Selected strategies for the synthesis of triphenylenes

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This *tutorial review* surveys the most useful strategies for the synthesis of triphenylenes. It is aimed at organic chemists in general and, in particular, synthetic chemists interested in the development of advanced materials for organic electronic devices. The synthetic strategies considered are classified according to the structures of their key intermediates. Selected examples illustrate the variety of target structures and the method(s) of choice for their synthesis.

More than forty years have passed since the publication of Buess and Lawson's review on triphenylenes.[1] Since then, a huge amount of information has been published on the structure, synthesis and properties of triphenylene (**1**) and of related compounds. Although some aspects of this work have been discussed in monographs or reviews,[2,3] no recent reviews have centered on synthesis. This paper aims to fill this gap by surveying research on the synthesis of substituted triphenylenes and some of their benzo-derivatives that has been published since the late 1950s. Polycyclic aromatic hydrocarbons in which a central ring is fused to more than three aromatic rings, as in coronene, fullerene and many extended systems, are not included, even though they formally contain the triphenylene nucleus. The purpose of this paper is to survey the procedures used to prepare triphenylenes through selected examples, and not to review the subject exhaustively.
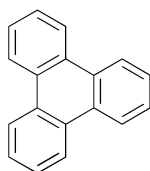
Fig. 1 Triphenylene.

Since the 1960s, interest in the chemistry of triphenylenes has increased continuously. Their planar rigidity and ability to support a variable number of functionalized arms of diverse types endow

them with great potential for supramolecular and materials chemistry. Particularly appealing are 2,3,6,7,10,11-hexasubstituted derivatives with medium-sized side chains, such as **2a–c** (Fig. 2).

These molecules self-associate to form discotic liquid crystals in which they are arranged in columns due to π-stacking of the aromatic rings and van der Waals interactions between their alkyl chains (Fig. 3).[4] Their liquid crystal behavior can be modified by changing their substitution pattern and/or the electronic properties of their substituents.

Recent efforts in this field have aimed at the preparation of mesophases formed by alternating electron-rich and electron-poor discotic molecules. For example, the mesophase of the electron-rich hexaalkoxytriphenylene **2a** (Fig. 2) is stabilized when it forms a 1:1 complex with the non-mesogenic electron-poor hetero-triphenylene **3**, which raises the mesophasic-isotropic transition temperature from 99.5 to 240 °C.[5]

As a consequence of overlap between the orbitals of neighboring molecules within the columns of the mesophases described above, charge can move easily along these columns. This property is potentially exploitable in photoconductive devices, optical data storage devices, photovoltaic solar cells and light-emitting diodes. As Buess and Lawson predicted in 1960,[1] the range of applications of triphenylene thus continues to grow.

Synthesis of the triphenylene moiety

Although many different synthetic strategies can be devised for the synthesis of triphenylenes, most of the practical syntheses reported to date may be formally classified into the six types shown in

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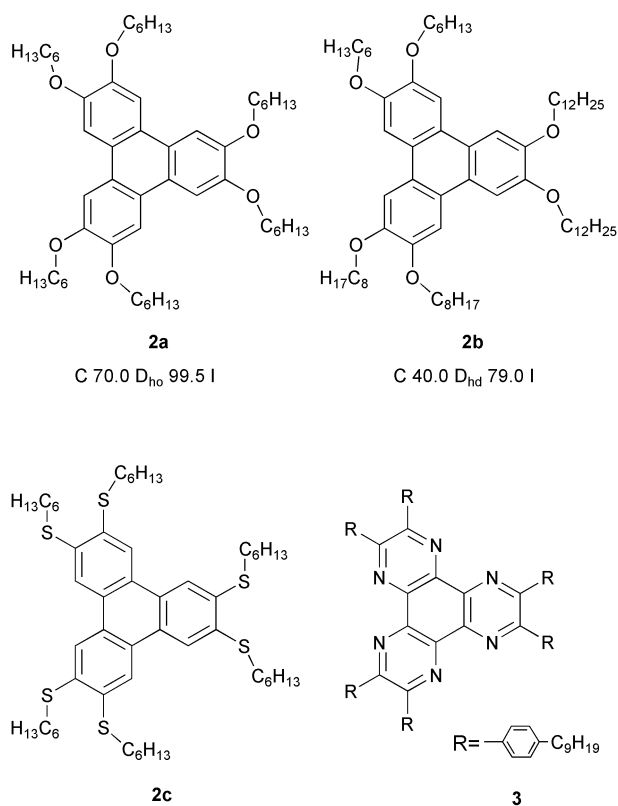
2a

C 70.0 D$_{ho}$ 99.5 I

2b

C 40.0 D$_{hd}$ 79.0 I

R=—⟨⟩—C$_9$H$_{19}$

2c

3

Fig. 2 2,3,6,7,10,11-Hexasubstituted triphenylene derivatives with medium-sized side chains. Phase transition temperatures (°C): C, crystalline phase; D, columnar mesophase; I, isotropic phase.
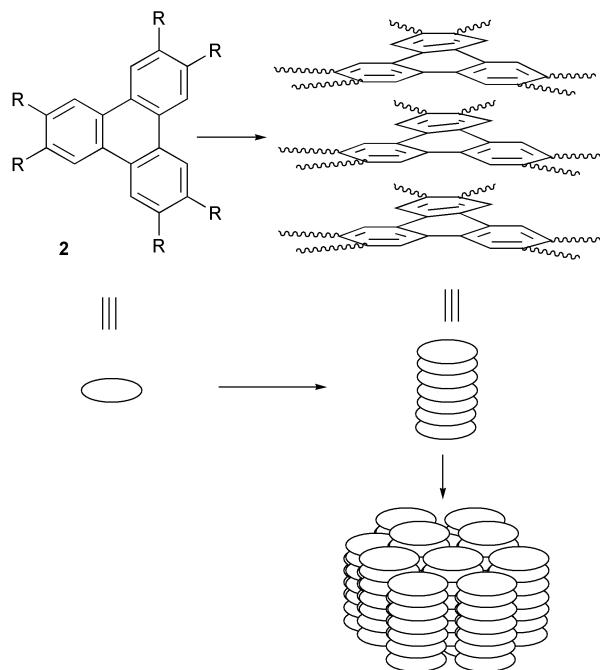

Fig. 3 Self-association of substituted triphenylene.

Scheme 1, where solid lines represent the structures of the key intermediates and dashed lines represent the bonds or fragments that become part of the triphenylene in the final step(s) of the synthesis.

