PROGRESS TOWARD THE SYNTHESIS OF (+)-ZOANTHENOL

AND

THE DEVELOPMENT OF AN ASYMMETRIC TSUJI ALLOYATION REACTION

Thesis by
Douglas Carl Behenna

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To my parents

for their constant support
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ABSTRACT

The stereoselective synthesis of all carbon quaternary stereocenters is an important problem in synthetic chemistry due to their common occurrence in bioactive compounds. The zoanthamine class of marine natural products highlights the challenge in constructing such stereocenters. After a summary of the isolation, structure determination, and biological activities of the zoanthamine natural products, published approaches toward their chemical synthesis are reviewed.

Synthetic strategies toward the carbocyclic portion of zoanthenol focus on the synthesis of the three challenging quaternary stereocenters located on the central C ring. An unusual acid-mediated S_N1' cyclization of a nucleophilic arene with an allylic alcohol forms the B ring and diastereoselectively constructs the benzylic C(12) quaternary stereocenter. However, difficulties with late-stage installation of the remaining C(9) quaternary stereocenter compelled the use of C ring synthons containing the vicinal C(9) and C(22) stereocenters installed at an early stage in the synthesis. Desymmetrization of a meso-anhydride containing vicinal quaternary stereocenters accomplishes this goal in an enantioselective fashion. Several C ring synthons bearing the vicinal quaternary stereocenters are elaborated with A ring fragments, and several methods for the formation of the C(11)-C(12) bond in these systems are explored. Ultimately, a radical conjugate addition strategy provides the carbocyclic core of zoanthenol with the correct relative configuration of all three quaternary stereocenters.

