(d, 1 H, J = 10.8 Hz), 3.51 (d, 1 H, J = 10.8 Hz), 4.29 (dq, 1 H, J = 6.10 Hz), 10.3 (br s, 1 H). Anal. Calcd for $C_{11}H_{17}O_3I$: C, 40.78; H, 5.29; I, 39.17. Found: C, 41.02; H, 5.38; I, 38.82.

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Supplementary Material Available: X-ray crystallographic data for iodolactone **13** and iodotetrahydrofuran **18** (6 pages). Ordering information is given on any current masthead page.

An Enantioselective Central-Axial-Central Chiral Element Transfer Process Leading to a Concise Synthesis of (+)-Sterpurene: Intramolecular Diels-Alder Reactions of Vinylallene Sulfoxides[1a,b]

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Abstract: The intramolecular Diels-Alder (IMDA) reaction of vinylallene sulfoxide **19** as the diene component occurs in a rapid and stereoselective manner at room temperature to give tricyclic **20** in good yield. Sulfoxide **19** cyclizes ~140 times faster than the corresponding hydrocarbon **15a**. It was also shown that *gem*-dimethyl substitution on the tether linking the vinylallene and vinyl group accelerates the rate of cyclization by only a factor of ~2.6. Treatment of enantiomerically enriched diene propargyl alcohol **6** with benzenesulfenyl chloride gave vinylallene sulfoxide **4** which cyclized in a highly enantio- and diastereoselective fashion to afford optically active tricyclic sulfoxide **5**. Sulfoxide **5** was converted in two steps to the novel sesquiterpene fungal metabolite (+)-sterpurene, thus establishing its absolute configuration. By use of 2D NMR techniques, most of the proton and carbon signals in the ^1H and ^{13}C NMR spectra of sterpurene (**8**) and the precursor diene **33** were assigned.

The intramolecular Diels-Alder (IMDA) reaction has been the subject of numerous synthetic and mechanistic studies,[2] but there has been a relative paucity of work on the vinylallene[3] variant of this reaction.[4] Although the intermolecular[5] vinylallene Diels-Alder reaction appears to have been first reported in 1960, the first definitive example of a vinylallene IMDA reaction was not reported until 1982.[4a] Inspection of Dreiding models of the hydrindane precursor **1** and the decalin precursor **2** (Scheme I) suggests that the cyclization of **1** should be considerably more facile than that of **2** due to the distorted overlap and eclipsing interactions present in the conformation of **2** leading to the decalin system **3b**. In contrast, there is excellent overlap (and no eclipsing interactions) in the conformation of **1** leading to the hydrindane system **3a**. Moreover, because of the shorter tether in **1** compared to that in **2**, cyclization of **1** should be entropically facilitated. A brief inquiry into this matter by Snider suggests that the cyclization of a vinylallene system to give a hydrindane is more facile than that of the homologous vinylallene leading to the decalin system.[4c,6]

Scheme I

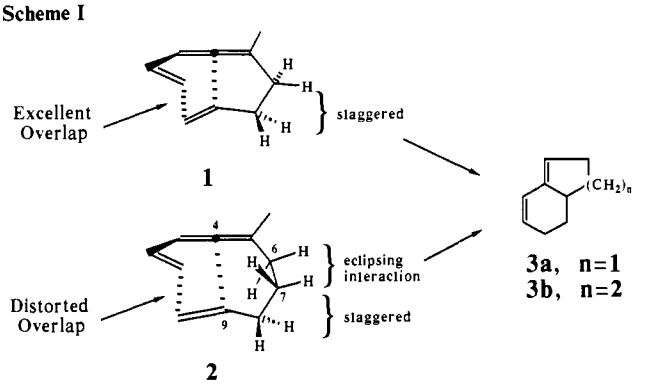
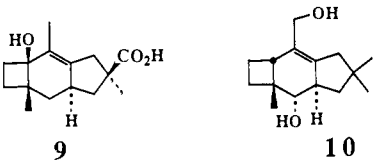


Chart I



(1) (a) A preliminary account of this paper has appeared. See: Gibbs, R. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 4062. (b) This paper is taken in part from the Ph.D. Dissertation of R. A. Gibbs, University of California, Riverside, CA, August 1988. (c) Analytical Chemical Instrument Facility, UC Riverside.

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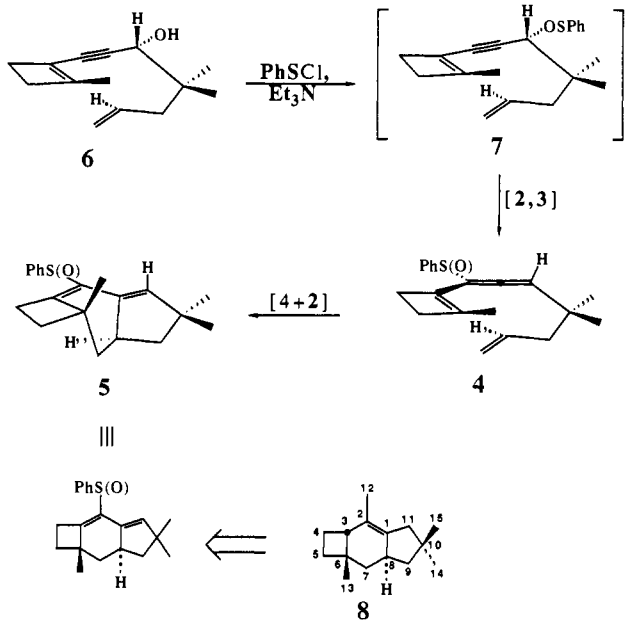
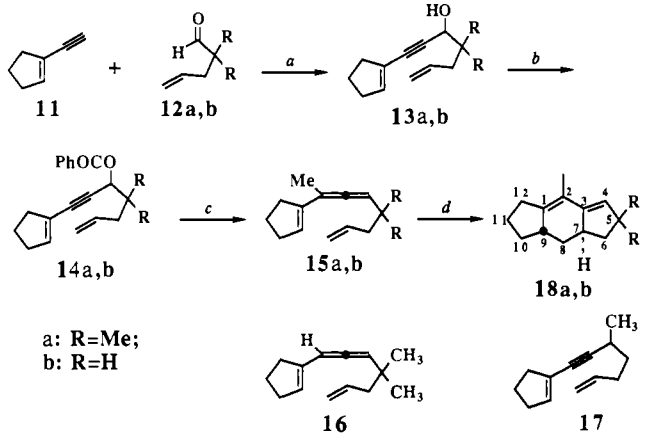
0002-7863/89/1511-3717$01.50/0

Scheme II



Scheme III[a]



[a](a) **11**, *n*-BuLi, Et_2O, 0 °C, 30 min; **12a,b**, 0 °C to room temperature, 2 h (**13a**, 96%; **13b**, 60%); (b) PhCOCl, DMAP, pyridine, room temperature, 3 h (**14a**, 92%; **14b**, 80%); (c) MeMgBr, CuI, LiBr, THF, 0 °C to room temperature, 7 h (**15a**, 50%; **15b**, 50%); (d) **15a**, C_6H_6, reflux, 4 h (95%); **15b**, isooctane, reflux, 3 h (94%).

However, a systematic examination of the hydrindane producing vinylallene IMDA reaction has not been carried out, particularly in connection with taking advantage of the chirality of the allene. Indeed, of the previously reported studies of chiral allanes in cyclization reactions,[7] only a few have been directed toward synthetic goals.[7j,m] Accordingly, we have initiated a systematic investigation of the Diels–Alder reaction and other pericyclic processes of allenes in order to develop insight into structure-activity patterns and to apply these processes in a manner that will take advantage of the axial chiral element present in substituted allenes.

It was expected that due to the rigid nature of the vinylallene moiety, the IMDA reaction of a vinylallene would proceed in a completely stereoselective fashion. As shown in Scheme II, vinylallene **4** should undergo an IMDA reaction to afford only tricyclic sulfoxide **5** with an anti ring junction between rings A and C.[8] This implies that if the precursor propargyl alcohol **6** were prepared in an enantioselective manner, then its central chiral element would be transferred to the axial chiral element of **4**[9–11] and subsequently to the two new central chiral elements in **5** in an entirely selective manner. It was the main goal of this study to demonstrate the feasibility of this type of chiral element transfer[8] process by applying this method to the preparation of a substance whose absolute stereochemistry could be easily established. In this connection, we were attracted to the unusual 4/6/5 tricyclic sesquiterpene (+)-sterpurene (**8**),[12–15] a metabolite of the fungus *Stereum purpureum*, the causitive agent of the so called "silver leaf disease" of a variety of shrubs and trees. Besides sterpurene, the related metabolites sterpuric acid (**9**)[12,15c] and 7,12-dihydroxysterpurene (**10**) have also been isolated and characterized (Chart I).[14b] It was anticipated that the tricyclic sulfoxide **5** could be readily transformed into optically active sterpurene (**8**).

