FEATURE ARTICLE

An Approach to Botrydianes: On the Steric Demands of a Metal Catalyzed Enyne Metathesis

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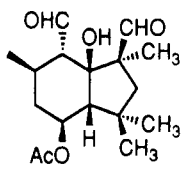
The synthetic scope of a transition metal catalyzed enyne metathesis as a synthesis of 1-alkenylcycloalkenes is tested. Contrary to normal expectations based upon the important sensitivity of transition metal catalyzed reactions to steric effects, severe steric congestion enhances the effectiveness of the reaction. While palladium based catalysts are generally preferred, a platinum catalyst also effects these novel cyclorearrangements.

Introduction

The fungus *Botrytis cinerea* is a serious plant pathogen afflicting numerous agricultural crops including lettuce, tomatoes, grapes, and strawberries. Examination of the neutral metabolites in this fungus had led to the isolation of a novel class of sesquiterpene antibiotics, the botrydianes,[1] represented by botrydial[1a] **1** and deacetyldihydrobotrydial[1e] **2** which do not obey the simple isoprene rule yet are derived from farnesyl pyrophosphate.[2] Envisioning a Diels–Alder strategy to this novel family based upon the cyclohexene **3** reduces the synthetic problem to a facile synthesis of the diene **4** (eq. 1). Our discovery of unusual palladium catalyzed enyne metathesis using tetralkoxycarbonylpalladacyclopentadiene[3] **6** as illustrated in eq. 2[4] suggests the ready availability of a 1-vinylcyclopentene from a 1,6-enyne in which the terminal diene carbons derive from the original olefin. Applying this concept to diene **4** indicates its precursor should be the 1,6-enyne **5** – a substrate of unprecedented steric demands in bearing quaternary centers adjacent to both the olefin and acetylene. To put the steric strain in perspective, we performed molecular mechanics calculations utilizing Macromodel of three hypothetical cyclobutene intermediates I–III which, as expected, reveal the high steric strain associated with the substitution pattern desired. Nevertheless, the relative effectiveness of the reaction depends upon comparing the differences in energy between the ground states of the starting materials and the transition states for the three cases (which should resemble I–III) which most likely will be less (or perhaps even inverted!) than the above differences because of the effect of these substituents in differentially destabilizing the ground states of the reactants. To test the steric limits of our enyne metathesis, we embarked upon a study of the reactivity of this 1,6-enyne and related substrates which is the topic of this paper.



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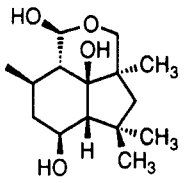

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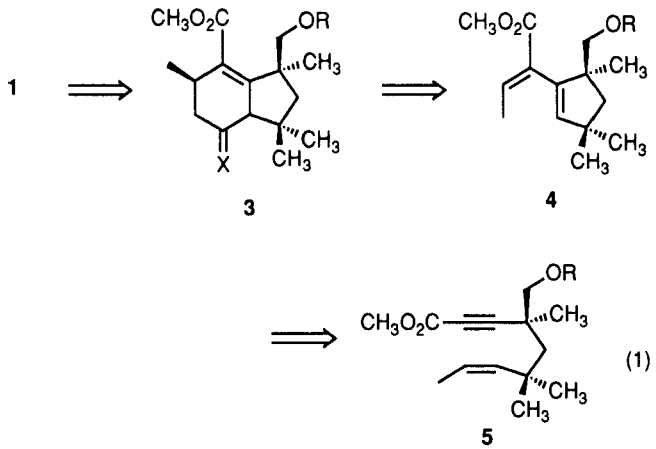
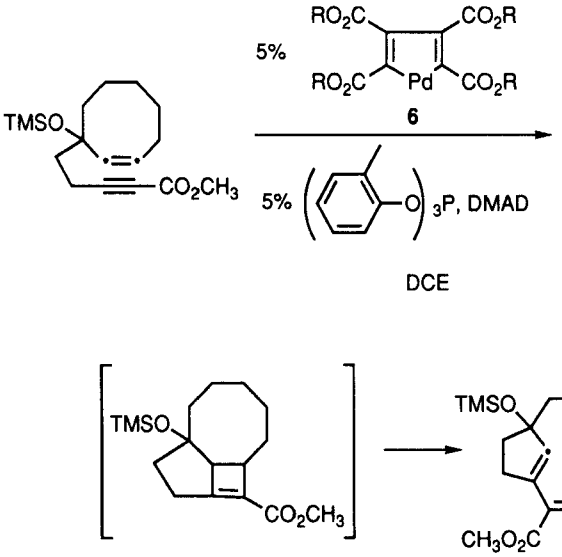


(1)

3 **4** **5**



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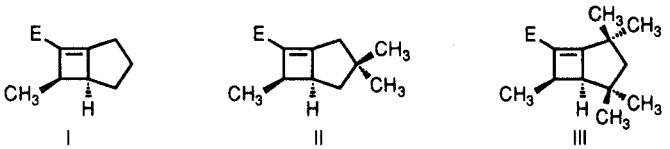
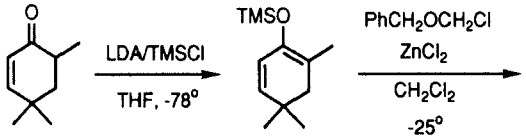


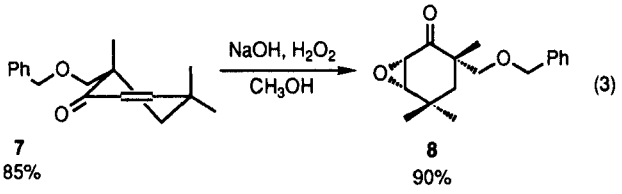
I 57.9 kcal/mol II 58.9 kcal/mol III 64.1 kcal/mol

Enyne Synthesis

Employing the Eschenmoser fragmentation of epoxy ketones to synthesize acetylenes[5] leads to the known

4,4,6-trimethylcyclohex-2-enone[6] as our starting material. Standard hydroxymethylations or enolate alkylations with benzyloxymethyl chloride are troublesome at best or fail. A very satisfactory solution employs a Lewis





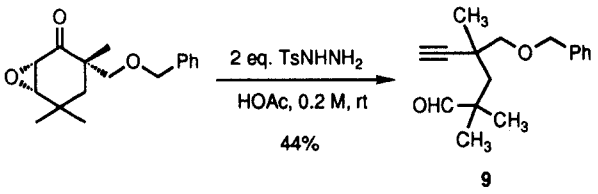
(3)

acid catalyzed alkylation of the corresponding enol silyl ether[7] to give the monoalkylcyclohexenone **7** (eq. 3). Standard nucleophilic epoxidation[8] to epoxy ketone **8** sets the stage for the Eschenmoser fragmentation. Spectral data suggest epoxide **8** is stereohomogeneous. Assuming the conformation of **7** depicted is preferred, topside attack is strongly sterically inhibited by the two axial methyl groups. Thus, steric strain combines with the stereoelectronic preference for axial addition of the peroxide anion to favor assignment of stereochemistry as shown.

The requisite fragmentation proved troublesome. The problem derives from the fact that hydrazone formation is slow, probably due to steric interference from the quaternary center adjacent to the carbonyl group, but that fragmentation of the hydrazone is fast. The acetylenic aldehyde is unstable to the conditions required to form the initial hydrazone and thus, begins to decompose before all of the epoxy ketone is converted to hydrazone.

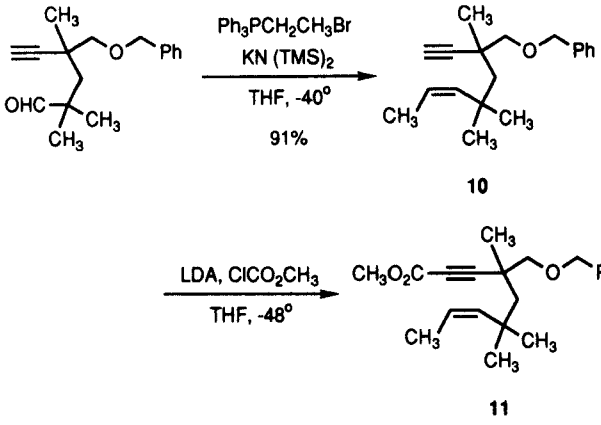
In accord with these notions, alternatives to *p*-toluenesulfonylhydrazine such as the 2,4-dinitrophenyl[9] or mesityl[10] derivatives give poorer results and 1-amino-2-phenylaziridine[11] essentially fails.