These efforts toward the synthesis of zoanthenol highlight the difficulty in generating enantioenriched α-quaternary cycloalkanones derived from ketones with multiple acidic α-hydrogens. The first direct catalytic enantioselective access to such products is achieved by the application of chiral bidentate phosphinoaxazoline (PHOX) ligands to Tsuji’s non-enantioselective allylation reactions. Cyclic allyl enol carbonates, silyl enol ethers, and allyl β-ketoesters all provide uniformly excellent yields and high enantioselectivity in the reaction. The limitations on the substrate scope of the reaction are discussed. Preliminary studies into the mechanism of these allylation reactions with prochiral enolate fragments suggest that they occur by a different mechanism than the outer-sphere nucleophilic attack commonly proposed in the alkylation of prochiral allyl fragments.
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<th>Abbreviation</th>
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<td>CAN</td>
<td>ammonium cerium (IV) nitrate</td>
</tr>
<tr>
<td>Cbz</td>
<td>benzyloxycarbonyl</td>
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<tr>
<td>CCDC</td>
<td>Cambridge Crystallographic Data Centre</td>
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<tr>
<td>comp</td>
<td>complex</td>
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<td>CSA</td>
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<td>Cy</td>
<td>cyclohexyl</td>
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<td>d</td>
<td>doublet</td>
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<tr>
<td>dba</td>
<td>dibenzylideneacetone</td>
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<tr>
<td>DBU</td>
<td>1,8-diazabicyclo[5.4.0]undec-7-ene</td>
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<tr>
<td>DCC</td>
<td>1,3-dicyclohexylcarbodiimide</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2-dichloroethane</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane or methylene chloride</td>
</tr>
<tr>
<td>DEAD</td>
<td>diethyl azodicarboxylate</td>
</tr>
<tr>
<td>DIBAL</td>
<td>diisobutylaluminum hydride</td>
</tr>
<tr>
<td>DIOP</td>
<td>2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane</td>
</tr>
<tr>
<td>DIPA</td>
<td>diisopropyl amine</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>DMA</td>
<td>N,N'-dimethylacetamide</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-dimethylaminopyridine</td>
</tr>
<tr>
<td>dmdba</td>
<td>3,5,3',5'-dimethoxydibenzylideneacetone</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-dimethoxyethane</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMP</td>
<td>Dess-Martin periodinane</td>
</tr>
<tr>
<td>DMPU</td>
<td>N,N'-dimethyl propylene urea</td>
</tr>
<tr>
<td>DMS</td>
<td>dimethylsulfide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
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<tr>
<td>DPPB</td>
<td>1,4-bis(diphenylphosphino)butane</td>
</tr>
<tr>
<td>DPPE</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>dr</td>
<td>diastereomeric ratio</td>
</tr>
<tr>
<td>ee</td>
<td>enantiomeric excess</td>
</tr>
<tr>
<td>E</td>
<td>entgegen olefin geometry</td>
</tr>
<tr>
<td>EI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>equiv</td>
<td>equivalent(s)</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>FAB</td>
<td>fast atom bombardment</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
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<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>Grubbs II</td>
<td>Grubbs’ second generation metathesis catalyst</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>[H]</td>
<td>reduction</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>hv</td>
<td>light</td>
</tr>
<tr>
<td>$^1$H</td>
<td>proton</td>
</tr>
<tr>
<td>$^3$H</td>
<td>tritium</td>
</tr>
<tr>
<td>HMDS</td>
<td>hexamethyldisilazide or hexamethyldisilizane</td>
</tr>
<tr>
<td>HMPA</td>
<td>hexamethylphosphoramide</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatography</td>
</tr>
<tr>
<td>HRMS</td>
<td>high resolution mass spectroscopy</td>
</tr>
<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>$\eta^n$</td>
<td>eta; $n =$ number of atoms coordinated to metal</td>
</tr>
<tr>
<td>IC$_{50}$</td>
<td>concentration required for 50% growth inhibition</td>
</tr>
<tr>
<td>imid.</td>
<td>imidazole</td>
</tr>
<tr>
<td>IR</td>
<td>infrared spectroscopy</td>
</tr>
<tr>
<td>$J$</td>
<td>coupling constant</td>
</tr>
<tr>
<td>$k_n$</td>
<td>rate constant, $n$ refers to various reactions, negative $n$ indicates reverse reaction</td>
</tr>
<tr>
<td>kcal</td>
<td>kilocalories</td>
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<tr>
<td>KHMDS</td>
<td>potassium hexamethyldisilazide</td>
</tr>
<tr>
<td>L</td>
<td>liter</td>
</tr>
<tr>
<td>LAH</td>
<td>lithium aluminum hydride</td>
</tr>
<tr>
<td>LDA</td>
<td>lithium diisopropylamide</td>
</tr>
<tr>
<td>LD$_{50}$</td>
<td>Lethal Dosage to kill 50% of test population</td>
</tr>
<tr>
<td>LiHMDS</td>
<td>lithium hexamethyldisilazide</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$m$</td>
<td>meta</td>
</tr>
<tr>
<td>m</td>
<td>multiplet or milli</td>
</tr>
<tr>
<td>$\mu$</td>
<td>micro</td>
</tr>
<tr>
<td>M</td>
<td>mega, metal, or molar</td>
</tr>
<tr>
<td>$m/z$</td>
<td>mass to charge ratio</td>
</tr>
<tr>
<td>$m$-CPBA</td>
<td>$meta$-chloroperbenzoic acid</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>$(R,R)$-Me-DUPHOS</td>
<td>$(-)$-1,2-Bis((2R,5R)-2,5-dimethylphospholano)benzene</td>
</tr>
<tr>
<td>MEK</td>
<td>methyl ethyl ketone</td>
</tr>
<tr>
<td>MH-60</td>
<td>mouse myelohybridoma cells</td>
</tr>
