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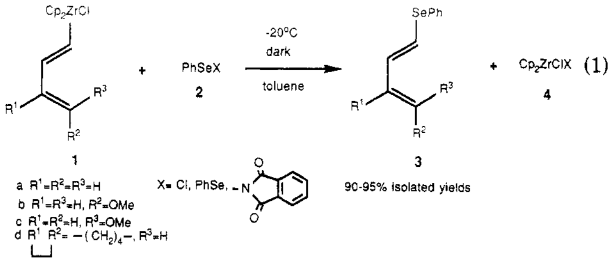
Communications

Transmetalation from Zirconium to Selenium. Stereoselective Preparation of 1-Phenylseleno 1,3-Dienes and Isomerization under Photochemical and Thermal Conditions

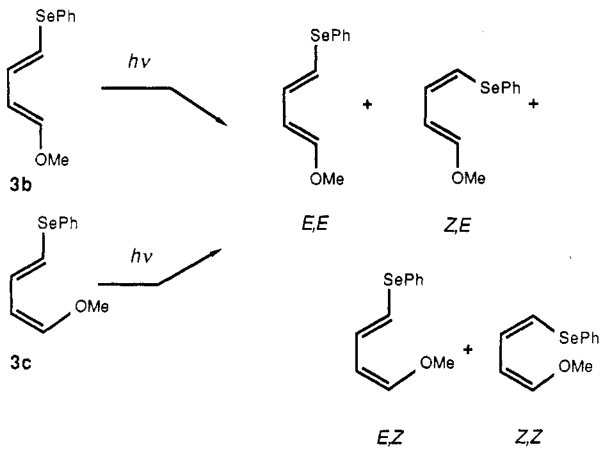
Summary: Functionalized 1-phenylseleno 1,3-dienes **3** synthesized via transmetalation from zirconium to selenium undergo facile photochemical and thermal isomerization.

Sir: The broad synthetic utility of the Diels–Alder cycloaddition reaction has fueled interest in the stereocontrolled synthesis of heterosubstituted 1,3-dienes.[1] While many oxygen-, nitrogen-, and sulfur-functionalized 1,3-dienes[2] are now available, we are aware of only two reports on the preparation of 1,3-dienes substituted at the 1-position with selenium. A methoxyselenation–elimination sequence on simple dienes has been communicated;[3] however, the assignment of stereochemistry was superficial and ambiguous. The other report involves the preparation, stereochemical analysis and reactivity of 1-(phenylseleno)-2-(trimethylsiloxy)-4-methoxy-1,3-butadiene.[4] Herein we report (i) the first example of transmetalation from zirconium to selenium[5] to generate 1-phenylseleno 1,3-dienes and (ii) the remarkably facile geometric isomerization of certain selenium-substituted 1,3-dienes under both photochemical and thermal conditions.

We have previously reported the preparation of (*E*)-1-bis(cyclopentadienyl)chlorozirconium 1,3-dienes **1** and their subsequent transmetalation to tin.[6] We have now found that zirconium dienyl derivatives **1a–d** rapidly transmetalate, in almost quantitative yields, to selenium by reaction with *N*-(phenylseleno)phthalimide[7] **2** (*N*-PSP) at −20 °C in toluene to generate the 1-phenylseleno 1,3-dienes **3a–d** (eq 1). The use of the *N*-PSP **2** is preferred over PhSeCl or PhSeSePh as the product phthalimido zirconium complex **4** is very insoluble and facilitates separation of the desired selenium substituted 1,3-diene **3**.



Scheme I



In the absence of light this reaction is completely stereoselective. However, if the reaction is performed in the presence of room light (fluorescent), mixtures of geometric isomers are obtained. From **3a** an *E*/*Z* (2:1) mixture is produced; however, more interestingly both **3b** and **3c** are obtained as a mixture *of all four possible stereoisomers* (Scheme I). Compound **3d** is stereochemically stable to this isomerization process. That this isomerization process occurs after transmetalation was established by careful isolation of the dienes **3a–c** at low temperature in the absence of light. ^{1}H NMR spectral analysis at −20 °C of these compounds showed conclusively that only one stereoisomer was present and that transmetalation had occurred with retention of configuration at the 1-position. If the probe temperature is increased to 25 °C and even to as high as 90 °C (in the absence of light), no geometric isomerization is observed after 1 h (vide infra). However, exposure of a 0.20–0.25 M solution of **3a–c** (C_6D_6, C_7D_8, or CD_2Cl_2) in a 5-mm NMR tube to fluorescent light at room temperature resulted in complete isomerization in approximately 1 h (not optimized). As shown in Scheme I, exposure of a solution of the *E,E* isomer **3b** to room light leads to the same mixture of isomerized products as obtained by similar photolysis of the *E,Z* isomer **3c**;[8] continued exposure of this mixture to fluorescent light (48 h) leads to no change in the composition. That these are equilibrium ratios is evident upon disturbing the equilibrium by addition of pure **3b** or **3c** to the photolyzed mixture; upon further irradiation, the original composition is reestablished.

Isomerization also occurs thermally in the dark, albeit sluggishly. Heating solutions of **3a–c** in toluene-d_8, protected from light, for approximately 48 h generated the isomerized 1,3-dienes in similar equilibrium ratios[8] as observed upon exposure to room light. However, the composition of the mixtures leading up to the final equilibrium ratios were different for the thermal process as compared to the photochemical reaction. Once again, the cyclic diene **3d** proved thermally stable to isomerization.

