Acknowledgment. This work was supported by grants from the National Institutes of Health (GM-38767, L.Q.; GM-30306, O.P.A.). We are grateful to Dr. Vasilios Papaefthymiou for providing the Mössbauer spectrum of 1 and Dr. A. S. Borovik for fruitful discussions and valuable assistance.

Supplementary Material Available: Tables of atomic positional and thermal parameters for $[Fe_2L_2O(OBz)]BPh_4$ (6 pages). Ordering information is given on any current masthead page.

Diastereofacialselectivity in Intramolecular Pauson-Khand Cycloaddition: Highly Stereoselective Synthesis of Pentalenene

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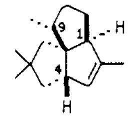
Our interest in expanding the scope of the intramolecular Pauson-Khand cyclopentenone synthesis recently led to our successful demonstration of this reaction's viability in the preparation of the angularly fused triquinane ring system.[1] In order to test the degree of stereocontrol available in this process we sought an efficient route to an enyne system which would be suitable for elaboration via cycloaddition into triquinane natural products. Herein we describe a synthesis of (±)-pentalenene (1)[2,3]



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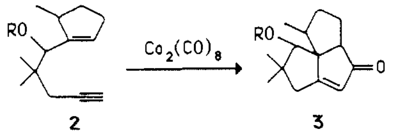
which makes use of (1) a novel approach to the generation of the quaternary center via conjugate addition-alkylation, (2) an efficient application of dissolving metal reduction to remove an otherwise intractable protecting group, and (3) a gratifyingly large kinetic diastereofacialselectivity in the Pauson-Khand cycloaddition itself, utilizing only the methyl group at the lone stereocenter in the precursor enyne to direct ring-closure in the required direction.

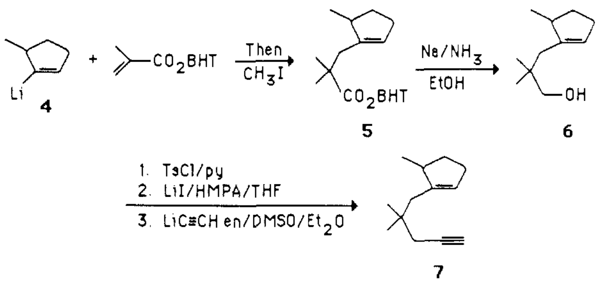
In our previous study the then unavoidable presence of an extraneous protected alcohol in the cycloaddition precursor (2, $R = CH_2OCH_3$) had two unfavorable effects: the products of



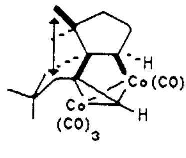
cycloaddition (3) were chemically unstable with respect to fragmentation reactions, and steric interference involving the protected alcohol overwhelmed any stereocontrol that the methyl group might have imparted to the cycloaddition process, resulting mostly in products with the undesired stereochemistry at C-9 (exclusively so for one of the diastereomers of 2).

As a result we turned to conjugate addition of the readily available 5-methylcyclopentenyllithium (4)[4] to methacrylate as a possible approach to the deceptively simple enyne required. Attempts to form and utilize either an organocopper[5] or organocuprate[6] derivative of 4 were, however, unsuccessful. Cooke's report of conjugate addition resulting from the reaction of organolithium reagents with BHA and BHT esters of α,β-unsaturated acids[7] then attracted our attention. Due to the availability of simple oxidative methods for subsequent removal of the BHA moiety, it is the preferred group for protection of an ester from 1,2-addition. Unfortunately, 4 fails entirely to add to BHA methacrylate.

Reaction of 4 with BHT methacrylate is extremely efficient, however, and in situ methylation of the resulting enolate gives 5 in 90% overall yield. This result would be of little value unless some means of removal of the BHT fragment (from a neopentyl ester, no less!) could be found. Not surprisingly, 5 is quite effective at resisting attack by nucleophiles: it is recovered unchanged after reaction with either $LiAlH_4$ for 5 h in refluxing THF or "Super-Hydride" ($LiEt_3BH$) for 18 h in THF at 25 °C. Fortunately, 5 succumbs to attack by solvated electrons; treatment with 10 equiv of Na in liquid NH_3 containing 4 equiv of ethanol affords alcohol 6 in a modest but usable 45% yield.[8] The sequence 4 → 6 is unprecedented in its simplicity, especially considering that the Sakurai approach[9] is inapplicable here due to the need to control the regiochemistry of the alkene. Conversion of 6 to enyne 7 is achieved in 34% overall yield as shown.[10]



The control of stereochemistry at C-9 in syntheses of angularly fused triquinanes in general and pentalenene in particular has been achieved with varying success. It has generally been found that greater success has resulted from sequences that set the stereochemistry in a ring-forming step.[3c,e,g,l] We hoped that the $Co_2(CO)_6$ complex of alkyne 7 would similarly display a preference for reaction on the face of the alkene opposite to the methyl substituent. Examination of models of the presumed intermediate made it far from obvious, however, that any single interaction would be capable of directing the cycloaddition in the desired direction. The only likely candidate appeared to be a 1,3-pseudodiaxial interaction that develops between the endo substituent at C-9 and the propargylic methylene group (arrow, below).



