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Gas-Phase Electrophilic Attack of a Double Bond Exhibits Stereoselectivity

Philip S. Mayer and Thomas Hellman Morton*

Department of Chemistry, University of California, Riverside, California 92521-0403

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Addition of oxygen-stabilized carbocations to alkenes has been known for 85 years.[1] It has broad synthetic utility for making carbon−carbon bonds, as Scheme 1 depicts.[2−7] Hosomi−Sakurai allylation represents one application.[2] In a recently reported example, anodic oxidation generates alkoxycarbenium ions in solution, which then attack allylsilanes ($X = CH_2, Y = CH_3$),[3] followed by departure of trimethylsilyl cation. Under different conditions, the silicon bridges between two vicinal carbons, giving cyclic ethers via internal attack by oxygen.[4] In other instances (cf. the Mukaiyama aldol condensation,[5] where $X = O$), the silyl group moves from one oxygen to the other, and the R_2 group is lost.

In contrast to the aforementioned isomerizations, intramolecular transfer of silicon from carbon to oxygen is poorly documented for cationic intermediates,[6,7] even though it is well-known in anions.[5b] This communication reports neutral products arising from addition of protonated acetaldehyde (**1**) to allyltrimethylsilane in the gas phase. Unprecedented stereoselectivity is observed.

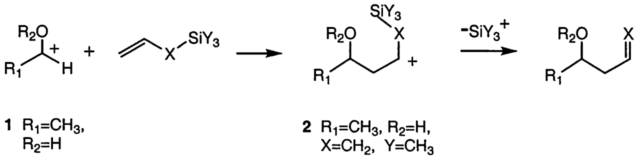
Density functional theory (DFT) calculations predict that ion **1** approaches the double bond with a tilted orientation.[8] The plane of the cationic sp^2 center makes a 66° angle with the plane of the double bond in a transition state for addition, as drawn in Scheme 2. Other transition states may also be accessible, but the tilt of the cation favors a synclinal orientation of the methyl group relative to the double bond. The final neutral product distribution from this gas-phase addition displays kinetic control, which suggests that the adduct ions retain memory of the geometry of initial approach.

A mass spectrometric experiment provides background for the neutral product study. When the hypothesized addition intermediate, ion **2**, is generated independently, its metastable ion decompositions show that the TMS group shifts from carbon to oxygen to form **3**. Protonation of $Me_3SiCH{=}CHCH_2CHOHCH_3$ gives a conjugate acid ion, which fragments unimolecularly via loss of trimethylsilanol, loss of pentadiene, or loss of propene.[9] In all three cases, silicon−oxygen bonds must have been formed. DFT calculations[8] predict that isomerization of **2** to the most stable conformation of **3** should be exothermic by $\Delta H = -19$ kcal mol^{-1}.

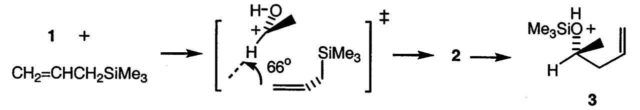
Scheme 3 summarizes the most abundant unimolecular dissociations.[9] Paths *i* and *ii* yield C_5 products. C−O bond cleavage (path *i*) gives $C_5H_9^+$ and trimethylsilanol. 1,2-Elimination, either from **3** (via path *ii*) or directly from **2** (to produce ion−neutral complexes that contain water and the allylic $Me_3SiCH_2CH{=}CHCHCH_3^+$ ion, which then expel protonated trimethylsilanol), gives pentadienes.

Schemes 1−3 summarize outcomes expected for the ion−molecule reaction of protonated acetaldehyde (**1**) with allyltrimethylsilane. The bimolecular reaction to yield *trans*-piperylene (*E*-**4**) plus protonated trimethylsilanol (products of path *ii*) has a calculated $\Delta H = -38$ kcal mol^{-1}.[8] If path *i* were to produce the most stable $C_5H_9^+$ ion, it would be 5 kcal mol^{-1} more favorable than path *ii*.[10]

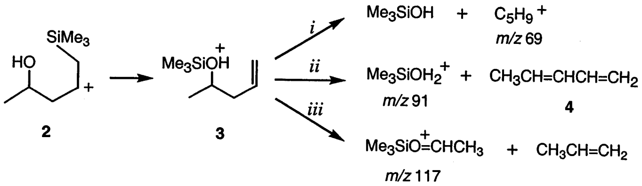
Scheme 1. Electrophilic Attack of a Double Bond by an Oxygen-Stabilized Carbocation



