Fused Polycyclic Aromatics via Electrophile-Induced Cyclization Reactions: Application to the Synthesis of Graphite Ribbons

Marc B. Goldfinger and Timothy M. Swager*,†

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania Philadelphia, Pennsylvania 19104

Received April 26, 1994

The study and subsequent development of conjugated organic polymers is an area which has provided enormous opportunities for researchers over the past several years. Recognized applications of these materials include their use in light-emitting diodes (LEDs), nonlinear optical (NLO) devices, lightweight batteries, and sensory devices. The growing number of uses and performance requirements for these materials is driving the need for ever more complex structures. A factor often limiting development of many structurally complex materials is synthetic methodology. In this report we describe the synthesis of one such structurally complex material, an all-carbon conjugated ladder polymer or graphite ribbon.[1,2] Critical to this synthesis was the development of a novel electrophile-induced cyclization reaction which provides a powerful new route to fused benzenoid aromatic hydrocarbon systems[3] in high to quantitative yields.

We chose to pursue an all-carbon framework as a result of the observation that conjugated polymers which display the highest conductivities have all-carbon backbones. Polyacetylene in particular has been reported to display conductivities as high as that of copper.[4] However, due to its inherent instability, extensive development of polyacetylene has not been realized. An all-carbon conjugated system with an increased degree of two-dimensional structure, such as a ladder polymer, should maintain interesting electronic and optical properties while attaining increased stability relative to polyacetylene. Our approach was to synthesize a single-strand poly(p-phenylene)[5,6] substituted with latent acetylenic functionality poised for postpolymerization chemistry. In the reaction's simplest form, the attack of an electrophile (E+) on a substituted 2-(ethynyl)biphenyl (Scheme 1) would provide a substituted phenanthrene.

To explore this new cyclization reaction we chose to study the model compound **3** (Scheme 2) for characterization and optimization purposes. Compound **3** is readily synthesized by Pd catalyzed Suzuki cross-coupling of 2,5-dimethoxyphenylboronic acid with the aryl halide **2** in 96% isolated yield. Compound **1** is synthesized by chemoselective Pd(0)/Cu(I) coupling at the

Scheme 1
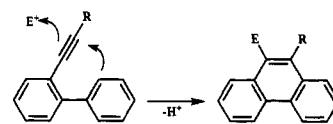
iodide positions of 1,4-dibromo-2,5-diiodobenzene[7] with 2 equiv of 4-(dodecyloxy)ethynylbenzene.

We first investigated cyclization of **3** with the I(pyridine)₂BF₄ reagent developed by Barluenga,[8,9] which when treated with 2 equiv of triflic acid (TfOH) liberates free I⁺BF₄⁻, a highly reactive source of electrophilic iodine. According to ¹H and ¹³C NMR evidence, a mixture of cyclization products was formed, suggesting that free TfOH must be competing with I⁺ in the cyclization. In fact, using TfOH alone produces a single compound, **5**. We have since found that milder conditions employing trifluoroacetic acid (TFA) are equally effective and produce *quantitative* yields of **5**, a bright yellow compound. Additionally, we have found that reaction of **3** with I(pyridine)₂BF₄ which has been treated with only 1 equiv of TfOH gives exclusively one cyclization product, **6**, in 96% isolated yield.

The reaction mechanism likely involves electrophilic attack at the acetylenic carbon attached to the central ring of the terphenyl moiety. The regiochemistry of the carbocation formation is directed by resonance stabilization, and electrophilic attack of the carbocation on the 6 and 6″ positions of the outer terphenyl rings, followed by loss of a proton, completes the cyclization. Consistent with this proposed mechanism are the results of attempted cyclizations of the identical model compound lacking only the p-alkoxy groups on the phenylethynyl moiety. Reaction with I⁺ gives complex mixtures, while no reaction is observed on treatment with TFA. Furthermore, we have found that the presence of the alkoxy (methoxy) groups, located on the terminal rings of the terphenyl moiety, is kinetically favorable but not essential for the success of the reaction, as **7** is produced from **4** in 100% isolated yield.

