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Synthesis of Geodesic Polynuclear Arenes and Fullerenes by Intramolecular Aryl–Aryl Coupling

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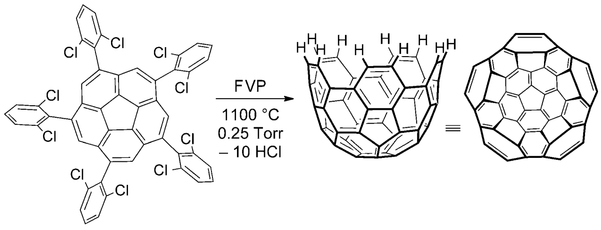
aryl–aryl coupling · flash vacuum pyrolysis · fluoroarenes · fullerenes · geodesic polynuclear arenes

Dedicated to Professor François Diederich on the occasion of his 60th birthday

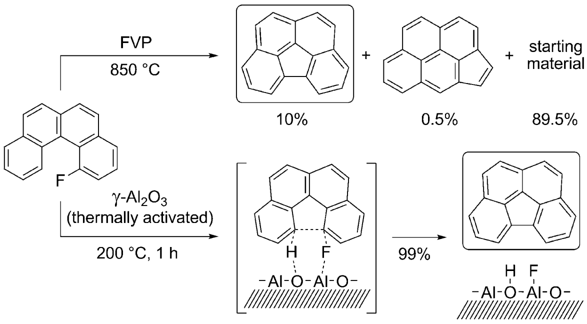
The discovery of fullerenes and carbon nanotubes has spurred interest in geodesic π-systems.[1,2] Higher fullerenes beyond C_{60} and C_{70} can occur as a variety of constitutional or stereoisomers, the number of which increases rapidly with size, and they are difficult to isolate in pure form from the soot produced by vaporization of graphite in an electric arc or by incomplete combustion of hydrocarbons in fuel-rich flames.[3] Therefore, the exploration and exploitation of the interesting properties of carbon spheroids and nanotubes call for a targeted, rational synthesis of isomerically pure species in macroscopic amounts. The dome-shaped geodesic polycyclic aromatic hydrocarbons (PAHs) corresponding to the end-caps of carbon nanotubes are popularly called "buckybowls".

Considerable methodological progress has led to the synthesis of a variety of geodesic polynuclear arenes[1,2] and a few well-defined fullerenes[4,5] over the last two decades. In the future, it may also provide access to structurally uniform nanotubes by growth of a honeycomb section on the rim of a buckybowl dictating the "roll-up" orientation of the cylindrical graphene lattice.[6] Most syntheses of "bowls" and "balls" currently focus on the "stitching up" of functionalized or pristine PAHs that include all C-atoms of the target compound in the correct positions ("crushed fullerenes"). The "stitching" consists of intramolecular aryl–aryl couplings which introduce the missing C–C connections, thereby generating new pentagons and hexagons and leading to more highly fused systems. Pentagons introduce curvature and strain into the carbon framework. To provide the required energy, the C_{Ar}–C_{Ar} couplings are often brought about at high temperature using flash vacuum pyrolysis (FVP). The entropic gain related to the elimination of small fragments (H, Hal) under these conditions constitutes a major driving force of the reaction.

FVP was the key step in the prepartion of a number of geodesic polynuclear arenes[2] (Scheme 1) as well as in the first rational synthesis of C_{60} by Scott et al.[4] Gas-phase temperatures between 1000 and 1300 °C provide enough thermal energy to distort the starting PAHs and to generate highly reactive intermediates, often aryl radicals that trap twisted conformations by intramolecular C_{Ar}–C_{Ar} coupling. Initial radical formation is markedly facilitated by Br or Cl substituents because C–Cl and C–Br bonds are weaker and undergo easier homolytic cleavage than C–C or C–H bonds. Accordingly, halogenated starting materials generally provide better yields than pure PAHs. Hydrogen 1,2-shifts, which may occur after radical generation, allow the introduction of Cl or Br at a position neighboring the strategically ideal, but sterically often congested position at the mouth of a cove or fjord region in the starting arene, thereby facilitating its synthesis.[2] Once curvature develops, a cyclodehydrogenation cascade may take place and completely "zip up" appropriately designed systems to deep bowls or fullerenes.[4,5] Somewhat surprising in view of the strength and difficult activation of C–F bonds, even polynuclear fluoroarenes have recently been successfully subjected to FVP-promoted C_{Ar}–C_{Ar} coupling (Scheme 2).[8] The reaction, in these cases, was proposed



Scheme 1. Synthesis of geodesic polynuclear arene $C_{50}H_{10}$ by FVP of 1,3,5,7,9-pentakis(2,6-dichlorophenyl)corannulene.[7]



Scheme 2. Synthesis of benzo[*ghi*]fluoranthene (framed) by 1,5-elimination of HF from 1-fluorobenzo[*c*]phenanthrene and concomitant C_{Ar}–C_{Ar} coupling across the cove region, either by FVP (top) or by reaction with activated aluminium oxide (bottom).

