

Perylene Synthesis by the Parallel Cycloaromatization of Adjacent Eneidyne

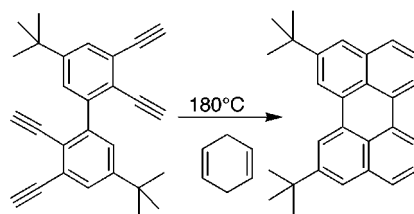
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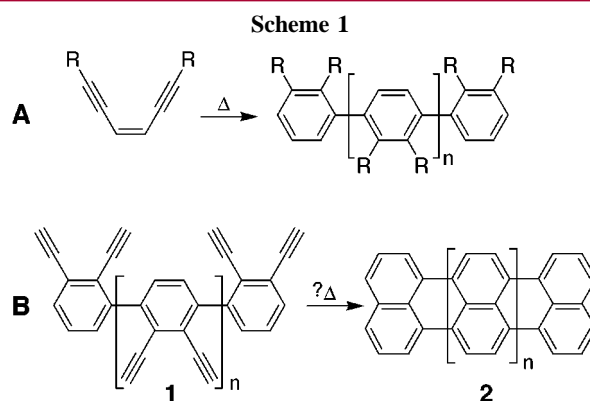
ABSTRACT



As part of an investigation into new synthetic routes to poly(*peri*-naphthalene), the synthesis and cycloaromatization of tetraethynylbiphenyls is described. The temperature-dependent cyclization of biphenyls containing unsubstituted alkynes provides the desired perylene in good yield.

A promising target for the preparation of conducting organic polymers is poly(*peri*-naphthalene) (PPN, **2**). Numerous theoretical treatments of this system have predicted a low band gap for the polymer,¹ while attempted syntheses of this material by the vacuum-pyrolysis of 3,4,9,10-perylenetetracarboxylic dianhydride² have provided insoluble, yet air-stable materials with conductivities as high as 1100 S cm⁻¹. While no synthesis of substituted, characterizable derivatives of this polymer have been reported, solubilized oligomeric species (called rylenes³) have been prepared from oligo-naphthalene precursors by reductive coupling with potassium metal followed by oxidation, or by heating in an oxidative alkali melt.⁴

Recent reports of the use of the Bergman cycloaromatization reaction⁵ to prepare poly(*p*-phenylenes)⁶ and other



highly cross-linked phenylene systems⁷ (Scheme 1, **A**) have led us to consider an alternative method for the synthesis of PPN and its oligomers (Scheme 1, **B**) which utilizes the

(1) (a) Tanaka, K.; Ueda, K.; Koike, T.; Yamabe, T. *Solid State Commun.* **1984**, *51*, 943. (b) Brédas, J. L.; Baughman, R. H. *J. Chem. Phys.* **1985**, *83*, 1316. (c) Bakhshi, A. K.; Ladik, J. *Synth. Met.* **1989**, *30*, 115. (d) Viruela-Martin, R.; Viruela-Martin, P. M.; Orti, E. *J. Chem. Phys.* **1992**, *97*, 8470. (e) Karabunarliev, S.; Baumgarten, Müllen, K.; Tyutyulkov, N. *Chem. Phys.* **1994**, *179*, 421.

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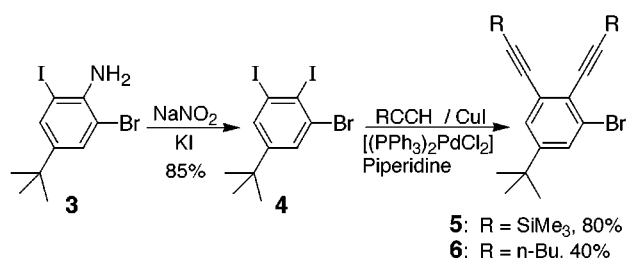
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thermal cycloaromatization of polymeric or oligomeric arenediynes such as **1** to form the desired PPN or rylene. Because cycloaromatization is strictly a thermal process, this parallel implementation of the reaction will be amenable to a wide variety of functional groups on the arene unit, which will allow the preparation of solubilized oligomers and polymers. We report here our first model studies on the synthesis and parallel cycloaromatization of some 2,3,2',3'-tetraethynylbiphenyls, the effects of substitution on the cycloaromatization reaction, and the cyclization temperature dependence for the formation of a 2,11-disubstituted perylene.

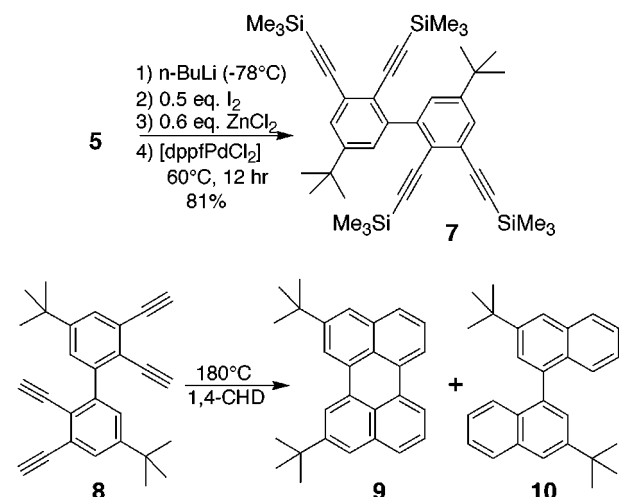
Substituted biphenyl tetrayne **7** was prepared in three high-yielding steps from halogenated aniline **3**.⁸ Diazotization/iodination of **3** in acetic acid followed by selective palladium-catalyzed alkyne coupling to the iodine functionalities led to the bromo enediynes **5** and **6** in fair to good yields (Scheme 2).

