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Pentalenes—From Highly Reactive Antiaromatics to Substrates for Material Science

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C–C coupling · dimerization · electronic materials · hydrocarbons · reduction

There appears to be a consistent pattern in hydrocarbon chemistry: in a "heroic" phase, hydrocarbons expected to possess unusual structural and electronic properties, and often endowed with a very high chemical reactivity, are prepared for the first time by the pioneers in the field. After this phase, often characterized more by failures than successes, the field lies dormant, sometimes for decades, and then is taken up again with new vigor—usually because new preparative routes have been discovered, and erstwhile "unattainable" compounds have become "normal" starting materials. Adamantane, [2.2]paracyclophane, the triquinacenes, and the dendralenes are examples of this development.

As far as pentalene (**1**, Scheme 1) is concerned, the "discovery phase" ended in the 1970s with the celebrated studies of Hafner and his students, who showed that not only **1** could be prepared and identified, but also other derivatives could be obtained by their methods.[1] As antiaromatic 4*n* hydrocarbons (formally they are "short-circuited" cyclooctatetraenes), many of these compounds are short-lived and undergo, for example, dimerization reactions readily. Still it was possible to prepare the first isolable pentalene, 1,3,5-tri-*tert*-butylpentalene (**2**), a deep blue, thermally stable solid.[2] The most remarkable, theoretically expected, electronic property of **2** is the alternation of its double bonds: NMR studies showed that the energy barrier between **2** and its valence isomer **2′** amounts to roughly 4 kcal mol^{-1}, with the delocalized, antiaromatic structure **3** serving as the transition state.

An alternative well-established means of stabilizing reactive organic compounds is their annulation to aromatic ring systems. In the case of pentalene (**1**) this would mean preparing benzopentalene (**4**) and dibenzopentalene (**5**). Both of these compounds have been known for a long time: hydrocarbon **5**, in fact, just celebrated its 100th anniversary, having been prepared first by Brand in 1912.[3]

To deliberately employ pentalenes as building blocks for more complex structures requires high-yielding and highly regioselective routes—and these have been reported in the last few years with increasing frequency. This development is driven by two trends: a growing number of efficient synthetic routes to these compounds on the one hand, and their rapidly increasing application as novel components in "electronic materials" (see below) on the other.

In the syntheses of derivatives of **4** and **5** the substituents can be in either olefinic or aromatic positions; and in principle they can be introduced either early or late in the synthesis. Most routes prefer the first alternative, and in the majority of cases it presently is the olefinic position (i.e. positions 5 and 10 in **5**) which carries the substituent. Not surprisingly, it is easier to synthesize derivatives of the symmetrical parent compound **5** than of the unsymmetrical system **4**. And as a rule of thumb it can be stated that "soft" synthetic methods, for example, catalytic reactions, have replaced "harsh" ones, for example, pyrolytic routes.

In 1999 Youngs and co-workers described the formation of the dibenzopentalene derivative **7** on treatment of the 1-ethynyl-2-iodobenzene precursor **6** under typical Sonogashira conditions (Scheme 2).[4] What was a singular observation at that time has since become a general route to dibenzopentalenes: the metal-induced dimerization of different types of ethynyl aromatics.

Thus in one of its structurally simplest variants, Saito and co-workers reduced tris(isopropyl)silylethynylbenzene (**8**) with lithium and isolated (besides an open-chain dimer of **8**) the dibenzopentalenide **9**, which upon oxidation with iodine provided the dibenzo[*a*,*e*]pentalene derivative **10** in excellent yield, from which the dihalides 11 were prepared (Scheme 3).[5]

In another, catalytic C,H-activation route Segawa, Itami, and co-workers have dimerized various arylacetylenes to obtain the correspondingly substituted dibenzopentalenes.[6] Thus diphenyacetylene (**12**, tolane) can be dimerized in the presence of $PdCl_2$, AgOTf, and *o*-chloranil to the diphenyldibenzopentalene **13** in good yield (Scheme 4).

According to first mechanistic experiments this new annulation occurs by way of an *ortho*-selective, electrophilic aromatic C,H palladation initiated by alkyne–palladium precoordination. Several cases have been reported[6] on the application of this process to unsymmetrical arylacetylenes leading to the corresponding unsymmetrical dibenzopentalene derivatives.