Conditions that accelerate hydrazone formation work best. Since acid catalysis promotes hydrazone formation, studies varying acid strength and concentration lead to the best conditions identified to date as outlined in eq. 4. Using a 0.2 M solution of substrate **8** in glacial acetic acid with 2 equivalents of *p*-toluenesulfonylhydrazine gives the desired aldehyde in a reproducible 44% yield.



(4)

The instability of aldehyde **9** (it decomposes completely after 2 days at room temperature) demands its immediate further transformation by Wittig olefination to enyne **10** and methoxycarbonylation to the desired enyne **11** (eq. 5).



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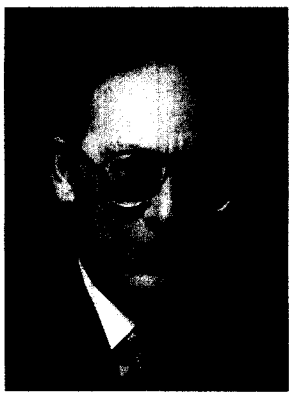
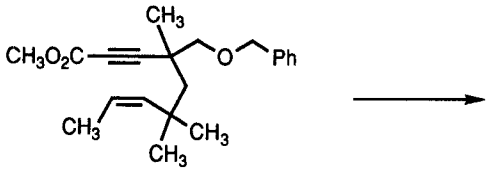
Bibliographical Sketch



Barry M. Trost was born in Philadelphia, Pennsylvania in 1941 where he began his university training at the University of Pennsylvania (BA, 1962), he obtained a Ph. D. degree in Chemistry just three years later at the Massachusetts Institute of Technology (1965). After twenty-two years on the faculty at the University of Wisconsin-Madison, he joined the faculty at Stanford as Professor of Chemistry in 1987 and became Tamaki Professor of Humanities and Sciences in 1990. Developing new reactions and reagents that are chemo-, regio-, diastereo-, and enantioselective from which emanate novel synthetic strategies for the total synthesis of bioactive and novel molecules constitute the theme for his research. In recognition of his many contributions, Professor Trost has received a number of awards, some of which are the ACS Award in Pure Chemistry (1977), the Baekeland Award (1981), ACS Award for Creative Work in Synthetic Organic Chemistry (1981), the Centenary Medal of the Royal Society of Chemistry-London (1981–82), the first Allan R. Day Award of the Philadelphia Organic Chemists' Club (1983), the Chemical Pioneer Award of the American Institute of Chemists (1983), the Alexander von Humboldt Stiftung Award (1984), MERIT Award of NIH (1988), Hamilton Award (1988), Arthur C. Cope Scholar Award (1989), Guenther Award in the Chemistry of Essential Oils and Related Products (1990), the Dr. Paul Janssen Prize (1990) and a Pfizer Senior Faculty Award (1992). Professor Trost has been an active teacher of both graduate and undergraduate students and has been recognized for excellence in teaching by receipt of one of the first ASSU Awards for Graduate Teaching.

Palladium Catalyzed Enyne Metathesis

Exposing enyne **11** to 5 mol% palladacycle **6** (R = CH_3, TCPC), 5 mol% tri-*o*-tolylphosphite (TOTPO), and 1.1 equivalents dimethyl acetylenedicarboxylate (DMAD) in 1,2-dichloroethane (DCE) at 60 °C effects smooth conversion in 15 hours to the desired vinylcyclopentene **12** (85% yield) (eq. 6). The spectral data secure the structural assignment. The *E*-enoate is indicated by the vinyl methyl



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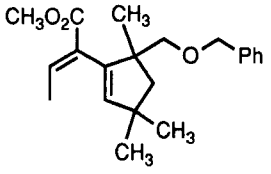
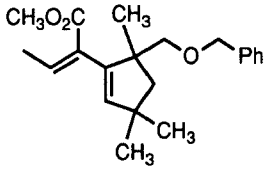


12 (6)

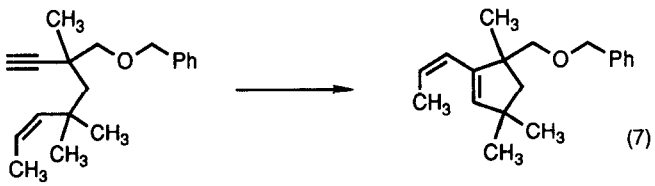
group (δ = 1.77, d, J = 7.1 Hz) coupled to the acyclic vinyl proton at δ = 6.91 (q, J = 7.1 Hz). The cyclopentene substitution is indicated by the isolated vinyl proton (δ = 5.28, s) and an isolated AB pattern for the methylene group (δ = 1.89 and 1.59, J = 13.3 Hz). The geometry of **12** as *E* is established by comparison to the *Z* isomer **13** obtained as a minor product after equilibration. For the latter, the vinyl proton occurs upfield (δ = 5.91) and the vinyl methyl protons downfield (δ = 1.80) compared to the *E* isomer as a result of the anisotropy of the ester group.



13

Using the more favorable catalyst $TCPC^{TFE}$ (**6**, R=CH_2CF_3) effects metathesis in only 1 hour at 60 °C. The enoate **12** is the exclusive product and is obtained in > 99% isolated yield!

Metathesis is usually promoted over other cycloisomerization pathways by placing an electron withdrawing ester group on the acetylene. Thus, we explored the importance of the effect of this substituent by subjecting the parent acetylene **10** to the metathesis catalysts (eq. 7).



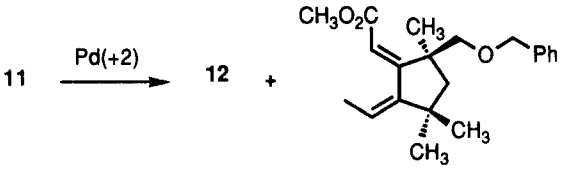
10 **14** (7)

Using 5 mol% TCPC as catalyst with all other variables the same as in the metathesis of **11**, the metathesis product **14** is still the only one obtained in 62% yield but somewhat more slowly requiring 60 hours at 60 °C compared to 15 hours at 60 °C for **11**. The reaction time is dramatically shortened by using the more active fluorinated catalysts $TCPC^{TFE}$ and $TCPC^{HFB}$ (**6**, R=$CH_2C_3F_7$) to 22 hours (66% yield) and 1 hour (68% yield), respectively. The exclusive formation of the metathesis product in all cases is noteworthy.

Extensive NMR studies reveal the structure of the isomeric product as the vinylcyclopentene **14**. The *Z*-propenyl side chain is clearly indicated by the absorptions for the protons of the methyl group (δ = 1.76, dd, J = 7, 2 Hz) and of the olefin (δ = 5.67, dq, J = 12, 7 Hz and δ = 5.84, dq, J = 12, 2 Hz). The substitution of the cyclopentene is verified by the absorptions for the isolated vinyl proton (δ = 5.45, s) and isolated methylene group (AB at δ = 2.10 and 1.55, J = 13.2 Hz).

Related Cycloisomerizations

The extraordinary propensity of these heavily substituted enyne substrates to undergo the enyne metathesis induced us to examine their propensity to undergo the related cycloisomerizations with palladium catalysts (eq. 8).[12]



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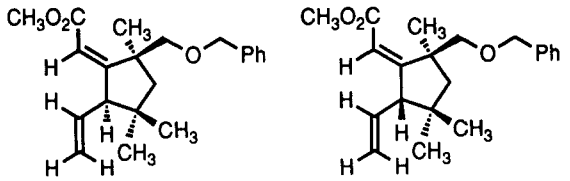
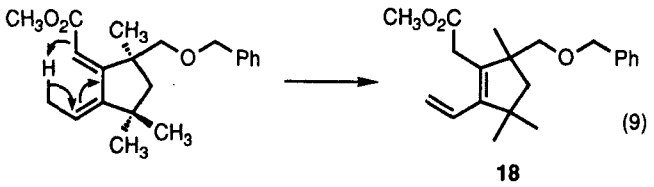


16 **17** (8)

Warming a solution of enyne **11** and 5% palladium acetate or bis(triphenylphosphine)palladium acetate in benzene[13] at 70 °C gives a mixture of four cycloisomers **12**, **15**, **16**, and **17** in approximately a 4:1:1:2 ratio in 78–83% yields. This is the first example in which the metathesis product **12** is obtained with palladium acetate based catalysts. Use of *N,N'*-bis(benzylidene)ethylenediamine (BBEDA) as ligand[14] completely suppresses metathesis and gives a 1:1:2 mixture of the normal cycloisomers **15**:**16**:**17**.

