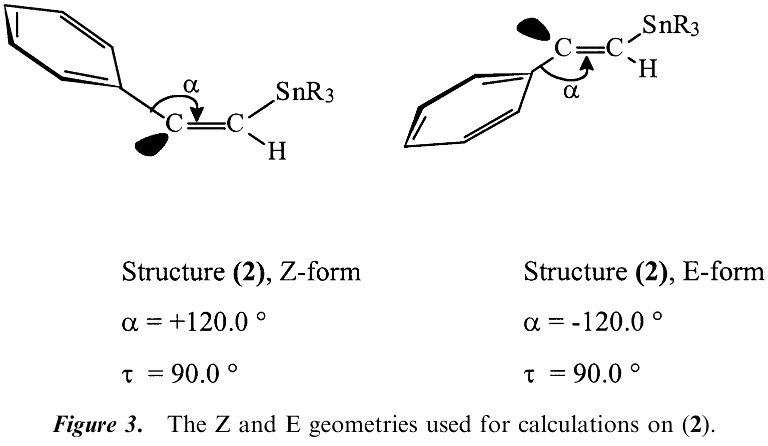


Figure 2. Nomenclature schematic for structures (**1**) and (**2**).

double bonded carbons and tin atom was set to 0.0° (phenyl ring in the plane with the carbon-carbon double bond, Figure 2).

A SCF geometry optimization was then performed. The same dihedral angle was set to 90.0° (phenyl ring out of plane with the carbon carbon double bond, Figure 2), and optimized.

After the structures (**1**) and (**2**) were optimized and found to be minima, a single point energy was computed for the E and Z forms of structure (**2**). These structures were built starting from the optimized geometry of (**1**) with $\tau = 90.0°$. The bond angle, α in Figure 3 (formed by the



Structure (**2**), Z-form
$\alpha = +120.0°$
$\tau = 90.0°$

Structure (**2**), E-form
$\alpha = -120.0°$
$\tau = 90.0°$

Figure 3. The Z and E geometries used for calculations on (**2**).

phenyl carbon, radical carbon and olefinic carbon) set to +120.0° [Z-form of (**2**)] and −120.0° [E-form of (**2**)].

For structures (**1**) and (**2**) the dihedral angle, β, formed by the double bonded carbons, tin atom and the first carbon of an aliphatic group on tin was set to 0.0° and constrained (Figures 2 and 4). The structure was optimized, and the procedure repeated for $\beta = 60°$ (*i.e.* tri-substituted tin group was rotated 60.0°).

The above procedures were performed with tin trisubstituted with methyl, ethyl, propyl, and butyl groups.

RESULTS AND DISCUSSION

The PM3 operator has been successfully parameterized for tin-containing compounds[11], and semi-empirical calculations are well-established as useful and reliable tools for structure analysis[12–15]. The $\langle S^2 \rangle$ value for doublet radicals should be 0.75. In these calculations we obtained a value of 1.3, indicating reasonable levels of spin contamination. Considering we are seeking a qualitative explanation of experimental results, we deemed these values acceptable. All optimizations resulted in reasonable geometries for the organotin compounds studied (*i.e.*, $r_{C=C} \sim 1.3–1.4$ Å, $r_{C\text{-}Sn} \sim 2$ Å) and indicated a consistent match with experimental facts. Attempts to optimize either of the structures in Figure 3 failed, with the initial geometries always collapsing to (**1**) in the optimization procedure. Thus, we chose to set α in Figures 2 and 3 to a typical value for an olefinic system (120.0 °) and then calculate single point energies to use for comparisons with structure (**1**).

The data in Table I indicates the intermediate radical (substitution, **R**, on the tin atom: methyl, ethyl, propyl and butyl) favors sp-hybridization of (**1**) by approximately 14–15 kcal mol^{-1} compared to the Z isomer of

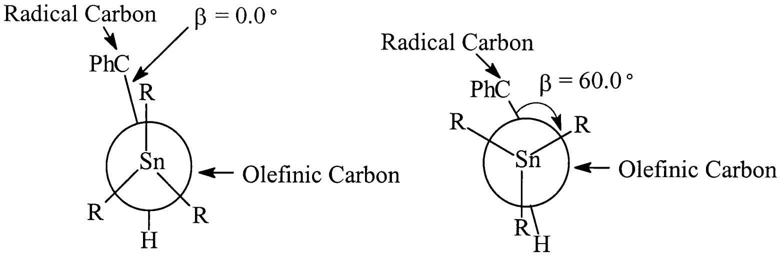


Figure 4. Newman projection schematic for dihedral angle β.

Table I. Relative Energies of Radicals (**1**) a–d and (**2**) a–d

	α	ΔH_f°(kcal mol^{-1})	ΔE **2-1** (kcal mol^{-1})
Sructure (**1**) Group on tin			
a. methyl	−3.66	66.40	
b. ethyl	−2.13	55.09	
c. propyl	−1.20	40.02	
d. butyl	−1.23	24.11	
Sructure (**2**), Z form Group on tin			
a. methyl	+120.00	81.68	15.28
b. ethyl	+120.00	70.29	15.20
c. propyl	+120.00	54.87	14.85
d. butyl	+120.00	38.68	14.57
Sructure (**2**), E form Group on tin			
a. methyl	−120.00	87.69	21.29
b. ethyl	−120.00	77.03	21.94
c. propyl	−120.00	62.74	22.72
d. butyl	−120.00	No convergence	(–)

structure (**2**). There are two possible reasons for the large difference in energy between structures (**1**) and (**2**): (**1**) electronic delocalization of the radical into the aromatic ring, and (**2**) a *gauche* interaction between the aryl ring and the trialkyltin group. We feel the former consideration is more important than the latter for the following reasons. First, delocalization of the radical electron into the aromatic ring is known to stabilize the planar benzyl radical by approximately 11–14 kcal mol^{-1} relative to its non-planar conformer[14,15].