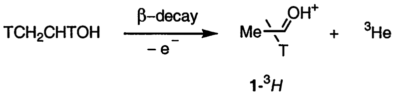
Scheme 2. Addition of Protonated Acetaldehyde Ions to Allyl-TMS



Scheme 3. Decomposition Pathways of Isomerized Adduct Ions



We have examined the neutral products corresponding to Schemes 1−3 in the gas phase. Radiolabeled **1** is generated by nuclear decay of tritiated ethanol.[11] When the ethanol contains more than one tritium atom, the resulting carbocation, **1**-^3H, retains tritium, as eq 1 depicts. Condensation products formed by reactions of tritiated ions with neutral reactants will also be radiolabeled. In particular, the neutral products (such as **4**) from condensation of **1**-^3H with allyltrimethylsilane can be identified and quantitated on the basis of their radioactivity.



$$\mathrm{TCH_2CHTOH} \xrightarrow[-e^-]{\beta\text{-decay}} \mathrm{Me\text{–}C(T){=}OH^+} + {}^3\mathrm{He} \qquad (1)$$

Gaseous tritiated ethanol was allowed to decay at room temperature in a sealed glass bulb in the presence of a mixture of allyltrimethylsilane, methanol, trimethylamine (to serve as a proton sink), and 1 atm of helium (to allow initially formed ions to thermalize before reacting).[11,12] Aliquots were taken over an interval of 1.5−2.5 × 10^8 s. Small amounts of the products expected from the gas-phase Sakurai reaction—$CH_3CHOHCH_2CH{=}CH_2$ (4-penten-2-ol) and its trimethylsilyl ether—were recovered. The most prevalent tritiated product with >3 carbons, however, was *Z*-1,3-pentadiene (*cis*-piperylene, *Z*-**4**).

Neutral products were analyzed by radio-gas chromatography using three separate GC columns connected to a proportional flow counter.[13] Table 1 lists the observed condensation products. Since *cis*-piperylene is notoriously difficult to separate from vinylcyclopropane by gas chromatography,[14] selected C_5H_8 isomers were also assayed by an independent method: addition of unlabeled carrier, conversion to a solid derivative, and recrystallization.

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* To whom correspondence should be addressed. E-mail: morton@citrus.ucr.edu.

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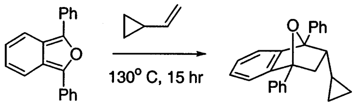
Table 1. Yields of Radiolabeled Condensation Products from 2.2 to 2.5 × 10^8 s Decay of Multiply Tritiated Ethanol in the Presence of a Mixture of Allyltrimethylsilane, Methanol, and Trimethylamine

	yield relative to *Z*-**4** (by GC)	recovered radioactivity, %
ethanol		68
1,4-pentadiene	0.15 ± 0.04	
cis-piperylene (*Z*-**4**)	1.00	0.8
vinylcyclopropane		0.08
trans-piperylene (*E*-**4**)	0.05 ± 0.02	0.04
methyl acetate	1.8 ± 0.40	1.3
$CH_3CHOHCH_2CH{=}CH_2$	0.13 ± 0.05	
$CH_3CH(OSiMe_3)CH_2CH{=}CH_2$	0.15 ± 0.01	
$CH_3CHOHCH_2CH{=}CHSiMe_3$	<0.01	

The percent recovered radioactivity corresponding to unreacted ethanol was quantitated by making its *N*-phenylurethane.[11] Diels−Alder reactions with *N*-phenylmaleimide (NPM) were used to make crystalline derivatives of *cis*- and *trans*-piperylene.[15] NPM does not react with vinylcyclopropane under the conditions where it adds to dienes. Since formation of vinylcyclopropane is a plausible outcome of the gas-phase reaction,[16] a solid derivative of vinylcyclopropane was prepared via the Diels−Alder reaction with 1,3-diphenylisobenzofuran (DBIF), as eq 2 shows.[17]



(2)

The tritiated ethanol in the reaction bulb had a specific activity of 5 × 10^4 Ci/mol (compared with a value of 5.8 × 10^4 Ci/mol for a compound with exactly two tritia per molecule).[18] One-third of the tritium undergoes nuclear decay in 2.2 × 10^8 s. Monotritiated ethanol decays to give products that contain no tritium, which are not detected. The more highly tritiated ethanols yield radioactive ions, whose neutral condensation products are listed in Table 1.