Besides providing the full experimental details of the preliminary communication, we describe new results concerning structural effects on the reactivity profile of the IMDA reaction in a model system (5/6/5 skeleton) related to the sterpurene (4/6/5) system. In particular, we have examined the effects of *gem*-dimethyl and sulfoxide substituents on the vinylallene IMDA reaction, and these results are described first.

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(8) This kind of sequential central–axial–central chiral element transfer process appears to be precedented only by the example recently reported by this laboratory. (a) Okamura, W. H.; Peter, R.; Reischl, W. *J. Am. Chem. Soc.* **1985**, *107*, 1034. (b) For further studies on the electrocyclization of allenyldienes, see: Elnagar, H. Y.; Okamura, W. H. *J. Org. Chem.* **1988**, *53*, 3060.

(9) (a) For examples of the intramolecular transfer of a central chiral element to an axial chiral element, see ref 10 and: Meyers, A. I.; Wettlaufer, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 1135 and references cited therein. (b) For a discussion of stereochemical nomenclature, see: Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319.

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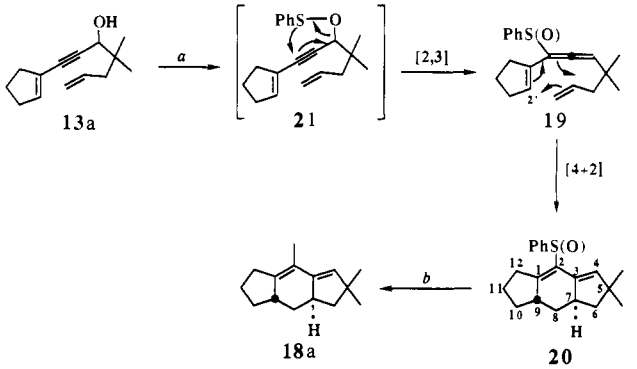
Results and Discussion

Model Systems. Because of the ready availability of enyne **11**[16] and aldehydes of the type **12**,[17] vinylallenes leading to the 5/6/5 ring system were selected for study. Propargyl alcohols of the type **13** were easily prepared in good yield (Scheme III). Treatment of **13a** (**13b**) with benzoyl chloride and catalytic *N,N*-(dimethylamino)pyridine (DMAP) in pyridine afforded benzoate **14a** (**14b**), which was converted to the desired vinylallene **15a** (**15b**) via an S_N2' displacement with excess MeMgBr·LiBr·CuI using the reaction conditions described by MacDonald and coworkers.[18] The allene **15a** was purified (separated from the reduction product **16**,[19] which was the major contaminant) by preparative HPLC and then used directly in the cycloaddition studies. The desmethylallene **15b** was similarly purified, but, in this case, the major byproduct was the enyne **17**, a product of a formal S_N2 displacement.

During the purification of **15a**, small amounts of IMDA cyclization product **18a** could be detected, suggesting that the desired cyclization occurred slowly even at room temperature. In order to quantitatively determine the half-life of the cyclization reaction, a small sample of vinylallene **15a** was heated in an NMR tube in C_6D_6 at 78 °C. The half-life for the Diels–Alder cyclization reaction was determined (by ^1H NMR) to be ~33 min at this temperature. The half-life of **15a** in $CDCl_3$ at room temperature (23 °C) was determined to be ~91 h. This is an exceptionally rapid rate for an uncatalyzed, unactivated IMDA reaction. As discussed earlier, the facility of this process may be attributed to the notion that vinylallenes such as **15a** are topographically especially well suited to undergo an IMDA reaction to afford hydrindanes (Scheme I). In contrast, Houk and Lin found that the cyclization of 1,3,8-nonatriene to afford a hydrindane system was only 45% complete after 90 h at 162 °C.[20] For preparative purposes, **15a** was heated at 80 °C (refluxing C_6H_6) for 4 h to afford **18a** as a single diastereomer (^1H and ^{13}C NMR spectrum) in 95% yield.

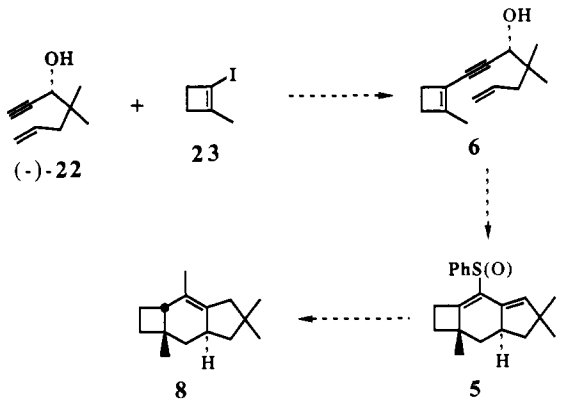
It was found that the cyclization of desmethyl **15b**[21] to afford **18b** was complete after 3 h at 100 °C (refluxing isooctane). Since the cyclization of **15b** to afford **18b** was complete (94% isolated yield of **18b**) after only 3 h at ~100 °C, the IMDA reaction of the *gem*-dimethylvinylallene **15a** was less than ~4 times faster than the IMDA reaction of **15b**. In more quantitative experiments, it was determined that the half-life of IMDA cyclization of **15b** was ~87 min at 78 °C (C_6D_6). Thus, the *gem*-dimethyl effect affords only an ~2.6 acceleration in rate at 78 °C. This appears surprising in view of the fact that *gem*-dimethyl substitution typically accelerates cyclization reactions by a factor of 10^2–10^3.[22] For example, Jung recently reported that in a furan IMDA reaction, *gem*-dimethyl substitution caused a rate acceleration of up to ~10^3.[23,24] However, Boeckmann and Ko found that in another system, introduction of a *gem*-dimethyl group in the chain linking the diene and dienophile caused a rate acceleration by a factor of only ~4,[25] very similar to the present vinylallene case. A rationale for the origin of this variation is incomplete at this time, and further studies are in progress.

Scheme IV[a]



[a] (a) PhSCl, Et_3N, CH_2Cl_2, −78 °C, 2 h; room temperature, 5 h (85%); (b) MeMgBr, Ni(dppp)Cl_2, THF, reflux, 19 h (57%).

Scheme V



A sulfoxide-substituted model system (racemic) was also investigated. Propargyl alcohol **13a**, when treated with benzenesulfenyl chloride in the presence of triethylamine[10,26] at −78 °C followed by stirring the mixture for 5 h at room temperature, afforded diene sulfoxide **20** (isolated in 85% yield as a mixture of two sulfoxide diastereomers, i.e., epimeric at sulfur) as depicted in Scheme IV. The ratio of diastereomer A (less polar isomer) to diastereomer B (more polar isomer) was 1.0–12.7 (by integration of appropriate signals of the ^1H NMR spectrum of the crude mixture).

The structure of sulfoxide **20** was assigned primarily on the basis of the similarity of its spectral data to that of sulfoxide **5**, which was converted into sterpurene (vide infra). Further confirmation of the structure of **20** was provided by its conversion to **18a** with methyl magnesium bromide and nickel [1,3-bis(diphenylphosphine)propane] dichloride [(Ni(dppp)Cl_2].[27] The hydrocarbon diene **18a** proved to be identical with the product obtained from the IMDA reaction of vinylallene **15a**.

In order to determine the half-life for the IMDA reaction of vinylallene sulfoxide **19**, propargyl alcohol **13a** was treated with benzenesulfenyl chloride as described above with the exception that the reaction was worked up after ~$^1/_2$ h at room temperature. The ^1H NMR of the crude reaction mixture showed a mixture of vinylallene **19** and the two diastereomers of **20**. The structure of vinylallene **19** was assigned on the basis of the similarity of

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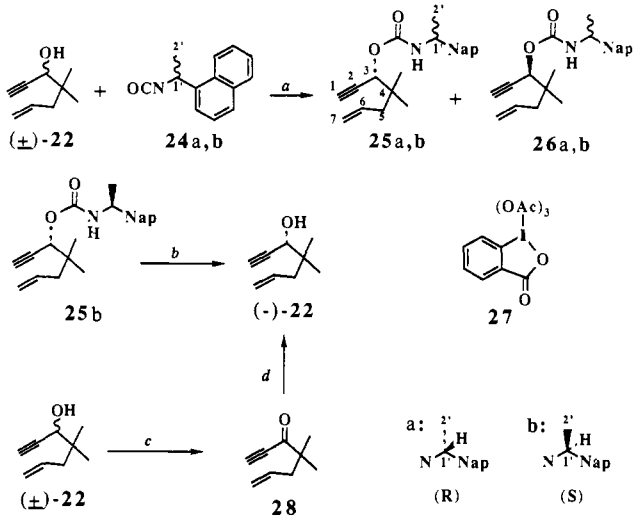
Scheme VI[a]