Second, if a *gauche* interaction is responsible for the enhanced stability then we anticipate the energy difference between (**1**) and (**2**) would increase as (**2**) would become less stable from bulky steric interactions. The fact that the energy difference with increasing steric bulk actually decreases is convincing evidence that the latter argument is not valid, or that it is valid but that the effect is conveniently the same for both (**1**) and (**2**), a coincidence we deem unlikely. The fact that (**1**) is lower in energy compared to both isomers of (**2**) does not account for the experimental result that the Z isomer is formed preferentially to the E product. However, careful examination of radical (**1**) shows a steric preference for hydrogen abstraction by (**1**) (from R_3SnH) that can only occur from the plane that contains the olefinic hydrogen, and is opposite to the bulky tin group. Support of this analysis is shown by a plot of the SOMO mapped onto the electron density (Figure 5). Such a plot for the E-isomer of (**2**) shows a larger electron density coefficient on the face *syn* to tin. Radical attack in this region is unfavorable due to the steric interaction of the large trisubstituted tin group. The same plot generated for (**1**) (Figure 5) shows a larger coefficient on the face *anti* to tin. If hydrogen abstraction from the tin hydride were to occur in this region, R_3SnH would have an unobstructed reaction plane in which to interact with (**1**).

Finally, it seemed to us that rotation of the trisubstituted tin group would also hinder hydrogen abstraction *syn* to tin. The data in Table II show that for (**1**) there is only about 0.1 kcal/mol barrier to rotation of the tin group regardless of the substitution. Most likely, the tin group is freely rotating under the experimental reaction conditions, and thus hydrogen abstraction in the face *syn* to tin (yielding the E-product) is even more unlikely.

Similar results were obtained for calculations on the structure of the intermediate radical in the hydrostannation of conjugated enynes. In this case also the experimental kinetic product is that of *anti* addition followed by free radical catalyzed isomerization to the more stable product[6,7].

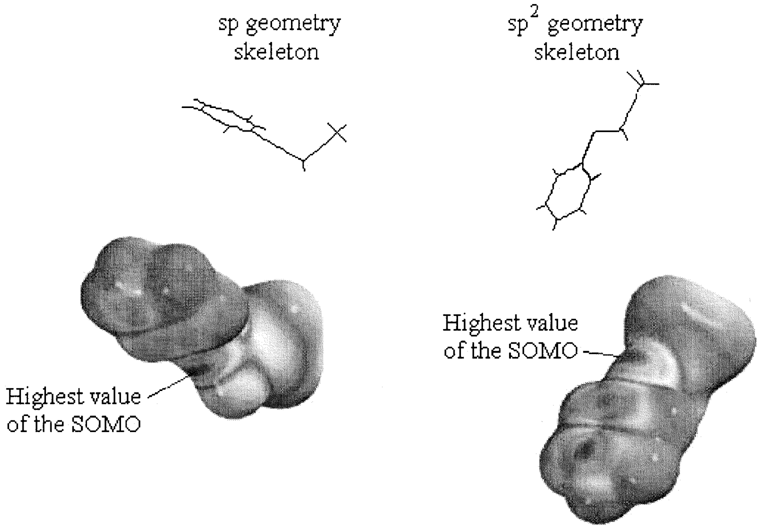


Figure 5. Mapped values of the SOMO for (**1**) and E isomer of (**2**).

Table II. Rotational Barriers Around the Olefinic Carbon-Tin Bond in (**1**) a–d

0° Rotomer Group on Tin	ΔH_f°(kcal mol^{-1})	60° Rotomer Group on Tin	ΔH_f°(kcal mol^{-1})	Barrier to Rotation (kcal mol^{-1})
a. methyl	66.369	a. methyl	66.509	0.113
b. ethyl	55.940	b. ethyl	56.045	0.105
c. propyl	40.651	c. propyl	40.753	0.102
d. butyl	24.476	d. butyl	24.582	0.106

CONCLUSIONS

In summary, semi-empirical calculations using the PM3 Hamiltonian indicate the radical species formed in the addition of trisubstituted tin hydride across the triple bond of phenylacetylene leads to an intermediate with an sp-geometry at the radical carbon. The reaction proceeds to form the Z product for a number of reasons. First, there is a small barrier to tin group rotations hindering hydrogen abstraction *syn* to tin. There is a nearly unhindered reaction plane *anti* to tin. A trialkyltin hydride is quite sizable and does not readily fit in the reaction plane necessary to form the E product. Finally, the value of the SOMO is highest where radical attack occurs. The value of the SOMO is highest *anti* to the tin group in the sp-structures. Radical attack forms the Z product. Experimentally, the kinetic product isomerizes and the thermodynamically more stable E isomer is isolated.

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