| Higher Acenes

Strategies for the Synthesis of Higher Acenes

Ruth Dorel[a] and Antonio M. Echavarren*[a,b]

Abstract: The outstanding performance of pentacene-based molecules in molecular electronics, as well as the predicted enhanced semiconducting properties of extended acenes, have stimulated the development of new synthetic methods and functionalization strategies for the preparation of stable and soluble acenes larger than tetracene with the aim of obtaining improved functional materials.

1. Introduction

Acenes are a class of polycyclic aromatic hydrocarbons (PAHs) consisting of planar sets of linearly fused benzene rings and have been the subject of extensive study due to their distinctive optoelectronic properties, which make them appealing materials for use in molecular electronic devices[1] such as organic field-effect transistors (OFETs),[2] organic light-emitting diodes (OLEDs),[3] or photovoltaic cells.[4] In contrast to the smallest members of the series, which can be extracted from petroleum resources, acenes higher than tetracene are not found in nature and therefore can only be accessed by multi-step syntheses. The promising semiconducting properties of pentacene,[5] as well as the improved electronic properties predicted theoretically for larger homologues,[6] have prompted renewed interest among the synthetic community in the development of new strategies for the preparation of higher acenes. Nonetheless, both the preparation and the application of extended acenes as functional materials are limited by the fact that their solubility and stability shrink as the number of annealed rings grows. Higher acenes typically decompose through photoinduced oxidation[7] and through dimerization or oligomerization processes,[8] which have been in part attributed to the open-shell character in the ground state theoretically predicted for acenes larger than pentacene.[9]

The unstable nature of larger acenes can also be explained in terms of Clar aromatic sextets.[10] Any acene possesses only one aromatic sextet, spread over the whole conjugated system (Figure 1). This leads to a rapid decrease in the HOMO–LUMO gap and to an increase in the chemical reactivity with each

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additional fused ring,[11] which therefore makes the synthesis of the higher members of the series a formidable challenge. Indeed, despite the fact that seminal reports on the synthesis of acenes higher than pentacene were disclosed as early as 1939,[12] the unstable nature of these materials has precluded their unambiguous description until recently.
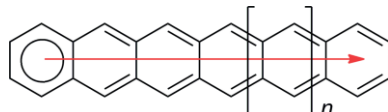

Figure 1. Clar sextet in acenes.

The reactivity of acenes is strongly influenced by the substituents attached to the aromatic core, and therefore, in order to circumvent the intrinsic photo-instability of higher acenes, a number of functionalization strategies have been developed.[13] Hence, steric blocking of the most reactive centermost ring minimizes intermolecular reactions, thus preventing dimerization, whereas the incorporation of substituents that electronically influence the acene core is a common approach to reducing the propensity for photooxidation.

In recent years a wide variety of stabilized acenes bearing different functionalities have been synthesized with the aim of improving their processability and optoelectronic properties. However, there is no general approach for the synthesis and functionalization of linearly condensed ring systems. Several reviews have been published on the synthesis and properties of functionalized higher acene[13,14] and heteroacene derivatives,[14d,15] as well as on general methods for the synthesis of PAHs.[16] The aim of this microreview is to provide a comprehensive survey of the different strategies that have been pursued for the preparation of stabilized acene derivatives larger than tetracene. The discussion is organized according to the type of precursor that leads to the acene core, as illustrated in Figure 2.

2. Acenes through Retrocycloaddition

One approach to larger acenes is through the use of stabilized masked precursors bearing solubilizing groups that can be cleanly removed to afford the parent acene.[17] This strategy has allowed not only the preparation of new acene-based devices but also access to unsubstituted larger acenes up to nonacene,[14a] which – because of their high reactivity – need to be isolated in inert matrices.

2.1. Thermally Induced Eliminations

A pioneering work in this area reported in 1996 described the formation of pentacene in a film after deposition of tetrachlorobenzene-pentacene adduct precursor **4a** through a thermally induced retro-Diels–Alder process.[18] This precursor and its brominated analogue **4b**, which was also converted into pentacene in the solid state, were prepared through the Diels–Alder cycloaddition of **3** and the corresponding tetrahalothiophene dioxides at high pressure (Scheme 1).[19] Similarly, the thermolysis of **5**, produced by hydrogenation of **3** on Pd/C, gave rise to pentacene upon elimination of ethane at 250 °C.
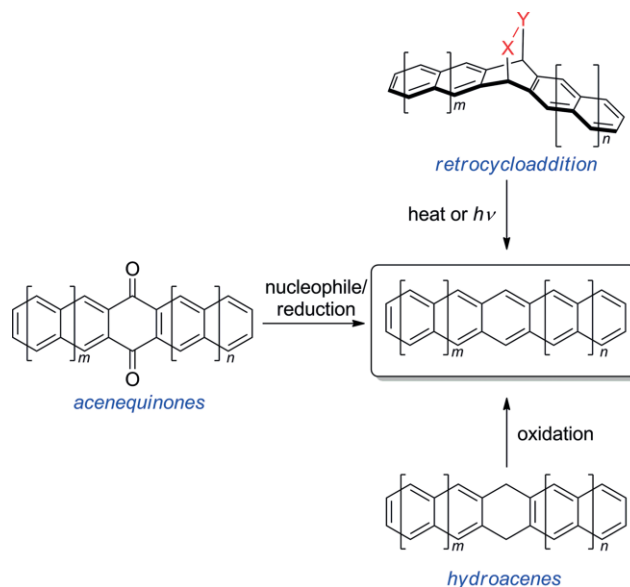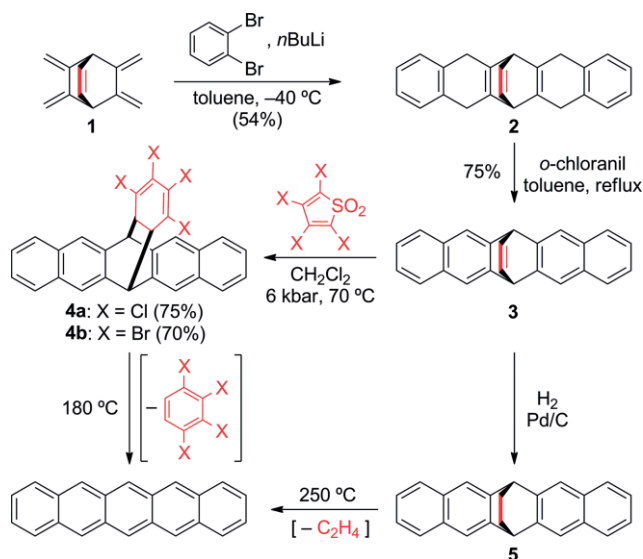

Figure 2. Approaches to higher acenes.