Polymer **8**, analogous to compound **3**, was prepared by cross-coupling of 1,4-didecyloxybenzene-2,5-diboronic acid with **2**. Similarly, polymer **9** was prepared by cross-coupling of **2** with 1,4-didodecylbenzene-2,5-diboronic acid,[10] and both rigid-rod polymers are soluble in CHCl₃, CH₂Cl₂, and THF. In optimizing these polymerizations, we determined that catalyst deactivation, which limits the molecular weight, could be eliminated by reducing the catalyst loading to 0.3 mol %. This key modification resulted in an increase in molecular weights (GPC, polystyrene standards, THF eluent) from M_n = 4000–6000 g/mol to M_n = 45 000–55 000 g/mol. Additional factors leading to high conversion during polymerization included using nitrobenzene/water as solvent and KOH as base. Polymer **8**, a light yellow solid with an intense blue fluorescence (430 nm), has straightforward ¹H and ¹³C NMR spectra. Polymer **9**,[12] a white solid which is also blue emissive, displays a more complex ¹H NMR spectrum. The NMR and greater bandgap of **9** are consequences of twisting of

(1) For other reports on graphite ribbons, see: (a) Schlüter, A. D. *Adv. Mater.* **1991,** *3,* 282 and references therein. (b) Koch, K. H.; Müllen, K. *Chem. Ber.* **1991,** *124,* 2091. (c) Grubbs, R. H.; Kratz, D. *Chem. Ber.* **1993,** *126,* 149. (d) For an example of a heterocyclic conjugated ladder polymer, see: Tour, J. M.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993,** *115,* 4935.

(2) A graphite ribbon with a very similar architecture was recently reported: Chmil, K.; Scherf, U. *Makromol. Chem., Rapid Commun.* **1993,** *14,* 217.

(3) This reaction affects a transformation similar to the Mallory photocyclization, which has been widely used in the synthesis of fused polycyclic aromatics. For a review, see: Mallory, F. B.; Mallory, C. W. *Organic Reactions;* Wiley & Sons: New York, 1984; Vol. 30, p 1.

(4) Naarmann, H.; Theophilou, N. *Synth. Met.* **1987,** *22,* 1.

(5) For examples of poly(p-phenylene)s prepared by cross-coupling chemistry, see: (a) Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W. J. *Polymer* **1989,** *30,* 1060. (b) Rehahn, M.; Schlüter, A.-D.; Wegner, G. *Makromol. Chem.* **1990,** *191,* 1991. (c) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991,** *113,* 7411. (d) Scherf, U.; Müllen, K. *Makromol. Chem., Rapid Commun.* **1991,** *12,* 489. (e) Scherf, U.; Müllen, K. *Macromolecules* **1992,** *25,* 3546. (f) Reference 1c.

(6) For a recent review on polyphenylenes, see: Tour, J. M. *Adv. Mater.* **1994,** *6,* 190.

