An Alkyne Metathesis-Based Route to ortho-Dehydrobenzannulenes

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Received

Abstract: An application of alkyne metathesis to 1,2-di(prop-1-ynyl)arenes, producing dehydrobenzannulenes, is described. An efficient method for selective Sonogashira couplings of bromiodoarenes under conditions of microwave irradiation is also reported.

Keywords: alkyne metathesis, 1,2-di(prop-1-ynyl)arenes, dehydrobenzannulenes, microwave irradiation, Sonogashira coupling

Alkyne metathesis (Scheme 1) has not been used widely in organic syntheses until recently, even though the first reports of its homogeneous, catalytic version date back to as early as 1974 with results of Mortreux et al.¹ A resurgence of the field occurred in the 1990s, based on the work by the groups of Bunz² and Fürstner,³ which includes examples of ring closures, one notably leading to a meta-dehydrobenzannulene system.^{2c}

Scheme 1

We report here the investigation of the potential of alkyne metathesis in the construction of dehydrobenzannulenes (Scheme 2).⁴ This class of molecules is interesting in several respects – it provides attractive ligands to transition metal complexes,⁵ models for subunits of graphyne, a novel allotrope of carbon,⁶ precursors to ordered carbon nanostructures,⁷ scaffolds for molecules on which to study supramolecular phenomena,⁸ and materials with interesting photophysical properties.⁹ Our need for an efficient synthetic entry into substituted derivatives stems from our quest for the first members of the circular phenylenes, such as antikekulene.¹⁰ As representative targets, we directed our initial efforts to examples of tribenzocyclene **1**, as in Scheme 3, and subsequently the more challenging tetrabenzocyclene **2**, as well as the fused systems **3** and **4**. The parent **1a** and its derivatives have received considerable attention as synthetic targets,⁴ whereas a substituted version of **2**^{8f} and parent **3**^{6c} have been prepared for the first time only recently, the latter two through relatively long sequences.

Scheme 2

Following the lead of the literature,^{2,3} we chose 1-propynylarenes as the starting materials to be subjected to ring closure, because the second alkyne to be formed on metathesis, 2-butyne, is removed readily from the reaction mixture. The requisite diynes **6** were accessed by Sonogashira reaction of appropriately substituted iodoarenes (Scheme 3, Table 1).¹¹ The respective couplings of otherwise unsubstituted and of alkyl- or alkoxy-substituted iodoarenes proceeded cleanly, in good to excellent yields (entries 1-4, 7-9, 11 in Table 1).¹²

To retain the potential of subsequent introduction of further alkyne substituents,¹⁰ tribenzocyclenes bearing bromine substituents were also of interest. Their preparation required the selective alkynylation of bromiodoarenes (entries 5,6,10 in Table 1). While such is often achievable at room temperature,¹³ we noticed significant overalkynylation in systems **5e**, **f**, and **j**. Monitoring the course of the reaction to the point of optimal conversion proved difficult, because of the use of closed systems under the positive pressure of propyne.

Scheme 3 Reagents and conditions: (i) propyne, $PdCl_2(PPh_3)_2$, CuI , NEt_3 (or NEt_3/DMF), Δ ; (ii) $(Me_3CO)_3W\equiv CMe_3$, toluene, 80 °C.

We therefore turned our attention to microwave-assisted Sonogashira couplings^{14,15} executed in a Smith Synthesizer. Application of this technique allowed the dipropynylation of three isomers of dibromodiiodobenzene at 100-110 °C (entries 5,6,10 in Table 1) with excellent selectivity in less than 20 minutes.¹⁶ Monitoring the change in pressure during the course of the reaction (Figure 1) provided a convenient gauge of its progress. The results of all propynylation reactions, both “classical” and microwave-assisted, are summarized in Table 1.

Figure 1 Pressure changes as a function of reaction time in Pd-catalyzed propynylation of **5** in a Smith Synthesizer. There is an initial pressure increase, as heating commences. The reaction starts at $t \sim 5$ min, causing the propyne pressure to drop, and ends at $t \sim 15$ min). The heater was turned off at $t \sim 44$ min.