<tr>
<td>MIC</td>
<td>minimal inhibitory concentration</td>
</tr>
<tr>
<td>min</td>
<td>minute(s)</td>
</tr>
<tr>
<td>mol</td>
<td>mole(s)</td>
</tr>
<tr>
<td>mol%</td>
<td>percentage used based on moles</td>
</tr>
<tr>
<td>MOM</td>
<td>methoxymethyl</td>
</tr>
<tr>
<td>$(R)$-MOP</td>
<td>$(R)$-$(+)$-2-(Diphenylphosphino)-2'-methoxy-1,1'-binaphthyl</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
</tr>
<tr>
<td>Ms</td>
<td>methanesulfonyl</td>
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<tr>
<td>MS</td>
<td>molecular sieves</td>
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<tr>
<td>MTPA</td>
<td>$\alpha$-methoxy-$\alpha$-(trifluoromethyl)phenylacetic acid</td>
</tr>
<tr>
<td>MVK</td>
<td>methyl vinyl ketone</td>
</tr>
<tr>
<td>N</td>
<td>normal</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------------------------------</td>
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<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
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<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<td>NOE</td>
<td>nuclear Overhauser effect</td>
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<td>o</td>
<td>ortho</td>
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<td>[O]</td>
<td>oxidation</td>
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<td>para</td>
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<td>prostaglandin</td>
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<tr>
<td>Ph</td>
<td>phenyl</td>
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<tr>
<td>pH</td>
<td>hydrogen ion concentration in aqueous solution</td>
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<tr>
<td>Ph-H</td>
<td>benzene</td>
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<td>PHOX</td>
<td>phosphinooxazoline</td>
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<td>pivaloyl</td>
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<td>PMA</td>
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<tr>
<td>PMB</td>
<td>p-methoxybenzyl</td>
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<td>PMBM</td>
<td>p-methoxybenzyloxymethyl</td>
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<tr>
<td>p.o.</td>
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<tr>
<td>ppm</td>
<td>parts per million</td>
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<tr>
<td>PPTS</td>
<td>pyridinium p-toluenesulfonate</td>
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<tr>
<td>Pr</td>
<td>propyl</td>
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<td>i-Pr</td>
<td>isopropyl</td>
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<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
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</tr>
<tr>
<td>psi</td>
<td>pounds per square inch</td>
</tr>
<tr>
<td>Py or Pyr</td>
<td>pyridine</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
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<tr>
<td>QUINAP</td>
<td>(R)-(+)-(2-Diphenylphosphino-1-naphthyl)isoquinoline</td>
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<tr>
<td>R</td>
<td>alkyl group</td>
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<tr>
<td>R</td>
<td>rectus (configurational)</td>
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<tr>
<td>Red-Al</td>
<td>sodium bis(2-methoxyethoxy)aluminum hydride</td>
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<td>R&lt;sub&gt;f&lt;/sub&gt;</td>
<td>retention factor</td>
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<td>SAR</td>
<td>structure-activity relationship</td>
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<td>TBAF</td>
<td>tetrabutylammonium fluoride</td>
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<td>tetrabutylammonium triphenylfluorosilicate</td>
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<td>TBDPS</td>
<td>(tert)-butyldiphenylsilyl</td>
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<td>(tert)-butyldimethylsilyl</td>
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<td>temperature</td>
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<td>TES</td>
<td>triethyldimethylsilyl</td>
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<tr>
<td>Tf</td>
<td>trifluoromethanesulfonyl</td>
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<td>Full Form</td>
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<td>trifluoroacetic acid</td>
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<td>tetrahydrofuran</td>
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<td>triisopropylsilyl</td>
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<td>TLC</td>
<td>thin-layer chromatography</td>
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<td>tetramethylethylenediamine</td>
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<td>turnover number</td>
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<td>TPAP</td>
<td>tetrapropylammonium perruthenate</td>
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<td>TROC</td>
<td>trichloroethoxycarbonyl</td>
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<td>Ts</td>
<td>( p )-toluenesulfonyl or ( p )-toluenesulfonic</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>visual wavelength</td>
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<td>volume per volume</td>
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<td>w/v</td>
<td>weight per volume</td>
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<tr>
<td>X</td>
<td>halide or trifluoromethanesulfonate</td>
</tr>
<tr>
<td>Z</td>
<td>zusammen olefin geometry</td>
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