Syntheses of types I–IV are characterized by the preparation and isolation of terphenyl, biphenyl, naphthyl and phenanthryl compounds, respectively, as key intermediates. In type V syntheses, triphenylenes are constructed by trimerization of three units, the precursors of the peripheral rings. In type VI, the final products are constructed on the central ring. However, not all syntheses afford
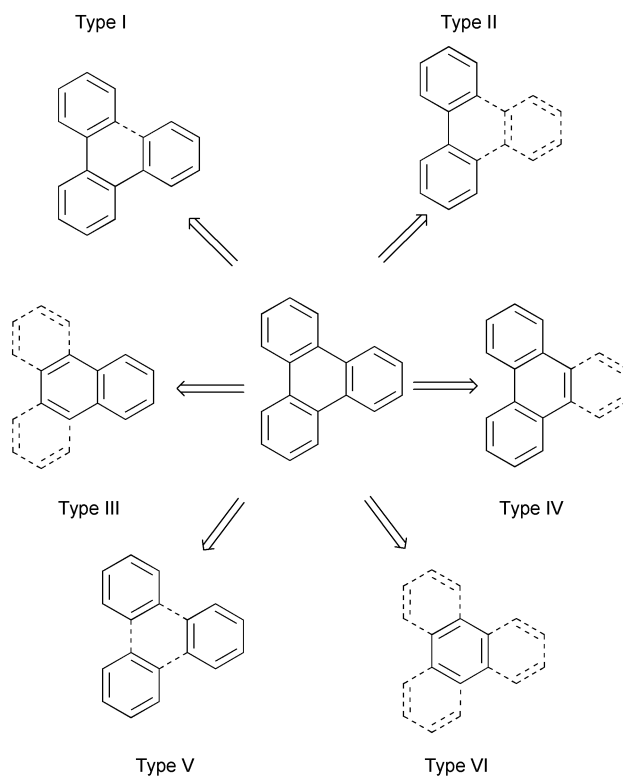

Scheme 1

the final triphenylene in one step from the key intermediate shown in Scheme 1. For example, there are methods for the one-pot trimerization of arenes that, though formally of type V, probably involve a multistep mechanism *via* intermediates corresponding to type II or even type I.
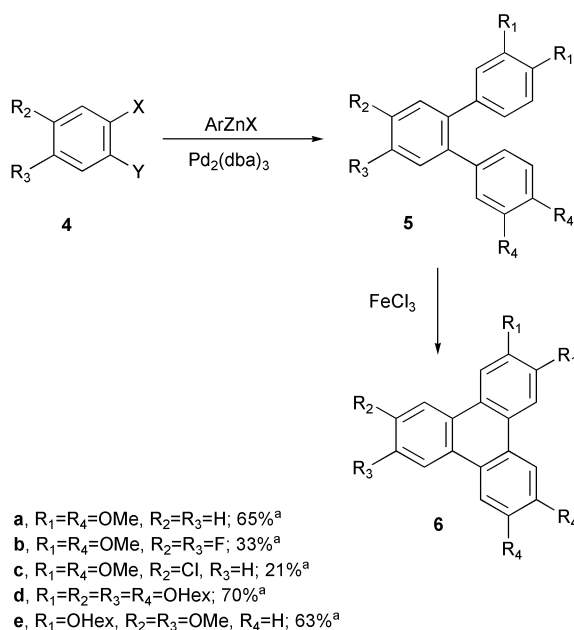
Type I syntheses

The key step of these routes is the cyclization of a terphenyl.
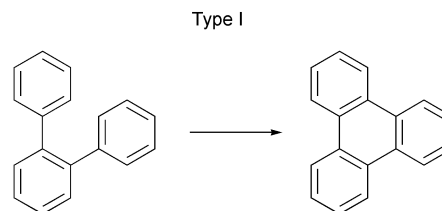
Oxidative cyclization. Oxidative coupling is a classic procedure for the formation of biaryl bonds that has been used extensively for the biomimetic synthesis of natural products. It was initially developed for the coupling of phenols using a plethora of oxidizing agents, among which K$_3$Fe(CN)$_6$ and FeCl$_3$ have been the most frequently used. In the past 20 years, coupling protocols of this type have been based on new oxidizing agents such as Tl(OCOCF$_3$)$_3$, VOCl$_3$, VOF$_3$ and MoCl$_5$, which can be used for the coupling of phenols and phenyl ethers. For preparation of the terphenyl, Ullman coupling, for many years the method of choice, has of late been replaced by palladium-catalyzed couplings.
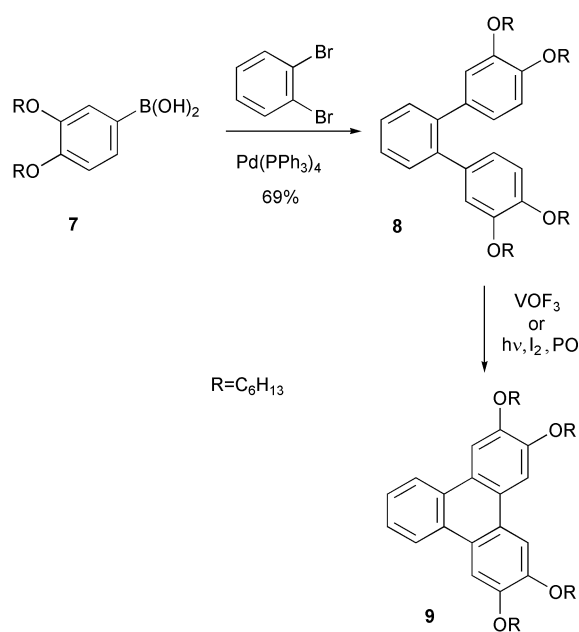
By this method, symmetrically and unsymmetrically substituted triphenylenes **6** have been prepared from arenes **4** by palladium-catalyzed coupling with arylzinc halides followed by oxidative cyclization with FeCl$_3$/H$_2$SO$_4$ (Scheme 2).[6,7] It is interesting to note that when X = I and Y = Br, two different arylzinc derivatives may be used in successive steps, the first coupling with the more reactive iodide and the second with the bromide

A similar strategy has been used to synthesize the tetrasubstituted triphenylene **9**, terphenyl **8** being prepared by Suzuki coupling of boronic acid **7** with *o*-dibromobenzene (Scheme 3).[8]

Scheme 2

a, $R_1=R_4=OMe$, $R_2=R_3=H$; 65%[a]
b, $R_1=R_4=OMe$, $R_2=R_3=F$; 33%[a]
c, $R_1=R_4=OMe$, $R_2=Cl$, $R_3=H$; 21%[a]
d, $R_1=R_2=R_3=R_4=OHex$; 70%[a]
e, $R_1=OHex$, $R_2=R_3=OMe$, $R_4=H$; 63%[a]

[a]Overall yields for the two steps (terphenyl formation and cyclization)

Scheme 3

2,3,6,7,10,11-Hexasubstituted triphenylenes have been obtained by this procedure starting from substituted dihalides **4**.[9] The same methodology has been used for the synthesis of a hexaalkoxybenzo[*b*]triphenylene mesogen, starting from a *o*-dibromonaphthalene.[10] As above, the use of compounds **4** with X = I, Y = Br allows the introduction of two different boronic acids **7** in successive steps.[11,12]