With this route to *o*-dipropynylated arenes in hand, the feasibility of alkyne metathesis to tribenzocyclynes could be tested. Three catalytic systems are presently most popular: a) a mixture of $Mo(CO)_6$ and *p*-chlorophenol, typically used in *o*-dichlorobenzene at high temperatures (130-150 °C),^{2,3b,3e} b) the better defined $(Me_3CO)_3W\equiv CMe_3$ which is active at lower temperatures (80 °C in, e.g., toluene),^{3b,d,e,g} and (c) a less-defined alternative based on Mo amido complexes.^{3c,d,f} Due to the simplicity of a), this catalyst was used in our first experiments with **6a** as the substrate. Under a variety of conditions – performing the reaction at decreased pressure, under a constant stream of nitrogen (both of which served to remove 2-butyne formed), or with variable catalyst loading – not even trace amounts of **1a**

Table 1 Propynylation Reactions

Entry	Iodoarene ^a	Product	Conditions/Yield
1			25 °C / 22 h 95%
2			25 °C / 26 h 57%
3			25 °C / 48 h 81%
4			25 °C / 96 h 91%
5			110 °C / 3.75 min (microwave) 71%
6			110 °C / 20 min (microwave) 60%
7			25 °C / 44 h 76%
8			25 °C / 22 h 93%
9			90 °C / 36 h 77%
10			100 °C / 2 min (microwave) 64%
11 ^b			90 °C / 60 h 28%

^a Ref. 11. ^b Penta(prop-1-ynyl)benzene was obtained as a side product in 32% yield.

(GC/MS) were detectable. The only occasional product was a metathesis dimer, 1,1'-(1,2-ethynediyl)bis[2-(prop-1-ynyl)]benzene, generated in approximately 2% yield (by GC/MS analysis).

Gratifyingly, turning to catalyst b), the reaction proceeded cleanly to give **1a** in 54% yield as the only isolable product (entry 1 in Table 2). This preparation is superior in terms of yield and simplicity compared to other recently published approaches.^{5,6c,17}

Encouraged by this result, scope and limitations were investigated, summarized in Table 2. A rather simple trend was observed – sterically more crowded bisortho-substituted precursors did not undergo cyclization (entries 4,6 in Table 2), whereas bismetasubstituted ones did (entries 2,3,5 in Table 2). This outcome was not particularly dependent on electronic effects – both electron withdrawing (Br) and electron donating (OMe and Me) substituents were tolerated as long as they were located in meta positions; interestingly, substrates with resonance donors as substituents (Br and OMe) reacted more slowly (~2-4 times) than their unsubstituted or alkylsubstituted counterparts.

To provide an intramolecular test for the proposed steric trend, substrate **6g** was investigated, in which the two alkyne units are differentiated by bearing an ortho- and a meta-methyl group, respectively. It should react only once, to give the product of metathesis of the sterically less crowded triple bond. Indeed, the system produced solely **7** in 55% yield (Scheme 4).

Scheme 4

While the yields of the products depicted in Table 2 are modest, the simplicity and straightforward execution of the method would seem to make it that of choice for the rapid synthesis of specific derivatives, in particular when such are endowed with interesting novel topologies. As a consequence, and to explore the possibility of ring closure cross metathesis, we targeted the parent hydrocarbons **2-4**. To our delight, equimolar proportions of **6a** and **6h** converted directly to the new tetrabenzocyclone **2** in 19% yield!¹⁹ Even more impressive was the finding that **6a** and **6i** (4:1) underwent six fold metathesis to furnish **3** in 6% yield. This compound, as previously reported,¹⁰ was extremely insoluble in common organic solvents, probably to the detriment of the isolated yield. Finally, not unexpectedly in light of the results described above, hexapropynylbenzene **6k** was inert to metathesis with **6a** (on route to **4**) and even simple propynylbenzenes.

