Selective [2+2+2] Cycloaddition of Nickel-Benzyne and an Asymmetric 1,3-Diyne: An Iterative Route to Substituted [n]Acenes

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Abstract: A new iterative route to substituted acenes is reported that centers on regioselective cycloaddition of a nickel-benzyne and 1-trimethylsilyl-1,3-pentadiyne. The five-step sequence installs two fused aromatic rings and two methyl substituents onto the backbone in 27% overall yield.

Key words: alkynes, cycloaddition, fused-ring systems, nickel, regioselectivity

Linearly fused [n]acenes 1 have garnered attention because of the interesting electronic and optical properties conferred on these compounds by the conjugated ring systems (Figure 1). Substituted naphthalenes and anthracenes have been used extensively as energy transfer agents and as fluorescent sensors. Naphthacene (1, n = 1) and especially pentacene (1, n = 2) have been intensively studied for their use in thin film transistors for organic light emitting diodes and for their potential use in photoluminescent and photonic devices. Further interest has been stimulated by theoretical predictions that as the chain extends to nine fused rings or more, the triplet state may become the ground state, which would lead to materials with unique optical and electronic properties.

Figure 1

Despite this interest in the acene chain architecture, general and reliable syntheses of substituted oligoacenes remain scarce, rendering the theoretical predictions of the electronic properties unsubstantiated. One problem commonly encountered is the insolubility of even oligomeric acenes, resulting in low yields and poor characterization as the chain is elongated. Using step-wise syntheses, the longest chain to be synthesized is heptacene (1, n = 3), prepared by a double Diels–Alder cycloaddition with p-quinone, followed by reduction and oxidation procedures to prepare the fully conjugated chain. Similar protocols involving Diels–Alder cycloadditions of substituted dienes and dienophiles to generate substituted oligoacenes containing 3–7 fused rings have since been reported.

Recently, iterative approaches to oligoacene syntheses have appeared. Anthony and coworkers published a procedure wherein each new ring was constructed via a three-step sequence starting from 1,2-bis-trimethylsilyl-1,3-pentadiyne benzene (2, n = 1, Scheme 1). Each iteration involved exchange of the silyl groups for bromines using N-bromosuccinimide (NBS) and silver nitrate, thermal Bergman cyclization, and coupling of the resultant 2,3-dibromoacene with trimethylsilylethynyl zinc chloride to afford the homologated dialkynyl arene 3 in 57–68% overall yield for the three steps. This sequence was executed twice to form the dialkynyl anthracene; however, upon extension to form the fourth ring, insolubility of the product prevented isolation and further reaction.

Takahashi has also published an iterative method for the construction of oligoacenes wherein two rings – a nonaromatic and an aromatic ring – were introduced in a five-step sequence that afforded substituted oligoacenes (Scheme 2). The sequence involved reduction of tetraalkyl phthalate 4 to the diol, conversion of the diol to the dibromide, and nucleophilic displacement of the bromides with alkynyl lithium to form a diyne. Reaction of the diyne with Cp2ZrBu4 formed the zirconacyclopentadiene which reacted with dimethyl acetylene dicarboxylate (DMAD) in the presence of copper(I) chloride to yield dihydroanthracene diesters 5 (n = 1) in 45–60% overall yields. Repeating this sequence afforded a 40–60% overall yield of tetrahydropentacenes (5, n = 2). In the case of the propyl-substituted five-ring compound, oxidation with chloranil provided a 33% yield of substituted pentacene 6, which was fully soluble in a range of organic solvents. Although further homologation to the seven-ring compound (5, n = 3) was reported, oxidation to the substituted heptacene was not.

Nonetheless, the use of a zirco-
nium and copper mediated cycloaddition of three
substituted alkynes to install substitution on the acene
backbone is noteworthy.

Scheme 2

We have recently reported the reaction of symmetric 1,3-
diyne 16 with nickel benzyne (Equation 1). It was found
that reaction of nickel benzene 7 with two equivalents of
conjugated diyne 8 led to the preferential formation of
the 2,3-dialkynyl naphthalenes 9. The other possible iso-
ers 10 and 11 were not observed, except in one case
where isomer 10 was formed due to increased steric de-
mand on the alkyne substituent [R = CH(CH3)O
<sub>t-Bu</sub>].