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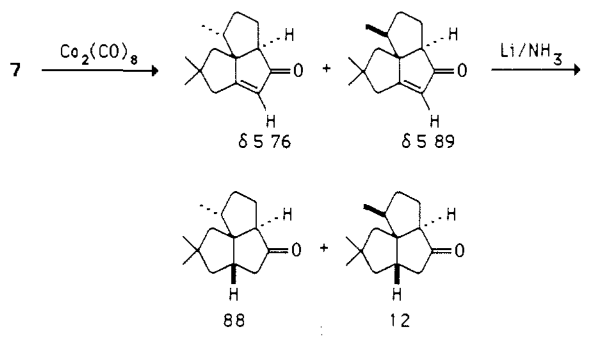

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In the event, heating of 7-$Co_2(CO)_6$ in heptane at 110 °C (sealed tube) gives 51% of an 88:12 ratio of enones. The products have readily resolved proton NMR resonances at δ 5.76 (major isomer) and δ 5.89 (minor isomer), respectively, but no information concerning the stereochemistry of the major product could be inferred at this point. Reduction (Li/NH_3, 89%) gives a mixture of saturated ketones **8** whose major constituent clearly possesses the desired configuration at C-9, based on superimposability of its NMR signals with those of the minor constituent in spectra obtained by Piers for a 42:58 mixture of isomers of **8**. Completion of the synthesis of pentalenene was achieved by following the published procedure; spectroscopic data for the product were identical in all respects with that of authentic (±)-pentalenene.[11,12]

The interactions associated with the intramolecular Pauson–Khand reaction are more than sufficient to give rise to usable stereoselectivity in relatively complex situations. The interaction above is not obviously greater than those that give rise to rather modest *regio*selectivities in some intermolecular versions of the reaction.[13,14] The difference in transition state energy between endo and exo C-9 methyl leading to the intermediate shown is about 1 kcal/mol. Apparently the transition state associated with alkene insertion in the intramolecular process is more product-like, consistent with the high stereoselectivities found by Magnus in Pauson–Khand syntheses of substituted bicyclic systems.[15] It was necessary in the latter cases to generate the controlling interaction by attachment of a bulky group to the alkyne terminus. In our system this is unnecessary, as the control elements are already present in the framework of the incipient tricyclic itself.

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(11) We are extremely grateful to Prof. Edward Piers of the University of British Columbia for providing us with details of his conversion of **8** into **1** and for supplying IR and NMR spectra of these compounds for comparison purposes.

(12) Satisfactory spectroscopic data for all compounds (300 MHz ^{1}H NMR, ^{13}C NMR, IR) and satisfactory elemental analyses for compounds **5** and **6** were obtained.

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[*n*]Staffanes: A Molecular-Size "Tinkertoy"[1] Construction Set for Nanotechnology. Preparation of End-Functionalized Telomers and a Polymer of [1.1.1]Propellane

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Nanotechnology,[2] custom design and construction of molecular-size mechanical structures, has been a subject of speculation for some time.[3] We have telomerized and polymerized [1.1.1]propellane (**1**) and obtained a family of end-functionalized inert, insulating, transparent, and straight beams with a van der Waals radius of 2.3 Å and a length increment of 3.35 Å for use as construction elements. We propose the trivial name [*n*]staffanes for the parent hydrocarbons.[4] Presently, we describe a one-step synthesis of singly functionalized telomers [***n***]**2**, with emphasis on the esters [***n***]**2a** and the acids [***n***]**2b**, including a low molecular weight polymer **[poly]2a**. A one-step preparation of doubly end-functionalized telomers of **1** will be reported separately.[5]

Previously described molecules of this type were the formal telomers [***n***]**3** of [2.2.2]propellane, originated by Zimmerman,[6] known up to $n = 2$, and used as spacers in studies of energy[6] and electron[7] transfer. Unlike the synthesis of [***n***]**2**, the preparation of the higher members of this series is laborious.

[1.1.1]Propellane[8] (**1**) is readily accessible from methallyl dichloride.[9] The formation of telomer side-products up to $n = 3$ during radical addition of cyanogen bromide to **1** has been detected,[10] and very recently a low-molecular weight polymer was obtained from a related monomer, 2,4-trimethylene-**1**, by anionic polymerization.[11]

We have detected the formation of numerous telomers under radical addition conditions, [***n***]**2a** – [***n***]**2i**, n = 1–4 or 5, and isolated many of them in pure state. Their relative amounts depend on the choice of reactant concentrations. Chlorocarbonylation of [***n***]**2a**, n = 2, 3, yielded derivatives of [***n***]**2j**. Some of the attempted telomerization reactions did not proceed smoothly; e.g., the reaction of $PhCH_2Br$ with **1** yielded some **[2]2k** and bibenzyl in addition to **[1]2l**.

Efficient preparation of [***n***]**2a** requires ether-free solutions of **1**, obtained in a 15% yield based on methallyl dichloride by substituting TMEDA for ether in the Szeimies synthesis. In a typical procedure, a 1.4 M solution of **1** in pentane (65 mL) reacted with methyl formate (800 mL) upon irradiation in the presence of benzoyl peroxide (0.4 g). The individual telomers [***n***]**2a** were separated by crystallization of the acids and potassium salts and by sublimation. On the basis of methallyl dichloride, the overall three-step yields of purified materials were about 3% for n = 1, 2, about 1.5% for n = 3, 4, and about 0.8% for n = 5, with about 3% of **1** accounted for as higher molecular weight material. It is possible to find reaction conditions under which only the

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(1) Tinkertoy is a trade-mark of the Questor Education Products Company, used to designate a children's toy construction set consisting of straight beams and connectors.

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