Benzannulation via Ruthenium-Catalyzed Diol−Diene [4+2] Cycloaddition: One- and Two-Directional Syntheses of Fluoranthenes and Acenes
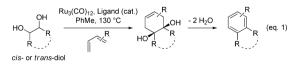
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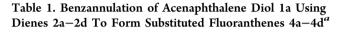
Ⓢ Supporting Information

ABSTRACT: A new benzannulation protocol is described and applied to the synthesis of polycyclic aromatic hydrocarbons. Ruthenium(0)-catalyzed diol−diene [4+2] cycloaddition delivers cyclohex-1-ene-4,5-diols, which are subject to aromatization upon dehydration or Nicholas diol deoxydehydration. Employing diol and tetraol reactants, benzannulation can be conducted efficiently in one- and two-directional modes, respectively, as illustrated in the construction of substituted fluoranthenes and acenes.
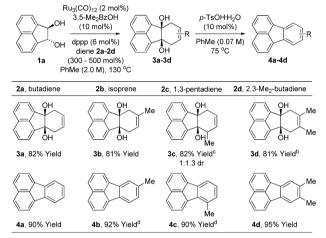
Polycyclic aromatic hydrocarbons (PAHs), including fluoranthenes and acenes, have attracted the interest of theoretical, physical experimental and materials chemists due to their electronic structure and potential utility vis-á-vis optoelectronic devices.[1] However, current methods for PAH construction are often lengthy and reliant upon methods that are not well suited for implementation on scale,[2] posing a barrier to the long-term goal of developing commercial manufacturing routes. In connection with ongoing studies on the catalytic C−C coupling of alcohols,[3] a byproduct-free protocol for the [4+2] cycloaddition of 1,2-diols with abundant conjugated dienes (butadiene and isoprene) employing an inexpensive ruthenium(0) catalyst was discovered in our laboratory.[4] It was recognized that aromatization of the diol containing cycloadducts via double dehydration would constitute a novel benzannulation strategy that could broaden access to tailored PAHs (eq 1).[5] Based on this novel

cycloaddition methodology, we herewith report a systematic investigation into the one- and two- directional benzannulation of diol and tetraol reactants, respectively, to furnish substituted fluoranthenes and acenes.

To establish the feasibility of this benzannulation strategy, our initial experiments focused on the cycloaddition of the racemic acenaphthalene derived *trans*-diol **1a** with dienes **2a**–**2d** (Table 1). For diol **1a**, a modification of our initially disclosed conditions[4] was required to obtain optimal isolated yields. Specifically, the ruthenium(0) catalyst generated from $Ru_3(CO)_{12}$ and 1,3-bis-(diphenylphosphino)propane (dppp)
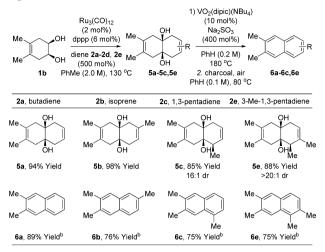
Table 1. Benzannulation of Acenaphthalene Diol 1a Using Dienes 2a−2d To Form Substituted Fluoranthenes 4a−4d[a]

[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further experimental details. [b]3,5-Me₂BzOH was not required. The ligand bis(1,2-diphenylphosphino)-benzene (dppPh) was used. [c]120 °C. [d]85 °C.
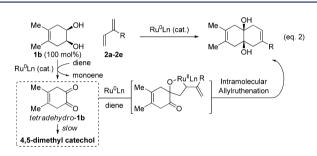
used in combination with 3,5-dimethylbenzoic acid (10 mol%) provided the best results. Under these conditions, *trans*-diol **1a** undergoes cycloaddition with dienes **2a**–**2d** to form the cycloadducts **3a**–**3d** in excellent yield with complete levels of *syn*-diastereoselectivity. Reactions of dienes **2a**–**2c** conducted in the absence of 3,5-dimethylbenzoic acid (10 mol%) were less efficient, resulting in a roughly 30% decrease in the isolated yield of cycloadducts **3a**–**3c**.[6] With cycloadducts **3a**–**3d** in hand, aromatization via double dehydration was attempted under the conditions of acid catalysis.[7] Gratifyingly, the products of benzannulation **4a**–**4d** were obtained in excellent yield.

To further evaluate the scope of this benzannulation protocol, the cycloaddition of *cis*-4,5-dimethylcyclohex-4-ene-1,2-diol **1b** with dienes **2a**–**2e** was attempted (Table 2). As the cycloaddition proceeds by way of a transient 1,2-dione *tetradehydro*-**1b**, the feasibility of using diol **1b** as a partner for cycloaddition was uncertain: tautomerization of *tetradehydro*-**1b** to form 4,5-dimethyl catechol may be faster than diene oxidative coupling (eq 2). Remarkably, use of the aforemen-

Table 2. Benzannulation of *cis*-4,5-Dimethylcyclohex-4-ene-1,2-diol 1b Using Dienes 2a–2c,2e To Form Substituted Naphthalenes 6a–6c,6e[a]

2a, butadiene	2b, isoprene	2c, 1,3-pentadiene	2e, 3-Me-1,3-pentadiene
5a, 94% Yield	5b, 98% Yield	5c, 85% Yield 16:1 dr	5e, 88% Yield >20:1 dr
6a, 89% Yield[b]	6b, 76% Yield[b]	6c, 75% Yield[b]	6e, 75% Yield[b]