Scheme 1. Synthesis of pentacene by a retro-Diels–Alder approach.

By this strategy, pentacene-based films have been accessed by means of thermally induced retro-Diels–Alder reactions from spin-coated solutions of the corresponding cycloadducts with different dienophiles including N-sulfinylbutylcarbamates,[20] dialkyl azodicarboxylates,[21] or diethyl ketomalonate,[22] which was also used to prepare a soluble precursor of hexacene.[23] The thermal elimination of lactam bridges has also been applied to the synthesis of other related PAHs such as twistacenes, which are benzo-fused acene derivatives bearing rigid terminal pyrene units.[24]

Acene films prepared by a solution-processed retro-Diels–Alder approach show higher mobilities in cases of substrates with smaller leaving groups, which has been attributed to lower levels of contamination of the resulting film by the eliminated groups.[25] Thus, stable carbonyl-bridged derivatives cleanly generate the corresponding acenes through cheletropic ther-

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mal decarbonylation. As an example, intermediate **6**, originating from a double-Diels–Alder reaction between an *ortho*-quinodimethane and 7-*tert*-butoxynorbornadiene, was obtained and transformed into pentacene precursor **7** by deprotection and oxidation of the secondary alcohol at the bridge (Scheme 2).[26] Precursor **7** underwent extrusion of CO at 150 °C, giving rise to pentacene in almost quantitative yield, whereas its less symmetrical isomer with the oxomethano bridge between C5 and C14 underwent the analogous elimination at temperatures below 130 °C.[27] This strategy has recently been applied to the preparation of 2-halopentacenes.[28] In a similar vein, ketal-bridged precursors afford pentacene through thermally induced elimination of CO_2 at higher temperatures.[29]
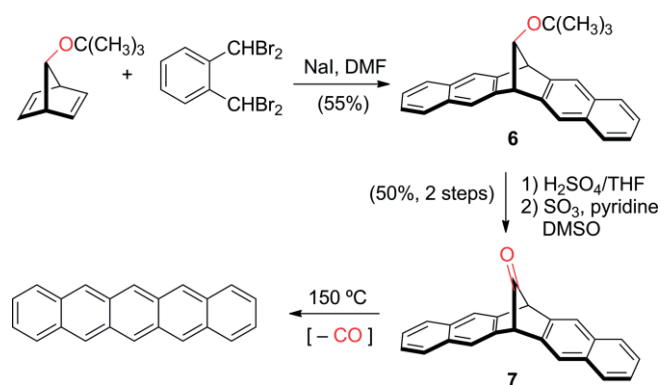
Scheme 2. Synthesis of pentacene through cheletropic thermal decarbonylation.

The synthesis of hexacene was also accomplished in the solid state from the corresponding carbonyl-briged precursor **11** by extrusion of CO at 180 °C under nitrogen (Scheme 3).[30] Com-

pound **11** was prepared in six steps from 3-amino-2-naphthoic acid, which reacted with 6,6-dimethylfulvene to form bicyclic intermediate **8** through a benzyne intermediate generated in situ. The Diels–Alder reaction between **8** and 1,4-anthraquinone delivered cycloadduct **9**, which gave rise to hexacene precursor **11** after reduction of the carbonyl moieties and oxidative cleavage of the bridging double bond. Single crystals of pure hexacene obtained by this method could be grown by physical vapor-transport (PVT), and its structure could thus be unambiguously established by X-ray diffraction for the first time. The semiconducting properties could also be examined on the crystals. Furthermore, in contrast to previous reports,[31] hexacene could be stored in the solid state under ambient conditions in the dark for more than one month without observation of significant degradation, although this acene was found to be extremely sensitive in solution under light.

2.2. Photochemically Induced Eliminations

Despite the fact that the thermolysis of acene precursors to generate the parent acenes is an important strategy for solution-processable OFET applications, the high temperatures required in the process often limit its applicability. In contrast, the photochemical conversion of suitable precursors into the corresponding conjugated acenes can be performed at or even below room temperature, which has motivated the synthesis of different types of photoconvertible acene precursors.[32]

The first example of photochemical synthesis of acenes was reported in 2005 for pentacene by using a Strating–Zwanenburg reaction starting from precursor **13**, which features
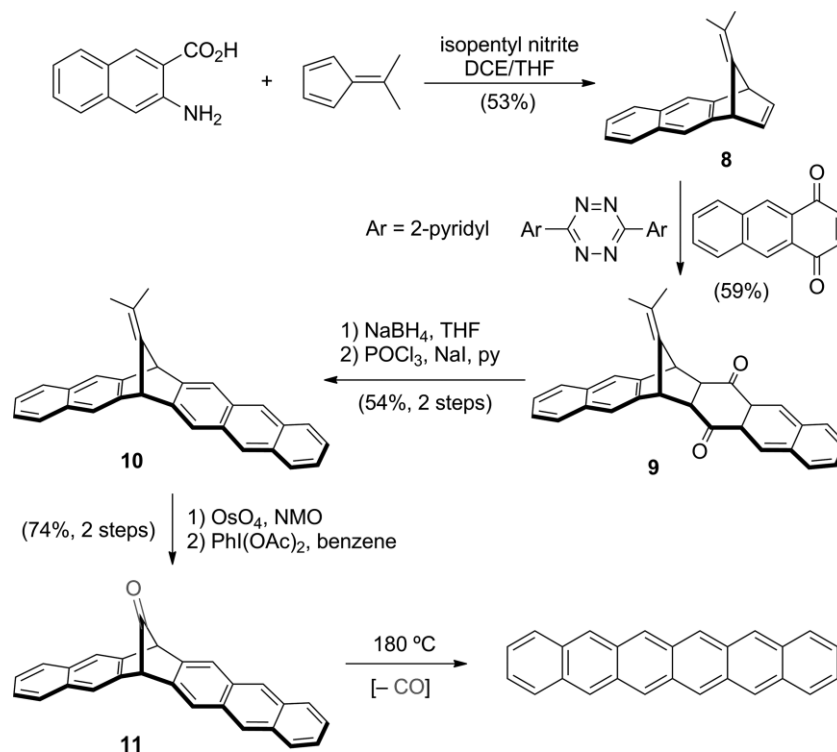
Scheme 3. Synthesis of hexacene through thermal decarbonylation.