We account for the condensation products as follows. A portion of **1**-^{3}H is produced in a highly vibrationally excited state. A mass spectrometric study shows that collisionally activated decomposition of ion **1** proceeds predominantly via expulsion of molecular hydrogen to form acetyl cation. Nucleophilic capture of tritiated acetyl cation by methanol accounts for the presence of methyl acetate among the radioactive neutral products, whose identity was confirmed by addition of unlabeled methyl acetate to an aliquot, conversion to acetanilide, and recrystallization.

It is hard to imagine how radiolabeled pentadienes might have arisen, except by addition of **1**-^{3}H to allyltrimethylsilane followed by decomposition via one of the paths drawn in Scheme 3. The high yield of *cis*-piperylene (*Z*-**4**) signals kinetic control.[19] While many reactions yield mixtures of pentadiene isomers, the vast majority form predominantly trans. Deprotonation of pentenyl ions in the gas phase gives a 1:2.3 ratio of trans to cis.[20] Thermal rearrangments of small-ring hydrocarbons generate 1,3-pentadiene mixtures,[14,21] but in no instance does cis exceed trans. Only two reactions have been reported to yield more cis than trans: Hofmann elimination[22] from pentenyltrimethylammonium and pyrolysis of *cis*-propenyl vinyldimethylsilane.[23] Neither precedent is relevant here: stereochemical preferences in both of those cases come from preservation of the geometry of the reacting species.

The novel stereoselectivity seen here results from a preferential elimination to produce *Z*-**4**. What determines that preference? The absence of $CH_3CHOHCH_2CH{=}CHSiMe_3$ among the neutral products suggests that **2** isomerizes to **3** rapidly. Once formed, **3** encounters an NMe_3 molecule within 10 ns. It seems unlikely that **3** reacts with the basic amine by any pathway other than proton transfer. However, the yield of *Z*-**4** is 7 times greater than that of the product of deprotonating **3**, $CH_3CH(OSiMe_3)CH_2CH{=}CH_2$, implying that adduct ions expel $Me_3SiOH_2^+$ before reacting with NMe_3.

We infer that unimolecular decomposition of **2** or **3** yields *Z*-**4**. Adduct ions initially contain 30−50 kcal mol^{-1} of internal energy when formed via Scheme 1,[8] but they collide with a helium atom within 0.1 ns. We speculate that (in the brief span of their lifetimes as vibrationally excited species) the methyl stays synclinal, as drawn for **3** in Scheme 2, which in turn reflects the geometry of electrophilic addition. Syn elimination (e.g., path *ii* of Scheme 3) from this conformer yields *Z*-**4**. The conjecture that elimination occurs faster than conformational equilibration invites further tests.

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(8) Calculations were performed at the B3LYP/6-31G** level (including zero-point energy and counterpoise corrections) using GAUSSIAN98.
(9) Chemical ionization with ammonia reagent gas gives the M + 1 ion (*m*/*z* 159), whose mass-analyzed ion kinetic energy (MIKE) spectrum shows *m*/*z* 69, *m*/*z* 91, and *m*/*z* 117 in an approximate ratio of 1:3:8.
(10) Based on the proton affinity difference between trimethylsilanol and *E*-**4** (Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413−656).
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(12) A 0.03 Ci sample of tritiated ethanol (corresponding to a partial pressure of 0.001 Torr), 20 Torr of allyltrimethylsilane, 20 Torr of methanol, and 3 Torr of trimethylamine were condensed in a 1 L silvered bulb; 1 atm of helium was introduced, the bulb was sealed, and the contents were allowed to warm to room temperature.
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(18) NMR analysis of the starting material shows that it contained roughly equal proportions of monotritiated, ditritiated, and tritritiated ethyl groups. We are grateful to Dr. Phil Williams for recording proton-decoupled one- and two-dimensional tritium NMR spectra.
(19) *trans*-Piperylene is more stable than the cis isomer. Extrapolation of the temperature-dependent equilibrium constant shows that trans predominates over cis at all temperatures <5000 K (Egger, K. W.; Benson, S. W. *J. Am. Chem. Soc.* **1965**, *87*, 3311−3314).
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