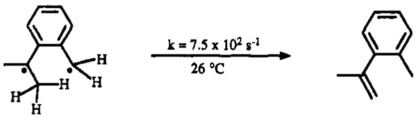
mmol, 74%) of **12** (Scheme II). Apparently, the benzenoid radical center in the initially produced biradical **9** was indeed trapped by the carbon–carbon double bond intramolecularly, forming preferentially a 5-membered ring in a fashion characteristic of the free-radical cyclization reaction,[16] to give a new biradical **10**, which then decayed to afford **12**.

Although on surface a reaction mechanism involving exchange of hydrogen atoms among **10** *intermolecularly* could account for the formation of **12**, this reaction pathway was not what actually occurred. Instead, **10** decayed through an *intramolecular* route with an initial [1,5]-sigmatropic hydrogen shift to form *o*-xylylene **11** followed by a second [1,5]-sigmatropic hydrogen shift to afford **12**. The existence of such an internal decay route was supported by the formation of **13** when deuterated enyne–allene **8d** was utilized (Scheme III). The migration of a deuterium atom to the benzylic position is consistent with the intramolecular pathway.

The transformation from **10** to **11** is likely to be facile; we estimate the heat of formation of **11** to be ca. 13 kcal/mol less than that of **10**, representing the difference in the bond dissociation energies of primary alkyl and benzylic C–H bonds.[17] Furthermore, the rigid structure of **10** should also enhance the rate of the hydrogen shift.[18] Biradical **11**, an *o*-xylylene derivative, is also expected to have a very short life time on the basis of the fact that **14** was reported to have a half-life of only 0.92×10^{-3} s at 26 °C ($k = 7.5 \times 10^2\ \mathrm{s}^{-1}$) (eq 1).[19]



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In summary, the reaction sequence outlined in Scheme I provides a facile route to a variety of enyne-allenes by using different combinations of readily available γ-(trimethylsilyl)allenylboranes and conjugated allenic aldehydes. The trapping experiment shown in Scheme II gives further evidence for the formation of α,3-dehydrotoluene species and also demonstrates a way for easy entry to many other new biradicals. Such new biradicals having a longer distance between the two radical centers could potentially exhibit very different DNA-cleaving properties and therapeutic values compared to the original biradicals by abstracting hydrogen atoms from other positions of the sugar-phosphate backbone of DNA.[20] Certainly, any facile intramolecular decay route must be eliminated in order to give these new biradicals a longer life time for hydrogen abstractions from DNA to take place. In addition, it should be noted that other synthetically useful *o*-xylylenes[21] could also be likewise prepared as shown in Scheme II.

Acknowledgment. The financial support of the National Science Foundation for the purchase of a JEOL GX-270 NMR spectrometer (RII-8011453) and an HP 5970B GC/MSD system (CHE-8913626) is gratefully acknowledged.

Supplementary Material Available: Experimental procedures, IR, MS, ^{1}H NMR and ^{13}C NMR spectral data and actual ^{1}H and ^{13}C NMR spectra of **1b**, **5a–d**, **7a–c**, **8a–d**, **12**, and **13** (37 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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A Facile Synthesis of 5-Methylene-1,3-cyclohexadienes (*o*-Isotoluenes) and 1,2,4,6-Heptatetraenes[†]

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Summary: Condensation between 4-methyl-2,3-pentadienal and γ-(trimethylsilyl)allylboranes **3**, **4**, and **16** followed by the Peterson olefination reaction afforded the corresponding *o*-isotoluenes and diene–allenes.

Since the first synthesis of 5-methylene-1,3-cyclohexadiene (*o*-isotoluene) by Bailey and Baylouny,[1] several different routes to this alicyclic isomer of toluene[2] and its benzologues[3] have been reported. However, almost all of these methods involved multistep synthesis and generally required gas-phase pyrolysis. Only limited quantities could be produced at a time. It is undoubtedly due to the lack of an efficient route to *o*-isotoluenes that a systematic investigation of this class of theoretically interesting and

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[†] Dedicated to Professor Gabor B. Fodor on the occasion of his 75th birthday.