a bicyclo[2.2.2]octane-2,3-dione framework (α-diketone precursor).[33] The synthesis of photoprecursor **13** was carried out by dihydroxylation of the etheno bridge of **3** to form diol **12**, followed by a double Swern oxidation (Scheme 4). Alternatively, **13** could also be prepared from the parent pentacene by Diels–Alder cycloaddition with vinylene carbonate, followed by hydrolysis under basic conditions. Irradiation of **13** in the absence of oxygen, to avoid the formation of endoperoxides, provided pentacene both in solution and in the solid state. Similarly, a solution of regioisomeric pentacene-5,14-dione in toluene was quantitatively converted into its parent pentacene.[34] The photodecarbonylation of α-diketone precursors has also been exploited for the preparation of functionalized pentacenes.[35] Furthermore, the conversion of the corresponding carbonyl-bridged precursors into pentacene[27] and hexacene[30] was also achieved photochemically in the absence of oxygen.
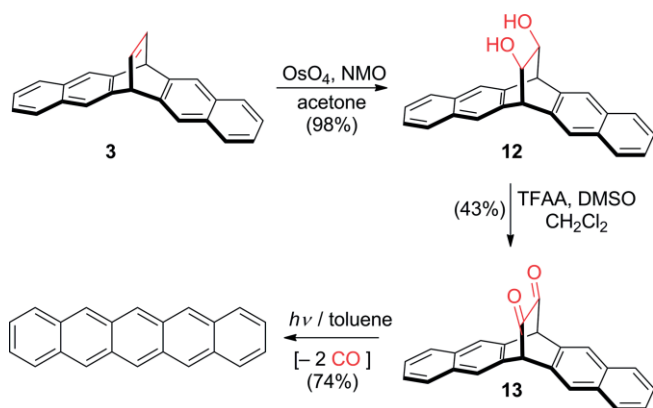
The synthesis of acenes larger than pentacene remained elusive until very recently when, after the successful synthesis of pentacene,[33] the photochemical conversion of stable α-diketone precursors was applied to the synthesis of hexacene[31] and larger acenes up to nonacene. However, higher unsubstituted acenes show a strong propensity for dimerization or oligomerization that can only be prevented by isolating these materials in an inert matrix. In fact, although some approaches to heptacene were already reported back in the 1940s and 1950s,[36] the characterization evidence for this molecule at that time was not enough to confirm the proposed structure, and therefore the existence of heptacene was for a long time controversial, leading to the conclusion that this acene represented the limit with respect to stability.

Only in 2006 could heptacene be unambiguously detected, upon generation in a polymer matrix by photodegradation of the corresponding α-diketone precursor.[37] Heptacene could not be isolated when the irradiation was performed in a toluene solution, and its lifetime in the solid matrix was less than 4 h due to the diffusion of oxygen into the matrix. This, however, was subsequently exploited to develop a method to determine the oxygen permeability of polymer films.[38] Moreover, when heptacene was generated analogously in a cryogenic inert-gas matrix it underwent a photoinitiated charge transfer to afford the corresponding radical ions.[39] Then, if the noble-gas matrix was evaporated and the sample allowed to warm to room temperature, heptacene was recovered as dimers or even higher oligomers,[40] which have been proposed to be thermodynamically more stable than the monomer.[8,41] These oligomeric species, when dissolved in concentrated sulfuric acid, give rise to heptacene dication, which shows a remarkable stability, lasting for over one year in solution.[42]

Scheme 4. Synthesis of pentacene from α-diketone precursor **13**.
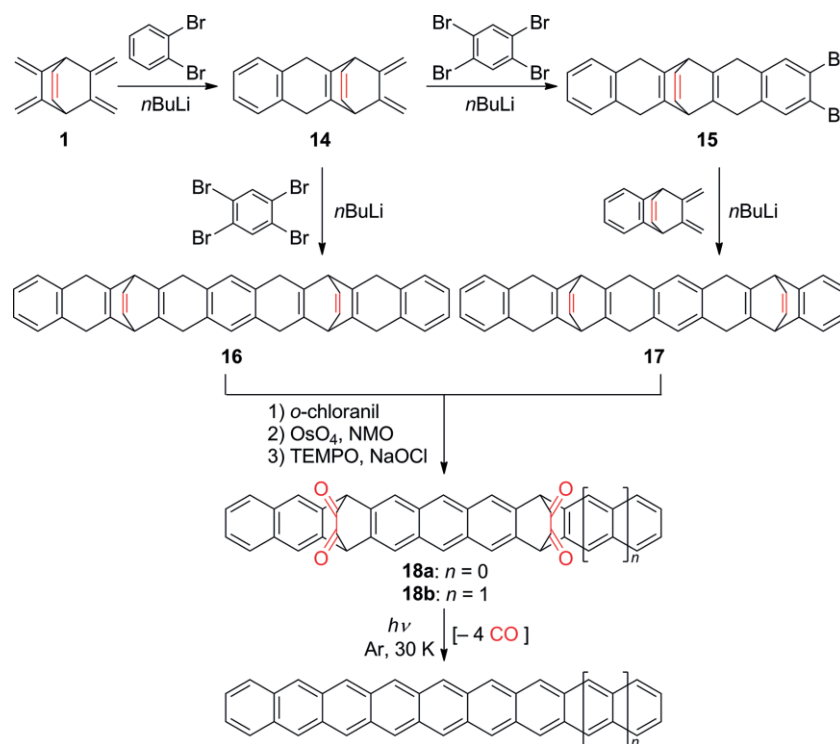
Scheme 5. Synthesis of octacene and nonacene.