Equation 1

The arrangement of the alkyne substituents on the newly-
formed naphthalene ring 9 observed in all but the most
sterically congested cases suggested the possibility of ex-
tending the ring system to an anthracene by means of a
Bergman cyclization (Scheme 3, 14 → 15). Such chain
extension would be analogous to that demonstrated by
Anthony and coworkers (see above, Scheme 1), but would
have the advantage of introducing solubilizing sidechains
onto the acene backbone. With appropriate choice of
diyne substituents, it should also be possible to access the
2,3-dibromoanthracene (15, R = Br). Since the nickel-
benzene complexes 13 are prepared from dibromoben-
zene 12, the formation of a 2,3-dibromoanthracene would
offer the opportunity for iterative oligoacene syntheses.
Toward this goal, we report herein on the regioselective
reaction of nickel-benzyne with the unsymmetric diyne 1-
trimethylsilyl-1,3-pentadiyne (16), and its elaboration to
the corresponding dibromooanthracene.

Scheme 3

Reaction of Unsymmetric Diynes

We chose the diyne 16 to investigate the selectivity of the
cycloaddition of nickel benzyne with unsymmetric
diyne 16 under conditions analo-
gous to those reported previously (Equation 2). However,
heating a mixture of nickel-benzyne 7 (1 equiv), diyne 16
(3 equiv), and Et<sub>3</sub>P (5 equiv) in degassed toluene at
60 ºC led to a disappointing 3% yield of product 17, with
a number of more polar by-products constituting the ma-
jority of the material. Upon lowering the reaction temper-
ature to 40 ºC, an increase in yield to 24% was observed;
however, at temperatures below 40 ºC the reaction did not
proceed. The structure of product 17 was assigned by the
symmetry evident in the NMR spectra, by analogy to the
previously isolated 1,4-dialkyl-2,3-dialkynyl naphtha-
lenes, and by the ease with which the trimethylsilyl alkyne
undergoes subsequent reaction (vide infra).
We speculated that the heating required to effect cyclization was contributing to undesired side-reactions of the starting materials and/or products. Thus, the reactivity of the nickel-benzyne was increased by omitting the electron-withdrawing fluorines and using more labile Et₃P ligands in place of the bidentate bis(dicyclohexylphosphino)ethane (dcpe) ligand. Reaction of nickel-benzyne, formed in situ by reduction of Ni(II) complex, with diyne in the presence of excess Et₃P at room temperature gave dialkynyl naphthalene in 62% yield for the two-step process (Equation 3). In comparison, nickel-fluorobenzyne complex is prepared in 68% yield, resulting in a 16% yield of difluoronaphthalene over two steps. It should be noted that to date, we have not observed any other isomers of [2+2+2] cycloaddition (e.g. similar to 10 or 11, Equation 1), although their formation cannot be ruled out given the modest yields of naphthalenes and isolated.

The formation of the 1,4-dialkyl-2,3-dialkynyl naphthalene product can be rationalized based on the mechanism proposed for the [2+2+2] cycloaddition of nickel-benzynes and alkynes (Scheme 4). The first step involves coordination of the diyne to nickel to give complex. Insertion into the alkyne occurs such that the new carbon-carbon bond is formed at the more accessible end of the diyne. Coordination of a second equivalent of diyne and subsequent insertion as before affords nickelacycle. Reductive elimination then provides product with concomitant release of nickel(0), which is sequestered by the added triethylphosphine.

The formation of dibromoanthracene constitutes completion of a five-step iteration to add two fused aromatic rings and two methyl substituents (Scheme 6). The complete cycle begins with insertion of nickel into one carbon-bromine bond of dibromobenzene to form complex. Formation of the nickel-benzyne and subsequent reaction with diyne yields dialkynyl naphthalene in 62% yield over the two steps. The selective formation of the 2,3-dialkynylnaphthalene allows the acene chain to be further extended upon conversion of the silyl alkynes to bromoalkynes and Bergman cyclization to afford the homologated dibromoarene in 27% overall yield for the five-steps.
Reactions were performed under an atmosphere of anhyd Ar utilizing standard Schlenk line techniques. All solvents were purified via distillation. IR spectra were recorded with a Perkin Elmer Spectrum BX spectrophotometer. All 1H and 13C NMR spectra were recorded on Varian Unity 400 or 500 MHz spectrometers using CDCl3. Electron Ionization (EI) mass spectra were obtained with Micromass 70 VSE spectrometer. All 1H and 13C NMR spectra were recorded on Varian Unity 400 or 500 MHz spectrometers using CDCl3. Electron Ionization (EI) mass spectra were obtained with Micromass 70 VSE spectrometer. The authors would like to thank Dr. Jian-Kang Jiang for preliminary experiments. Financial support from the University of Illinois is gratefully acknowledged.

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