Scheme 2



Enediyne **5** was homocoupled through a convenient one-pot reaction sequence (Scheme 3). Halogen–metal exchange

Scheme 3



with 1.0 equiv of butyllithium in THF at $-78\text{ }^{\circ}\text{C}$ was followed by the addition of 0.5 equiv of iodine, which

converted half of the material to the aryl iodide, and anhydrous zinc chloride (0.6 equiv), which converted the remaining aryllithium to the corresponding arylzinc species. Addition of a palladium catalyst and heating to $60\text{ }^{\circ}\text{C}$ overnight provided the desired biphenyl in 81% isolated yield. Biphenyl **7** was desilylated by treatment with sodium methoxide in methanol–THF, yielding tetrayne **8** in quantitative yield. Cycloaromatization of **8**, which required heating a 0.01 M solution of the tetrayne in 10:1 (v/v) benzene/1,4-cyclohexadiene to $180\text{ }^{\circ}\text{C}$ in a sealed steel bomb⁹ for 2 h, led to the desired perylene **9** as the major product (66% yield), along with a small amount ($\sim 10\%$) of the binaphthyl **10**.¹⁰

While several reaction trials involving variations in the concentration of the radical trap showed little change in the ratio of these two products,¹¹ the product distribution was found to depend strongly on the reaction temperature (Table 1), with higher temperatures leading to increasing amounts of the desired perylene.

Table 1. Temperature Dependence of Product Distribution for the Cycloaromatization of **8**

temp ($^{\circ}\text{C}$)	time (h) ^a	yield of 9 , %	ratio 9:10
140	48	23 ^b	1:1.3
160	6	51 ^b	2:1
180	2	66 ^c	5:1
210	<2	40 ^b	7:1

^a Time required for complete consumption of starting material. ^b GC yield. ^c Isolated yield.

A possible explanation for this temperature-dependent product distribution arises from a consideration of the most reasonable mechanism for the formation of perylene **9** from **8**. Previous studies have shown that the radical species formed by cycloaromatization react preferentially with other cycloaromatized species, rather than with uncycloaromatized enediyne.^{6b} If biphenyl **8** behaves in an analogous manner, both of the enediyne units in the biphenyl need to be in the cycloaromatized state in order to form the perylene. Because the rate of cycloaromatization increases with increasing temperature, at higher temperature it is more likely that both enediyne units on any single biphenyl will be in the cycloaromatized state.¹²

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(9) All of the cycloaromatization reactions were performed in sealed systems behind protective shielding.

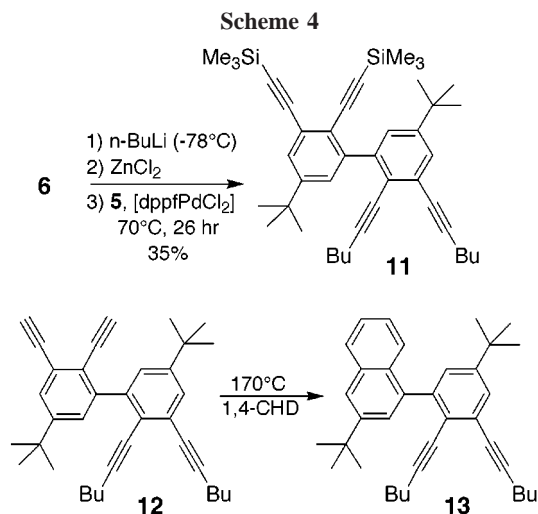
(10) For confirmation of structure, compound **10** was also synthesized by the homocoupling of 1-bromo-3-*tert*-butylnaphthalene, which was prepared by the cycloaromatization of desilylated **5**.

(11) Decreasing the concentration of the radical trap *did* lead to a significant decrease in overall yield.

(12) An alternative mechanism involves a 6-*exo* radical attack of one cycloaromatized enediyne unit on an alkyne on the adjacent, uncycloaromatized enediyne unit. Similar 6-*exo* radical cyclizations have been shown to be particularly inefficient. See, for example: Grisson, J. W.; Calkins, T. L.; Egan, M. *J. Am. Chem. Soc.* **1993**, *115*, 11744.

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To further explore the scope and mechanism of parallel cycloaromatization reactions, partially substituted tetrayne **12** was prepared. Because disubstituted enediynes do not undergo cycloaromatization at reasonable temperatures,¹³ all reaction products arising from the thermal reactions of desilylated **11** will result from interactions of the substituted enediyne unit with the adjacent cycloaromatized species. Biphenyl **11** was synthesized by an asymmetric coupling between bromo enediynes **5** and **6** as outlined in Scheme 4,



providing the desired biphenyl **11** in acceptable yield along with appreciable amounts of **7** as the major byproduct.

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Desilylation of **11** followed by cycloaromatization using conditions similar to those described for **8** led to naphthalene **13** as the sole isolable product in 20% yield, along with a number of side products which appear to have resulted from hydrogen abstraction from the alkyl side chains,¹⁴ and significant uncharacterizable tar—there was no evidence of any reaction products arising from the interaction of the cycloaromatized enediyne with the adjacent alkyne. The complete absence of the desired perylene from the reaction mixture has significant implications for the application of parallel cycloaromatization to the formation of larger rylene or polymer—solubilizing groups on these larger systems will have to be placed on the aromatic rings, rather than on the more easily substituted alkynes. We are currently investigating the effects of ring substitution on the subsequent cycloaromatization step, to be able to prepare larger oligomers and solubilized polymer.

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Supporting Information Available: Text giving experimental procedures for the preparation of compounds **4–7**, **9–11**, and **13**, along with their ^{13}C NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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