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Earlier attempts to generate nonacene by thermally induced extrusion of ethane were not successful, most likely because of the reactive anthracene subunit present in the required precursor.[19] Nevertheless, octacene and nonacene could be generated by photochemically induced bis(decarbonylation) of the corresponding α-diketone precursors **18** at 30 K in an argon matrix (Scheme 5).[43] The acene photoprecursors were conceived so that they did not contain any aromatic segment larger than anthracene, to ensure both stability and solubility, and therefore two α-diketone bridges were introduced per molecule. Thus, the acene backbones were constructed through sequences of Diels–Alder cycloadditions that gave rise to partially hydrogenated derivatives **16** and **17**, which were subjected to aromatization in the presence of o-chloranil, followed by a dihydroxylation/oxidation sequence similar to the one developed for the synthesis of pentacene precursors.[33,34]

3. Acenes from Acenequinones

Acenequinones are commonly used as starting materials for the preparation of acene derivatives by direct reduction of the carbonyl moieties or nucleophilic addition of organometallic species followed by reductive aromatization. These precursors are typically assembled either through Diels–Alder cycloadditions or through intramolecular Friedel–Crafts-type processes and exhibit improved solubility and stability when compared to to their acene counterparts.

3.1. Pentacene Derivatives

The addition of nucleophiles to acenequinones was used at an early stage to prepare pentacene derivatives with unique optoelectronic properties,[44] although the implementation of these materials in electronic devices was still hampered by their propensity to react with molecular oxygen in the presence of light. A breakthrough in device-oriented acene derivatives was reported in 2001, when the synthesis of 6,13-bis(triisopropylsilylethynyl)pentacene (**20**) from pentacenequinone **19** was reported (Scheme 6).[45] The (triisopropylsilyl)ethynyl substituents conferred enough solubility and stability to allow processing under ambient conditions as well as significantly improved conductivity in comparison with the parent pentacene, due to its arrangement in the solid state. Since then, several 6,13-dialkynylated pentacene derivatives have been prepared by this strategy.[46] The synthesis of unsymmetrically substituted 6,13-difunctionalized pentacenes from **19** was also achieved by controlling the stoichiometry of the two nucleophilic reagents relative to the quinone.[47]

Furthermore, the use of secondary amines as the nucleophiles in additions to **19** in the presence of a reducing agent to afford electron-rich 6,13-diaminopentacenes **21** has recently been described. These readily undergo a two-electron oxidation process that results in a structural change into a butterfly-like conformation of the pentacene moiety to provide **22**.[48]

Electron-deficient perfluoropentacene **24**, which shows good performance as an n-type semiconductor, was likewise
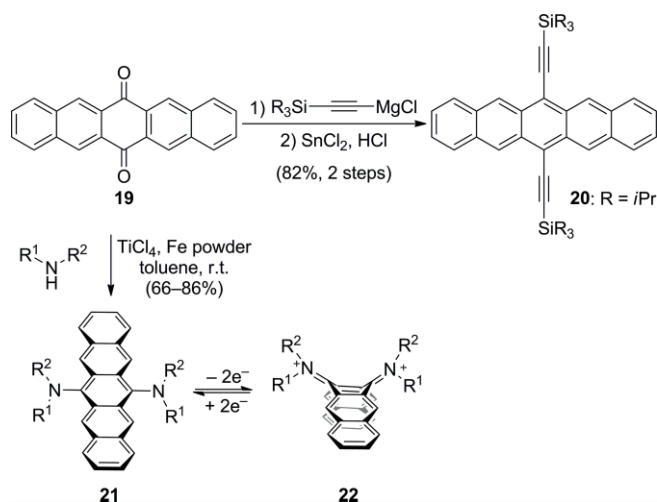
Scheme 6. Synthesis of bis(silylethynyl)pentacene and diaminopentacenes.

synthesized from quinone **23** by exhaustive fluorination with SF_4 followed by defluorination with Zn at 280 °C (Scheme 7).[49]
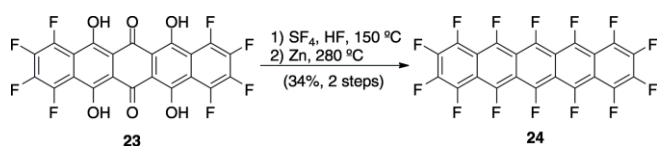

Scheme 7. Synthesis of perfluoropentacene.

6,13-Diarylpentacenes **25** undergo $FeCl_3$-mediated Scholl reactions to afford regioselectively bis(indeno)-annulated pentacenes **26**, which exhibit remarkably high photostability in solution (Scheme 8).[50]
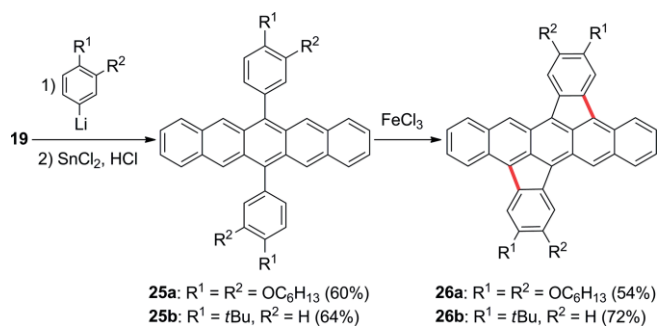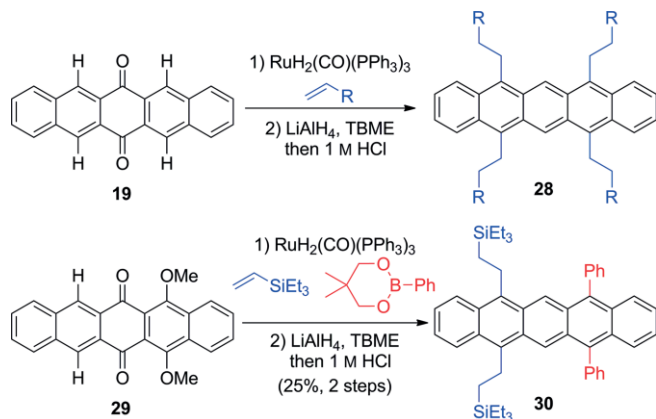

Scheme 8. Synthesis of bis(indeno)-annulated pentacenes **26**.