Spectroscopy allows ready assignment of all three isomers **15–17**. For **15**, the ethylidene moiety is identified by the peaks at δ = 1.87 (d, J = 7.3 Hz) and δ = 5.58 (m) and the methoxycarbonylmethylidene by peaks at δ = 5.96 (s) and 3.67 (s). The isolated cyclopentyl methylene group appears as an AB at δ = 2.00 and 1.46 (J = 13 Hz). Its geometry as *Z* is implicated by mechanistic considera-

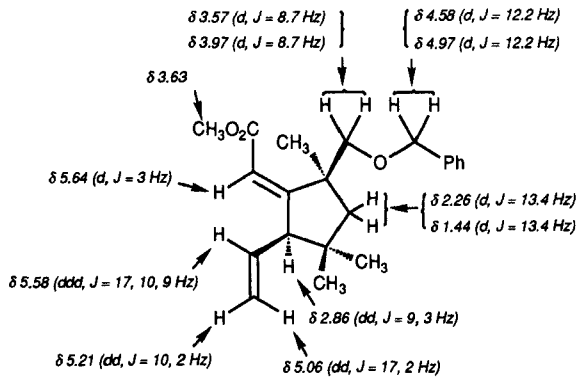
tions (*vide infra*) and is indicated by its smooth thermal isomerization upon GC analysis to the 1,5-hydrogen shift product **18** (eq. 9).



(9)

18

The structures of the two isomers **16** and **17** are clearly indicated by their nearly identical patterns as shown in Figure 1. On the other hand, the stereochemical assignment can only be speculated upon. A significant difference resides in the absorptions of the benzyloxymethylene group in which there is a larger degree of nonequivalence observed for these protons in **16** than **17**. For this reason, one may tentatively assign the vinyl group cis to this substituent in **16** and trans in **17** as depicted.



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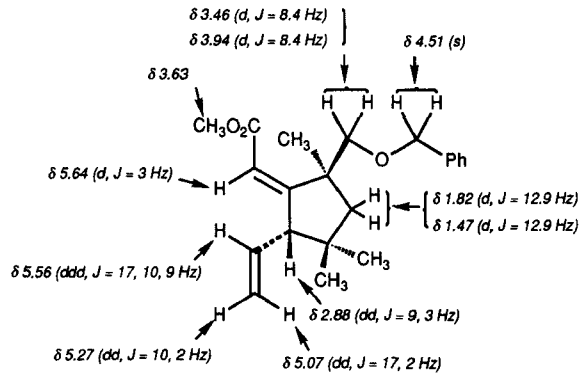
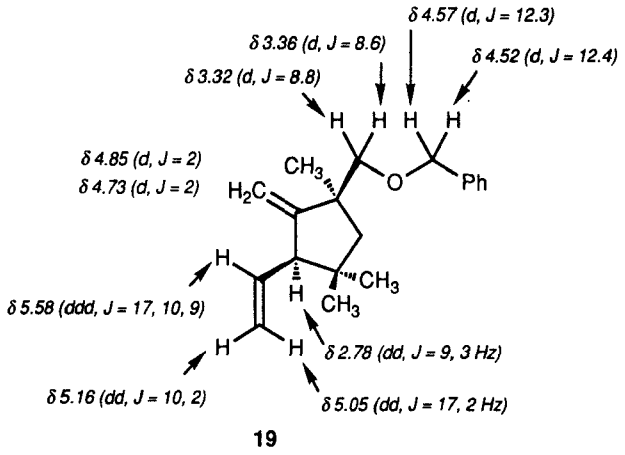


17

Figure 1. ^{1}H NMR Data for Ene Products 16 and 17

Enyne **10** undergoes exclusive Alder ene type chemistry upon treatment with 2.5% $(dba)_3Pd_2 \cdot CHCl_3$, 5% acetic acid, and 5% TPP in benzene[15] at room temperature to give a 90% yield of an approximately equimolar mixture of **19** and **20**. The spectral data unambiguously confirms the structural assignment except for stereochemistry which must be considered quite speculative based upon the same reasoning as before. None of the 1,3-diene nor metathesis product is observed under these conditions.



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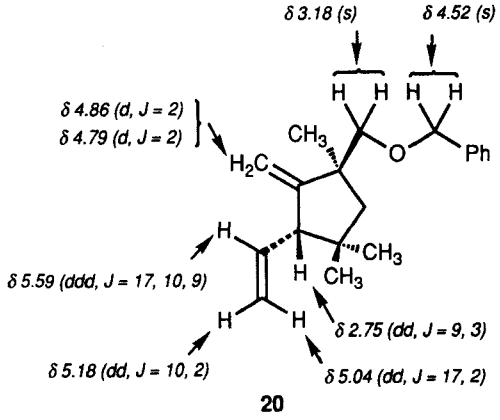
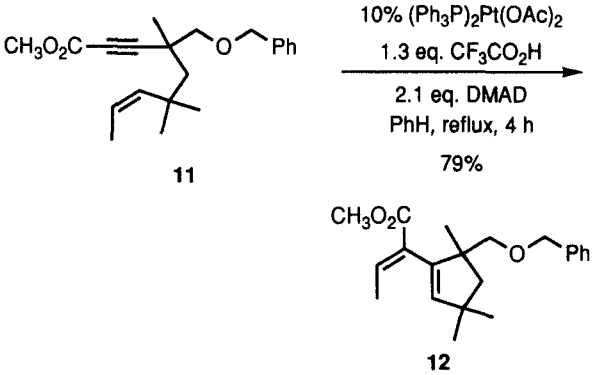


20

Platinum Catalysis

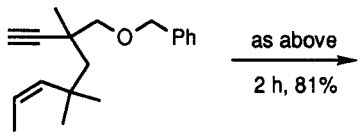
The hypothesis that the catalytic cycle for the metathesis involves a Pd(+2) – Pd(+4) catalytic cycle encouraged us to consider catalysis by platinum for which the Pt(+2) – Pt(+4) catalytic cycle is much more precedented.[16] Gratifyingly, the simple complex $(Ph_3P)_2Pt(OAc)_2$[17] effects metathesis of enynoate **11** as outlined in eq. 10. The yield is comparable to that obtained with TCPC but is significantly faster (4 h vs. 15 h). On the other hand, it is somewhat slower than use of TCPC[TFE].



11 **12**

(10)

The same conditions effect metathesis of the simpler enyne **10** but as a 1 : 3.4 ratio of *Z* and *E* isomers (eq. 11). The 15.8 Hz coupling constant of the vinyl protons in **21** clearly reveals the olefin geometry. Interestingly, flash vacuum thermolysis of the *Z* olefin **14** also leads to olefin isomerization. Further exploration of platinum complexes as metathesis catalysts merits consideration.



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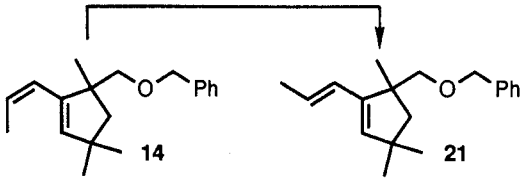
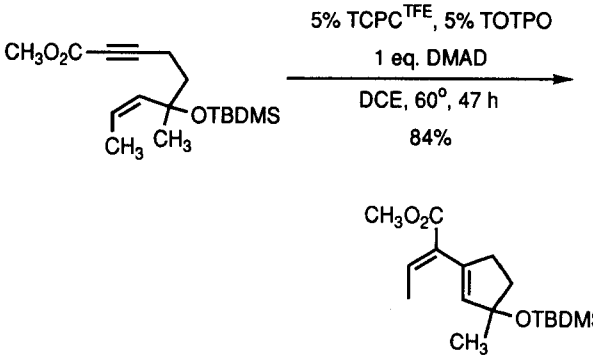


(11)

Discussion

General consideration of steric effects on transition metal catalyzed reactions leads one to predict that substrates like **10** and **11** should barely react. Quite the opposite is the situation; they are dramatically more reactive in the palladium catalyzed enyne metathesis than any other substrate examined to date. Notions regarding the normal effects of gem alkyl groups on nonmetal catalyzed reactions (Thorpe–Ingold effect) do not simply extrapolate to transition metal catalyzed reactions because of their great sensitivity to steric effects. Ancillary studies suggest that geminal substitution adjacent to the olefin permits metathesis (eq. 12); *whereas, geminal substitution at the propargylic position completely retards metathesis (eq. 13)*.[4] Apparently, fully substituting both the allylic and propargylic carbons has a synergistic effect such that the reaction becomes faster than either substitution pattern alone.