(7) Goldfinger, M. B.; Swager, T. M. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1993,** *34(2),* 755.
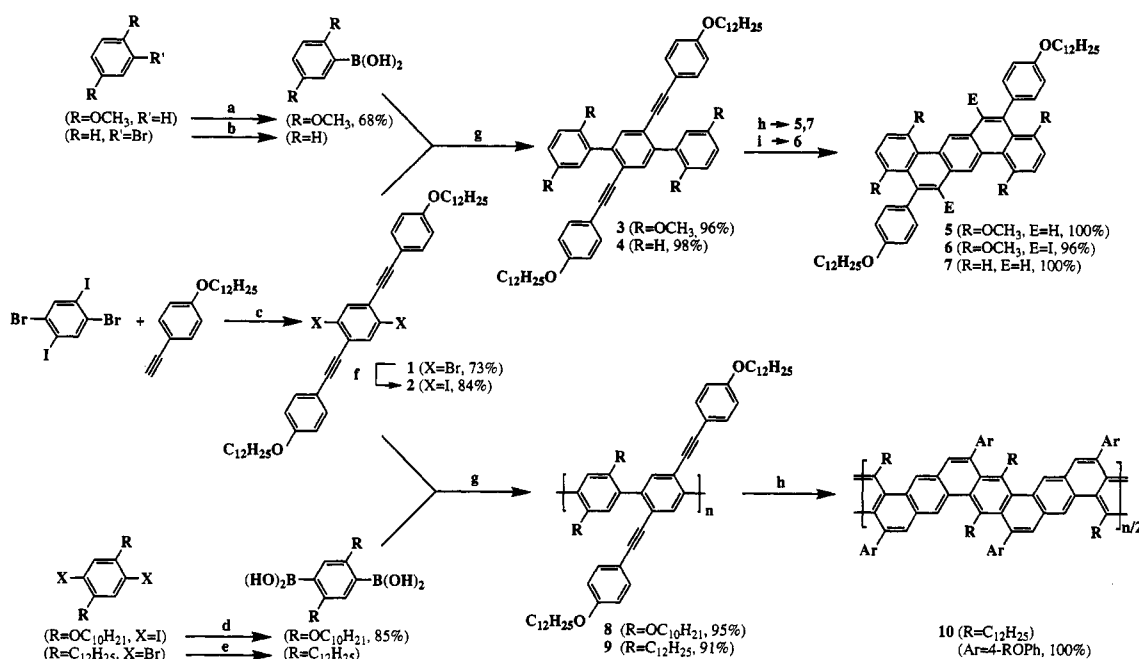
(8) (a) Barluenga, J.; Gonzalez, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 319. (b) Barluanga, J.; Rodriguez, M. A.; Gonzalez, J. M.; Campos, P. J. *Tetrahedron Lett.* **1990,** *31,* 4207.

(9) Barluenga has previously reacted I(pyridine)₂BF₄ with acetylenes and olefins to affect intramolecular carbocyclizations: Barluenga, J.; Gonzalez, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1546.

(10) 1,4-Dialkylbenzene-2,5-diboronic acids have previously been used in poly(p-phenylene) syntheses, see refs 5b, 5d, and 5e.

(11) Phenylboronic acid was synthesized by B(OMe)₃ quench of phenyllithium which was prepared according to the literature: Trepka, W. J.; Sonnenfeld, R. J. *J. Organomet. Chem.* **1969,** *16,* 317.

(12) Polymer **9**: Anal. Calcd for C₇₆H₁₁₂O₂: C, 86.30; H, 10.67. Found: C, 87.18; H, 11.05. Polymer **10**: Anal. Calcd for C₇₆H₁₁₂O₂: C, 86.30; H, 10.67. Found: C, 84.63; H, 10.29.

Scheme 2[a]

(R=OCH₃, R'=H)
(R=H, R'=Br)   —a→ (R=OCH₃, 68%)   —b→ (R=H)

3 (R=OCH₃, 96%)
4 (R=H, 98%)

5 (R=OCH₃, E=H, 100%)
6 (R=OCH₃, E=I, 96%)
7 (R=H, E=H, 100%)

1 (X=Br, 73%)
2 (X=I, 84%)

(R=OC₁₀H₂₁, X=I) —d→ (R=OC₁₀H₂₁, 85%)
(R=C₁₂H₂₅, X=Br) —e→ (R=C₁₂H₂₅)

8 (R=OC₁₀H₂₁, 95%)
9 (R=C₁₂H₂₅, 91%)

10 (R=C₁₂H₂₅)
(Ar=4-ROPh, 100%)

[a] (a) (i) t-BuLi (3 equiv), THF, (ii) B(OMe)₃ (5 equiv), (iii) HCl (1 M); (b) ref 11; (c) (Ph₃P)₂PdCl₂ (2 mol %), CuI (10 mol %), Bu₄NBr (10 mol %), 1:1 PhMe:HN(i-Pr)₂; (d) (i) t-BuLi (5 equiv), THF, (ii) B(OMe)₃ (8 equiv), (iii) HCl (1 M); (e) ref 5b; (f) (i) t-BuLi (5 equiv), THF, (ii) I₂ (3.5 equiv); (g) Pd(dba)₂ (0.3 mol %), Ph₃P (2.4 mol %), KOH (10 equiv), 6:1 PhNO₂:H₂O, 85 °C; (h) CF₃CO₂H (10–100 equiv/acetylene), CH₂Cl₂, 25 °C; (i) I(pyridine)₂BF₄ (2 equiv), CF₃SO₃H (2 equiv), CH₂Cl₂, −40 to 10 °C.

the polymer backbone, caused by the greater steric bulk of the alkyl groups. ¹H NMR of **9** taken at 90 °C shows a coalesced spectrum.