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[5] (a) Negishi, E.; Takahashi, T. *Aldrichimica Acta* **1985**, *18*, 31. (b) Transmetaltion from Zr in B, P, and S has been achieved in our laboratory, results of which will appear in future papers.

[6] Fryzuk, M. D.; Bates, G. S.; Stone, C. *Tetrahedron Lett.* **1986**, *27*, 1537.

[7] *N*-PSP was prepared according to: Nicolaou, K. C.; Claremon, D. A.; Barnett, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704.

[8] Equilibrium ratios obtained by photolysis were *E,E*/*E,Z*/*Z,Z*/*E,Z* 36:15:12:37 and by thermolysis were 34:11:13:42. These ratios were determined by integration of the methyl enol ether peaks in the ^{1}H NMR and are accurate to ±10%.

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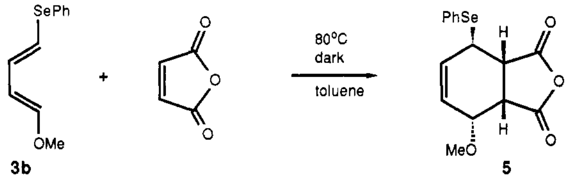
Preliminary mechanistic studies have so far been limited to the use of free radical inhibitors. Varying concentrations of 2,6-di-*tert*-butyl-4-methylphenol (BHT) or tetramethylpiperidinyloxy radical (TEMPONE) have no apparent effect on the photochemical isomerization process. However, the presence of 2 equiv of BHT does appear to retard the thermal isomerization of **3b** and **3c**. That the isomerization process may involve cyclobutene intermediates, via conrotatory electrocyclic reactions, is suggested by analogy to observations made by Trost et al.[9] in their attempt to prepare (*E*,*E*)-1-(phenylsulfinyl)-4-methoxy-1,3-butadiene. Such a mechanism can account for the stereochemical stability of **3d**.

Although this facile geometric isomerization process of 1-phenylseleno 1,3-dienes might be expected to reduce their usefulness in Diels–Alder-type chemistry, this is not the case. For example, heating an equilibrium mixture of all four possible stereoisomers of **3b** with maleic anhydride, at 80 °C in the dark, leads to a *single stereoisomeric product* **5** in good yield (greater than 80% by ^{1}H NMR). The stereochemistry was confirmed by ^{1}H NMR and NOEDIFF experiments. Thus the *E*,*E* stereoisomer is kinetically "milked" from the equilibrium. Compound **5** is also obtained in good yield by reaction of isomerically pure **3b** with maleic anhydride (eq 2).



(2)

Further studies on the mechanisms of both the photoinduced and thermally driven isomerization will be reported along with a more comprehensive study of the Diels–Alder reactivity of these new 1-phenylseleno 1,3-dienes.

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Supplementary Material Available: Experimental details, ^{1}H NMR spectra, and analytical data on compounds **3** and ^{1}H NMR and ^{1}H NMR NOEDIFF data on **5** (9 pages). Ordering information is given on any current masthead page.

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[10] Fellow of the Alfred P. Sloan Foundation (1984–1987).

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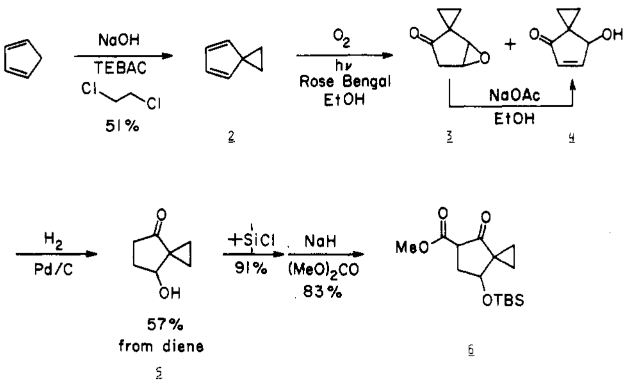
Synthesis of Pederol

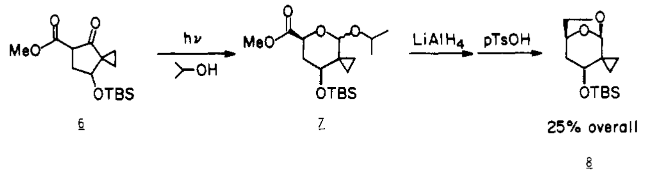
Summary: The synthesis of pederol, the "right half" of pederin, has been accomplished by using an oxacarbene intermediate to construct its pyran unit.

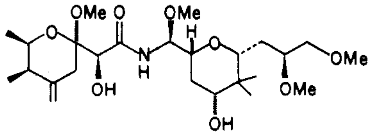
Sir: Despite considerable mechanistic study of the photochemical ring expansion of cycloalkanones to oxacarbenes,[3] its unique possibilities for selective organic synthesis have heretofore been unexploited. Reports have appeared only recently concerning cyclobutanone ring expansions that provide entries into tetrahydrofuran structures.[4] Tetrahydropyrans can also be produced by using this methodology.[5] We have undertaken the total synthesis of the naturally occurring compound pederin[6] (1) utilizing the photochemical generation of a 2-tetrahydropyranylidene as a key step. This initial report describes the preparation of the "right half" of pederin, pederol.

Scheme I



Scheme II





Pederin

1

The synthesis of the substrate for the photoreaction is summarized in Scheme I. It begins with cyclopentadiene, which is cycloalkylated with dichloroethane under improved conditions using phase-transfer catalysis.[7] This gives spiro[2.4]heptadiene (2) in 51% yield. Lots of 40 g

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[1] Research Fellow of the Alfred P. Sloan Foundation, 1986–1988.

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