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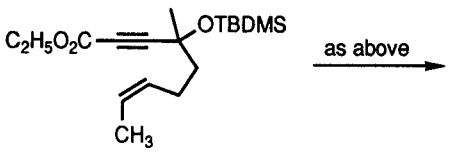
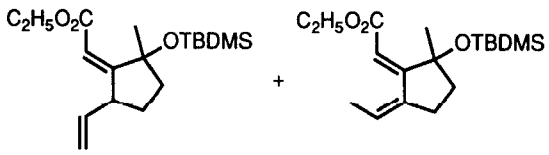
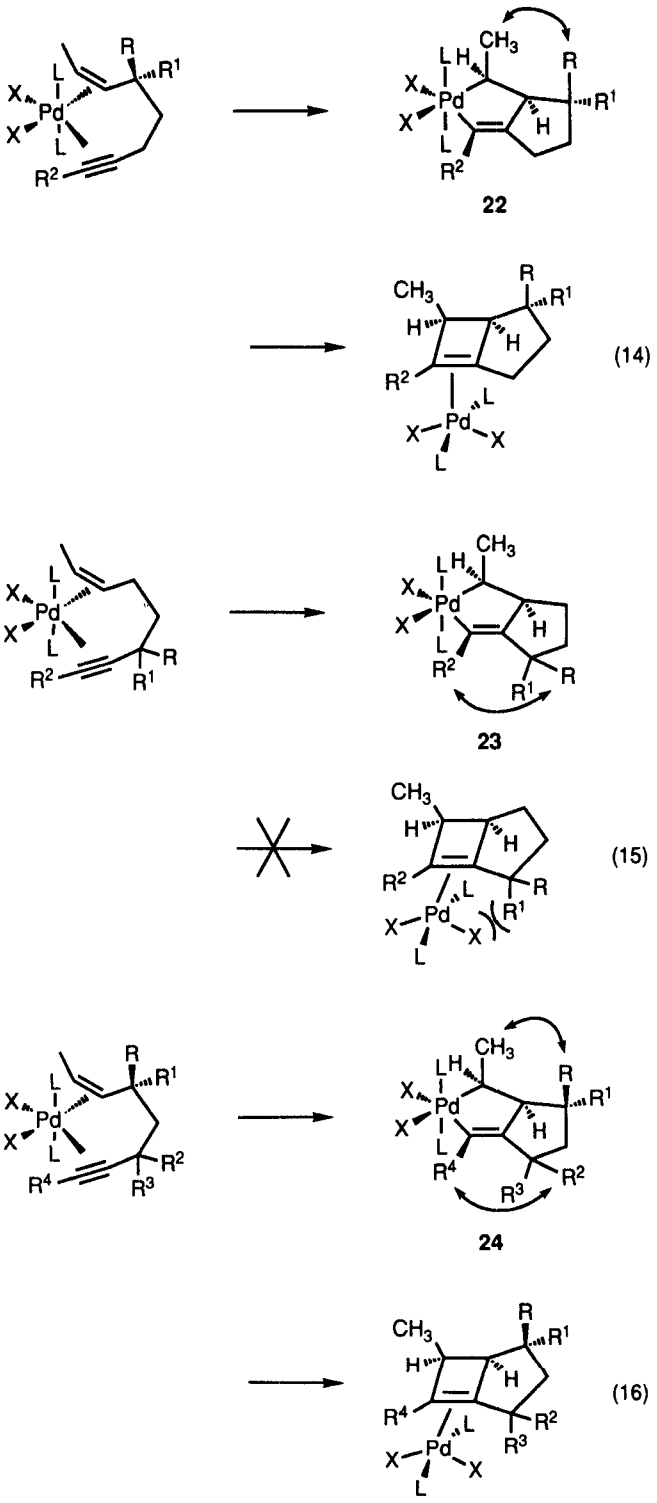




(13)

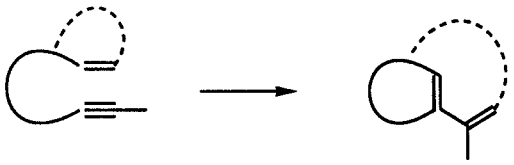
This effect becomes even more dramatic when one considers that unsubstituted terminal acetylenes normally do not participate very well in the metathesis reaction – proceeding either very slowly, or, more commonly, giving other cycloisomers in competition with the desired reaction.

In formulating a rationale for this dramatic steric acceleration, we must begin with a reasonable working hypothesis for the mechanism of this reaction. Strong evidence now exists for the intermediacy of cyclobutenes as depicted in eq. 2.[18] Given this intermediate, most reasonable precursors are metallacyclopentenes **22–24** formed by valence isomerization of a palladium (+2) complex in which the enyne serves as a bidentate liquid (eq. 14–16).



The steric interaction in **22** can be envisioned to have two consequences: (1) an acceleration of reductive elimination to the cyclobutene as a result of release of steric strain, and (2) inhibition of β-hydrogen elimination by preventing adaptation of the requisite conformer. In **23** (eq. 15), both of these effects are absent. Furthermore, the reductive elimination to the cyclobutene–palladium complex is disfavored by steric interactions between the transition metal complex and R. Incorporating substituents at both the allylic and propargylic systems leads to **24** which reintroduces the two factors favoring reductive elimination. The fact that this type of substitution has a strong acceleration demands more. A further steric strain in **24** that is somewhat relieved in the reductive elimination is between R^4 and R^2 which contributes an $A_{1,3}$ strain.[19] The synergism of the three effects may account for the extraordinary reactivity.

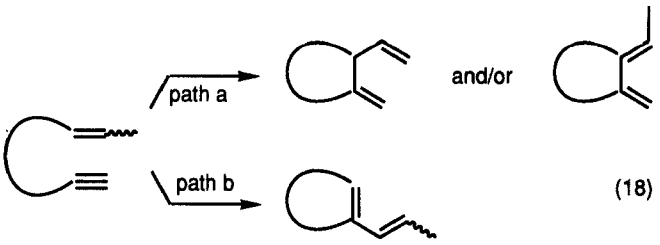
The facts that even palladium acetate leads to some metathesis products and that platinum acetate leads exclusively to metathesis products attest to the magnitude of these effects. The effectiveness of platinum acetate also lends support to the proposed mechanistic rationale.



(17)

Synthetically, the enyne metathesis reaction offers a novel and simple construct of 1-alkenylcycloalkenes from simple acyclic building blocks according to eq. 17. The accommodation of severe steric stress around the reacting centers combined with the high chemoselectivity suggests a broad scope for the process. In addition to the somewhat esoteric but very easily accessible palladacyclopentadiene catalysts, we can add bis(triphenylphosphine)platinum acetate as a catalyst although it does not appear to be as mild.[20] Further tuning of the platinum catalyst may increase its reactivity and selectivity.

The reactions of enyne **10** with the various palladacyclopentadiene catalysts **6** represent the first direct comparison of all three and the effect is remarkable. Going from **6** R = CH_3 to R = CH_2CF_3 to R = $CH_2C_3F_7$ progressively decreases the reaction time from 60 hour to 1 hour and speaks to the importance of the acceptor properties of this unit in facilitating the reaction. We believe this effect derives from facilitating the reductive elimination of the palladacylopentadiene **24** to the cyclobutene.[21] Five catalyst systems effect cycloisomerizations of enynes: (1) palladium acetate plus phosphine (or arsine or stibine) ligand,[13,22] (2) palladium acetate plus BBEDA as ligand,[14] (3) palladium(0) plus acetic acid and phosphine (or arsine or stibine) ligand,[15] (4) TCPC and the fluorinated esters,[3,4] and (5) platinum acetate plus phosphine. By choice of the appropriate ligand environment around palladium(+2), the same substrate can be channeled towards the ene and related type systems (eq. 18, path a) or the metathesis (eq. 18, path b). Catalyst systems 2 and 3 clearly direct reaction via path a. Catalyst systems 4



(18)

(especially the fluorinated esters) and 5 direct reaction via path b. Catalyst system 1 normally follows path a but can, in particularly favorable cases as those herein, direct reaction via both pathways. Further selectivity may be achieved with modification of the ligands. The synthetic versatility offered by catalyst design represents a continuing endeavor in our laboratories.