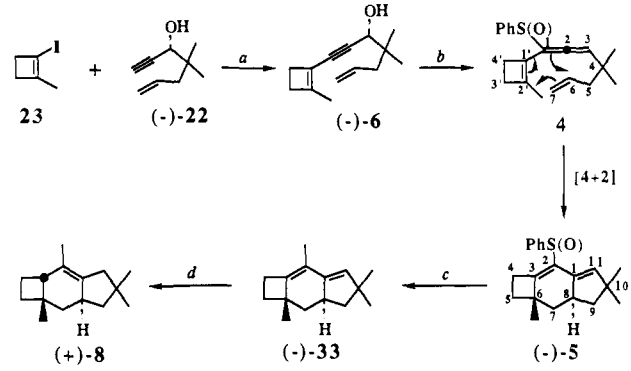
[a] (a) $Me_2NCH_2CH_2OH$, PhH, reflux, 48 h (**25a**, 39%; **25b**, 40%); (b) $HSiCl_3$, Et_3N, PhH, room temperature, 48 h (76%); (c) **27**, CH_2Cl_2, room temperature, 1 h (84%); (d) Darvon alcohol–$LiAlH_4$, Et_2O, −78 °C, 9 h; room temperature, 14 h (65%).

its ^1H NMR to that of the vinylallene sulfoxide **4** (vide infra). The mixture of **19** and **20** in $CDCl_3$ in an NMR tube was maintained at room temperature, and the ^1H NMR was recorded at various time intervals. In this manner, the half-life for the sulfoxide variant of the vinylallene intramolecular Diels–Alder reaction at room temperature (~23 °C) was estimated to be 39 min. The presence of the sulfoxide moiety thus accelerated the reaction at room temperature by a factor of ~140 relative to **15a** (methyl substituent in place of the phenylsulfinyl group).[28] This effect is most simply attributed to the electron-withdrawing phenylsulfinyl group acting to induce an inverse-demand IMDA cyclization reaction. Recently, Posner and his group have exploited the use of phenylsulfinyl-substituted dienes in inverse-demand intermolecular Diels–Alder reactions.[29]

(+)-Sterpurene. The synthetic plan for the preparation of sterpurene (**8**) involved first coupling the two fragments (−)-**22** and **23**[30,31] to produce diene propargyl alcohol **6** (Scheme V), which was to be treated with benzenesulfenyl chloride to afford **5**. It was anticipated that the latter could be readily transformed into (+)-sterpurene (**8**) as indicated earlier.

Propargyl alcohol (−)-**22** was prepared from 2,2-dimethyl-4-pentenal (**12a**, Scheme III), which was treated with lithium acetylide.[32] The racemic propargyl alcohol (±)-**22** was resolved according to the method developed by Pirkle.[33-36] Propargyl alcohol (±)-**22** and (*R*)-napthylethyl isocyanate **24a** were coupled, and the resulting mixture was separated by flash chromatography to afford in order of elution the desired (3*R*,1′*R*)-carbamate **25a** and (3*S*,1′*R*)-carbamate **26a** (Scheme VI). The absolute stereochemical assignments for **25a** and **26a** are based upon an empirical rule governing elution orders of naphthylethyl carbamates developed by Pirkle.[37] Unfortunately, there were technical difficulties using the (*R*)-isocyanate **24a**. The reaction between (±)-**22** and **24a** is not always *complete*, and the small amounts of residual (±)-**22** and **25a** were found not to be easily separable even by HPLC. Also, when **25a** was deprotected with trichlorosilane, it was found that the reaction had not always gone to completion. The resulting mixture of (−)-**22** and residual **25a** could of course also not be easily separated by HPLC.

Scheme VII[a]



[a] (a) $Pd(PPh_3)_2Cl_2$, CuI, Et_2NH, room temperature, 6 h (77%); (b) PhSCl, Et_3N, CH_2Cl_2, −78 °C, 2 h; room temperature, 38 h (70%); (c) MeMgBr, Ni(dppp)Cl_2, THF, reflux, 18 h (62%); (d) Na/NH_3, *t*-BuOH, −78 °C, 3 h (69%).

This problem was circumvented very simply. Alcohol (±)-**22** was coupled with the enantiomeric *S*-naphthylethyl isocyanate **24b**, and the resulting carbamates were again separated by flash chromatography to afford in order of elution (3*S*,1′*S*)-**26b** and (3*R*,1′*S*)-**25b**. Because **25b** and **26b** are enantiomers of **25a** and **26a**, respectively, the complementary empirical elution order rule described above was used to predict their configurations. The diastereomeric excess of flash chromatographically purified **25b** was determined by HPLC to be >99%. The latter was deprotected with trichlorosilane to afford alcohol (−)-**22** contaminated by small amounts of starting **25b**. This mixture was easily separated (in contrast to (−)-**22** and **25a**) by flash chromatography to give (−)-**22** ($[\alpha]_D$ −8.1 (*c* 4.00, $CHCl_3$)) in 76% yield. This material is estimated to be >99% enantiomerically pure within experimental error as evidenced by its method of preparation and conversion to (+)-sterpurene (vide infra).

An additional series of experiments were carried out to more firmly establish the absolute configuration of (−)-propargyl alcohol **22**. Racemic propargyl alcohol (±)-**22** was oxidized with the Dess–Martin periodinane reagent (**27**) to the corresponding ketone **28** in 84% yield.[38,39] The latter (**28**) was then reduced with Darvon alcohol–$LiAlH_4$ complex[40a,b] to afford primarily the same levorotatory enantiomer of **22** previously obtained from cleavage of carbamate **25b** ($[\alpha]_D$ −5.5 (*c* 4.0, $CHCl_3$)). The enantiomeric excess of (−)-**22** obtained from this reduction was determined to be 58%.[40c] It is known that the Darvon alcohol–$LiAlH_4$ complex reduces propargyl ketones to afford primarily (*R*)-propargyl alcohols.[40a,b] Thus the carbamate elution order and the stereochemical mode of reduction are taken to independently support the absolute configuration assigned to (−)-**22** as shown in Scheme VI.

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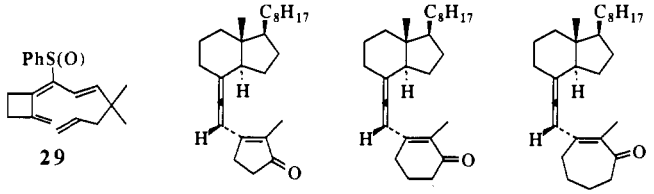
Chart II



29 30 31 32

With (−)-**22** in hand, its coupling[41-44] with vinyl iodide **23** using the Sonogashira procedure[42a] ($PdCl_2(PPh_3)_2$, CuI, Et_2NH) afforded the desired enyne (−)-**6** ($[\alpha]_D$ −13.2 (*c* 9.10, $CHCl_3$)) in 77% isolated yield (Scheme VII). Treatment of dienynol (−)-**6** with benzenesulfenyl chloride (−78 °C for 2 h and then room temperature for 40 h) afforded the desired tricyclic sulfoxide (−)-**5** in 70% yield (as a ~60:40 mixture of sulfur diasteromers). It was found that the major, less polar sulfoxide A possessed $[\alpha]_D$ −110.4 (*c* 1.25, $CHCl_3$) and the minor, more polar sulfoxide B possessed $[\alpha]_D$ −14.0 (*c* 1.10, $CHCl_3$). An attempt was made to determine the enantiomeric purity of the sulfoxides by HPLC on a chiral stationary phase column by the method of Pirkle.[45] A side-by-side comparison was made between optically active and racemic materials (prepared in the same manner as the former) as a control. The major diastereomer could not be resolved into its antipodes. The minor diastereomer was partially resolved, and although only one peak was detected for a sample of optically active (−)-**5**, a quantitative estimate of its enantiomeric excess could not be made.

The IMDA reaction was examined further (racemic series) by following the course of the cycloaddition reaction by ^1H NMR spectroscopy at various time intervals. Sulfoxide (±)-**4** was isolated, and it was found by monitoring the ^1H NMR spectrum of a sample maintained at room temperature that it cyclized to afford the desired diene sulfoxide (±)-**5** with $\tau_{1/2}^{23°C} \sim 12.4$ h. Vinylallene sulfoxide **4**, due to the presence of the allylic methyl group at $C_{2'}$, has the potential to undergo a [1,5]-sigmatropic hydrogen shift to afford tetraene **29** (Chart II). However, there was no evidence (e.g., the presence of exocyclic terminal methylene proton signals in the ^1H NMR spectrum) to indicate that the putative **29** had formed, and this was anticipated for a four-membered ring-fused vinylallene such as **4**. The [1,5]-hydrogen shift pathway should be retarded by a ring size effect which we have previously studied.[3b] Thus, rearrangement of the five-membered ring vinylallenone **30** requires heating at 140 °C for 24 h, whereas the six-membered ring vinylallenone **31** requires only 20 h at 100 °C to effect complete rearrangement. It has been noted that in the seven-membered ring case **32** the [1,5]-shift is even more rapid (3 h at 100 °C). Thus we anticipated the [1,5]-shift in a system such as **4** would be slow, and, in the event, experimentation revealed that the IMDA reaction proceeded satisfactorily.