Photocyclization. Soon after the discovery of the photocyclization of stilbene to phenanthrene, this procedure was applied to the synthesis of triphenylenes from terphenyls. For the preparation of triphenylene itself from *o*-terphenyl (**10**) it is very efficient, with yields of up to 90% (Scheme 4).[13]

The photocyclization approach is also efficient for symmetrically substituted triphenylenes such as **12a**, but unsymmetric substitution introduces the problem of regioselectivity and usually decreases the yield. For example, triphenylene **12b** was obtained in
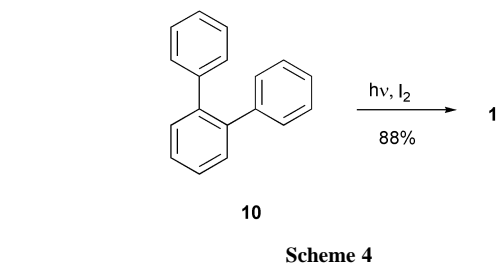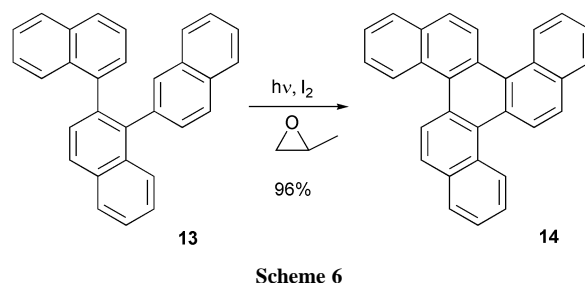

Scheme 4

only moderate yield by irradiation of the corresponding terphenyl with UV light in the presence of iodine (Scheme 5).[14] The terphenyls, **11a,b**, were obtained in low yield by Ullman coupling.

a, $R_1=R_3=H$, $R_2=OMe$, 72%
b, $R_1=R_2=Me$, $R_3=OMe$, 43%
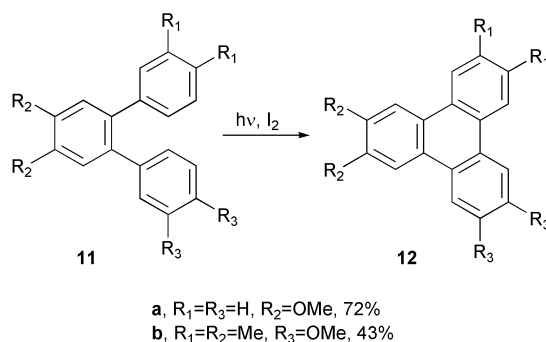
Scheme 5

Irradiation in the presence of iodine as oxidant and propylene oxide (PO) as acid scavenger also improved the yield of the cyclization of terphenyl **8** to triphenylene **9** (Scheme 3).[7] Under the same conditions, a tribenzoterphenyl derivative, **13** (obtained from 1-indanone in 4 steps and 47% yield), was cyclized to tribenzotriphenylene **14** (Scheme 6).[15]
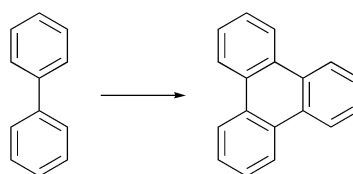

Scheme 6

Summing up, the most interesting aspect of type I procedures is the possibility of preparing unsymmetrically substituted triphenylenes. Although synthesis of the key terphenyl has frequently been a multistep, low-yielding, tedious process, palladium-catalyzed couplings such as those shown in Schemes 2 and 3 have improved the results of this approach.
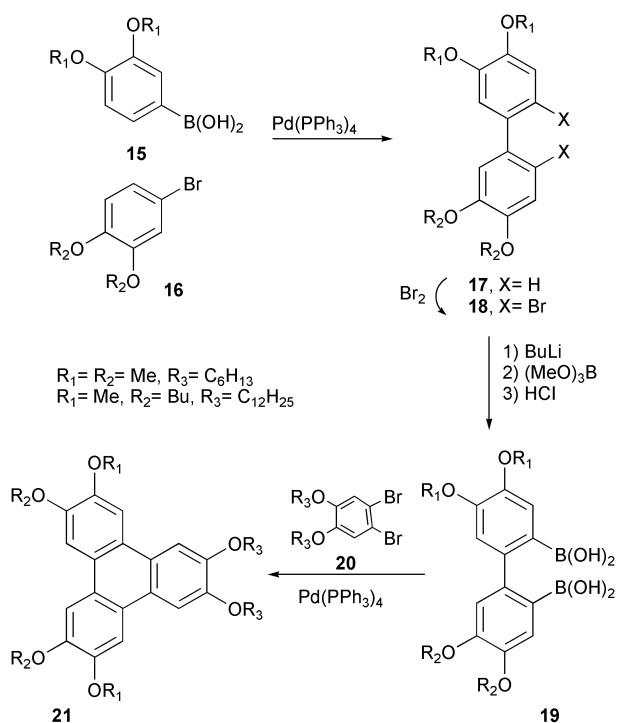
Type II syntheses

These strategies are characterized by the formation of triphenylene from a precursor containing two of the future peripheral rings linked by a biaryl bond.

Type II

Palladium-catalyzed coupling. An interesting synthesis of unsymmetrically substituted triphenylenes has been reported which
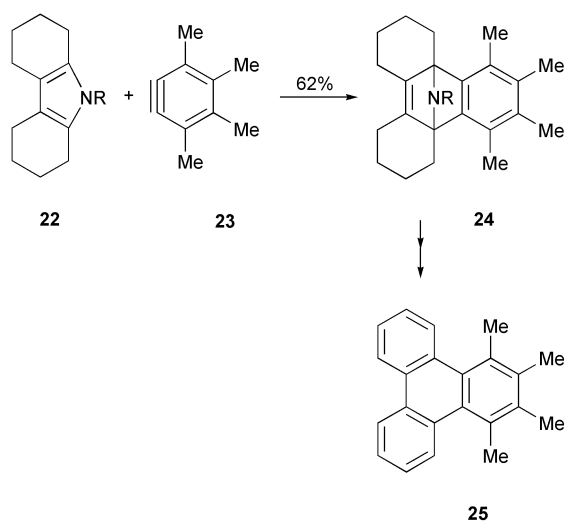
Scheme 7

includes three Suzuki-type reactions (Scheme 7). Pd(PPh₃)₄-catalyzed coupling of boronic acids **15** and aryl bromides afforded biaryls **17**, which were transformed into dibromides **18** by treatment with Br₂. Compounds **18** were then transformed into diboronic acids **19** by metal–halogen exchange with BuLi, treatment with B(OMe)₃, and hydrolysis with HCl. Finally, triphenylenes **21** were obtained by double Suzuki coupling between dibromides **20** and diboronic acids **19**.[16]

Diels–Alder cycloaddition. Inter- or intramolecular Diels–Alder reactions are key steps in several type II syntheses of triphenylenes.