On the other hand, the direct reduction of 6,13-pentacenequinones has been widely used for the preparation of pentacene derivatives without substituents on the centermost ring. The stepwise reduction of **19** via the corresponding diol provide the parent pentacene under mild reaction conditions with a purity comparable to that of a sample purified by sublimation (Scheme 9).[51] Quinone **19** can also be reduced to pentacene in one step by using a stronger reducing agent, albeit in lower yields.[52] This strategy has been used as the last step in the preparation of pentacene derivatives functionalized at the pro-cata positions.[53]

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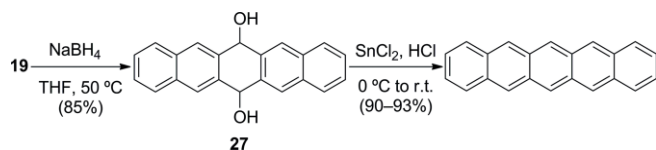
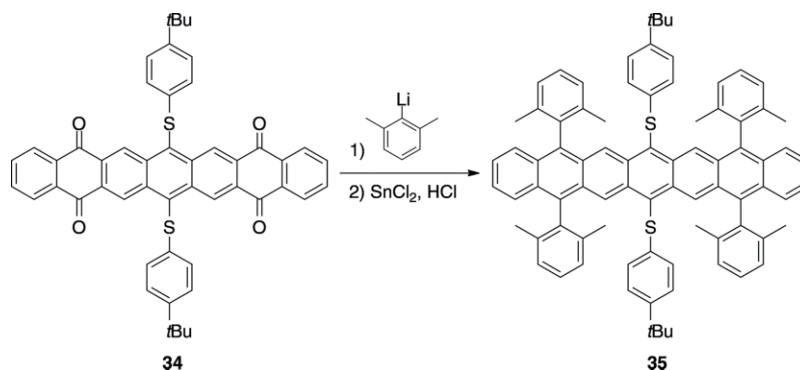Scheme 9. Synthesis of pentacene by reduction of **19**.

Acenequinones are suitable substrates for ruthenium-catalyzed carbonyl-directed C–H and C–O functionalization, and therefore 5,7,12,14-tetraalkylpentacenes **28** were prepared from **19** through tandem C–H alkylation/quinone reduction (Scheme 10).[54] Moreover, quinone **29** was converted into pentacenes of type **30**, which bears two alkyl and two aryl groups, through a chemoselective C–H alkylation/C–O arylation sequence followed by reduction of the quinone.

Scheme 10. Synthesis of pentacenes through Ru-catalyzed C–H alkylation/quinone reduction.

31b–**d**, for which the main decomposition pathway is dimerization rather than photooxidation.[56] Partial fluorination of the acene backbone gave rise to further stabilized hexacenes **32** suitable for device studies.[57] A series of dioxolane-functionalized hexacenes **33** with long-wavelength fluorescence was also prepared from the corresponding acenequinones.[58] In contrast, the analogous heptacene derivatives were not stable enough to be isolated.
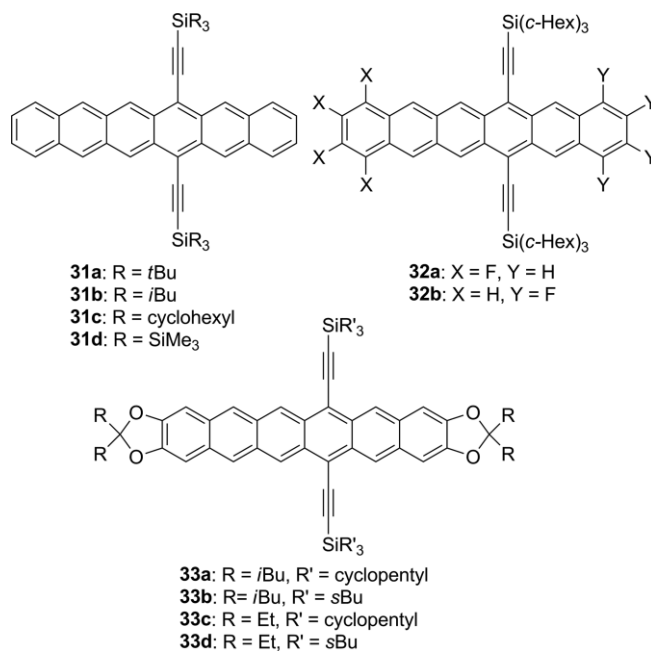

31a: R = *t*Bu
31b: R = *i*Bu
31c: R = cyclohexyl
31d: R = SiMe₃

32a: X = F, Y = H
32b: X = H, Y = F

33a: R = *i*Bu, R' = cyclopentyl
33b: R = *i*Bu, R' = *s*Bu
33c: R = Et, R' = cyclopentyl
33d: R = Et, R' = *s*Bu

Figure 3. Functionalized hexacenes from hexacenequinones.