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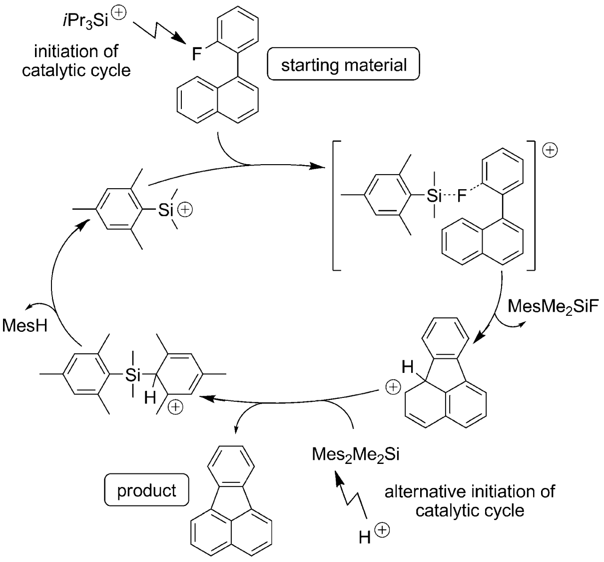
to proceed not through homolytic C–F bond cleavage and radicals, but through synchronous 1,5-elimination of HF across cove regions. Compared to bromo- or chloro derivatives, fluoroarenes benefit from a higher volatiliy in the sublimation process, sterically easier introduction of the halogen into the encumbered cove mouth, and greater inertness in precursory chemical transformations. Overall, FVP of halogenated PAHs provides a fairly general access to geodesic polynuclear arenes and fullerenes. Even so, an inherent disadvantage of the experimental setup is the rather limited amounts of compound that can be processed.

Low absolute yields affect also the preparation of polynuclear arenes and fullerenes such as C_{60} or $C_{57}N_3$ by surface-catalyzed cyclodehydrogenation of PAHs, even though the process per se is highly efficient.[9] It takes place after vacuum deposition and annealing of the precursor on a strongly interacting metal surface such as Pt(111) or Ru(0001). Besides, the convenient solution-based Pd^0-catalyzed intramolecular coupling between C_{Ar}–X (X = Cl, Br, I, OTf) and C_{Ar}–H has become an attractive method for the synthesis of geodesic PAHs.[10]

Shortly after Ozerov et al. achieved the silyl cation-promoted activation of aliphatic and benzylic C–F bonds, including the substitution of F by H,[11] Siegel et al. reported the difficult abstraction of fluoride from fluoroarenes.[12] The phenyl cation equivalents generated from Ar–F with extremely fluorophilic silyl Lewis acids[13] were used in intramolecular Friedel–Crafts type aryl–aryl coupling reactions (Scheme 3). Initially, stoichiometric amounts of the silyl cation $i\mathrm{Pr}_3\mathrm{Si}^+$ were used, most advantageously with hexachlorocarborane ($[CB_{11}H_6Cl_6]^-$) as a chemically stable, feebly nucleophilic and weakly coordinating counter-ion with a delocalized negative charge.[13] The acidic proton of the σ-complex in the intramolecular electrophilic aromatic substitution can be removed by a bulky Brønsted base. Alternatively, the proton was used to generate a mesityldimethylsilylium ($\mathrm{MesMe_2Si}^+$) ion by protodesilylation of the added silane $\mathrm{Mes_2Me_2Si}$, thereby sustaining a catalytic cycle which can be initiated either by R_3Si^+ or H^+ ions (Scheme 3).[12] Stoichiometric amounts of the silane are consumed as "fuel" in a reaction that can be abridged as C_{Ar}–F + C_{Ar}–H + C_{Ar}–Si → C_{Ar}–C_{Ar} + Si–F + C_{Ar}–H, and the main driving force of which is the exchange of a C_{Ar}–F for a very strong Si–F bond. This cyclization method appears well suited for the formation of PAHs by closure of five- or six-membered rings, and the preparation of the starting materials again benefits from the small size of fluorine. On the other hand, yields drop significantly in syntheses of more strained systems: Thus, the preparation of biphenylene from 2-fluorobiphenyl by closure of the four-membered ring failed.[12]



Scheme 3. Catalytic cycle for intramolecular C_{Ar}–C_{Ar} coupling by Friedel–Crafts type arylation with a phenyl cation equivalent as the electrophile. It is generated from a fluoroarene by abstraction of fluoride with a silyl cation. The cycle is initiated either by trialkylsilylium ions (trialkylsilylium hexachlorocarborate) or by protons (mesitylenium hexachlorocarborate). Mes = mesityl = 2,4,6-trimethylphenyl.

Very recently, Amsharov et al. reported a highly efficient solid-state 1,5-elimination of HF across the cove region of polynuclear fluoroarenes heated under vacuum with previously thermally activated γ-Al_2O_3 (Scheme 2).[14] Ring closure proceeds in nearly quantitative yield under relatively mild conditions, for example, heating at 150 °C for 20 h or at 200 °C for 1 h. An important driving force for the smooth reaction is the formation of a strong Al–F bond. Based on experimental observations, the rather mild process is proposed to proceed as a concerted reaction through a six-membered transition state with aromatic character and not to involve any reactive intermediates. This transition state may further account for the regiospecificity of the elimination which occurs only with F substituents in cove regions, making initial 1,2-elimination with aryne-type intermediates highly improbable. The annulation is furthermore chemoselective in the sense that chloro- and bromo-analogs are not transformed under the conditions of the reaction. Gratifyingly, Br substituents in other parts of the molecule are also left intact, which provides a handle for further functionalization of the produced arenes. Also, the solid-state transformation allows insoluble and unsublimable starting materials to be processed.

In summary, the new fluoroarene-based syntheses of bent polynuclear arenes benefit from a high degree of regio- and chemoselectivity, the small steric requirement of F, generally good yields, and the relative inertness of the C–F bond in prevenient synthetic steps. On the other hand, their potency to prepare highly strained systems appears to be lower than that of FVP but needs to be further explored. As opposed to the latter, they are probably not suited to trigger cyclodehydrogentation cascades that completely "stich up" tailored extended fluoroarenes. Specific polyfluoroarenes, which might alternatively be used, could constitute a synthetic challenge themselves. While representing convenient, efficient, and relatively mild substitutes for FVP in a number of cases, the new methods do not make pyrolysis dispensable for the time being.

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