Intermolecular Diels–Alder reactions of heterocyclic dienes **22** with aryne **23** lead to adducts **24**, which can be transformed into triphenylene **25** by heating followed by oxidation with DDQ (Scheme 8).[17]
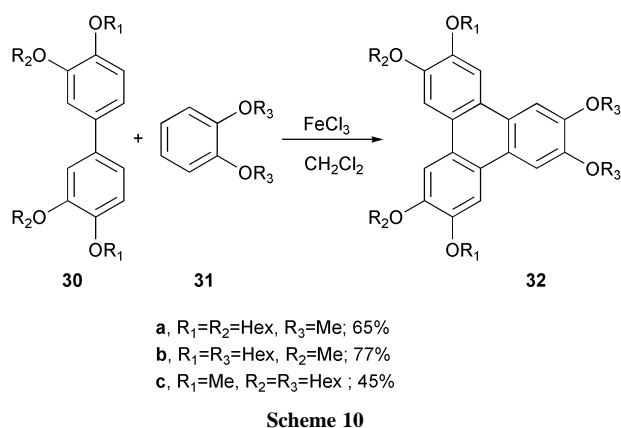

Scheme 8

Compound **29**, which contains two triphenylene units, has been obtained from **28** by a double Diels–Alder reaction, followed by aromatization with DDQ. Intermediate **28** was prepared by palladium-catalyzed coupling of diiodide **26** with two units of

iodide **27** (Scheme 9).[18] This strategy for the synthesis of **29** is rather unusual in that the central ring and one of the peripheral rings are formed in the same step.
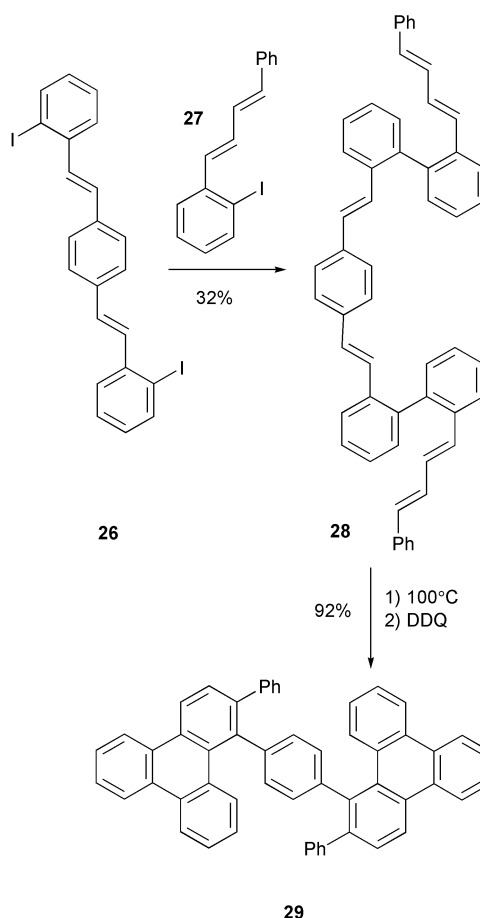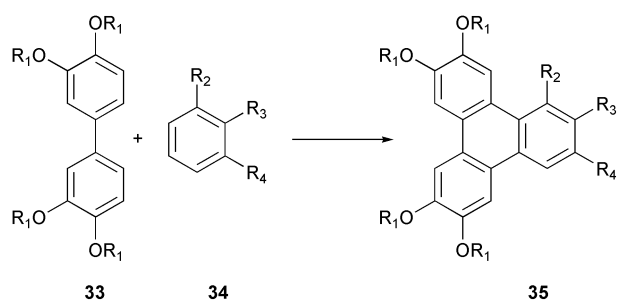

Scheme 9

Oxidative cyclizations. Cyclization by oxidation with FeCl₃ was extensively studied by Bushby and coworkers[19–22] and has been applied by other groups.[12,23] In a typical example, biaryls **30** were reacted with catechol derivatives **31** in the presence of FeCl₃ to afford triphenylenes **32** in moderate yields (Scheme 10).[19]

a, R₁=R₂=Hex, R₃=Me; 65%
b, R₁=R₃=Hex, R₂=Me; 77%
c, R₁=Me, R₂=R₃=Hex ; 45%

Scheme 10

Kumar and coworkers have applied other oxidizing agents, such as MoCl₅[24] and VOCl₃,[25] to the synthesis of triphenylenes with the substitution pattern of **32**. More unusual is the synthesis of triphenylenes **35**, which have substituents at position 1. For this purpose FeCl₃,[20,26] MoCl₅[26] and VOCl₃[25] have been used; Scheme 11 shows some representative examples.

To sum up, syntheses of types I and II have many features in common. The same type of couplings as are used to prepare

a, $R_1=R_2=R_3=C_4H_9$, $R_4=OC_4H_9$; 40%[25,26]
b, $R_1=C_5H_{11}$, $R_2=R_3=R_4=OC_{12}H_{25}$; 20%[25]
**c**, $R_1=C_6H_{13}$, $R_2=F$, $R_3=R_4=OCH_3$; 67%[20]

Scheme 11

terphenyls may be used to prepare the biaryl key intermediates of type II syntheses. In both cases, the key cyclization frequently has only moderate yield and is often complicated by the formation of regioisomers.

Type III syntheses

These routes are characterized by the formation of two of the peripheral rings of the triphenylene on a naphthalene nucleus.

Type III
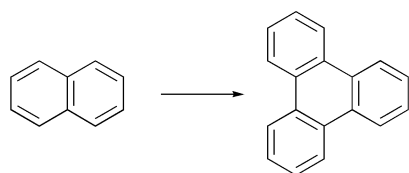
Diels–Alder cycloaddition. Most type III procedures have in common the use of the Diels–Alder reaction. For example, 1,2,3,4-tetrahydronaphthalene (**37**), generated *in situ* from **36** by metal–halogen exchange followed by elimination, has been reacted with furan to afford the bisadduct **38** in 41% yield. Deoxygenation by treatment with Pd/C and Mg followed by TFA yielded triphenylene (Scheme 12).[27]
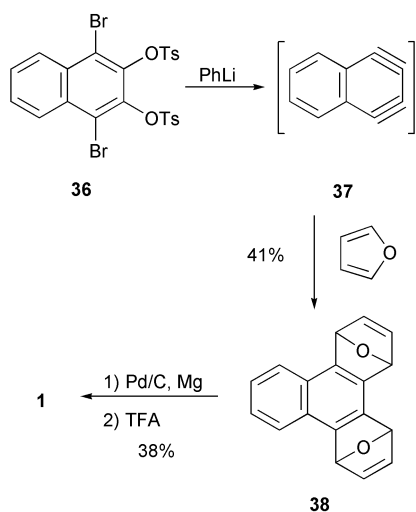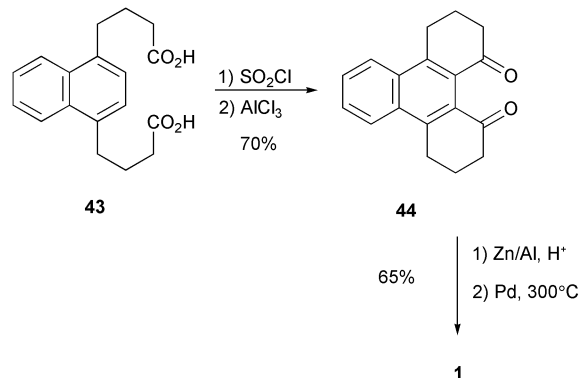
Scheme 12