3.2. Hexacene Derivatives

The silylethynylation strategy developed for the synthesis of pentacene derivatives[45,46a] was also applied for the preparation of stable derivatives of higher acenes. In the case of hexacene, (triisopropylsilyl)ethynyl substituents were not sufficient to obtain a stable derivative, and so alkyne units bearing the bulkier tri-*tert*-butylsilyl group were used instead to afford crystalline bis(silylethynyl)hexacene **31a** (Figure 3).[55] Subsequent studies demonstrated that other trialkylsilyl groups at the alkyne terminus also provide relatively stable hexacene derivatives
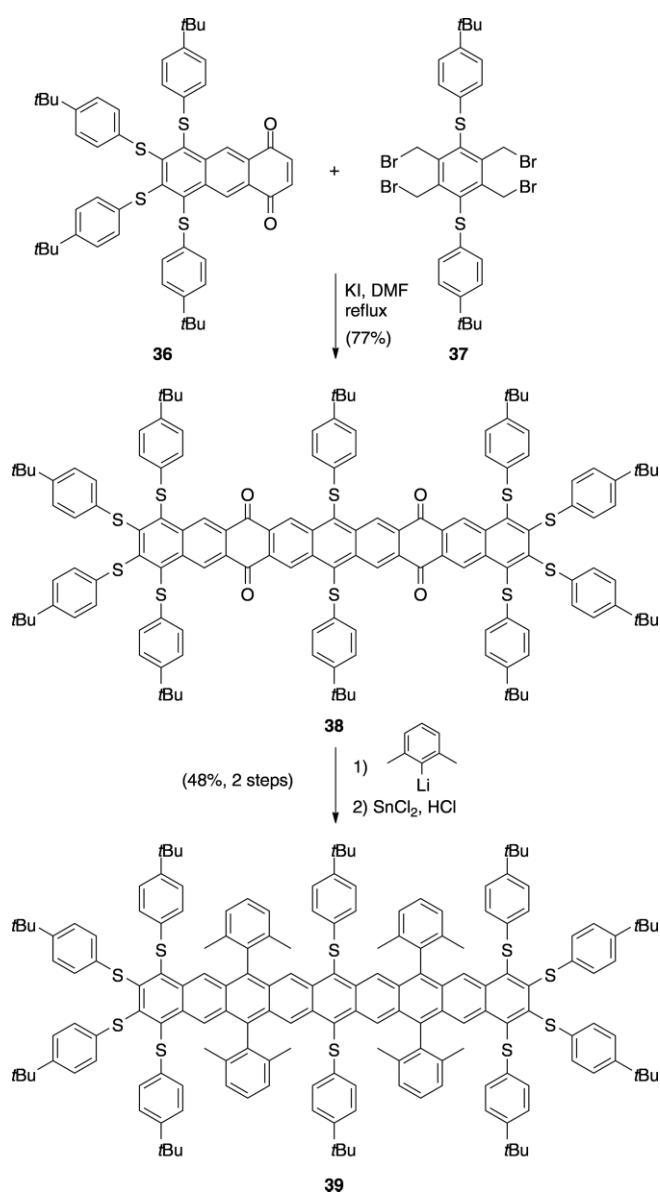
3.3. Heptacene Derivatives

The first crystalline heptacene was prepared from 7,16-heptacenequinone through a two-step sequence similar to the one developed for **20**, although in this case a larger tris(trimethylsilyl)silyl group was required on the alkyne in order to prevent decomposition of the heptacene derivative.[55] Later studies revealed that the inclusion of aryl substituents attached to the heptacene core further prevented dimerization processes, and therefore allowed the use of smaller triisopropylsilyl groups at the alkyne terminus.[59] *o,o*-Alkyl-disubstituted phenyl groups

Scheme 11. Synthesis of photooxidatively resistant heptacene **35**.

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are superior stabilizing groups towards dimerization due to the fact that the *o*-substituents lie directly above and below the π-system of the acenes, whereas thioalkyl and thioaryl substituents show a good performance in enhancing photooxidative resistance, as found first for pentacene derivatives.[60] Thus, a combination of these two strategies was applied in the synthesis of new heptacene derivative **35**, which is stable for weeks as a solid, for days in solution with exclusion of light, and for hours in solution when exposed to light and air (Scheme 11).[61]
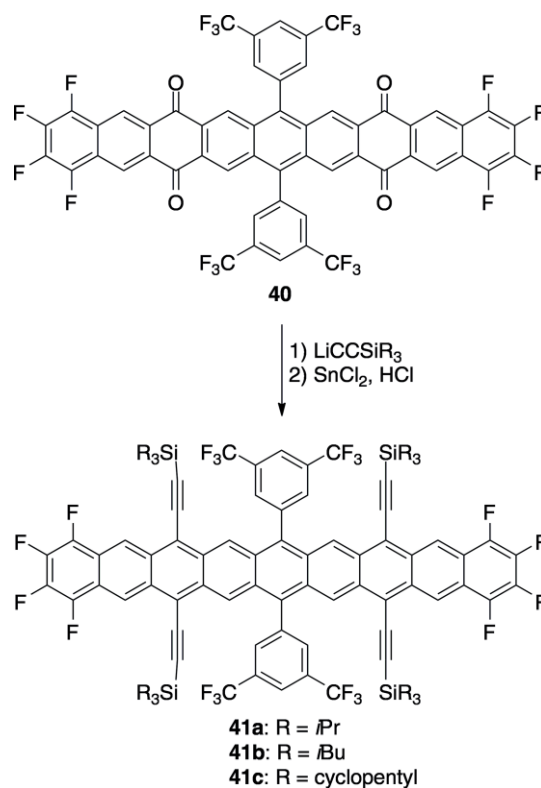
3.4. Nonacene Derivatives

The synthesis of the first nonacene derivative also relied on the use of both aryl and thioaryl groups as stabilizing agents.

Hence, the so-called "persistent nonacene" **39** was obtained through the nucleophilic addition of the corresponding aryllithium reagent to bis(quinone) **38**, which was in turn assembled through a double Diels–Alder reaction between **36** and the bis(diene) generated in situ from **37** (Scheme 12).[62] Nonacene derivative **39** was characterized by a set of solution-phase techniques including ^{1}H and ^{13}C NMR, UV/Vis/NIR, and fluorescence spectroscopy. However, the spectroscopic data provided for this compound appeared later to be more consistent with an endo-peroxide decomposition product rather than with a functionalized nonacene.[63]

With the aim of unambiguously assigning the optoelectronic properties of nonacene, stable and fully characterizable derivatives **41** were synthesized from bis(quinone) **40** with the aid of a combination of electron-withdrawing substituents and bulky (trialkylsilyl)ethynyl groups as the stabilizing agents (Scheme 13).[63] Exposing solutions of **41** to light and air led to complete decomposition within hours to form the corresponding endoperoxides, which showed spectroscopic profiles similar to those reported for **39**.[62]

Scheme 12. Synthesis of nonacene derivative **39**.