Table I. Assignments of the Signals in the ^1H and ^{13}C NMR Spectra of Diene **33**[a]

^1H NMR signal, δ[b]	assignment	^{13}C NMR, δ	assignment
1.01 (s)	C_{15}–$CH_{3\alpha}$	14.4	C_{12}
1.08 (s)	C_{14}–$CH_{3\beta}$	26.3	C_{15}
1.15 (s)	C_{13}–CH_3	26.9	C_{13}
1.23 (dd, 11.5, 11.5)	$H_{9\beta}$	27.1	C_4
1.32 (dd, 13.6, 5.2)	$H_{7\beta}$	29.8	C_{14}
1.67 (dd, 1.8, 0.8)	C_{12}–CH_3	34.7	C_5
1.79 (m)	$2H_5$	39.8	C_7
1.83 (dd, 13.6, 10.7)	$H_{7\alpha}$	41.8	C_8
1.90 (dd, 11.5, 6.9)	$H_{9\alpha}$	43.8	C_6 and C_{10}
2.54 (ddd, 14.7, 5.5, 5.5)	$H_{4\alpha}$	45.6	
2.79 (m)	$H_{4\beta}$	50.0	C_9
2.88 (m)	H_8	120.4	C_1, C_2, and C_3
5.26 (d, 2.6)	H_{11}	141.2	
		146.1	
		130.0	C_{11}

[a] Further details are presented in the Supplementary Material. [b] Multiplicities and coupling constants (Hz) are given in the parentheses.

Sulfoxide (−)-**5** was transformed into the optically active diene (−)-**33**, $[\alpha]_D$ −49.2 (*c* 1.25, $CHCl_3$), in 62% yield using a variant of the reaction conditions (MeMgBr, Ni(dppp)Cl_2, THF, reflux) described by Takei and Wenkert.[27] Diene **33** was then reduced[46] under Paquette's conditions (Na, *t*-BuOH, NH_3, THF)[46c] to afford (+)-sterpurene in 69% yield [(+)-**8**], $[\alpha]_D$ +66.3 (*c* 0.83, $CHCl_3$).[47,48] The observed optical rotation was identical within experimental error with that of natural sterpurene, ($[\alpha]_D$ + 65.3 (*c* 0.87, $CHCl_3$)),[49] thus demonstrating that the central–axial–central chiral element transfer process proceeded in a highly enantio- and diastereoselective fashion (presuming that the natural sterpurene[49] was optically and chemically pure) and also that the absolute stereochemistry of (+)-sterpurene is that which is shown in Scheme VII.

The CD spectrum of (+)-sterpurene exhibited a band at 223 nm (θ = −7600) and a more intense band at 205 nm (θ = +19 300) which is in the same position as the UV λ_{max}. This CD spectrum is similar to that seen for other tetrasubstituted olefins.[50] The positive sign of the π to π^* band at 205 nm agrees with that predicted by both the reversed octant rule developed for chiral olefins by Scott and Wrixon[51] and with the axial bond chirality sign convention for chiral olefins developed by Mazur and later investigators.[52] This provides further support for the assigned absolute configuration of (+)-sterpurene. Recently, Abell and Leech established that the absolute configuration of 7,12-dihydroxysterpurene (**10**) is the same as that which we have determined for sterpurene itself.[53]

NMR Studies of Sterpurene and Diene Precursor 33. In order to rigorously establish that the intramolecular Diels–Alder cyclization had proceeded in the expected manner, we independently

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(48) As discussed in greater detail in the Experimental Section, the originally reported (ref 1a) rotation of synthetic (+)-sterpurene ($[\alpha]_D$ +64.9 (*c* 1.54)) was slightly in error due to the presence of minor impurities.

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Table II. Assignments of the Signals in the ^1H and ^{13}C NMR Spectra of Sterpurene[a]

^1H NMR signal, δ[b]	assignment	^{13}C NMR, δ	assignment
0.67 (dd, 12.8, 11.1)	$H_{7\beta}$	17.8	C_{12}
1.05 (s)	C_{15}–$CH_{3\alpha}$	24.7	C_4
1.08 (s)	C_{14}–$CH_{3\beta}$	27.9	C_5
1.09 (m)	$H_{9\beta}$	29.3	C_{15}
1.21 (s)	C_{13}–CH_3	29.5	C_{13}
1.42 (m)	$H_{4\alpha}$	30.2	C_{14}
1.44 (m)	$H_{5\beta}$	36.9	C_{10}
1.51 (m)	C_{12}–CH_3	37.6	C_8
1.53 (dd, 12.8, 5.6)	$H_{7\alpha}$	38.0	C_6
1.66 (ddd, 11.8, 7.1, 1.3)	$H_{9\alpha}$	39.3	C_7
1.92 (ddd, 10.3, 10.3, 10.3)	$H_{5\alpha}$	44.4	C_{11}
2.07 (m)	H_3	44.6	C_3
2.09 (m)	H_{11}	48.6	C_9
2.13 (ddd, 16.7, 1.3, 1.3)	$H_{11'}$	127.7	C_2
2.36 (m)	$H_{4\beta}$	137.0	C_1
~2.6 (m)	H_8		

[a] Further details are presented in the Supplementary Material. [b] Multiplicities and coupling constants (Hz) are given in the parentheses.

determined the structure of diene **33** and sterpurene by the use of a variety of NMR techniques.[54,55] The complete assignment of the ^1H and ^{13}C NMR spectra for sterpurene would also be valuable for biosynthetic studies on this natural product. The strategy employed in these studies was to first assign all signals in the ^1H NMR spectrum and then use these assignments along with ^1H–^{13}C correlation experiments to assign the peaks in the ^{13}C spectrum.

The ^1H NMR spectrum of diene **33** was assigned on the basis of five pices of evidence: (a) coupling constants from the 500 MHz spectrum; (b) connectivity patterns from 500 MHz ^1H–^1H (COSY) 2D NMR experiments;[54,55] (c) 300 MHz NOE experiments; (d) 300 MHz decoupling experiments; and (e) calculated vicinal coupling constants determined from the MMX optimized structure of **33**.[56] Once all of the proton signals had been assigned, the carbon signals (with the exception of the quaternary carbon signals) were readily assigned by a 2D ^1H–^{13}C NMR experiment.[57] The ^1H and ^{13}C NMR assignments are summarized in Table I, and a detailed discussion of the assignments is presented in the Supplementary Material.

The same kinds of information were used to assign the ^1H NMR spectrum of sterpurene (**8**) as for the precursor diene **33**. An exception was that it was necessary to utilize the ^1H–^{13}C 2D NMR spectrum in order to unambiguously assign some of the proton signals. The ^1H NMR spectrum of sterpurene had previously been partially assigned by Ayer and Saeedi-Ghomi,[13] although in the present study two signals were reassigned.

With the proton spectrum completely assigned, the methyl, methylene, and methine signals in the ^{13}C NMR spectrum of sterpurene were readily assigned by a 2D ^1H–^{13}C NMR experiment. In order to assign the four quaternary carbons, a long range 2D ^1H–^{13}C correlation experiment was performed.[58] To verify the assignments, a selective heteronuclear NOE experiment was also performed. The ^1H and ^{13}C assignments are presented in Table II, and a detailed discussion of the spectra is given in the Supplementary Material.

Summary. It has been demonstrated that the intramolecular vinylallene Diels–Alder reaction leading to a hydrindane system proceeds in a highly enantio- and diastereoselective manner. The introduction of *gem*-dimethyl groups on the tether linking the vinylallene and olefin has only a modest accelerating effect.

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Table III. GC and GC/MS Analysis of Contaminants in Sterpurene

peak	relative % *a*	relative % *b*	*m/z*
1	1.6	1.9	190 (a desmethyl compound)
2	2.1	2.2	190 (a desmethyl compound)
3[c]	3.2	3.4	204 (isomer of sterpurene)
4[c]	87.3	85.8	204 (sterpurene)
5	2.0	2.5	218
6	4.0	4.2	218

[a] GC conditions: HP 5880A gas chromatograph, methyl silicone 10 m capillary column, injector temperature 200 °C, oven temperature 60–250 °C (6 °C/min rate of increase). [b] GC column: HP 5790A gas chromatograph (linked to a VG-ZAB mass spectrometer), DB5 capillary column, injector temperature 180 °C, oven temperature 40–250 °C (6 °C/min rate of increase). [c] In addition, a seventh peak was seen between peaks 3 and 4 (relative area: <1%) which possessed an *m/z* of 204 (isomer of sterpurene).

However, the sulfoxide moiety exerts a pronounced acceleration on the vinylallene IMDA reaction. This reaction has been employed as the key step in a highly stereoselective central–axial–central chiral element transfer process, which provided as means to a concise, enantioselective total synthesis of the novel sesquiterpene (+)-sterpurene. In this manner, the absolute configuration of this natural product has been determined. This new synthetic approach should be applicable to the enantioselective preparation of a wide variety of hydrindane systems.