A related approach starts from the naphthyl derivative **39** (previously obtained by a Diels–Alder reaction between 4,5-di-bromo-1,2-didehydrobenzene and furan). Adduct **39** is treated with NaNH₂ in the presence of furan to generate aryne **40** by double dehydrohalogenation, and **40** reacts with the furan to afford the triendoxide **41**, which can be transformed into triphenylene as
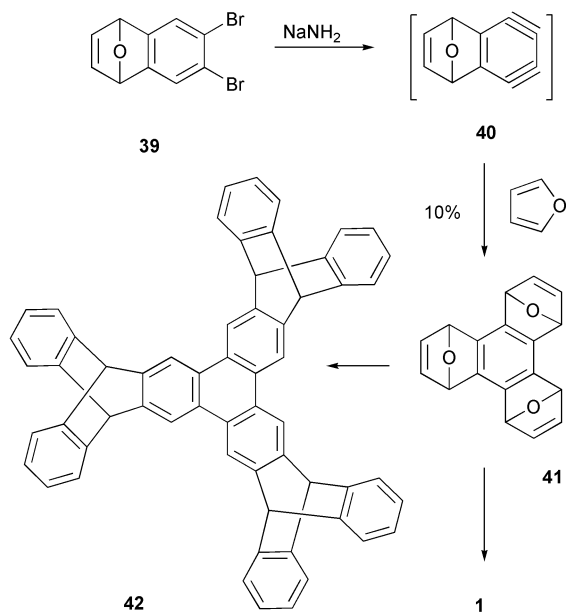
Scheme 13

Other methods. Triphenylenes have been obtained by classical Friedel–Crafts chemistry from functionalized naphthalenes such as **43**. The cyclization of **43** affords a diketone, **44**, which can be converted into triphenylene in moderate yield by Clemmensen reduction and palladium-catalyzed dehydrogenation (Scheme 14).[29]
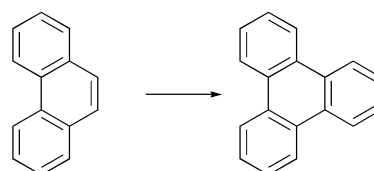
Scheme 14

Type IV syntheses

In these procedures the last peripheral ring of the triphenylene is formed on an isolated phenanthrene derivative.

Type IV

Diels–Alder reactions. The most useful procedure for type IV syntheses is the Diels–Alder reaction, for which the diene is frequently a phenanthrene with exocyclic double bonds at positions 9 and 10. For example, furan **45**, upon reaction with benzyne as

dienophile, affords a 48% yield of endoxide **46**, which can be deoxygenated to benzotriphenylene **47** by treatment with Fe₂(CO)₉ (Scheme 15).[30]


Scheme 15
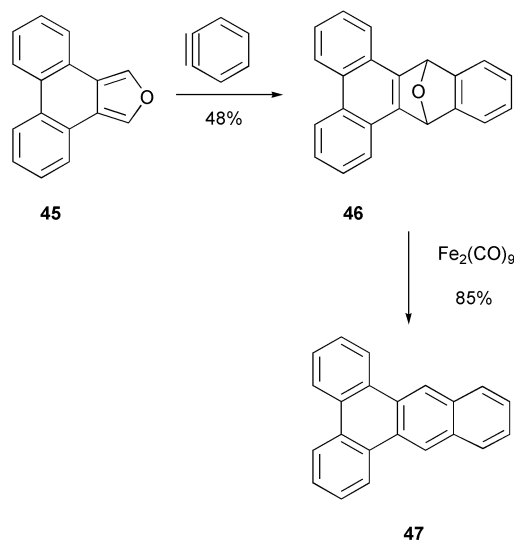
Occasionally the diene is formed by a double bond between positions 9 and 10 of the phenanthrene and the double bond of a vinyl substituent at position 9. For example, oxazine **49**, prepared from 9,10-phenanthrenequinone derivative **48**, undergoes Diels–Alder reactions with dimethyl acetylenedicarboxylate (DMAD) or a maleimide to yield bridged intermediates that through a retro-Diels–Alder reaction afford functionalized triphenylenes **50** and **51**, respectively (Scheme 16).[31]
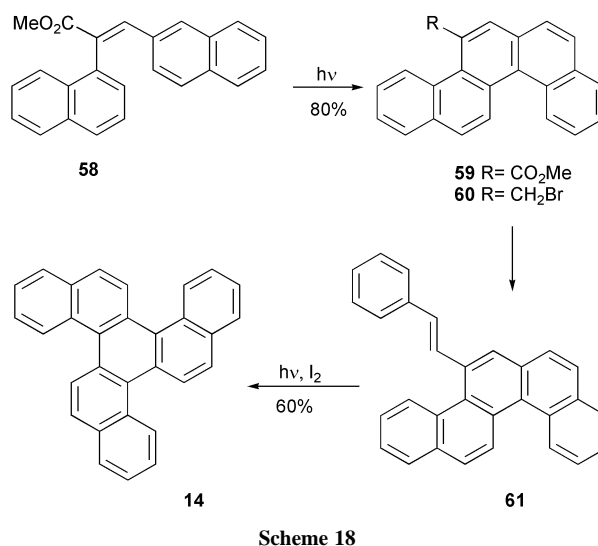

Scheme 16
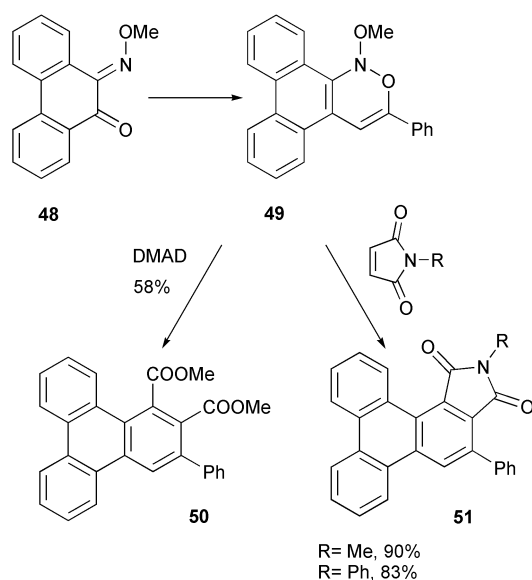
Reversed-role Diels–Alder reactions in which a phenanthrene derivative acts as dienophile have also been explored. To synthesize triphenylenoparacyclophane **57**, 9,10-didehydrophenanthrene (**52**), generated by treatment of 9-bromophenanthrene with sodium amide, was reacted with furan, affording variable yields of adduct **53**, which was deoxygenated with diiron nonacarbonyl to triphenylene **54**; transformation into dibromide **55** and dithiol **56**, followed by reaction of **56** with **55**, then gave a low yield of cyclophane **57** (Scheme 17).[32]