Returning to Youngs' approach with 1-ethynyl-2-haloarenes such as **6** as substrates, this route has been developed recently into a very effective way of making substituted dibenzopentalenes. Thus Kawase, Kubo, and their students

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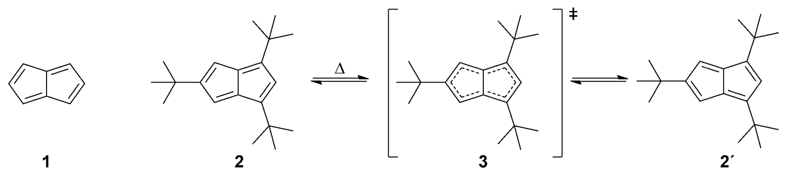
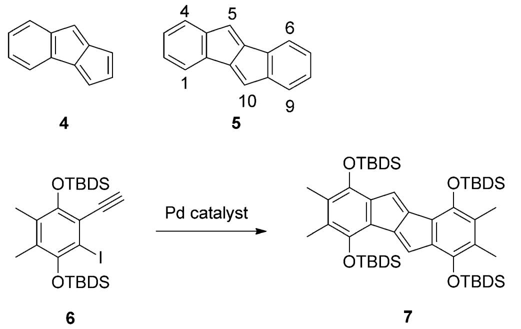


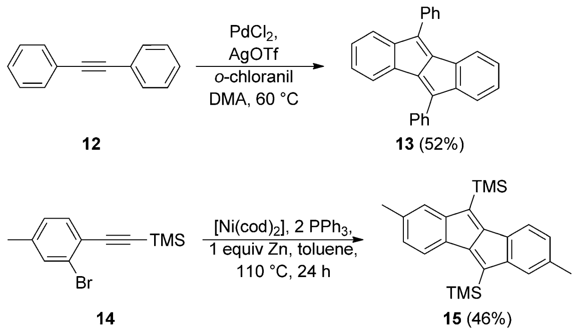
Scheme 1. Pentalene (**1**) and its stabilization.



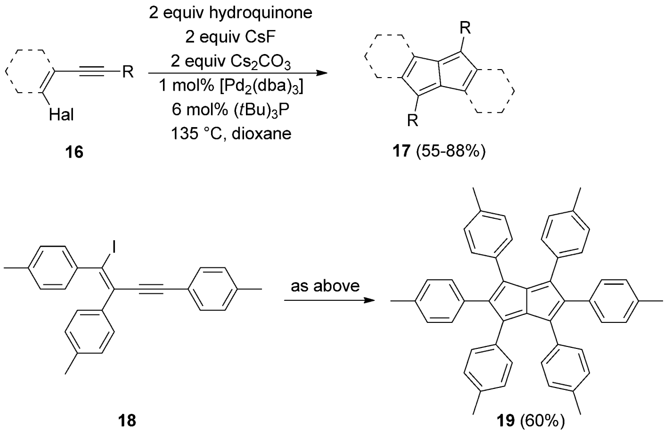
Scheme 2. Dibenzopentalene derivatives (**7**) from aromatic ethynyliodides (**6**) according to Youngs et al.[4] TBDS = *tert*-butyldimethylsilyl.

have reported on a nickel-mediated dimerization of various 2-bromo-1-ethynylbenzenes providing symmetrically substituted dibenzopentalenes in moderate yield in one step.[7] For example, under the conditions outlined in Scheme 4, the *ortho*-bromophenylacetylene **14** furnished the 5,10-disilylated dibenzopentalene **15** in 46 % yield. Functional groups (MeO, COOMe) could be introduced into **14**, leading to dibenzopentalenes carrying appropriate functionality for further transformations. More recent investigations have demonstrated that the substrates **14** may be replaced by the corresponding naphthalene derivatives to provide dinaphthopentalene diastereomers depending on the substitution pattern of the starting material.[8]

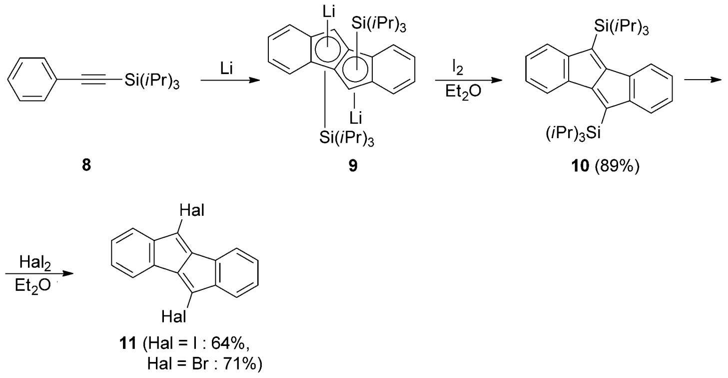
The presently most versatile and best yielding dimerization of this type has been reported by Tilley and Levi.[9] It involves the Pd-catalyzed homocoupling of haloenynes **16** (Scheme 5) and provides not only carbocyclic dibenzopentalenes but also derivatives with fused heterocyclic rings such as thiophenes. A particularly striking transformation was



Scheme 4. 5,10-Diphenyldibenzopentalene (**13**) from tolane (**12**) according to Itami et al. cod = 1,5-cyclooctadiene, DMA = dimethylacetamide, TMS = trimethylsilyl.