Experimental Section[59]

Preparation of Benzenesulfenyl Chloride. Distillation Method. A solution of sulfuryl chloride in CH_2Cl_2 (19.8 mL, 1.0 M, 19.8 mmol) was added to Ph_2S_2 (4.10 g, 18.9 mmol) in a 50 mL flask at 0 °C under N_2. The cooling bath was removed, and the mixture was stirred at ambient temperature for 4 h. The solvent was then removed by rotary evaporation, and the residue was distilled under reduced pressure to afford 1.09 g (20%) of pure PhSCl as a clear, dark red liquid (bp 33 °C (0.24 mm)).

In Situ Method. A solution of chlorine in CCl_4 (1.15 mL, 0.96 M, 1.10 mmol) was added to diphenyl disulfide (240 mg, 1.10 mmol) in a 10-mL flask under N_2 at 0 °C. The resulting mixture was stirred for 10 min and then warmed to room temperature to give an orange-red solution of PhSCl in CCl_4 (3.65 mL, 1.66 M, 2.20 mmol).

1-(2′-Methylcyclobut-1′-en-1′-yl)-1-(phenylsulfinyl)-4,4-dimethyl-1,2,6-heptatriene (4). A solution of PhSCl (0.45 mL, 1.44 M in CCl_4, 0.65 mmol; prepared via the in situ method) was added to a mixture of racemic propargyl alcohol (±)-**6** (102 mg, 0.50 mmol), triethylamine (0.18 mL, 131 mg, 1.30 mmol, distilled from CaH_2) and dichloromethane (10 mL, distilled from CaH_2) in a 50-mL flask at −78 °C under N_2. The reaction mixture was stirred for 2 h, and then the cooling bath was removed. After ~1 h, the reaction mixture was quenched with water (~2 mL) and added to a mixture of CH_2Cl_2 and saturated aqueous $NaHCO_3$ in a separatory funnel. The layers were separated, and the organic layer was dried ($MgSO_4$) and filtered. The solvent was removed to give the crude product, which was purified by flash chromatography (15% EtOAc/hexanes, 2.5 × 15 cm silica gel) to afford 70 mg (45%) of vinylallene sulfoxide **4**. A sample of vinylallene **4** was allowed to cyclize at room temperature in ~0.5 mL $CDCl_3$ in an NMR tube. The reaction rate was monitored by the change in the ratio of the peak at 5.60 (H_3 of one isomer of vinylallene **4**) and the peak at 5.18 (H_{11} for one diastereomer of the tricyclic sulfoxide **5**). The half-life measured in this manner was $\tau_{1/2}^{23°C}$ ~ 740 min (~12 h).

(−)-(6*S*,8*S*)- and (±)-(6*R,8*R**)-2-(Phenylsulfinyl)-6,10,10-trimethylcyclo[6.3.0.0^{3,6}]undeca-1(11),2-diene (5).** Racemic propargyl alcohol **6** (102 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (10 mL, distilled from CaH_2) under N_2 and cooled to −78 °C. Triethylamine (0.16 mL, 120 mg, 1.2 mmol, distilled from KOH) was added to the mixture followed by PhSCl (0.6 mmol, 87 mg, freshly distilled). The reaction mixture was stirred at −78 °C for 2 h and at room temperature for 40 h. Water (~2 mL) was added to quench the reaction, and then the mixture was diluted with CH_2Cl_2. The organic phase was separated, extracted with saturated aqueous $NaHCO_3$ (1×), dried ($MgSO_4$), filtered, and concentrated to give an orange oil. Flash chromatographic purification (15% EtOAc/hexanes, 3.0 × 18 cm silica gel) gave 119 mg (76%) of **5** (diastereomer A, major, less polar and diastereomer B, minor, more polar) as a diastereomeric mixture. A portion of this mixture was

(59) General experimental details are given in the Supplementary Material.

separated by HPLC (Rainin Dynamax 1.0 × 25 cm, 5 μm silica gel column, 15% EtOAc/hexanes) to give, in the following order of elution, diastereomer A as a white crystalline solid (mp 97–98 °C) and diastereomer B as a clear liquid. Integration of the peaks assigned to H_{11} in the NMR of the crude reaction mixture gave an A:B ratio of 61:39. Integration of the HPLC RI trace gave an A:B ratio of 62:38.

A freshly prepared CCl_4 solution of benzenesulfenyl chloride (0.40 mL, 1.66 M, 0.66 mmol; prepared by the in situ method) was added to a stirred mixture of (3*R*)-dienynol (−)-**6** (113 mg, 0.55 mmol) and triethylamine (0.19 mL, 140 mg, 1.39 mmol, distilled from CaH_2) in CH_2Cl_2 (11.6 mL, distilled from CaH_2) under N_2 at −78 °C. After 2 h, the cooling bath was removed, and the reaction mixture was stirred for 38 h at room temperature. The reaction mixture was then worked up, and the product was purified by chromatography in the same manner described above to give 120 mg (70%) of (6*S*,8*S*)-sulfoxide **5** (as a ~60:40 mixture). The major, less polar sulfoxide (isomer A) was found to possess $[\alpha]_D = -110.4$ (c = 1.25, $CHCl_3$). The minor, more polar sulfoxide (isomer B) was found to possess $[\alpha]_D = -14.0$ (c = 1.1, $CHCl_3$).

(±)- and (−)-1-(2′-Methylcyclobut-1′-en-1′-yl)-4,4-dimethyl-6-hepten-1-yn-3-ol (6). Cyclobutenyl iodide **23** (100 mg, 0.52 mmol) and racemic propargyl alcohol (±)-**22** (71 mg, 0.52 mmol) in a 25-mL flask under N_2 were dissolved in diethylamine (3 mL, distilled from BaO). To this mixture were added $Pd(PPh_3)_2Cl_2$ (36 mg, 0.052 mmol) and CuI (19 mg, 0.10 mmol). The flask was covered with aluminum foil and the reaction mixture was stirred for 6 h at room temperature. The Et_2NH was removed by rotary evaporation, and the residue was diluted with H_2O (~20 mL). The mixture was extracted with Et_2O (3 × 25 mL), and then the combined organic layers were dried ($MgSO_4$), filtered, and concentrated to give an orange residue. Flash chromatographic purification (10% EtOAc/hexanes, 2.5 × 15 cm silica gel) gave 94 mg (89%) of racemic alcohol (±)-**6**.

Optically pure (−)-(3*R*)-propargyl alcohol **22** (400 mg, 2.89 mmol) and cyclobutenyl iodide **23** (674 mg, 3.47 mmol) were coupled in the same manner described above [101 mg (0.145 mmol) $Pd(PPh_3)_2Cl_2$, 55 mg (0.289 mmol) CuI, 17.3 mL Et_2NH] to afford 453 mg (77%) of (3*R*)-dienynol (−)-**6** [$[\alpha]_D$ −13.2 (c 9.1, $CHCl_3$)].

The benzoate ester of (±)-**6** was also prepared. To a solution of dienynol (±)-**6** (258 mg, 1.26 mmol) in pyridine (4.5 mL, distilled from KOH) under N_2 at room temperature was added *N*,*N*-(dimethylamino)pyridine (DMAP, 12 mg) followed by benzoyl chloride (0.154 mL, 187 mg, 1.33 mmol). After 2 h, ether (50 mL) was added, and the mixture was washed with saturated aqueous $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL), dried ($MgSO_4$), filtered, and concentrated to give the crude product. Flash chromatography (95:5:0.5, hexanes/EtOAc/pyridine; 2.5 × 15 cm silica gel) afforded 208 mg (53%) of the desired racemic benzoate of (±)-**6** as a clear, viscous oil.

(±)- and (+)-1-Sterpurene, (3*R,6*R**,8*R**)- and (3*S*,6*S*,8*S*)-2,6,10,10-Tetramethyltricyclo[6.3.0.0^{3,6}]undec-1-ene (8).** A solution of sodium in liquid ammonia was prepared by introducing ~25 mg of sodium to ~25 mL of liquid ammonia at −78 °C in a 50-mL, three-necked flask equipped with a N_2 inlet and a dry ice condenser. To the resulting dark blue solution was then added a solution of (±)-diene **33** (12.5 mg, 0.060 mmol) and *t*-BuOH (0.020 mL, distilled from CaH_2) in THF (0.5 mL distilled from sodium/benzophenone ketyl), followed by 0.5 mL rinsing with THF. The reaction mixture was stirred for 3 h at −78 °C to −33 °C, quenched carefully with aqueous NH_4Cl (~2 mL), then warmed to room temperature, and stirred for ~3 h to allow the ammonia to evaporate. The reaction mixture was diluted with saturated aqueous NH_4Cl (20 mL) and then extracted with ether (3 × 25 mL). The combined ether extracts were washed with brine (1 × 20 mL), dried ($MgSO_4$), and carefully concentrated (due to the volatile nature of sterpurene) to give the crude reaction product. Flash chromatographic purification (100% hexanes, 1.0 × 21 cm silica gel) afforded 7.0 mg (56%) of (±)-1-sterpurene (**8**).