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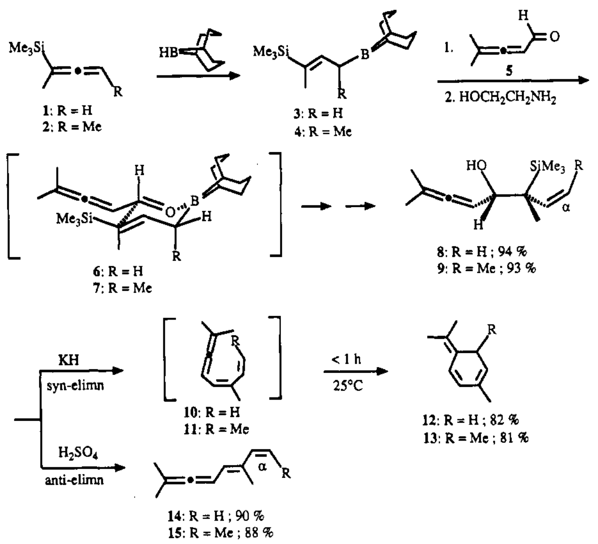
Scheme I

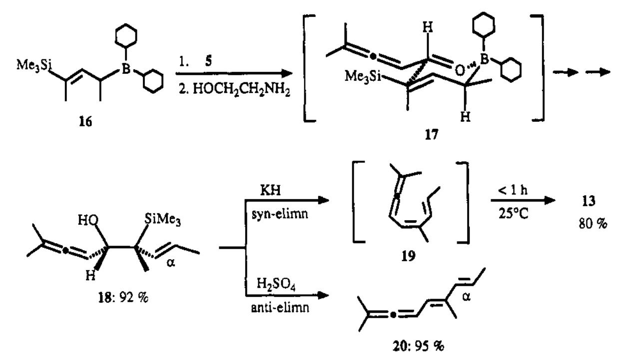


potentially synthetically useful compounds has not been made. Only a few studies of their chemical properties have been reported.[2-4] We describe here a simple and versatile route to *o*-isotoluenes as well as 1,2,4,6-heptatetraenes.

We recently reported a highly diastereoselective condensation reaction between aldehydes and γ-(trimethylsilyl)allylborane **3**, prepared from hydroboration of 3-(trimethylsilyl)-1,2-butadiene (**1**) with 9-borabicyclo[3.3.1]nonane, to afford, after the Peterson olefination reaction, the corresponding 1,3-butadienes.[5] We were attempting to extend this method to the synthesis of diene–allenes[6] by using the readily available conjugated allenic aldehydes[7] for condensation. Indeed, treatment of **3** with 4-methyl-2,3-pentadienal (**5**),[7] followed by 2-aminoethanol, produced **8** with high diastereomeric purity (de > 90%) (Scheme I). However, the use of KH to promote the Peterson olefination reaction resulted in the formation of **12**, an *o*-isotoluene derivative. Apparently, the initially formed diene–allene **10** underwent a facile electrocyclic reaction (<1 h, 25 °C), as observed previously for compounds with similar chemical structures,[2d,8] to afford **12**. On the other hand, treatment of **8** with concentrated H_2SO_4 produced the expected diene–allene **14**.

Condensation between **4**[9] and **5** was also highly diastereoselective (*RS*/*SR*:*RR*/*SS* > 98:2), leading to *o*-isotoluene **13** and diene–allene **15**. The preference for the *Z* geometry of the α double bond in **9** and consequently also in **14** (*Z*:*E* = 95:5) had been observed previously during the synthesis of the internal 1,3-butadienes.[9] This preference was attributed to the allylic methyl group at the carbon-1 position favoring the axial position in the chairlike transition state **7** to avoid a large steric interaction that would arise between the rigid bicyclic ligand on boron and the allylic methyl group if it were to assume the equatorial position.

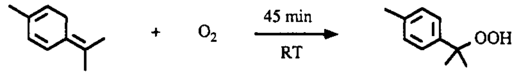
Scheme II



Similarly, by using **16**[9] for condensation with **5**, hydroxyallylsilane **18** was obtained with high diastereomeric purity (*RS*/*SR*:*RR*/*SS* > 98:2), leading to *o*-isotoluene **13** and diene–allene **20** (Scheme II). The α double bond in **18** and **20** has exclusively the *E* geometry (>98%) as observed earlier.[9] Apparently the less rigid cyclohexyl ligands could rotate away to avoid excessive nonbonded interaction with the allylic methyl group adopting the equatorial position in the transition state **17**. The 1,3-diaxial interaction with the methyl group at the carbon-3 position becomes the dominant factor in pushing the allylic methyl to the equatorial position, resulting in the formation of the *E* geometry for the α double bond.

We were pleasantly surprised to observe that *o*-isotoluenes **12** and **13** survived the presence of KH and $KOSiMe_3$, a byproduct of the Peterson olefination reaction, without tautomerization (<2%) to the corresponding much more stable benzene derivatives. These *o*-isotoluenes are thermally stable and could be purified by distillation under reduced pressure at 35 °C.