All new compounds gave satisfactory microanalysis (C ± 0.29, H ± 0.32) or HRMS (± 0.0031).

6-Benzyloxymethyl-4,4,6-trimethyl-2-cyclohexenone (7):
To a mixture of diisopropylamine (5.60 mL, 4.04 g, 40.0 mmol) and BuLi (1.5 M, 26.5 mL, 39.8 mmol) in THF (100 mL) cooled to −78 °C under N_2, was added a solution of 4,4,6-trimethyl-2-cyclohexenone (5.0 g, 36.2 mmol) in THF (10 mL). After the mixture had stirred for 1 h, TMSCl (6.90 mL, 5.91 g, 54.4 mmol) was slowly added dropwise. The mixture was allowed to gradually warm to r.t. and stirred an additional 1 h. After concentration by rotary evaporation, the residue was taken up in Et_2O and filtered through Celite to remove precipitated LiCl. The solution was again concentrated by rotary evaporation to afford 6.90 g (91 %) of the crude silyl enol ether which was used without any further purification. R_f (5:1 hexanes/EtOAc) 0.72.

IR (film): ν = 3025, 2950, 2900, 2860, 2810, 1665, 1445, 1405, 1380, 1358, 1330, 1250, 1190, 1095, 960, 905, 840, 750 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 5.55 (d, J = 9.8 Hz, 1 H), 5.39 (d, J = 9.8 Hz, 1 H), 2.03 (t, J = 1.2 Hz, 2 H), 1.63 (s, 3 H), 0.99 (s, 6 H), 0.17 (s, 9 H).

^{13}C NMR ($CDCl_3$): δ = 140.85, 136.67, 123.92, 111.26, 43.80, 31.75, 27.84, 16.46, 0.41.

MS (EI, 70 eV, relative percent): m/z = 210 (M+, 47), 195 (100), 179 (27), 105 (11), 73 (38).

To a solution of the crude silyl enol ether in CH_2Cl_2 under N_2 was added a catalytic amount of anhydr. $ZnCl_2$ at −30 °C. Benzyloxymethylchloride (1.2 equiv) was added dropwise via syringe. After 2 h, the mixture was hydrolyzed with water. The organic layer was removed and the aqueous layer was extracted with CH_2Cl_2 (2 ×). The combined organic fractions were washed with 5% $NaHCO_3$ (2 ×), washed with water, dried (Na_2SO_4), and concentrated by rotary evaporation. The crude residue was purified by flash chromatography (5:1 hexanes/EtOAc) to afford the desired product **7** in 80–85 % overall yield. R_f (5:1 hexanes/EtOAc) 0.38.

IR (film): ν = 3070, 3050, 3015, 2950, 2900, 2880, 1675, 1450, 1374, 1310, 1230, 1090, 825, 733, 695 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.34–7.27 (m, 5 H), 6.59 (dd, J = 10.1, 1.3 Hz, 1 H), 5.83 (d, J = 10.1 Hz, 1 H), 4.53 (d, J = 12.2 Hz, 1 H), 4.48 (d, J = 12.2 Hz, 1 H), 3.65 (d, J = 8.9 Hz, 1 H), 3.27 (d, J = 8.9 Hz, 1 H), 2.25 (d, J = 14.2 Hz, 1 H), 1.68 (dd, J = 14.3, 1.3 Hz, 1 H), 1.22 (s, 3 H), 1.18 (s, 3 H), 1.16 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 202.32, 158.11, 138.35, 128.20, 127.43, 127.39, 125.49, 75.89, 73.28, 45.53, 43.54, 32.84, 31.19, 29.86, 23.24.

MS (EI, 70 eV, relative percent): m/z = 258 (M^+, 0.3), 228 (0.7), 167 (17), 152 (8), 137 (8), 96 (83), 91 (100).

6-Benzyloxymethyl-2,3-epoxy-4,4,6-trimethylcyclohexanone (8):
A solution of **7** (8.0 g, 31.0 mmol) and 30% aq H_2O_2 (9.5 mL, 93 mmol) in MeOH (80 mL) was cooled in an ice/water bath. NaOH (15.5 mL of a 1 M solution) was slowly added dropwise; the

temperature was not allowed to rise above 5°C. The mixture immediately became cloudy. After complete addition, the mixture was gradually warmed to r.t. After 3 h, the mixture was poured into water and extracted with Et_2O (3×). The ether fractions were combined, washed with water, dried ($MgSO_4$), and concentrated by rotary evaporation. Purification by flash chromatography (5:1 hexanes/EtOAc) afforded 7.63 g (90%) of the epoxy ketone **8**. R_f (5:1 hexanes/EtOAc) 0.37.

IR (film): ν = 3075, 3050, 3020, 2950, 2860, 1702, 1470, 1455, 1370, 1100, 1030, 1005, 840, 740, 705 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.30 (m, 5H), 4.49 (s, 2H), 3.36 (m, 3H), 3.25 (dd, J = 4.3, 1.3 Hz, 1H), 2.10 (d, J = 14.0 Hz, 1H), 1.20 (dd, J = 14.0 Hz, 1.4, 1H), 1.18 (s, 3H), 1.16 (s, 3H), 1.05 (s, 3H).

^{13}C NMR ($CDCl_3$): δ = 210.18, 138.14, 128.23, 127.42, 127.31, 77.01, 73.15, 65.59, 56.46, 46.01, 41.87, 31.97, 28.45, 24.68, 23.79.

MS (EI, 70 eV, relative percent): m/z = 244 ($M^+ - CH_2O$, 0.5), 167 (1), 153 (1), 138 (8), 112 (9), 96 (12), 91 (100).

4-Benzyloxymethyl-2,2,4-trimethyl-5-hexynal (9):
To a solution of epoxy ketone **8** (1.00 g, 3.65 mmol) in glacial AcOH (18 mL) was added *p*-toluenesulfonylhydrazide (1.36 g, 7.30 mmol). After 15 min stirring at r.t., all the hydrazide dissolved and the mixture was clear and yellow. After 2.5 h, the mixture was poured into an Et_2O/water mixture. The aqueous layer was separated and the organic layer was washed several times with water until the aqueous layer was neutral. The organic layer was dried ($MgSO_4$) and concentrated by rotary evaporation. Purification by flash chromatography (10:1 hexanes/EtOAc) afforded 414 mg (44%) of the acetylenic aldehyde **9**. R_f (5:1 hexanes/EtOAc) 0.47.

IR (film): ν = 3315, 3090, 3065, 3035, 2970, 2930, 2870, 2710, 1723, 1452, 1365, 1090, 690 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 9.52 (s, 1H), 7.36–7.29 (m, 5H), 4.54 (d, J = 12.1 Hz, 1H), 4.48 (d, J = 12.1 Hz, 1H), 3.35 (d, J = 8.8 Hz, 1H), 3.27 (d, J = 8.8 Hz, 1H), 2.16 (s, 1H), 2.03 (d, J = 14.7 Hz, 1H), 1.73 (d, J = 14.7 Hz, 1H), 1.26 (s, 3H), 1.19 (s, 3H), 1.12 (s, 3H).

^{13}C NMR ($CDCl_3$): δ = 205.94, 138.00, 128.31, 127.57, 88.41, 76.79, 72.93, 71.61, 46.11, 44.65, 34.84, 26.60, 23.86, 22.65.

MS (EI, 70 eV, relative percent): m/z = 243 ($M^+ - CH_3$, 0.5), 162 (2), 143 (3), 137 (3), 121 (2), 109 (6), 105 (5), 91 (100).