Photocyclization. Photocyclization has been used for the synthesis of some benzotriphenylenes from phenanthrene deriva-

Scheme 17
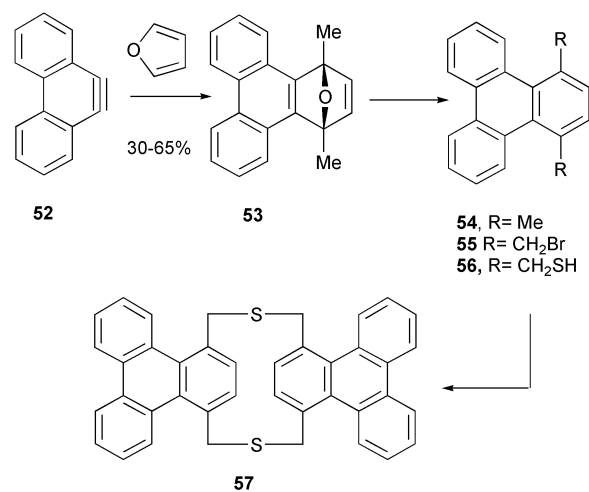
tives. Stilbenoid **58** was cyclized in 80% yield to **59**; reduction of **59** with lithium aluminium hydride, followed by treatment with HBr, afforded **60**, which was converted to stilbenoid **61**; and **61** was cyclized by irradiation with UV light in the presence of iodine, affording tribenzotriphenylene **14** in 60% yield (Scheme 18).[33]
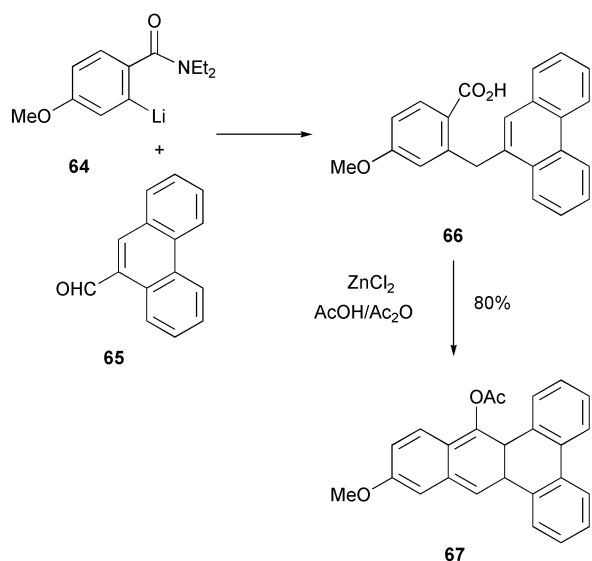

Scheme 18

Application of a similar procedure to heterostilbenoid **62** affords **63**; compound **62** can be prepared (albeit in low yield) by reaction of 9,10-phenanthrenequinone with 2-thienyllithium followed by didehydroxylation with Ti (Scheme 19).[34]
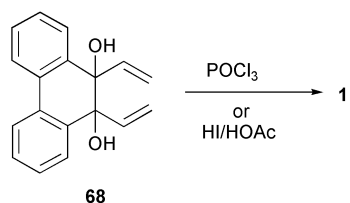

Scheme 19
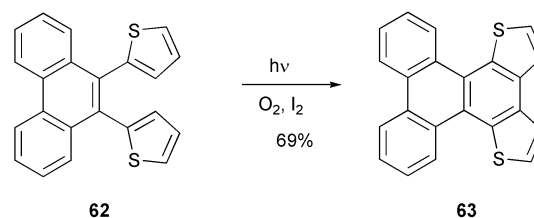
Other methods. Triphenylene **67** has been prepared from phenanthrene-9-carboxaldehyde (**65**) by addition of *o*-lithiated benzamide **64**, reduction and hydrolysis of the product to **66**, and Friedel–Crafts cyclization of **66** with ZnCl₂ in AcOH/Ac₂O, which presumably affords a ketone that under the reaction conditions undergoes enolization and acetylation to **67** (Scheme 20).[35]

Cationic cyclizations have been used to synthesize triphenylene from 9,10-phenanthrenequinone. The key intermediate, **68**, ob-
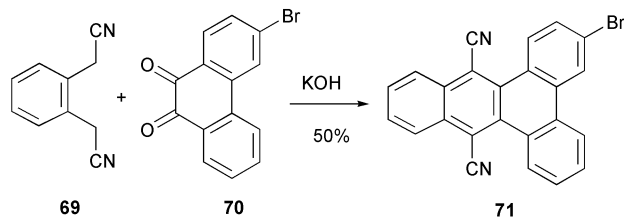
Scheme 20

tained in 34% yield by reaction of the quinone with vinyllithium, was cyclized and dehydrated to triphenylene in 74% or 71% yield by treatment with POCl₃ or HI/HOAc, respectively (Scheme 21).[36]
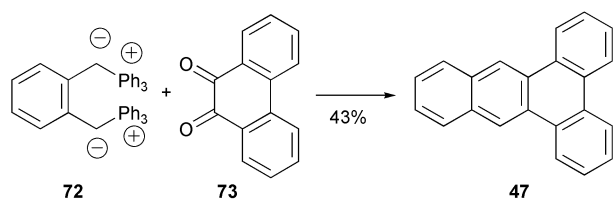

Scheme 21

Classical carbanion chemistry has been used for the preparation of functionalized triphenylenes: KOH-promoted condensation of dicyano compound **69** with phenanthrenequinone **70** led to triphenylene **71** (Scheme 22).[37]

Scheme 22
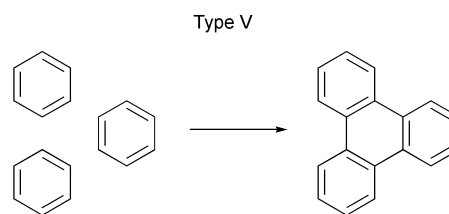
Benzotriphenylene **47** has been prepared in 43% yield by Wittig reaction of 9,10-phenanthrenequinone (**73**) and diylide **72** (Scheme 23).[37]

Scheme 23

Type V syntheses

In these, the central ring is constructed by formal trimerization of 6-membered rings. Since the early work of Mannich this has been the most widely used approach to the synthesis of triphenylenes.

Type V

Oxidative trimerization. Since the discovery of their liquid crystal nature and properties, most synthetic work on triphenylenes has aimed at hexaalkoxytriphenylenes. The method of choice, especially for symmetrically substituted alkoxytriphenylenes such as **2a**, is the oxidative trimerization of catechol derivatives **74** and **75** (Table 1).