The procedure described above was used to transform (−)-diene **33** (26 mg, 0.128 mmol) to (+)-1-sterpurene (with the exception that the temperature during the entire reaction was maintained at −78 °C) by using the same proportions of solvent and reagents. Flash chromatographic purification (100% hexanes, 1.5 × 20 cm silica gel) gave 18 mg (69%) of (+)-1-sterpurene, $[\alpha]_D$ +64.9 (c 1.54, $CHCl_3$); lit.[49] $[\alpha]_D$ +65.3 (c 0.87, $CHCl_3$).

A GC/MS experiment[60] later demonstrated that this sample of (+)-sterpurene was accompanied by five other minor compounds (Table III), each of which was present in from ~1.6 to 4.2% (average of 2.7% each). Reverse phase HPLC purification (Whatman M-9 ODS-2 Partisil 10 × 50 cm column, 100% acetonitrile) afforded sterpurene of greater than 97% purity (by ^1H NMR and capillary GC analysis). This material was found to possess an optical rotation of $[\alpha]_D$ +66.3 (c, 0.83, $CHCl_3$). The optical rotation of HPLC purified sterpurene was measured four times, using two different samples. The average rotation obtained was $[\alpha]_D$ +65.8 (average c 0.54, $CHCl_3$).

1-(Cyclopent-1′-en-1′-yl)-4,4-dimethyl-6-hepten-1-yn-3-ol (13a). Enyne **11** (2.03 g, 22 mmol)[16] was dissolved in ether (29 mL, distilled from Na/benzophenone ketyl) in a 100-mL flask under N_2. This mixture was cooled to 0 °C, and *n*-BuLi (13.2 mL, 1.52 M in hexanes, 20 mmol) was added dropwise via syringe to give a clear yellow solution of the acetylide anion. After 30 min, 2,2-dimethyl-4-pentenal (**12a**, 2.87 mL, 2.47 g, 22 mmol)[17] was added via syringe to the reaction mixture. After an additional 5 min, the cooling bath was removed, and the reaction was stirred at room temperature for 2 h. After water (~4 mL) was added to quench the reaction, K_2CO_3 was added to the mixture until a paste formed. The reaction mixture was diluted with additional ether, then dried ($MgSO_4$), and filtered. The solvent was removed, and the crude propargyl alcohol was distilled (Kugelrohr; bp 90–92 °C, 0.1 mm) to afford 3.91 g (96%) of **13a** as a clear, viscous oil.

1-(Cyclopent-1′-en-1′-yl)-6-hepten-1-yn-3-ol (13b). Enyne **11** (0.76 g, 8.2 mmol) was dissolved in ether (10 mL, distilled from Na/benzophenone ketyl) in a 50-mL flask under N_2. This mixture was cooled to 0 °C and *n*-BuLi (5.4 mL, 1.45 M in hexanes, 7.8 mmol) was added dropwise via syringe to give a clear yellow soliution of the acetylide anion. After 30 min, 4-pentenal[21] (1.04 g, 12.3 mmol) was added via cannula to the reaction mixture. After an additional 5 min, the cooling bath was removed, and the reaction was stirred at room temperature for 2 h. After water (~2 mL) was added to quench the reaction, K_2CO_3 was added to the mixture until a paste formed. The reaction mixture was diluted with additional ether, then dried ($MgSO_4$), and filtered. The solvent was removed, and the crude propargyl alcohol was purified by flash chromatography (10% EtOAc/hexanes, 5.0 × 15 cm silica gel) to afford 0.82 g (60%) of **13b** as a clear oil.

1-(Cyclopent-1′-en-1′-yl)-3-(benzoyloxy)-4,4-dimethyl-6-hepten-1-yne (14a). Propargyl alcohol **13a** (0.82 g, 4.0 mmol) was dissolved in pyridine (14 mL, distilled from KOH) in a 50-mL flask under N_2. To this solution was then added *N*,*N*-(dimethylamino)pyridine (DMAP, 38 mg, 0.14 mmol) followed by benzoyl chloride (0.49 mL, 0.59 g, 4.2 mmol). After 3 h at room temperature, the reaction mixture was taken up in ether, and the other solution was washed with saturated aqueous $NaHCO_3$ (1×) and brine (1×), dried ($MgSO_4$), and filtered. The solvent was removed to give the crude reaction product which was purified by flash chromatography (5% EtOAc/hexanes, 4.0 × 15 cm silica gel) to afford 1.1 g (92%) of benzoate **14a** as a clear viscous oil.

1-(Cyclopent-1′-en-1′-yl)-3-(benzoyloxy)-6-hepten-1-yne (14b). Propargyl alcohol **13b** (0.31 g, 1.76 mmol) was dissolved in pyridine (6.2 mL, distilled from KOH) in a 25-mL flask under N_2. To this solution was then added *N*,*N*-(dimethylamino)pyridine (DMAP, 17 mg) followed by benzoyl chloride (0.21 mL, 0.26 g, 1.85 mmol). After 3 h at room temperature, the reaction mixture was taken up in ether, and the ether solution was washed with saturated aqueous $NaHCO_3$ (1×), water (1×), saturated aqueous $CuSO_4$ (4×), and brine (1×), dried ($MgSO_4$), and filtered. The solvent was removed to give the crude reaction product which was purified by flash chromatography (5% EtOAc/hexanes, 3.0 × 15 cm silica gel) to afford 0.39 g (80%) of benzoate **14b** as a clear oil.

1-(Cyclopent-1′-en-1′-yl)-1,4,4-trimethyl-1,2,6-heptatriene (15a). Tetrahydrofuran (28 mL, distilled from Na/benzophenone ketyl) was added to a mixture of LiBr (0.57 g, 6.6 mmol, dried under vacuum at ~50 °C for several hours) and purified CuI (1.26 g, 6.6 mmol) in a 100 mL flask under N_2 at room temperature. The resulting mixture was stirred until a homogeneous yellow solution was obtained. This solution was cooled to 0 °C, and CH_3MgBr (2.73 M in ether, 2.39 mL, 6.5 mmol) was introduced via syringe. After 15 min, a solution of benzoate **14a** (0.34 g, 1.1 mmol) in THF (3 mL plus 2 mL rinsing) was added to the well-stirred greenish copper reagent suspension via cannula, and the reaction mixture was then allowed to warm to room temperature. After 3 h, an ~2 mL aliquot removed from the reaction mixture was added to ~2 mL saturated aqueous NH_4Cl, and the latter aliquot was worked up in the manner described below. The crude ^1H NMR of the aliquot indicated the presence of a mixture of the desired methylated vinylallene **14a** and reduced vinylallene **16** in a ratio of 60:40. This ratio was determined by integration (cut and weight method) of the peak at δ 5.18 assigned to H_3 of methylated vinylallene **14a** and the peak at δ 6.10 assigned to H_1 of reduced vinyalllene **16**. After ~7 h, the reaction was quenched with ~5 mL saturated aqueous NH_4Cl, and the mixture was taken up in ether (~150 mL). The resulting mixture was washed with saturated aqueous $NaHCO_3$ (1×) and brine (1×), dried ($MgSO_4$), and filtered. Removal of the solvent afforded the crude reaction product. The ^1H NMR of the crude product indicated a 76:24 mixture of the desired methylated vinylallene **15a** and reduced vinylallene **16**. After preliminary flash chromatographic purification (100% hexanes, 2.0 × 17 cm silica

(60) We thank Professor Thomas H. Morton for suggesting this experiment.

gel) the hydrocarbon mixture was separated by HPLC (100% hexanes, Whatman M10, 2.0 × 50 cm silica gel column, 7 mL/min, four recycles) to afford in the following order of elution: 19 mg (9%) of the cyclized hydrocarbon **18a**, 110 mg (50%) of the methylated vinylallene **15a**, and 27 mg (14%) of the reduced vinylallene.

1-(Cyclopent-1′-en-1′-yl)-1-methyl-1,2,6-heptatriene (15b). A solution of CH_3MgBr (2.70 mL, 3.00 M in ether, 7.9 mmol) was added to a well-stirred mixture of dry LiBr (697 mg, 8.0 mmol) and purified CuI (1.53 g, 8.0 mmol) in 34 mL of THF (distilled from Na/benzophenone ketyl) at 0 °C under N_2. The reaction mixture was stirred for 15 min at 0 °C, the propargylic benzoate **14b** (353 mg, 1.26 mmol) in 5 mL of THF was added dropwise, and the reaction mixture was then stirred for 7 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (~5 mL), and the mixture was taken up in ether. The organic layer was subsequently washed with saturated aqueous $NaHCO_3$ (1×) and brine (1×), dried ($MgSO_4$), and filtered. Concentration followed by flash chromatography (100% hexanes, 2.0 × 18 cm silica gel, ~5 mL fractions) afforded in the following order of elution: 110 mg (50%) of the desired vinylallene **15b** and 23 mg (10%) of the methyl-substituted enyne **17**.