As reported previously for 5-methylene-1,3-cyclohexadiene,[4d] *o*-isotoluene **12** was found to be very sensitive to oxygen, being rapidly and cleanly oxidized to the corresponding *p*-cymene hydroperoxide **21**[10] on brief exposure to air (eq 1). The autoxidation most likely proceeded



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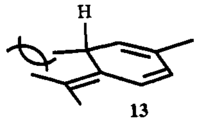
12 **21**

through a free-radical chain mechanism as proposed previously for 5-methylene-1,3-cyclohexadiene,[4d] and not through a one-step ene-type reaction, which requires singlet oxygen. The gain of aromaticity in the initiation as well as the propagation step is clearly responsible for the facile rate of reaction.

Surprisingly, **13** was found to be stable toward oxygen. Not a trace of the corresponding benzylic hydroperoxide was detected by ^{1}H NMR even after 2 h of exposure to air. This result is unexpected because normally the tertiary methine hydrogen in **13** should be more labile toward radical formation in both the initiation and the propagation steps.



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This unexpected observation perhaps could be attributed to the arising of a severe A$^{(1,3)}$ allylic strain[11] if 13 is forced to adopt the conformation with the C–H bond of the methine hydrogen parallel to the C–C π bonds. Such a conformation would be required in the transition states of the initiation and the propagation steps leading to the corresponding benzylic radical in order for them to benefit from aromaticity. It is likely that the benzylic radical center in the transition states would be pushed away from the parallel position with the C–C π bonds of the benzene ring, resulting in the loss of the resonance energy and the increase of the energy barrier. Consequently, 13 is much more stable than 12 toward air. On the other hand, 12 is free from severe allylic strain, and therefore is prone to autoxidation.

In summary, the reaction sequence outlined in Schemes I and II could be easily adopted for the synthesis of a variety of *o*-isotoluenes and diene–allenes by using different combinations of readily avalable γ-(trimethylsilyl)allylboranes and conjugated allenic aldehydes. With the development of such a facile route to *o*-isotoluenes, the chemical properties of these compounds can now be investigated and the large amount of energy (ca. 24 kcal/mol)[4b] to be gained from aromatization is ready to be exploited. The conjugated diene–allenes are synthetically useful for the preparation of polyenes through facile sigmatropic hydrogen shifts[12] and can also find applications in the Diels–Alder reaction utilizing the allene moiety as a part of the diene component.[6a,13]

Acknowledgment. The financial support of the National Science Foundation for the purchase of a JEOL GX-270 NMR spectrometer (RII-8011453) and an HP 5970B GC/MSD system (CHE-8913626) is gratefully acknowledged.

Supplementary Material Available: Experimental procedures, IR, MS, ^{1}H NMR, and ^{13}C NMR spectral data and actual ^{1}H and ^{13}C NMR spectra of 8, 9, 12, 13, 14, 15, 18, 20 (23 pages). Ordering information is given on any current masthead page.

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Diastereoselectivity in the Hydroxyl-Directed Cyclopropanation of Vinylorganometallic Compounds

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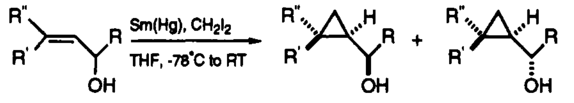
Summary: Olefins bearing silicon and/or tin substituents undergo highly diastereoselective cyclopropanation in the presence of Sm/CH$_2$I$_2$. The stereochemistry of the tin moiety has a dramatic effect on the rate of a subsequent transmetalation with MeLi.

Hydroxyl-directed reactions have found widespread use in organic synthesis. The directed epoxidation, osmylation, and hydrogenation reactions are a few of the now standard methods for the construction of multiple adjacent stereocenters.[2-4] Directed cyclopropanation reactions are also well-known and are of current interest.[5] Molander has recently reported highly diastereoselective cyclopropanation of allylic alcohols using Sm/CH$_2$I$_2$, eq 1.[6] The results of these studies may be summarized as follows: *Z* olefins undergo diastereoselective cyclopropanation with de's >100:1; *E* olefins also undergo cyclopropanation with selectivities which increase as the steric sizes of R and R″ increase. When R is small, the facial selectivity is reversed and modest selectivities are obtained (approximately 1:4–6).



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In light of the demonstrated utility of silylated[7] and stannylated[8] cyclopropanes, and our interest in the preparation of 1,1-dimetalated olefines bearing tin and/or silicon,[9] we undertook a study to evaluate the reactivity

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