Oxidative trimerizations of catechol derivatives using chloranil or FeCl₃ in sulfuric acid were reported throughout the 1960s. Bushby's group have recently optimized the experimental conditions for trimerization with FeCl₃, making this procedure very practical. The key modifications are the use of low concentrations of sulfuric acid for the reaction (0.3%) and the addition of methanol as reducing agent at the beginning of work-up; under these conditions, good yields of hexasubstituted triphenylenes with substituents ranging from OH to crown ethers or ramified chiral moieties have been obtained. Other oxidizing agents, such as MoCl₅ and VOCl₃, have been used with similar results (Table 1).

**Table 1** Selected examples of oxidative trimerization

Monomer	Reagent	Triphenylene (%)	Remarks	Ref.
74 (catechol, OR, OR)				
R = Me	FeCl₃/	86		38
Hexyl	0.3% H₂SO₄/	73		
Octyl	CH₂Cl₂	60		
R = Methyl	FeCl₃/	96		39
Pentyl	70% H₂SO₄	45		
Decyl		42		
R = Me	FeCl₃/SiO₂	89		40
Pentyl		86		
Hexyl		88		
Octyl		82		
R = Me	MoCl₅	74		24
Butyl		95		
Hexyl		94		
Decyl		80		
R = Pentyl	MoCl₅	64		41
R = (branched chain)	MoCl₅	44		42
R = Bu	VOCl₃	86		25
Pentyl		85		
Decyl		70		
75				
R = –(CH₂)₂OCH₂CH₂–	FeCl₃/H₂SO₄	25		43
R = (Me)CCH₂CO₂Et	MoCl₅	40	*anti/syn* = 3 : 1, chiral	44

Synthesis *via* organometallic intermediates. Triphenylenes have frequently been observed when dehydrobenzenes have been generated from organometallic intermediates. It has been shown that this is a multistep process that involves the formation of biaryl intermediates. The best yields have been obtained by decomposition of the magnesium and sodium derivatives **77**[45] and **79**[46] (Scheme 24).
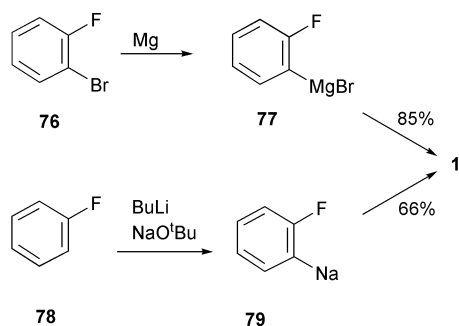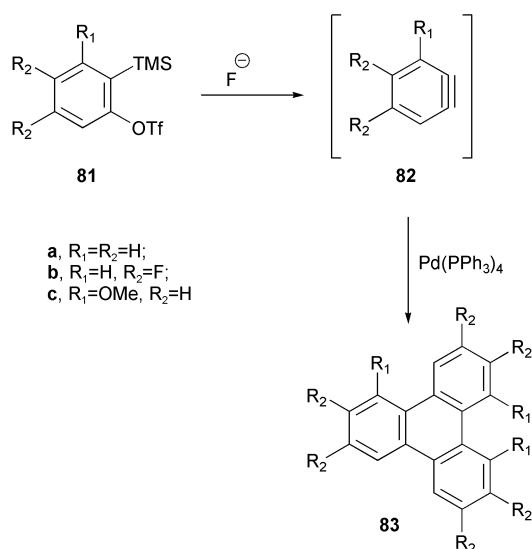

Scheme 24

The huge amount of work carried out during the 1990s on the reactivity of arenes and their derivatives with transition metals led to the discovery of new routes to triphenylenes. The first moderately efficient transition-metal-mediated synthesis of triphenylenes was discovered when 1,2-dibromobenzene (**80**) was treated with Ni(cod)$_2$/PPh$_3$, which gave compound **1** in 60% yield (Scheme 25).[47]
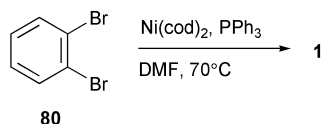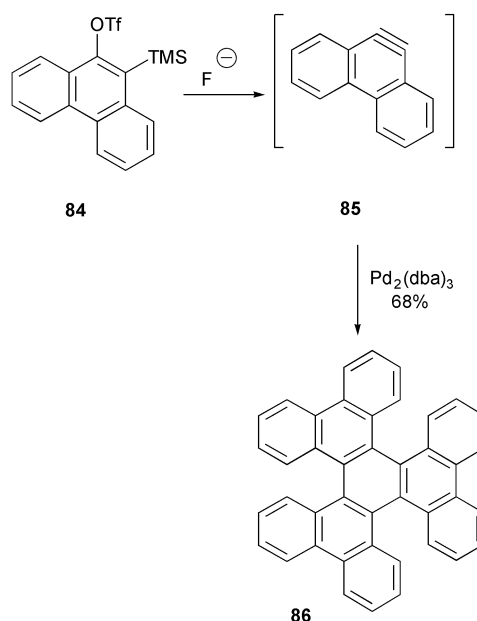

Scheme 25

A few years ago, the first aryne trimerizations to be promoted by catalytic amounts of a transition metal were reported.[48] When trimethylsilylaryltriflates **81** were subjected to aryne-forming conditions (CsF, acetonitrile) in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ (5–10%), triphenylenes **83** were obtained in good yields. Arynes **82** were proposed as possibly being the intermediates in these transformations (Scheme 26).


a, R$_1$=R$_2$=H;
b, R$_1$=H, R$_2$=F;
c, R$_1$=OMe, R$_2$=H

Scheme 26

This procedure has also been applied to the synthesis of benzotriphenylenes such as **86** from phenanthrene **84** (Scheme 27).[49]

Scheme 27

These palladium-catalyzed trimerizations should be particularly useful for the synthesis of triphenylenes with substituents other than OR and for strained benzoannelated triphenylenes, all of which are difficult to prepare by other methods.

Other methods. Mannich's original procedure, H$_2$SO$_4$-catalyzed trimerization of cyclohexanone (**87**), has scarcely been used since 1960, but variants have been developed that use catalysts such as HfCl$_4$, ZrCl$_4$, and Cp$_2$ZrCl$_2$ (Scheme 28).[50]
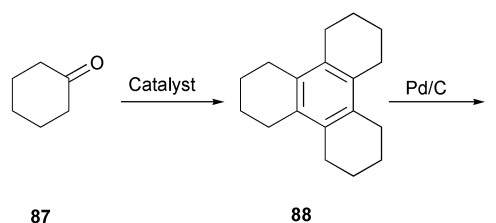
Catalyst	Yield (%)
HfCl$_4$	57
ZrCl$_4$	70
Cp$_2$ZrCl$_2$	41

Scheme 28

Scheme 29 shows a related example, the formal synthesis of triphenylene by trimerization of 1-methoxycyclohexene (**89**) with boron trifluoride etherate, followed by dehydrogenation.[51]
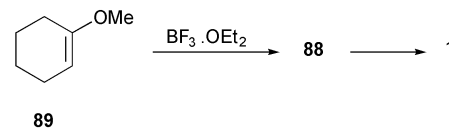
Scheme 29