(*Z*)-3-Benzyloxymethyl-3,5,5-trimethyl-6-octen-1-yne (10):
To a suspension of ethyltriphenylphosphonium bromide (1.86 g, 5.0 mmol) in THF (50 mL) cooled to −42°C ($MeCN/CO_2$ bath) was added potassium bis(trimethylsilyl)amide (9.2 mL, 4.6 mmol, 0.5 M in toluene). The mixture immediately turned from a cloudy white to yellow-orange. After stirring 1 h, a solution of the acetylenic aldehyde **9** (1.08 g, 4.2 mmol) in THF (10 mL) was added dropwise. After stirring for 30 min, the cooling bath was removed and the reaction warmed to r.t. After 1 h, the reaction mixture was clear and colorless. The precipitated KBr was removed by filtration through Celite. Ether was added and the organic solution was washed with sat. NaCl (2×), dried ($MgSO_4$), and concentrated by rotary evaporation. Purification by flash chromatography (12:1 hexanes/EtOAc) afforded 1.03 g (91%) of the desired 1,6-enyne **10**. R_f (10:1 hexanes/EtOAc) 0.55.

IR (film): ν = 3300, 3080, 3055, 3020, 2900, 2100, 1450, 1365, 1200, 1095, 1025, 735, 695 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.36–7.27 (m, 5H), 5.40 (dq, J = 12.1, 1.7 Hz, 1H), 5.24 (dq, J = 12.1, 7.2 Hz, 1H), 4.58 (s, 2H), 3.37 (d, J = 8.7 Hz, 1H), 3.34 (d, J = 8.7 Hz, 1H), 2.17 (s, 1H), 1.78 (d, J = 14.3 Hz, 1H), 1.71 (dd, J = 7.2, 1.7 Hz, 3H), 1.64 (d, J = 14.3 Hz, 1H), 1.30 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H).

^{13}C NMR ($CDCl_3$): δ = 140.44, 138.48, 128.26, 127.48, 127.42, 121.89, 90.20, 78.31, 73.15, 70.34, 49.72, 37.32, 35.61, 30.66, 30.44, 26.20, 14.33.

MS (EI, 70 eV, relative percent): m/z = 255 ($M^+ - CH_3$, 0.2), 179 (2), 149 (12), 147 (8), 135 (6), 121 (13), 107 (9), 105 (8), 91 (100).

Methyl (*Z*)-4-Benzyloxymethyl-4,6,6-trimethyl-7-nonen-2-ynoate (11):
To a solution of diisopropylamine (0.57 mL, 0.41 g, 4.1 mmol) in THF (20 mL) at −78°C was added BuLi (2.9 mL, 4.1 mmol, 1.40 M in hexanes) dropwise. After stirring for 30 min, a solution of enyne **10** (731 mg, 2.7 mmol) in THF (7 mL) was added all at once. After stirring for 1 h, methyl chloroformate (375 μL, 459 mg, 4.9 mmol) was added. The mixture was allowed to gradually warm to r.t. and stirred an additional hour. The mixture was poured into an Et_2O/water mixture and the phases were separated. The organic layer was washed with sat. NaCl, dried ($MgSO_4$), and concentrated by rotary evaporation. Purification by flash chromatography (8:1 hexanes/EtOAc) afforded 752 mg (85%) of the 1,6-enynoate **11**. R_f (5:1 hexanes/EtOAc) 0.36.

IR (CCl_4): ν = 3080, 3055, 3020, 2950, 2860, 2220, 1720, 1450, 1430, 1250, 1210, 1095, 1025, 750, 695 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.35–7.26 (m, 5H), 5.36 (dq, J = 12.1, 1.6 Hz, 1H), 5.26 (dq, J = 12.1, 7.0 Hz, 1H), 4.57 (d, J = 12.3 Hz, 1H), 4.54 (d, J = 12.3 Hz, 1H), 3.75 (s, 3H), 3.40 (d, J = 8.8 Hz, 1H), 3.37 (d, J = 8.8 Hz, 1H), 1.83 (d, J = 14.3 Hz, 1H), 1.71 (dd, J = 7.1, 1.5 Hz, 3H), 1.68 (d, J = 14.3 Hz, 1H), 1.34 (s, 3H), 1.25 (s, 3H), 1.24 (s, 3H).

^{13}C NMR ($CDCl_3$): δ = 154.26, 139.73, 138.14, 128.28, 127.51, 122.43, 94.53, 77.21, 74.87, 73.16, 52.44, 49.38, 37.14, 35.98, 30.58, 30.40, 25.30, 14.27.

Methyl (2*E*)-2-[5-Benzyloxymethyl-3,3,5-trimethyl-1-cyclopentenyl]-butenoate (12):
To a solution of 1,6-enynoate **11** (127 mg, 0.388 mmol) in 1,2-dichloroethane (5 mL) was added $TCPC^{TFE}$ (10.3 mg, 0.016 mmol, 4%), tri-*o*-tolylphosphite (5.5 mg, 0.016 mmol, 4%), and DMAD (53 μL, 61.2 mg, 0.431 mmol). The mixture was heated at 60°C for 1 h. After concentration by rotary evaporation, the residue was purified by flash chromatography (15:1 hexanes/EtOAc) to afford 125.8 mg (99%) of the cyclized diene **12**. R_f (10:1 hexanes/EtOAc) 0.41.

IR (CCl_4): ν = 3040, 2960, 2870, 1720, 1455, 1435, 1260, 1225, 1100, 1030, 700 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.29 (m, 5H), 6.91 (q, J = 7.1 Hz, 1H), 5.28 (s, 1H), 4.47 (d, J = 12.2 Hz, 1H), 4.38 (d, J = 12.3 Hz, 1H), 3.62 (s, 3H), 3.24 (d, J = 8.4 Hz, 1H), 3.20 (d, J = 8.4 Hz, 1H), 1.89 (d, J = 13.2 Hz, 1H), 1.77 (d, J = 7.1 Hz, 3H), 1.59 (d, J = 13.3 Hz, 1H), 1.17 (s, 3H), 1.12 (s, 3H), 1.11 (s, 3H).

^{13}C NMR ($CDCl_3$): δ = 168.05, 142.14, 139.86, 138.89, 138.78, 131.02, 128.13, 127.17, 78.49, 72.86, 53.41, 51.47, 50.15, 43.41, 30.75, 30.24, 24.71, 15.52.

MS (EI, 70 eV, relative percent): m/z = 237 ($M^+ - CH_2Ph$, 0.2), 220 (4), 207 (5), 175 (15), 147 (23), 91 (100).

Using the same conditions as above, reaction of **11** (21.1 mg, 64.2 μmol, 5%) TCPC (1.4 mg, 3.5 μmol, 5%), tri-*o*-tolylphosphite (1.2 mg (3.4 μmol, 5%), and DMAD (8.7 μL, 10.0 mg, 70.6 μmol) after 15 h afforded 15 mg (85%) of the identical product.

Methyl (2*Z*)-2-[5-Benzyloxymethyl-3,5,5-trimethyl-1-cyclopentenyl]-butenoate (13):
To a solution of *E*-enoate **12** (15.0 mg, 46 μmol) in MeOH (400 μL) was added KOH (35 μL, 110.4 mg in 0.5 mL MeOH, 46 μmol). The mixture was heated to reflux. Monitoring the reaction by GC showed formation of the *Z*-stereoisomer. The ratio of *E*- and *Z*-isomers fluctuated with prolonged heating. After 24 h, the reaction was cooled to r.t. and quenched with 1 M HCl. The aqueous mixture was extracted several times with Et_2O, the organic layer was dried ($MgSO_4$) and concentrated by rotary evaporation. Purification by flash chromatography (10:1 hexanes/EtOAc) afforded a mixture of *E*- and *Z*-isomers in a ratio of 9:1, respectively. The minor isomer **13** could be separated by preparative GC. R_f (10:1 hexanes/EtOAc) 0.41.

^1H NMR ($CDCl_3$): δ = 7.32 (m, 5H), 5.91 (q, J = 7.1 Hz, 1H), 5.38 (s, 1H), 4.52 (d, J = 12.3 Hz, 1H), 4.46 (d, J = 12.3 Hz, 1H), 3.71 (s, 3H), 3.32 (d, J = 8.8 Hz, 1H), 3.28 (d, J = 8.9 Hz, 1H), 2.03 (d,

J = 13.2 Hz, 1 H), 1.80 (d, J = 7.2 Hz, 3 H), 1.53 (d, J = 13.1 Hz, 1 H), 1.16 (s, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H).

MS (EI, 70 eV, relative percent): m/z = 222 (21), 220 (29), 175 (98), 147 (94), 91 (100).