(7*R,9*S**)-2,5,5-Trimethyltricyclo[7.3.0.0^{3,7}]dodeca-1,3-diene (18a). Method A.** Vinylallene **15a** (44 mg, 0.22 mmol) was dissolved in benzene (4.3 mL, distilled from Na/benzophenone ketyl) in a 25-mL flask equipped with West condenser under N_2. This solution was refluxed for 4 h and then cooled to room temperature. The solvent was removed to afford 42 mg (95%) of the desired tricyclic product **18a**. For spectral purposes, a small sample of hydrocarbon **18a** was purified by HPLC (100% hexanes, Whatman M10, 2.0 × 50 cm silica gel column, 7 mL/min, four recycles). The half-life for the Diels–Alder reaction was determined in the following manner. A sample of vinylallene **15a** (~8 mg) was dissolved in benzene-d_6 (~0.5 mL), placed in an NMR tube under N_2, and then heated in an oil bath at 78 °C. The tube was removed from the bath at several intervals, and the spectrum of the mixture was recorded. The peak at δ 5.59 assigned to $H_{2'}$ of the vinylallene **15a** and the peak at δ 5.30 assigned to H_4 of the tricycle **18a** were integrated by the cut and weight method, and the ratio of these two peaks was used to determine the half-life for this reaction ($\tau_{1/2}^{78°C}$ ~ 33 min). A sample of **15a** (~5 mg) was also dissolved in $CDCl_3$ (~0.5 mL) and allowed to stand at room temperature. The NMR spectrum of the resulting mixture was then measured at several intervals, and the half-life at room temperature was determined in the same manner as described above ($\tau_{1/2}^{23°C}$ ~ 91 h).

Method B. To a solution of sulfoxide **20** (110 mg, 0.35 mmol, diastereomeric mixture) and Ni(dppp)Cl_2 ([1,3-bis(diphenylphosphino)-propane]nickel(II) chloride; 24 mg, 0.035 mmol) in THF (9.2 mL, distilled from Na/benzophenone) under N_2 at room temperature was added CH_3MgBr (0.96 mL, 2.73 M in ether, 2.6 mmol). The resulting mixture was then refluxed for 19 h, cooled to room temperature, and quenched with saturated aqueous NH_4Cl (~2 mL). The reaction mixture was taken up in ether and the ether extract was washed with saturated aqueous $NaHCO_3$ (1×) and brine (1×), dried ($MgSO_4$), filtered, and concentrated. The crude reaction product was absorbed on Na_2SO_4, the solvent was removed, and the mixture was separated by flash chromatography (100% hexanes, 2.0 × 19 cm silica gel) to afford 40 mg (57%) of the hydrocarbon **18a**, identical by ^1H NMR with the material produced from the thermolysis of vinylallene hydrocarbon **15a**.

(7*R,9*R**)-2-Methyltricyclo[7.3.0.0^{3,7}]dodeca-1,3-diene (18b).** A solution of vinylallene **15b** (51 mg, 0.30 mmol) in 5 mL of isooctane (distilled from $LiAlH_4$) was heated at reflux temperature (100 °C) for 3 h. The reaction was monitored by TLC (100% hexanes). The reaction mixture was then cooled to room temperature, the solvent was removed, and the residue purified on the chromatotron (1 mm silica gel, 100% hexanes) to afford 48 mg (94%) of the desired Diels–Alder product **18b**. By a method similar to that described in the preceding section for the IMDA reaction of **15a** to **18a**, the half-life for the conversion of **15b** to **18b** in C_6D_6 was determined to be $\tau_{1/2}^{78°C}$ ~ 87 min (and $\tau_{1/2}^{23°C}$ ~ 250 h in $CDCl_3$ in a separate experiment).

(7*R,9*S**)-2-(Phenylsulfinyl)-5,5-dimethyltricyclo[7.3.0.0^{3,7}]dodeca-1,3-diene (20).** A solution of PhSCl (0.71 mL, 1.68 M in CCl_4, 1.2 mmol; prepared via the in situ method) was added to a solution of propargyl alcohol **13a** (204 mg, 1.0 mmol), triethylamine (0.33 mL, 242 mg, 2.4 mmol, distilled from CaH_2), and CH_2Cl_2 (20 mL, distilled from CaH_2) at −78 °C under N_2. The reaction mixture was stirred for 2 h at −78 °C and then for 5 h at room temperature. After water (~2 mL) was added to quench the reaction, the reaction mixture was taken up in additional CH_2Cl_2 (40 mL), and then the CH_2Cl_2 extract was washed with saturated aqueous $NaHCO_3$ (1 × 25 mL), dried ($MgSO_4$), and filtered. The solvent was removed to give the crude sulfoxide as an orange oil. Flash chromatography (15% EtOAc/hexanes, 2.5 × 16 cm silica gel) afforded 266 mg (85%) of sulfoxide **20** as a mixture of two diastereomers. Integration of the peaks assigned to H_4 in the ^1H NMR of the crude material gave a ratio of the minor, less polar isomer A to the major, more polar isomer B of 1.0:12.7. For analytical purposes, these isomers were separated by HPLC (Whatman M10 2.0 × 50 cm silica gel column, 15% EtOAc/hexanes, 9.5 mL/min) to afford pure isomer B as a white solid, mp 92–93 °C. The minor, less polar isomer A under these conditions was not separated from an aromatic impurity.

In a separate experiment, an identical amount of propargyl alcohol **13a** was treated in the same manner described above with the exception that the reaction was worked up after ~1/2 h at room temperature. The crude NMR showed a mixture of vinylallene **19** and the two diastereomers of **20**. The rate of the Diels–Alder reaction at room temperature was then followed by ^1H NMR. The signals assignable to the allene sulfoxide intermediate were as follows: δ ($CDCl_3$) 4.9–5.1 (2 H, C_7-CH_2, m), 5.59 (1 H, H_3, narrow m), 5.6–5.8 (1 H, H_6, m), 6.17 (1 H, $H_{2'}$, narrow m). The peak at δ 6.17 assigned to $H_{2'}$ of the vinylallene **19** and the peaks at δ 5.35 and 5.89 assigned to H_4 of the two cyclized sulfoxide diastereomers (**20**) were integrated by the cut and weight method to determine the fraction of starting material remaining at several different time points. It was found that vinylallene sulfoxide **19** cyclized with a $\tau_{1/2}^{23°C}$ ~ 39 min.

(±)-4,4-Dimethyl-6-hepten-1-yn-3-ol (22). A 50-mL graduated cylinder (fitted with a septum and a nitrogen inlet) was filled with 40 mL of THF under N_2 and cooled to −78 °C. Acetylene was passed through this solution until the total volume increased by ~3.5 mL (~85 mmol). The acetylene solution was added via cannula to a 500-mL flask containing 50 mL of THF at −78 °C. After the transfer was complete, the graduated cylinder was thoroughly flushed with N_2 (~30 min) to remove any acetylene gas. *n*-Butyllithium (17.9 mL, 50 mmol, 2.80 M in hexanes) was added to a 100-mL flask containing 20 mL of THF at −78 °C. The resulting solution was then added dropwise *slowly* via the cannula to the flask containing the acetylene/THF solution. After the addition was complete, the solution of lithium acetylide was stirred for ~15 min, and then 2,2-dimethyl-4-pentenal (**12a**, 5.87 mL, 5.05 g, 45 mmol) was added neat via syringe. The reaction mixture was stirred for 30 min at −78 °C and 14 h at room temperature, quenched with H_2O (~5 mL), treated with K_2CO_3 until a paste formed, dried ($MgSO_4$), and concentrated to give the crude reaction product. Distillation (Kugelrohr, 100–105 °C, ~40 mm) afforded 6.04 g (97%) of propargyl alcohol (±)-**22**.

(−)-(3*R*)-4,4-Dimethyl-6-hepten-1-yn-3-ol (22). To (3*R*,1′*S*)-naphthylethyl carbamate **25b** (1.3 g, 3.9 mmol, prepared from (*S*)-(+)-1-(1-naphthyl)ethyl isocyanate **24b** and racemic propargyl alcohol (±)-**22** in benzene (37.5 mL, distilled from sodium/benzophenone ketyl) under N_2 in a 100-mL flask was added triethylamine (0.64 mL, 0.46 g, 4.6 mmol). A mixture of trichlorosilane (0.49 mL, 0.62 g, 4.6 mmol) in benzene (9.4 mL) was added dropwise (slowly) via a 20 gauge cannula to the carbamate mixture. The resulting mixture was stirred at room temperature for 48 h and then poured slowly into 100 mL of vigorously stirred saturated aqueous NH_4Cl. The layers were separated, the aqueous layer was extracted with ether (4 × 50 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated to give the crude reaction product. Flash chromatography (10% EtOAc/hexanes, 5 × 15 cm silica gel) afforded 0.40 g of alcohol (−)-**22** (76% yield; $[\alpha]_D$ −8.1 (*c*, 4.0, $CHCl_3$)). When the (3*R*,1′*R*)-naphthylethyl carbamate **25a** (prepared from (*R*)-(−)-1-(1-naphthyl)ethyl isocyanate and racemic propargyl alcohol (±)-**22**) was treated with trichlorosilane using the same conditions as described above, the optically active alcohol (−)-**22** could not be separated chromatographically from a small amount of remaining unreacted (3*R*,1′*R*)-carbamate **25a**.