The same authors have observed an interesting trimerization of 1-cyanocyclohexene (**90**), which in the presence of LDA affords **91** (Scheme 30).[51]
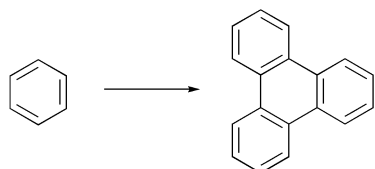
Type VI syntheses

Few syntheses of triphenylenes by one-pot formation of the peripheral rings have been reported. This is rather surprising, since this procedure allows the synthesis of compounds that are difficult to prepare by most classical procedures. For example, acid-
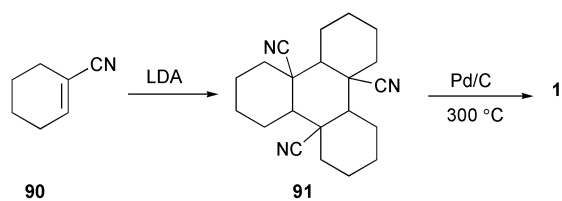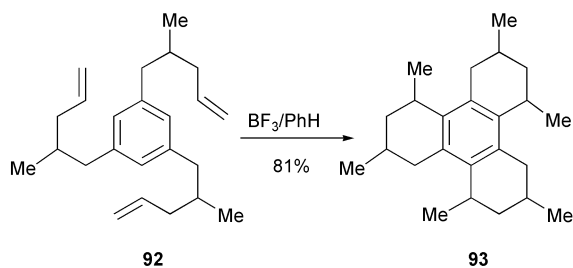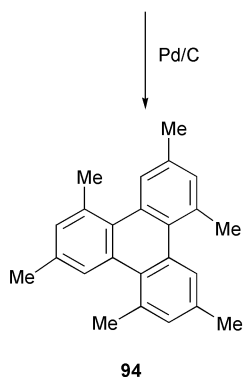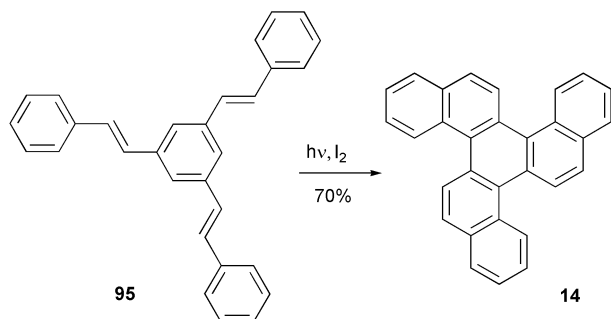
Scheme 30

Type VI

catalyzed cyclization of **92** leads to **93**, which by dehydrogenation with palladium on carbon can be transformed into **94** (Scheme 31).[52]
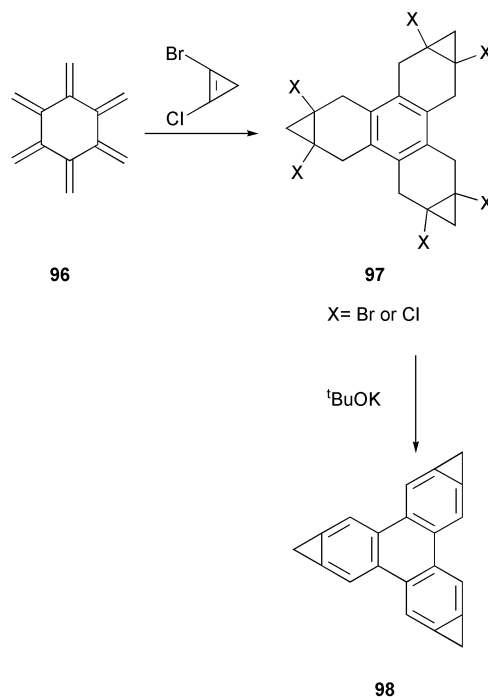

Scheme 31

Photochemical cyclization. A similar strategy, but based on photocyclization of stilbene **95**, has been used for the synthesis of tribenzotriphenylene **14** (Scheme 32).[53]

Scheme 32

Diels–Alder cycloaddition. In a completely different approach to the formation of the external rings that has recently been

reported, the key reaction is a cycloaddition between hexaradialene **96** and 1-bromo-2-chlorocyclopropene. Treatment of the resulting mixture of adducts **97** with potassium *tert*-butoxide produced the tris(cyclopropa)triphenylene **98** in 20% yield (Scheme 33).[54]

X= Br or Cl

Scheme 33

Heterocyclic analogs

In recent years there has been growing interest in the synthesis and properties of aza-analogs of triphenylene. Most aza-triphenylenes (**100** and **102** are typical examples) have been prepared using one of the following strategies: condensation of hexaaminobenzene (**99**) with 1,2-dicarbonyl derivatives (Scheme 34),[55] and condensa-
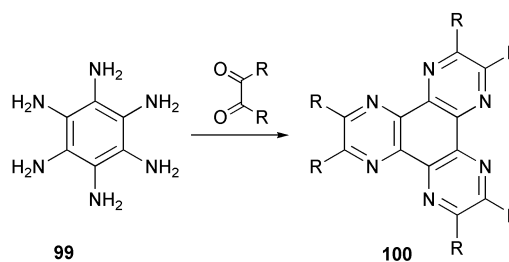
Scheme 34

tion of hexaketocyclohexane (**101**) with 1,2-diaminoethylene derivatives (Scheme 35).[56]
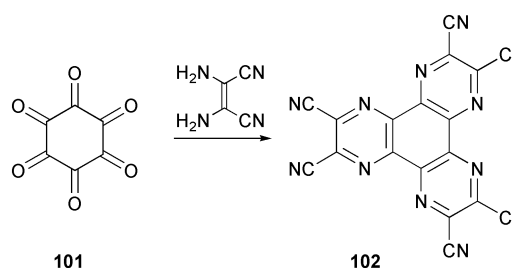
Scheme 35

Conclusion

Most of the methods discussed in this review are appropriate for the preparation of triphenylene itself or simple benzo-derivatives. The

synthesis of substituted triphenylenes requires more careful evaluation of the alternatives. The triphenylenes that have been most intensively studied, due to their liquid crystal properties, are those with alkoxy substituents. If these substituents are distributed symmetrically (usually at positions 2,3,6,7,10 and 11), oxidative trimerization is the method of choice: the starting materials are usually easily available, the trimerization procedure is simple, and the yields are good. Palladium-catalyzed trimerization is also a very promising method because it is very mild, is not limited to alkoxy substituents, and works efficiently even in the synthesis of strained compounds. For the preparation of triphenylenes with unsymmetric substitution, sequential methods are more appropriate, especially syntheses of types I and II. The utility of syntheses of types III and IV depends on the availability of the key naphthalenes and phenanthrenes.

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