[a]Yields are of material isolated by silica gel chromatography. dipic = 2,6-pyridinedicarboxylate. See Supporting Information for further experimental details. [b]Isolated yield after two steps.
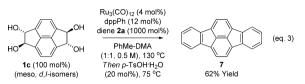

tioned conditions in the absence of a carboxylic acid cocatalyst led to formation of cycloadducts 5a–5c,5e in excellent yield with complete levels of *syn*-diastereoselectivity. Only in the case of 2,3-dimethylbutadiene 2d was cycloaddition thwarted due to competing formation of 4,5-dimethyl catechol. Presumably, because diene 2d does not incorporate a monosubstituted olefin, oxidative coupling of diene 2d with *tetradehydro*-1b is slow with respect to tautomerization to form the catechol.[8]

Cycloadducts 5a–5c,5e are not at an appropriate oxidation level for direct aromatization under the conditions of acid-catalyzed dehydration, and their exposure to acid catalysts was complicated by competing pinacol rearrangement. Consequently, diol deoxydehydration (DODH)[9] followed by aerobic dehydrogenative aromatization of the resulting trienes was explored as a means of accessing naphthalenes 6a–6c,6e. Using the DODH method of Nicholas,[9f] which employs an inexpensive dioxovanadium catalyst, the cycloadducts 5a–5c,5e were converted to corresponding trienes in good yield. As the trienes were generated as mixtures of olefin regioisomers, the DODH reaction mixture was filtered through Celite and the crude trienes were exposed to activated charcoal (DARCO KB) in the presence of air to deliver the substituted naphthalenes 6a–6c,6e in good yield (Table 2).

Having established effective protocols for one-directional benzannulation, the feasibility of two-directional benzannulation was explored through the double cycloaddition of butadiene 2a with the pyracylene-based tetraol 1c, which is prepared in 3 steps from acenaphthalene.[10] Optimal conditions involve use of the ruthenium(0) catalyst derived from
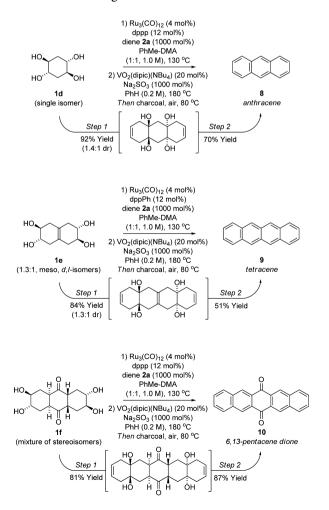
Ru₃(CO)₁₂ and bis(1,2-diphenylphosphino)benzene (dppPh). Aromatization of the double cycloadduct proceeded smoothly *in situ* simply upon introduction of an acid catalyst to furnish indeno[1,2,3-*cd*]-fluoranthene 7 in 62% isolated yield over the two-step sequence (eq 3).
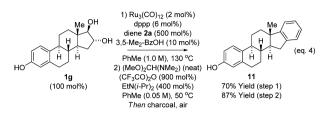

Inspired by these results, two-directional syntheses of a homologous series of acenes were undertaken. Cyclohexane tetraol 1d[11] undergoes ruthenium(0)-catalyzed double cycloaddition with butadiene 2a in a remarkable 92% yield to provide the indicated tetraol, which upon double DODH[9] followed by aerobic dehydrogenative aromatization of the resulting tetraene provides anthracene 8. An analogous two-step sequence converts octahydronaphthalene-tetraol 1e[11] to tetracene 9. Finally, the tricyclic tetraol 1f, prepared in 3 steps from benzoquinone through Diels–Alder cycloaddition,[11] is converted to 6,13-pentacene dione 10 (Scheme 1).

The present benzannulation protocol may have impacts beyond PAH construction. For example, the reaction of estriol 1g with butadiene 2a occurs efficiently in the absence of a

Scheme 1. Two-Directional Double Benzannulation of Tetraols 1d–1f Using Butadiene 2a To Form Acenes 8–10

phenolic protecting group. The resulting cycloadduct (not shown) is converted to the benzannulated steroid **11** in 87% yield via DMF-acetal-mediated DODH followed by exposure to activated charcoal in the presence of air (eq 4).[12]

In summary, a new protocol for benzannulation based on ruthenium(0)-catalyzed diol−diene [4+2] cycloaddition is described. Employing diol and tetraol reactants, benzannulation can be conducted efficiently in one- and two-directional modes, respectively, as illustrated in the construction of substituted fluoranthenes and acenes. Application of this methodology to the direct modification of abundant renewable polyols such as ethylene glycol, glycerol, and cellulose is underway.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Experimental procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(10) As described in the Supporting Information, the tetraketone corresponding to tetraol **1c** was prepared from acenaphthalene in two steps using a combination of literature procedures. Reduction of the tetraketone to form the tetraol **1c** required use of $NaBH(OAc)_3$, as use of more reactive hydride sources (e.g., $NaBH_4$, $LiAlH_4$, $LiBHEt_3$) led to decomposition. Although 1,2-diketones are reported to undergo reductive [4+2] cycloaddition, when using *o*-quinones the yields of product were prohibitively low.

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