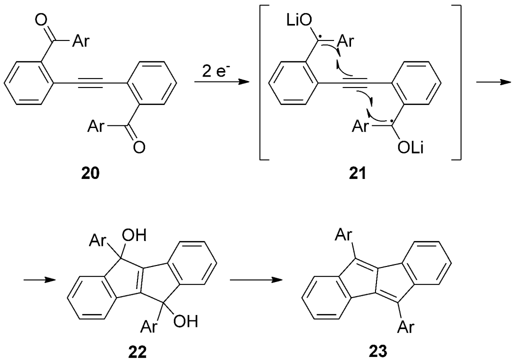
Scheme 5. Dibenzopentalenes (**17**) from halogenoenynes according to Tilley and Levi.[9] dba = dibenzylideneacetone.



Scheme 3. Dibenzopentalene dihalide derivatives (**11**) from ethynylbenzenes (**8**) according to Saito et al.[5]

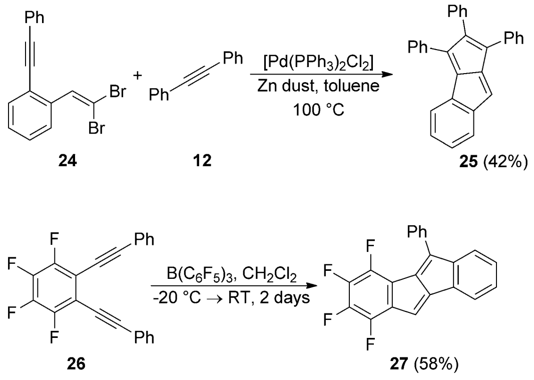
reported for the iodoenyne **18**, which was converted in high yield into the fully substituted pentalene derivative **19**.

A unique route to substituted dibenzopentalenes, in which all of carbon atoms of the future product are already present in the starting material, has been described by Yamaguchi and co-workers.[10] The substrates, *o,o′*-bis(arylcarbonyl)diphenylacetylenes **20**, are subjected to a reductive intramolecular double cyclization by reaction with lithium naphthalenide (Scheme 6). The initially generated diyl **21** undergoes a double radical 5-*endo-dig* cyclization to give the diol **22**, which is produced together with the final hydrocarbon **23**. A control experiment showed that **22** is indeed a precursor of **23**.



Scheme 6. 5,10-Diaryldibenzopentalenes (**23**) by reductive cyclization according to Yamaguchi et al.[10]

Returning to unsymmetrical benzannelated pentalenes, the parent system **4** was evidently prepared by Lothrop already in the early 1940s, although he assumed that he had synthesized biphenylene.[11] Recently two (variable) approaches to unsymmetrical benzopentalenes have been reported. Diederich and co-workers exploit a carbopalladation reaction cascade (Scheme 7),[12] whose mechanism may be similar to that of the homocoupling of enynes described by Levy and Tilly (Scheme 5). Application of this reaction to the dibromide **24**, a readily available precursor, and diphenylacetylene (**12**) produces the tribenylbenzopentalene **25** in good yields. The process allows the variation of substituents in both reaction partners, leading to numerous unsymmetrical benzopentalenes which display redox amphoteric behavior and possess small HOMO–LUMO gaps, making them interesting components for application in the construction of OFETs (organic field-effect transistors).[8]



Scheme 7. Unsymmetrical benzo- (**25**) and dibenzopentalene derivatives (**27**) according to Diederich et al.[12] and Erker et al.[13]

Unsymmetrical dibenzopentalenes have been synthesized in another single-step transformation recently reported by Erker, Yamaguchi, and co-workers.[13] In this case 1,2-bis(phenylethynyl)benzenes were employed as substrates and isomerized by an intramolecular cyclization using the strong Lewis acid $B(C_6F_5)_3$ as shown in Scheme 7 for the tetrafluoro derivative **26**. The cyclization product **27**, a red solid, was generated in 58 % yield. The transformation may be applied to other *o*-bis(phenylethynyl)benzene derivatives and presumably proceeds via a dipolar intermediate which subsequently undergoes an intramolecular electrophilic aromatic substitution.

It will be interesting to observe the generalization of all these new syntheses and the applications of the formed benzopentalenes in organic material science. Needless to say, the pentalene core of these molecules can also be modified, and has, for example, been replaced by s- and as-indacene moieties.[14]

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