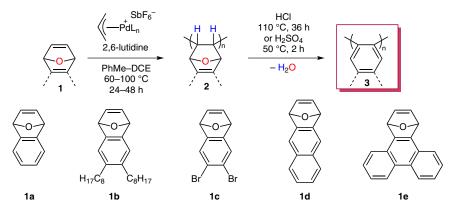
Materials and

Unnatural Products

S. ITO,* K. TAKAHASHI, K. NOZAKI* (THE UNIVERSITY OF TOKYO, JAPAN) Formal Aryne Polymerization: Use of [2.2.1]Oxabicyclic Alkenes as Aryne Equivalents *J. Am. Chem. Soc.* **2014**, *136*, 7547–7550.

Poly(o-arylene)s from [2.2.1]Oxabicyclic Alkenes as Monomers



Plausible mechanism of the polymerization:

Significance: The instability of aryne has prevented its polymerization to form poly(*o*-arylene)s. Only few examples of oligomeric *o*-arylenes through iterative coupling reactions are reported. Ito, Takahashi, and Nozaki report the synthesis of poly(*o*-arylene)s via polymerization of [2.2.1]oxabicyclic alkenes, followed by acid-catalyzed dehydration.

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Comment: In this chain-growth polymerization, the co-solvent and the additive 2,6-lutidine play key roles. Toluene may stabilize the cationic palladium catalyst species and may hinder β -oxygen elimination (the termination step). Dichloroethane (DCE) solubilizes the palladium catalyst in toluene. 2,6-Lutidine produces polymer **2** with high yields and a low polydispersity index.

Key words

poly(o-arylene)s

chain-growth polymerization

palladium



809