1-Iodo-2-methylcyclobutene (23).[30a,31] To a cooled (−78 °C) solution of 4-bromo-1-butyne[61] (2.00 g, 15.0 mmol) in pentane (30 mL, distilled from $LiAlH_4$) under N_2 was added *n*-BuLi (9.6 mL, 15.0 mmol, 1.56 M in hexanes) dropwise. After 30 min at −78 °C, a solution of dichlorobis(η^5-cyclopentadienyl)zirconium (zirconocene dichloride, 4.38 g, 15.0 mmol) and trimethylaluminum (2.96 mL, neat, 2.16 g, 30 mmol) in CH_2Cl_2 (30 mL, distilled from CaH_2) was added via cannula, and then the reaction mixture was brought to room temperature. After 3 h, the reaction was recooled to −78 °C, and a solution of iodine (5.71 g, 22.5 mmol) in ether (35 mL, distilled from Na/benzophenone ketyl) was added. The reaction mixture was warmed to 0 °C for ~15 min and then poured into a well-stirred mixture of ice and 5% aqueous HCl. The layers were separated, the aqueous phase was extracted with ether (3×), and the combined organic layers were washed with saturated aqueous $NaHCO_3$ (3×), saturated aqueous $Na_2S_2O_3$ (1×), and brine (1×), then dried

(61) (a) Daniels, S. B.; Cooney, E.; Sofia, M. J.; Chakravarty, P. K.; Katzenellenbogen, J. A. *J. Biol. Chem.* **1983**, *258*, 15046. (b) For an alternative method for the preparation of 4-bromo-1-butyne, see: Eglinton, G.; Whiting, M. C. *J. Chem. Soc.* **1950**, 3650.

($MgSO_4$), and concentrated. Kugelrohr distillation (bp 90 °C, ~25 mm) of the residue gave 1.68 g (58%) of vinyl iodide **23** as a clear, pale yellow liquid (~90% pure by ^1H NMR).

(3*R*,1′*S*)-4,4-Dimethyl-6-hepten-1-yn-3-yl *N*-[1′-(1-Naphthyl)ethyl]-carbamate (25b). Racemic propargyl alcohol (±)-**22** (1.16 g, 8.40 mmol), (*S*)-(+)-1-(naphthyl)ethyl isocyanate **24b** (1.74 g, 8.83 mmol), *N*,*N*-dimethylethanolamine (3 drops, distilled from NaOH), and benzene (18.7 mL, distilled from sodium/benzophenone ketyl) were placed in a 50-mL flask equipped with a West condenser, and the resulting mixture was then refluxed under N_2 for 48 h. The reaction mixture was cooled to room temperature, the solvent was removed, and the residue was purified by flash chromatography (10% EtOAc/hexanes, 8.0 × 23 cm silica gel) to afford the expected diastereomers in the following order of elution: (3*S*,1′*S*)-isomer **26b** followed by the desired (3*R*,1′*S*)-isomer **25b** (1.14 g, 40%). For analytical purposes, a mixture of the diastereomers was separated by HPLC (Rainin Dynamax 2.24 × 25 cm, 5 μm silica gel column, 10% EtOAc/hexanes, 9 mL/min flow rate) to afford (3*S*,1′*S*)-isomer **26b** (retention time = 26 min) and (3*R*,1′*S*)-isomer **25b** (retention time = 38 min). A sample of the (3*R*,1′*S*)-isomer **25b** obtained by flash column purification was analyzed by HPLC: integration (cut and weigh method) of the RI trace indicated a ratio of **25b**/**26b** of 119:1 (de > 99%).

(6*R,8*R**)- and (6*S*,8*S*)-2,6,10,10-Tetramethyltricyclo[6.3.0.0^{3,6}]-undeca-1(11),2-diene (33).** To a solution of sulfoxide (±)-**5** (diastereomeric mixture, 56 mg, 0.18 mmol) in THF (4.9 mL, distilled from sodium/benzophenone ketyl) under N_2 was introduced [1,3-bis(diphenylphosphino)propane]nickel(II) dichloride (Ni(dppp)Cl_2, 12 mg, 0.018 mmol) followed by methylmagnesium bromide (2.73 M in ether, 0.49 mL, 1.35 mmol). The reaction mixture was refluxed for 14.5 h, cooled to room temperature, and quenched with saturated aqueous NH_4Cl (~2 mL). Ether was added, and then the organic extract was washed with brine, dried ($MgSO_4$), filtered, and concentrated. Flash chromatographic purification (hexanes, 1.5 × 20 cm silica gel) gave 24 mg (66%) of pure (±)-**33**.

Optically active sulfoxide (−)-**5** (distereomeric mixture; 74 mg, 0.24 mmol) was treated in the same manner described above [16 mg (0.024 mmol) Ni(dppp)Cl_2, 0.65 mL (1.78 mmol) MeMgBr (2.73 M in ether), 6.4 mL THF] to afford 30 mg (62%) of pure (6*S*,8*S*)-diene (−)-**33** ($[\alpha]_D$ −49.2 (*c* 1.3, $CHCl_3$)).

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Registry No. (±)-**4** (isomer 1), 119904-10-8; (±)-**4** (isomer 2), 119904-11-9; (−)-**5** (isomer 1), 114636-41-8; (−)-**5** (isomer 2), 114715-41-2; (±)-**5** (isomer 1), 119904-14-2; (±)-**5** (isomer 2), 119904-15-3; (−)-**6**, 114636-39-4; (±)-**6**, 119904-12-0; (±)-**6** benzoate, 119795-88-9; (±)-**7**, 119795-76-5; (+)-**8**, 79579-56-9; (±)-**8**, 81370-74-3; **9**, 79367-59-2; **11**, 1610-13-5; **12a**, 5497-67-6; (±)-**13a**, 119795-77-6; (±)-**13b**, 119795-90-3; (±)-**14a**, 119795-78-7; (±)-**14b**, 119795-91-4; (±)-**15a**, 119795-79-8; (±)-**15b**, 119795-89-0; (±)-**16**, 119795-80-1; (±)-**17**, 119795-81-2; (±)-**18a**, 119795-82-3; (±)-**18b**, 119795-93-6; **19**, 119795-83-4; (±)-**20** (isomer 1), 119795-84-5; (±)-**20** (isomer 2), 119905-58-7; (±)-**21**, 119795-85-6; (−)-**22**, 114715-40-1; (±)-**22**, 114636-42-9; **23**, 92144-00-8; **24a**, 42340-98-7; **24b**, 73671-79-1; **25a**, 119818-77-8; **25b**, 114636-44-1; **26a**, 119795-86-7; **26b**, 119795-92-5; **27**, 87413-09-0; **28**, 119795-87-8; (−)-**33**, 114636-43-0; (±)-**33**, 119904-13-1; $HC{\equiv}C(CH_2)_2Br$, 38771-21-0.

Supplementary Material Available: Spectral data for all new compounds, discussion of resonance assignments for diene **33** and sterpurene, procedures for the preparation of (−)-**22** (via Chirald reduction of **28**), **25a**, **28**, and detailed procedures for the 2D NMR experiments (31 pages). Ordering information is given on any current masthead page.

Novel Lactam Synthesis by Use of a Combination System of Carbonylation and Nitrogenation[1]

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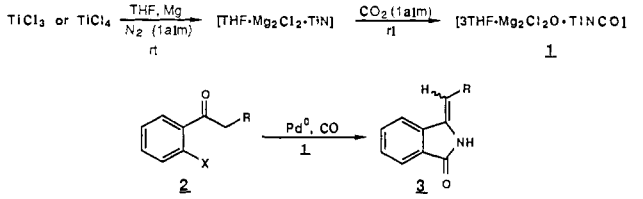
Abstract: An amide unit was constructed from aryl halide and titanium–isocyanate complex prepared from $TiCl_4$ under atmospheric pressure of molecular nitrogen and carbon monoxide in the presence of a palladium catalyst. With this combination system of carbonylation and nitrogenation, isoindolinone and quinazolinone derivatives were synthesized from *o*-halophenyl alkyl ketone in one step. The reaction proceeds through the oxidative addition of enol lactone, generated by palladium-catalyzed carbonylation to *o*-halophenyl alkyl ketone, to titanium–isocyanate complex.

Compared to the impressive development of molecular nitrogen fixation by a variety of transition metal,[2] incorporation of nitrogen into organic compounds using these nitrogen–metal complexes has received only scant attention. Therefore, the use of dinitrogen gas in organic synthesis is still a major challenge. Recently, we have reported[3] a new nitrogenation method for amide and imide

Scheme I



(1) This is paper 2 of the series "Incorporation of Molecular Nitrogen into Organic Compounds".

(2) For reviews: (a) Dilworth, J. R.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 8, 1073. (b) George, T. A. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pinolet, L. H., Ed.; Plenum Press: New York, 1983; p 405. (c) Hidai, M. In *Molybdenum Enzyme*; Spiro, T. G., Ed.; Wiley: New York, 1985; p 285.

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