5-Benzyloxymethyl-1-[(*Z*)-1-propenyl]-3,3,5-trimethylcyclopentene (14):

To a solution of 1,6-enyne **10** (21.9 mg, 81 μmol) in 1,2-dichloroethane (800 μL) was added $TCPC^{HFB}$ (4.3 mg, 4 μmol, 5%), tri-*o*-tolylphosphite (1.5 mg, 4 μmol, 5%), and DMAD (11 μL, 12.7 mg, 89 μmol). The mixture was heated at 60 °C for 1 h. After concentration by rotary evaporation, the residue was purified by flash chromatography (20:1 hexanes/EtOAc) to afford 15.0 mg (68%) of the cyclized diene **14**. R_f (10:1 hexanes/EtOAc) 0.36.

IR (CCl_4): ν = 3035, 3025, 2970, 2940, 2870, 1460, 1370, 1110, 700 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.33–7.25 (m, 5 H), 5.73 (d, J = 11.7 Hz, 1 H), 5.70 (dq, J = 11.4, 5.3 Hz, 1 H), 5.42 (s, 1 H), 4.51 (s, 2 H), 3.26 (d, J = 8.9 Hz, 1 H), 3.22 (d, J = 8.9 Hz, 1 H), 1.95 (d, J = 13.2 Hz, 1 H), 1.78 (d, J = 5.3 Hz, 3 H), 1.49 (d, J = 13.2 Hz, 1 H), 1.13 (s, 3 H), 1.10 (s, 3 H), 1.09 (s, 3 H); (C_6D_6): δ = 7.30–7.06 (m, 5 H), 5.84 (m, 1 H), 5.67 (dq, J = 11.6, 6.9 Hz, 1 H), 5.45 (s, 1 H), 4.33 (s, 2 H), 3.24 (d, J = 8.7 Hz, 1 H), 3.20 (d, J = 8.8 Hz, 1 H), 2.10 (d, J = 13.2 Hz, 1 H), 1.76 (dd, J = 6.9, 1.8 Hz, 3 H), 1.55 (d, J = 13.2 Hz, 1 H), 1.28 (s, 3 H), 1.18 (s, 3 H), 1.17 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 140.72, 139.63, 138.99, 128.18, 128.07, 127.34, 127.22, 123.47, 77.88, 73.13, 51.88, 49.37, 43.47, 31.11, 30.48, 24.75, 15.16.

MS (EI, 70 eV, relative percent): m/z = 270 (M^+, 0.2), 255 (0.6), 179 (2.5), 164 (28), 149 (86), 121 (41), 107 (45), 91 (100).

Using the same conditions as above, reaction of **10** (81.4 mg, 0.30 mmol), $TCPC^{TFE}$ (8.0 mg, 0.012 mmol, 4%), tri-*o*-tolylphosphite (4.0 mg, 0.011 mmol, 3.8%), and DMAD (44 μL, 47.4 mg, 0.33 mmol), afforded after 22 h, 54 mg (66%) of the identical product.

Using the same conditions as above, reaction of **10** (24.3 mg, 90 μmol) TCPC (1.3 mg, 3.3 μmol, 4%), tri-*o*-tolylphosphite (1.2 mg, 3.4 μmol, 4%) and DMAD (12 μL, 13.8 mg, 98 μmol), afforded after 60 h, 15 mg (62%) of the identical product.

Cyclization of Methyl (*Z*)-4-Benzyloxymethyl-4,6,6-trimethyl-7-nonen-2-ynoate with Palladium(II) Acetate:

To a solution of 1,6-enynoate **11** (10.2 mg, 31 μmol) in benzene (310 μL) was added $Pd(OAc)_2$ (0.4 mg, 2 μmol, 6%). The mixture was heated at 70 °C for 22 h. After evaporation of the solvent, the residue was purified by flash chromatography (15:1 hexanes/EtOAc) to afford 8.0 mg (78%) of a mixture of metathesis product **12**, 1,4-dienes **16**, **17**, and 1,3-diene **15**, 3.5:1.4:2.3:1, respectively. Compound **12** and **16** could be separated from the isomeric mixture by preparative GC at 190 °C (isothermal) for separate characterization.

With BBEDA–Palladium(II) Acetate:

To a solution of 1,6-enynoate **11** (14.5 mg, 44 μmol) in benzene (220 μL) was added $Pd(OAc)_2$ (0.4 mg, 2 μmol, 5%) and BBEDA (1.0 mg, 4 μmol, 10%). The mixture was heated at 70 °C for 27 h. After evaporation of the solvent, the residue was purified by flash chromatography (12:1 hexanes/EtOAc) to afford 12.6 mg (87%) of a mixture of 1,4-dienes **16**, **17**, and 1,3-diene **15**, 1:2:1, respectively. Compound **16** could be separated from the isomeric mixture by preparative GC at 190 °C (isothermal).

With $(Ph_3P)_2Pd(OAc)_2$:

To a solution of 1,6-enynoate **11** (15.1 mg, 46 μmol) in benzene (400 μL) was added $Pd(PPh_3)_2(OAc)_2$ (1.6 mg, 2 μmol, 5%). The mixture was heated at 70 °C for 31 h. After evaporation of the solvent, the residue was purified by flash chromatography (12:1 hexanes/EtOAc) to afford 12.6 mg (83%) of a mixture of metathesis product **12**, 1,4-dienes **16**, **17**, and 1,3-diene **15**, 4:2:1:1, respectively. Compounds **12** and **16** could be separated from the isomeric mixture by preparative GC at 190 °C (isothermal).

Methyl (*Z*)-[5-Benzyloxymethyl-(*Z*)-2-ethylidene-3,3,5-trimethyl-1-cyclopentylidene]acetate (15):

R_f (10:1 hexanes/EtOAc) 0.43.

^1H NMR ($CDCl_3$): δ = 7.30 (m, 5 H), 5.96 (s, 1 H), 5.58 (m, 1 H), 4.51 (s, 2 H), 3.72 (s, 2 H), 3.67 (s, 3 H), 2.00 (d, J = 13.0 Hz, 1 H), 1.87 (d, J = 7.3 Hz, 3 H), 1.46 (d, J = 13.0 Hz, 1 H), 1.39 (s, 3 H), 1.07 (s, 3 H), 1.05 (s, 3 H).

Methyl (*Z*)-[(2*S,5*R**)-5-Benzyloxymethyl-3,3,5-trimethyl-2-vinyl-1-cyclopentylidene]acetate (16):**

R_f (10:1 hexanes/EtOAc) 0.43.

IR (film): ν = 2952, 2927, 2867, 1724, 1641, 1194, 1174, 1093, 1028, 1000 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.33 (m, 5 H), 5.64 (d, J = 2.5 Hz, 1 H), 5.58 (ddd, J = 17.0, 10.2, 9.2 Hz, 1 H), 5.21 (dd, J = 10.2, 2.2 Hz, 1 H), 5.06 (dd, J = 17.1, 2.1 Hz, 1 H), 4.58 (d, J = 12.2 Hz, 1 H), 4.47 (d, J = 12.1 Hz, 1 H), 3.97 (d, J = 8.7 Hz, 1 H), 3.63 (s, 3 H), 3.57 (d, J = 8.7 Hz, 1 H), 2.86 (dd, J = 9.2, 2.5 Hz, 1 H), 2.26 (d, J = 13.4 Hz, 1 H), 1.44 (d, J = 13.9 Hz, 1 H), 1.41 (s, 3 H), 1.00 (s, 3 H), 0.78 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 135.89, 128.38, 127.72, 127.68, 127.44, 119.03, 114.62, 76.79, 73.23, 64.40, 52.56, 47.06, 40.20, 28.96, 25.54, 23.56.

MS (EI, 70 eV, relative percent): m/z = 298 (2), 220 (5), 207 (14), 205 (16), 147 (24), 145 (28), 91 (100).

Methyl (*Z*)-[(2*R,5*R**)-5-Benzyloxymethyl-3,3,5-trimethyl-2-vinyl-1-cyclopentylidene]acetate (17):**

R_f (10:1 hexanes/EtOAc) 0.43.