Table 2 Tribenzocyclones by Alkyne Metatheses Catalyzed by $(\text{Me}_3\text{CO})_3\text{W}\equiv\text{CCMe}_3^a$

Entry	Starting material	Cyclone	Conditions/ Yield
1 ^b			80 °C, 8 h 20 mol% cat. 54%
2 ^c			80 °C, 24 h 20 mol% cat. 27%
3 ^d			80 °C, 140 h 20 mol% cat. 28%
4			80 °C, 96 h 20 mol% cat. no reaction
5			80 °C, 120 h 20 mol% cat. 12%
6			80 °C, 96 h 20 mol% cat. no reaction

^a Ref. 19. ^b Ref. 20. ^c Ref. 21. ^d Ref. 4.

Cyclone **2** constitutes the parent of a di-*tert*-butyl derivative synthesized as part of a series of phenylacetylene macrocycles adorned with solubilizing substituents.^{8f} It is,

nonetheless, quite soluble in common organic solvents, exhibiting strong, green fluorescence. Its ^1H -NMR spectrum contains a characteristic peak due to the proton inside the macrocycle at $\delta = 8.05$ ppm (CDCl_3). The less benzofused system **8** shows the analogous absorption at $\delta = 7.82$ ppm (CDCl_3),²² possibly (but not necessarily) a reflection of increased dehydro[18]annulene diatropism. The aromaticity of cyclynes as measured by the ring current criterion is a topic of renewed current scrutiny.²³

The X-ray crystal structure of **2**,²⁴ shown in Figure 2, is only slightly distorted from ideal planarity – the dihedral angle between the planes of the respective meta- and ortho-fused rings is 7.1° . The intraannular hydrogen-hydrogen distance is 2.29 Å; in comparison, in **8** this distance is 2.57 Å – a possible indication of the greater flexibility of the system.²² The compound crystallizes in the $C2/c$ space group, with four molecules of **2** in the unit cell.

Figure 2 X-ray crystal structure of **2**

While **3** is known,^{6c} its ^1H -NMR spectrum could not be obtained due to seemingly poor solubility. We have found **3** sufficiently soluble in CDCl_3 to allow for such a measurement. The molecule gives rise to an AA'BB' multiplet for the peripheral aromatic hydrogens at $\delta = 7.19$ and 7.44 ppm, instead of the expected ABCD pattern, reflecting local symmetry, and a singlet at $\delta = 7.34$ ppm for the protons on the central benzene ring. These appear shielded relative to the corresponding ring hydrogens in 1,2,4,5-tetraethynylbenzene, which resonate at $\delta = 7.63$ ppm (CDCl_3) – an indication of the effect of the two neighboring paratropic cyclyne moieties.²³

In summary, we have shown that alkyne metathesis can be a potentially useful method for the construction of benzocyclynes. Although as yet the yields are only

moderate, for certain targets, this drawback is compensated for by a synthetic approach that is short and straightforward. Current work is aimed at improving catalyst efficiency to render this strategy more broadly applicable.

Acknowledgements

This work was facilitated by the National Science Foundation (CHE-0071887) and the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy, under Contract DE-AC03-76SF00098. The Center for New Directions in Organic Synthesis is supported by Bristol-Myers Squibb as a Sponsoring Member and Novartis as a Supporting Member. We would like to thank Prof. Alois Fürstner and Mr. Günter Seidel (Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, Germany) for catalyzing the initiation of this effort with a generous sample of $(\text{Me}_3\text{CO})_3\text{W}\equiv\text{CCMe}_3$. We are also indebted to Personal Chemistry, Inc. for providing us with access to a Smith SynthesizerTM, Prof. John Anthony (University of Kentucky) for communicating the experimental route to 1,4-dibromo-2,3-diiodobenzene, Prof. Sethuraman Sankamaram (Indian Institute of Technology, Madras) for helpful correspondence, and Prof. Uwe Bunz (University of South Carolina) for stimulating advice.

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An Alkyne Metathesis-Based Route to *ortho*-Dehydrobenzannulenes

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