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COMMUNICATIONS

Published on Web 10/28/2006

Uncatalyzed Zirconium-Mediated Biphenylation of *o*-Dihalobenzenes To Form Triphenylenes

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Received August 2, 2006; E-mail: king@chem.unr.edu

Aryl−aryl bond forming reactions are ubiquitous in synthesis.[1] Zirconium has, however, played a limited role in this field. Buchwald reported a Pd-mediated reaction of a Zr−benzyne complex with benzenes or biphenyls to give biphenyls or terphenyls.[2] Takahashi reported a Cu-mediated reaction of an alkyl zirconocyclopentadiene with *o*-diiodobenzenes to give alkyl-substituted naphthalenes.[3]

We report herein the uncatalyzed reaction of $[Zr(biphe)_3][(Li\cdot(THF)_4)_2]$ (**1**),[4] where biphe is 2,2′-biphenyldiyl, with *o*-dihaloarenes to give triphenylenes (Scheme 1). The reaction is noteworthy from a synthetic viewpoint because it is a new disconnection for the synthesis of polycyclic aromatic hydrocarbons (PAHs). The closest reported analogue is the double nucleophilic aromatic substitution reaction of dilithiobiphenyl with hexafluorobenzene to afford 1,2,3,4-tetrafluorotriphenylene.[5] The reaction is noteworthy from an organometallic viewpoint because it is a rare, if not unprecedented, example of an uncatalyzed, Zr-mediated aryl−aryl bond formation.

The scope is broad. The reaction works with all halogens (Scheme 1). Dichloro-, dibromo-, and diiodobenzene give higher yields (14, 26, and 48%) than difluorobenzene (2%). Substituents are tolerated: 4,5-dibromoveratrole or 4,5-dibromo-*o*-xylene react with **1** to give the corresponding 2,3-disubstituted triphenylene.

This method provides rapid entry into 2,3-disubstituted triphenylenes, which may be useful as discotic liquid crystals.[6] The reaction of 1,2-diiodo-4,5-dihexylbenzene with **1** gave 2,3-dihexyltriphenylene in 8% yield (Scheme 1).

Multiple biphenyldiyl moieties can be introduced in a single step. The reaction of 1,2,4,5-tetrabromobenzene with **1** afforded tetrabenz[a,c,h,j]anthracene in 17% isolated yield (Scheme 1).

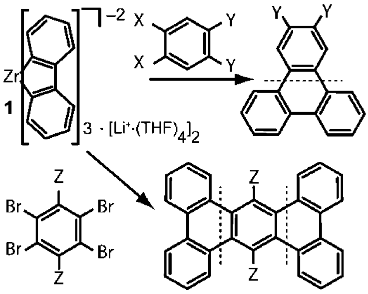
Strained molecules can be produced. The reaction of **1** with tetrabromo-*p*-xylene gave 9,18-dimethyltetrabenz[a,c,h,j]anthracene (**2**) in 20% yield. This molecule is slightly more strained (35 kcal/mol, B3LYP/6-31+G*) than Pascal's analogous 9,18-diphenyltetrabenz[a,c,h,j]anthracene **3**[7] (34 kcal/mol, B3LYP/6-31+G*). Like **3**,[8] **2** is easily reduced−excess **1**, which is presumably a reductant, gives the corresponding 9,18-dihydro product as a major component.

This reaction works in a variety of conditions: in toluene, dioxane, or THF solution, or with neat liquid reagents. The best procedure utilizes toluene at 25 °C with sufficient solvent to dissolve all reactants. Most reactions are complete after 20 min.

This unoptimized reaction is not ideal. Significant amounts of quaterphenyl are produced, which may arise from the oxidation of **1** or zirconates derived from **1** upon workup or from a reductive elimination step. The yields vary from poor to modest.

We are uncertain of the mechanism. Double nucleophilic aromatic substitution is unlikely since electron-rich dihalobenzenes, such as 4,5-dibromoveratrole, are good substrates. A mechanism involving the reductive generation of benzyne from the *o*-dihaloarene and its subsequent insertion into Zr−(biphe) bonds is also possible. Trapping experiments, however, do not support this mechanism−the reaction of *o*-dibromobenzene with **1** in the presence of a 10-fold excess of furan proceeded normally and did not produce detectable (GC−MS) amounts of the trapping product, 1,4-dihydro-1,4-epoxynaphthalene.

Scheme 1. Substitution of *o*-Dihalides by 2,2′-Biphenyldiyl



X	Y	Yield (%)
F	H	$2^{\dagger}$
Cl	H	$14^{\dagger}$
Br	H	$26^{\dagger}$
I	H	$48^{\dagger}$
Br	OMe	$61^{\ddagger}$
Br	Me	$66^{\ddagger}$
I	Hex	$8^{\ddagger}$

Z	cmpd	Yield (%)
H		$17^{\ddagger}$
Me	**2**	$20^{\ddagger}$

†GC ‡isolated

A mechanism involving oxidative insertion of Zr into an aryl−halogen bond may operate. Since the Zr center is d^0, reduction would have to precede oxidative insertion. The formation of quaterphenyl suggests this may occur. σ-Bond metathesis, perhaps involving electron transfer, is another possibility.

This transformation enables a new disconnection for the synthesis of PAHs: the double substitution of two *o*-halogens with a biphenyldiyl moiety to give a triphenylene fragment. The reaction tolerates functionality and can generate strained molecules. This reaction is a rare example of an uncatalyzed aryl−aryl bond formation reaction involving Zr.

Acknowledgment. This work was supported by the National Science Foundation (CHE-0449740).

Supporting Information Available: Strain definitions, geometries, synthetic procedures, and NMR spectra for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA065602I

10.1021/ja065602i CCC: $33.50