^1H NMR ($CDCl_3$): δ = 7.30 (m, 5 H), 5.64 (d, J = 2.6 Hz, 1 H), 5.56 (ddd, J = 17.1, 10.2, 9.1 Hz, 1 H), 5.27 (dd, J = 10.2, 2.3 Hz, 1 H), 5.07 (dd, J = 17.1, 2.2 Hz, 1 H), 4.51 (s, 2 H), 3.94 (d, J = 8.4 Hz, 1 H), 3.63 (s, 3 H), 3.46 (d, J = 8.4 Hz, 1 H), 2.88 (dd, J = 9.0, 2.6 Hz, 1 H), 1.82 (d, J = 13.0 Hz, 1 H), 1.47 (d, J = 12.8 Hz, 1 H), 1.39 (s, 3 H), 1.01 (s, 3 H), 0.86 (s, 3 H).

MS (EI, 70 eV, relative percent): m/z = 328 (M^+, 2), 298 (2), 220 (11), 207 (37), 147 (46), 133 (27), 91 (100).

Methyl (5-Benzyloxymethyl-3,3,5-trimethyl-2-vinyl-1-cyclopentenyl) acetate (18):

Preparative GC at 190 °C (isothermal) of a mixture of **15**, **16**, and **17** afforded a mixture of the title compound and **17**. R_f (10:1 hexanes/EtOAc) 0.43.

^1H NMR ($CDCl_3$): δ = 7.32 (m, 5 H), 6.23 (dd, J = 17.9, 11.7 Hz, 1 H), 5.37 (dd, J = 17.9, 2.0 Hz, 1 H), 5.20 (dd, J = 11.7, 2.1 Hz, 1 H), 4.48 (d, J = 12.4 Hz, 1 H), 4.42 (d, J = 12.4 Hz, 1 H, 3.55 (s, 3 H), 3.27 (s, 2 H), 3.16 (d, J = 1.6 Hz, 2 H), 1.82 (d, J = 13.2 Hz, 1 H), 1.53 (d, J = 13.2 Hz, 1 H), 1.20 (s, 3 H), 1.17 (s, 3 H), 1.12 (s, 3 H).

MS (EI, 70 eV, relative percent): m/z = 328 (M^+, 2), 220 (11), 207 (37), 147 (46), 133 (27), 91 (100).

(2*S,5*R**)-5-Benzyloxymethyl-1-methylene-3,3,5-trimethyl-2-vinylcyclopentane (19): and (2*S**,5*R**)-5-Benzyloxymethyl-1-methylene-3,3,5-trimethyl-2-vinylcyclopentane (20):**

To a solution of 1,6-enyne **10** (20.3 mg, 75 μmol) in benzene (0.75 mL) was added $Pd_2(dba)_3 \cdot CHCl_3$ (2.0 mg, 2 μmol, 2.5%), PPh_3 (1.0 mg, 4 μmol, 5%), and AcOH (0.2 μL, 0.2 mg, 4 μmol, 5%). The mixture was stirred at r.t. for 7 h. After concentration by rotary evaporation, the residue was purified by flash chromatography (15:1 hexanes/EtOAc) to afford 18.2 mg (90%) of a diastereomeric mixture of 1,4-dienes (**19**:**20**, 1:1.2). The diastereomers were separated by preparative GC.

19: R_f (10:1 hexanes/EtOAc) 0.57.

IR (film): ν = 3070, 3030, 2955, 2930, 2865, 1452, 1366, 1095, 915, 890, 735, 695 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.31 (m, 5 H), 5.58 (ddd, J = 17.0, 10.1, 9.3, 1 H), 5.16 (dd, J = 10.2, 2.4 Hz, 1 H), 5.05 (dd, J = 17.1, 1.8 Hz, 1 H), 4.85 (d, J = 2.8 Hz, 1 H), 4.73 (d, J = 2.1 Hz, 1 H), 4.57 (d, J = 12.3 Hz, 1 H), 4.52 (d, J = 12.4 Hz, 1 H), 3.36 (d, J = 8.6 Hz, 1 H), 3.32 (d, J = 8.8 Hz, 1 H), 2.78 (dt, J = 9.2, 2.6 Hz, 1 H), 1.19 (d,

J = 13.5 Hz, 1 H), 1.37 (d, J = 13.5 Hz, 1 H), 1.19 (s, 3 H), 0.99 (s, 3 H), 0.73 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 161.88, 138.87, 136.50, 128.23, 127.39, 117.76, 105.39, 78.33, 73.22, 60.74, 50.83, 44.67, 40.94, 29.30, 28.77, 23.58.

MS (EI, 70 eV, relative percent): m/z = 270 (M^+, 1), 179 (10), 164 (9), 149 (21), 135 (19), 121 (16), 107 (26), 91 (100).

20: R_f (10:1 hexanes/EtOAc) 0.57.

IR (film): ν = 3070, 3030, 2955, 2930, 2865, 1452, 1366, 1095, 915, 890, 735, 695 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.31 (m, 5 H), 5.59 (ddd, J = 17.1, 10.1, 9.2 Hz, 1 H), 5.18 (dd, J = 10.2, 2.4 Hz, 1 H), 5.04 (dd, J = 17.1, 2.4 Hz, 1 H), 4.86 (d, J = 3.0 Hz, 1 H), 4.79 (d, J = 2.4 Hz, 1 H), 4.52 (s, 2 H), 3.18 (s, 2 H), 2.75 (dt, J = 9.2, 2.8 Hz, 1 H), 1.79 (d, J = 13.1 Hz, 1 H), 1.43 (d, J = 13.2 Hz, 1 H), 1.20 (s, 3 H), 0.98 (s, 3 H), 0.81 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 161.43, 138.91, 136.56, 128.21, 127.27, 117.99, 106.15, 80.83, 73.20, 61.27, 51.26, 44.70, 40.60, 28.11, 25.60, 23.62.

MS (EI, 70 eV, relative percent): m/z = 270 (M^+, 0.1), 179 (5), 164 (5), 149 (52), 136 (20), 121 (16), 107 (27), 91 (100).

5-Benzyloxymethyl-1-[(*E*)-1-propenyl]-3,3,5-trimethylcyclopentene (21):

To a solution of 1,6-enyne **10** (19.6 mg, 72 μmol) in benzene (250 μL) was added $Pt(OAc)_2(PPh)_3$ (6.0 mg, 7.2 μmol, 10%), DMAD (18.7 μL, 21.6 mg, 152 μmol), and trifluoroacetic acid (7.2 μL, 10.7 mg, 94 μmol). The mixture was heated at 70 °C for 2 h. After concentration by rotary evaporation, the residue was purified by flash chromatography (15:1 hexanes/EtOAc) to afford 15.9 mg (81%) of an inseparable mixture of *E*:*Z* regioisomers (**14**:**21**, 3.4:1). R_f (10:1 hexanes/EtOAc) 0.36.

^{1}H NMR ($CDCl_3$): δ = 7.33 (m, 5 H), 5.87 (m, 2 H), 5.48 (s, 1 H), 4.53 (s, 2 H), 3.35 (d, J = 8.9 Hz, 1 H), 3.30 (d, J = 8.9 Hz, 1 H), 1.99 (d, J = 13.2 Hz, 1 H), 1.74 (m, 3 H), 1.50 (d, J = 13.2 Hz, 1 H), 1.16 (s, 3 H), 1.08 (s, 3 H), 1.06 (s, 3 H); (C_6D_6): δ = 7.30–7.06 (m, 5 H), 5.97 (dd, J = 15.8, 1.4 Hz, 1 H), 5.88 (m, 1 H), 5.47 (s, 1 H), 4.38 (d, J = 12.5 Hz, 1 H), 4.32 (d, J = 12.5 Hz, 1 H), 3.34 (d, J = 8.7 Hz, 1 H), 3.31 (d, J = 8.8 Hz, 1 H), 2.16 (d, J = 13.3 Hz, 1 H), 1.62 (dd, J = 6.4, 1.4 Hz, 3 H), 1.59 (d, J = 13.2 Hz, 1 H), 1.28 (s, 3 H), 1.14 (s, 3 H), 1.12 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 142.98, 138.92, 137.23, 127.46, 127.42, 127.27, 125.76, 125.61, 77.52, 77.21, 51.07, 50.75, 42.41, 30.89, 30.26, 24.89, 18.76.

MS (EI, 70 eV, relative percent): m/z = 270 (M^+, 0.1), 255 (0.2), 164 (21), 149 (61), 121 (33), 107 (37), 91 (100).

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