Scheme 13. Synthesis of nonacene derivatives **41**.
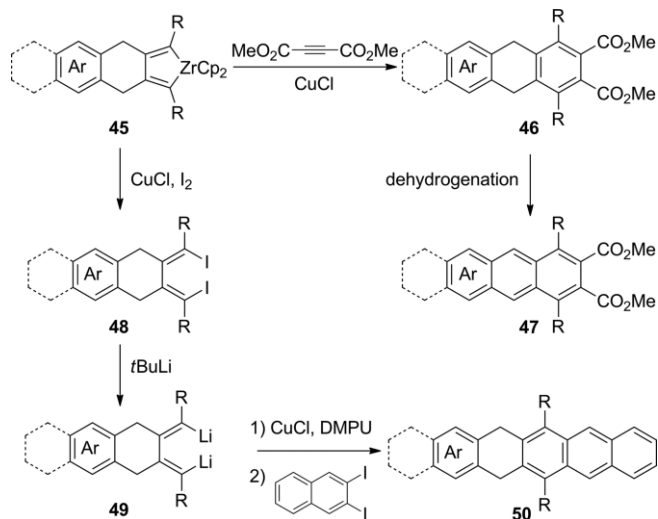
4. Acenes from Hydroacenes

Partially saturated acenes, which exhibit remarkably improved solubility and stability in comparison with the corresponding parent acenes and acenequinones, have been described as "hydrogen-protected" acenes that can reveal the conjugated acene upon oxidation.[64]

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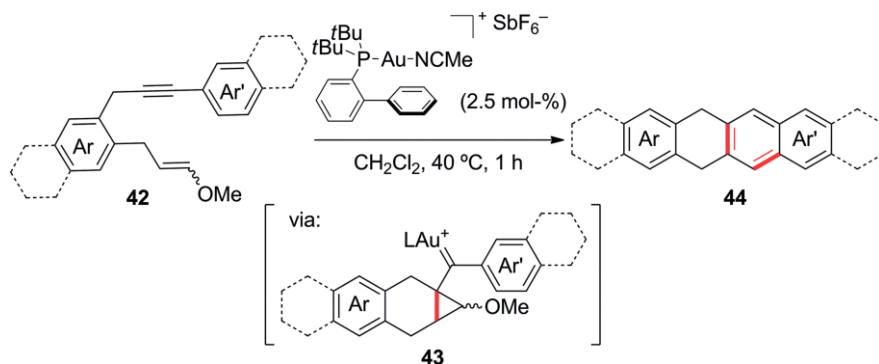
Scheme 14. Gold(I)-catalyzed synthesis of hydroacenes.

4.1. Methods for the Synthesis of Hydroacenes

The formation of six-membered rings through [4+2] cycloaddition reactions typically provides partially saturated systems that can subsequently be dehydrogenated to the aromatic counterparts.[16] Alternatively, partially hydrogenated acene derivatives can be accessed through the reduction of acenequinones.[65] The first systematic synthesis of hydroacene derivatives to be developed involved the direct reduction either of acenes or of acenequinones with HI in acetic acid at reflux temperature.[64] However, the harsh reaction conditions and low regioselectivities obtained for systems larger than tetracene limit the applicability of this approach. More recently, the preparation of functionalized hydroacenes **44** has been described under mild reaction conditions through the gold(I)-catalyzed cyclization of 1,7-enynes **42**, presumably via intermediates of type **43** (Scheme 14).[66] This transformation proceeded in the presence of a wide range of functional groups and allowed the synthesis of unsubstituted hydroacenes with up to nine linearly fused rings, such as tetrahydrononacene. Importantly, 1,7-enynes **42** are obtained in a highly modular manner by straightforward Sonogashira coupling of iodoarenes with relatively simple synthons.
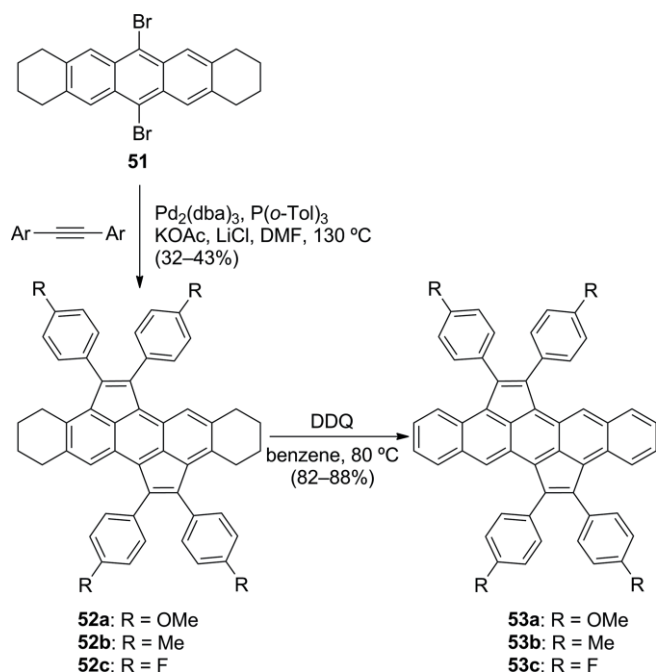
Zirconacyclopentadienes **45**, produced by treatment of diynes with Negishi reagent (Cp$_2$ZrBu$_2$),[67] are versatile building blocks for the assembly of linearly fused six-membered rings. Thus, the cycloaddition of **45** with electron-deficient alkynes or alkenes has been applied to the synthesis of functionalized dihydroacenes of type **46**, which can be converted either into the corresponding acenes **47** by dehydrogenation or into larger hydroacene derivatives through an iterative sequence (Scheme 15).[68] Moreover, the iodination/lithiation of **45** gives rise to 1,4-dilithiobutadienes **49**, which can be coupled with diiodoarenes in the presence of CuCl to afford dihydroacenes of type **50**.[69]
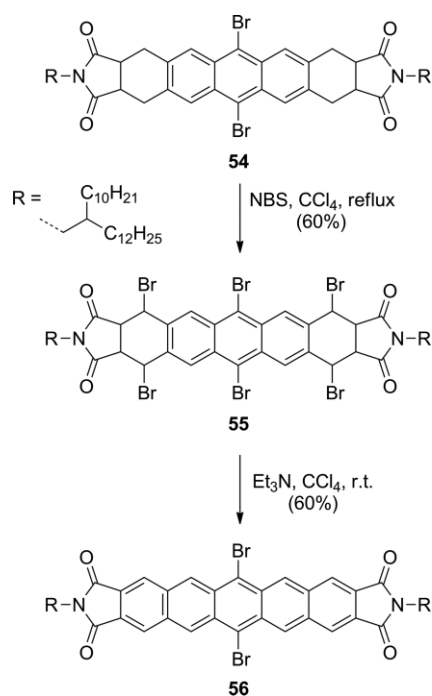
4.2. Dehydrogenation of Hydroacenes