CH₂Cl₂ solutions of polymer **8** react with TFA to give deep red/brown materials. The presence of free decanol in the reaction mixture suggests that additional acid-catalyzed side reactions were occurring. IR indicates that the acetylenes are consumed; however, assignment of the exact nature of the side reaction is made difficult by the rigid structure which manifests a very broad NMR spectrum. The defect sites are most clearly apparent in the luminescence spectrum, which shows two emission channels at 500 and 575 nm. Although ¹H NMR indicates that the loss of decanol occurs to the extent of only ~10%, the emission band at 575 nm due to the defects is dominant. This effect is likely due to the migration of excitons to local minima created in the bandgap by the defect sites, but more importantly it provides our most sensitive probe for unwanted structural defects in the cyclized polymers.

CH₂Cl₂ solutions of polymer **9** treated with TFA produce graphite ribbon **10**[12] as a yellow/orange solid and show a single emission band at 507 nm. Polymer **10**'s absorption edge appears at 478 nm (λ_max = 340 nm and a strong shoulder at 364 nm), which is a substantial red shift from **9**'s band edge, which appears at 380 nm (λ_max = 341 nm).[13] In the IR spectrum, the acetylene stretch observable for **9** at 2214 cm⁻¹ is absent in **10**, and as expected distinct changes are observable in the aromatic C–H bending regions. ¹H NMR evidence also agrees with trends observable in the model systems **5, 6,** and **7**. The protons on the 3' and 6' positions of the central ring of **4** appear at 7.68 ppm and shift downfield to 9.14 ppm after cyclization to **7**. In polymer **9**, the analogous protons appear at 7.66 ppm and shift to 8.97 ppm after cyclization to **10**. Due to its large rigid structure, **10**'s

¹³C NMR (500 MHz) has broad unresolved aromatic resonances in the regions of 113–115, 126–135, 136–139, and 157–159 ppm. This spectrum is consistent with **10**'s structure, since very similar aromatic groupings are observed for **5, 6,** and **7** and all cyclized products rigorously lack acetylenic resonances. The high solubility and the monomodal nature of the GPC trace taken after cyclization, indicate that the reaction is exclusively intramolecular in nature, i.e., the material is not cross-linked. In addition, a molecular weight decrease of ~30% is observed by GPC after cyclization, indicative of the smaller effective volume of the boardlike **10** as opposed to the cylindrically shaped **9**.

In conclusion, we have introduced a novel electrophile-induced cyclization/isomerization reaction which constitutes a versatile new route to fused polycyclic aromatic hydrocarbons. We have demonstrated the utility of this reaction by synthesizing the all-carbon conjugated ladder polymer or graphite ribbon **10**. Future investigations will focus on synthetic routes to a variety of topologically interesting structures including helicenes, helical polymers, and other molecules with high degrees of steric strain. Additional studies will be aimed at gaining a more detailed understanding of the reaction mechanism.

Supplementary Material Available: Experimental procedures and characterization data for all new compounds reported (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(13) Although Chmil and Scherf (ref 2) report a large bathochromic shift for λ_max on conversion from precursor to ladder polymer, the absorbance trends observed for our system are in complete agreement with those of our model compounds. Compound **3**: UV–vis (λ, nm (relative intensity)) 364 (0.84), 342 (λ_max = 1); luminescence spectrum (λ, nm) 395. Compound **5**: UV–vis (λ, nm (relative intensity)) 430 (0.27), 406 (0.23), 376 (0.44), 358 (0.44), 320 (λ_max = 1), 280 (0.70); luminescence spectrum (λ, nm (relative intensity)) 440 (1), 466 (0.55).