The aromatization of hydroacenes has been extensively used over the last decades to prepare the corresponding acene derivatives. Indeed, the first synthesis of pentacene was accomplished by Clar in 1929–1930 through the oxidation of 6,13-dihydropentacene.[70] Similarly, pentacene was later obtained from 5,14-dihydropentacene in quantitative yield by dehydrogenation on Pd/C.[71] Since then, the dehydrogenation of hydropentacenes has become a common strategy for the synthesis of functionalized pentacene derivatives.[72] In a recent example, the Pd-catalyzed cyclopentannulation of **51** with internal alkynes leads to **52**, which are converted into stabilized cyclopentannulated pentacenes **53** by dehydrogenation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, Scheme 16).[73]

An alternative aromatization strategy was employed for the synthesis of 6,13-dibromopentacene-2,3:9,10-bis(dicarboximide) (**56**), a suitable building block for the synthesis of stable pentacene derivatives (Scheme 17).[74] Thus, whereas the dehydrogenation of **54** with DDQ or Pd/C resulted in the recovery of unreacted starting material, quadruple benzylic bromination followed by treatment with triethylamine provided **56** in 36 % yield over the two steps (Scheme 17).

The dehydrogenation of hydroacenes has also been applied in the synthesis of the highest known members of the acene family. The first reports on the synthesis of hexacene were based on Diels–Alder approaches to access polyhydrogenated hexacenes such as **68**, which was aromatized in the last step to afford the corresponding acene (Scheme 18).[12,36b] Some years


Scheme 15. Synthesis of hydroacenes via zirconacyclopentadienes.

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Scheme 16. Synthesis of cyclopentannulated pentacenes **53**.

52a: R = OMe
52b: R = Me
52c: R = F

53a: R = OMe
53b: R = Me
53c: R = F

Scheme 17. Alternative dehydrogenation of hydropentacene **54**.

R = C10H21 / C12H25

later, the synthesis of hexacene by dehydrogenation of dihydro-hexacene at high temperature on CuO was described.[75] Subli-mation of the crude mixtures obtained through these methods afforded a dark green solid, the structure of which was assigned as that of hexacene on the basis of spectral analyses. Neverthe-less, later reports on the unstable nature of hexacene[30,31] cast some doubts on the identity of this material.
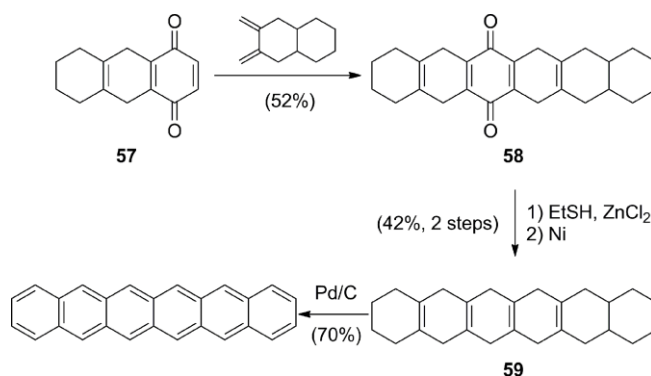
Scheme 18. Early synthesis of hexacene.

Hexahydrotetraphenylheptacene **60** was dehydrogenated with DDQ and trapped with C$_{60}$ fullerene by means of [4+2] cycloadditions to form stable *cis*-trisadduct **61** (Scheme 19).[76] In addition, the late-stage aromatization of hydroacene deriva-tives has been exploited in the synthesis of the photoprecursors of octacene and nonacene.[43]
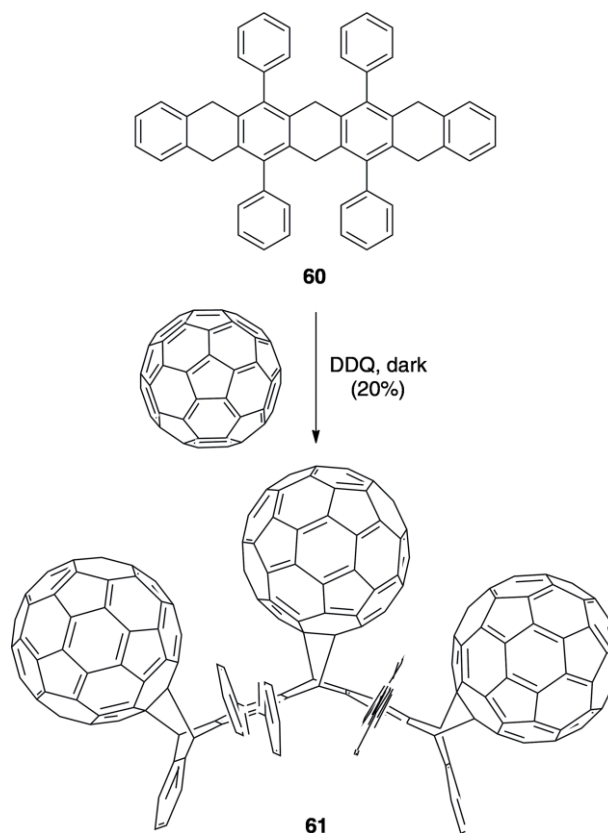
Scheme 19. Synthesis of **61**.

5. Conclusions

Acenes higher than pentacene are deceptively simple mol-ecules that, despite their highly symmetrical structures, cannot be readily accessed because of their high sensitivity in solution towards oxidation and dimerization or oligomerization.

Whereas functionalization of the aromatic systems through, for example, silylethynylation or arylation provides sufficient stabilization to higher acenes for their isolation and characterization, the preparation and application of the parent hydrocarbons is still limited by their intrinsic photo-instability, and only the photoinduced decarbonylation of carbonyl-bridged precursors combined with matrix isolation techniques has allowed the synthesis of the acene series up to nonacene. Thus, the development of methods for the straightforward synthesis of acenes larger than heptacene stable enough to be used in molecular electronics still remains a significant challenge. With the advent of new cycloaddition methods, more convergent strategies have been developed for the preparation of stable precursors of higher acenes, which could eventually allow for the synthesis of even larger acenes.

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