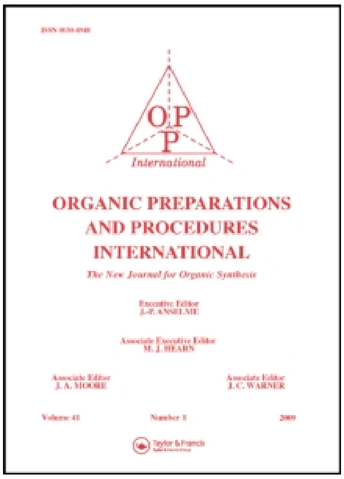


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

MAIN METHODOLOGIES FOR THE SYNTHESIS OF RADIALENES. AN UPDATE

Florence Geneste[a]; Alec Moradpour[a]
[a] Laboratoire de Physique des Solides UA2 du CNRS, University of Paris-Sud, Orsay cedex, FRANCE

To cite this Article Geneste, Florence and Moradpour, Alec(1999) 'MAIN METHODOLOGIES FOR THE SYNTHESIS OF RADIALENES. AN UPDATE', Organic Preparations and Procedures International, 31: 5, 507 — 536

To link to this Article: DOI: 10.1080/00304949909355336

URL: http://dx.doi.org/10.1080/00304949909355336

ORGANIC PREPARATIONS AND PROCEDURES INT., 31 (5), 507-536 (1999)

MAIN METHODOLOGIES FOR THE SYNTHESIS OF RADIALENES. AN UPDATE

Florence Geneste and Alec Moradpour *

Laboratoire de Physique des Solides
UA2 du CNRS, University of Paris-Sud
F-91405 Orsay cedex, FRANCE

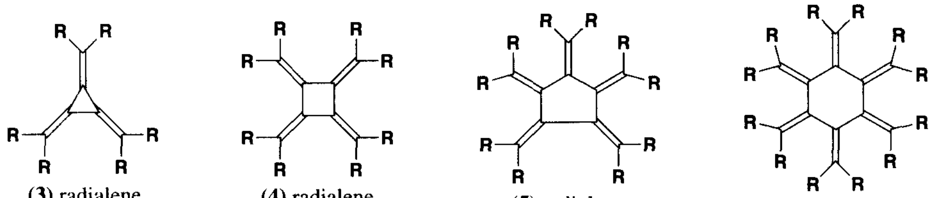
MAIN METHODOLOGIES FOR THE SYNTHESIS OF RADIALENES. AN UPDATE

Florence Geneste and Alec Moradpour *

Laboratoire de Physique des Solides
UA2 du CNRS, University of Paris-Sud
F-91405 Orsay cedex, FRANCE

INTRODUCTION

Radialenes defined as "alicyclic compounds in which all ring carbon atoms are sp^2-hybridized and carry as many exocyclic double bonds as possible", have attracted much attention for their unique molecular properties, as well as their potentially interesting behavior as components of solid state materials, after the isolation of the first radialene in the early sixties. Interest for this highly aesthetic series of molecules includes the challenging aspects of working out the corresponding high yield syntheses.



(3) radialene (4) radialene (5) radialene (6) radialene

Scheme 1

Although the above definition might include a larger family of compounds, we will restrict the present review to the syntheses of radialenes in which each carbon of the central alkane ring is involved in an exocyclic double bond, as illustrated in (*Scheme 1*).

The preparation and the properties of radialenes have been very nicely reviewed recently.[1] The synthetic aspects were discussed according to the sizes of the central rings of the radialene compounds. The present review, as an alternate viewpoint, is aimed at examining more specifically the methodologies involved throughout these syntheses, and at pointing out general strategies if any, to the preparation of a desired radialene.

It is divided into two main parts: (i) the reactions leading to the construction of the radialenes inner rings, and (ii) the ultimate formations of the radial double bonds that result in the radialene structures from available rings. For both parts we will emphasize the more broadly applicable and high yield reactions.

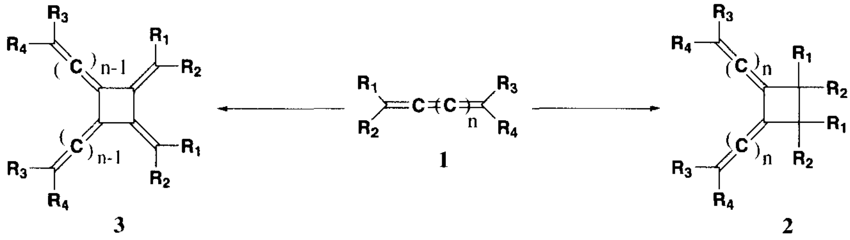
I. CONSTRUCTION OF THE RADIALENES INNER RINGS

Several radialenes have been elegantly prepared using processes involving the construction of the central rings with the simultaneous introduction of the exocyclic double bonds. These processes include: (i) cumulene cycloadditions and, (ii) carbenoid cyclooligomerizations.

1. Cumulene Cycloadditions

a. Thermal Reactions

The cyclodimerizations of compounds containing cumulated double bonds, such as cumulenes (**1**), might result either in the formation of cyclobutanes **2** or lead to (4)radialenes **3** depending on the double bonds which react (*Scheme 2*).



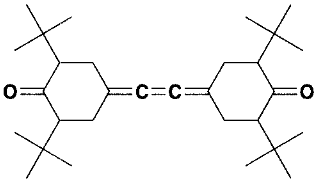
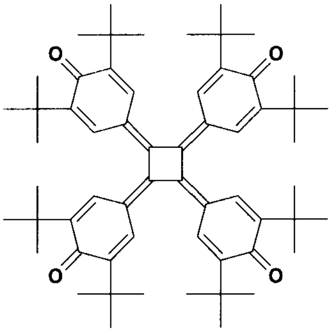
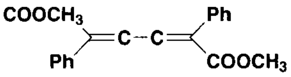
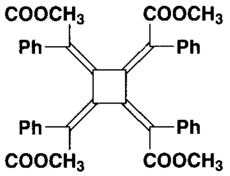
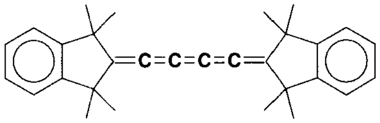
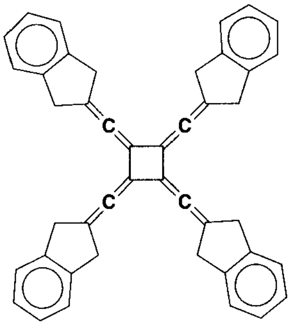
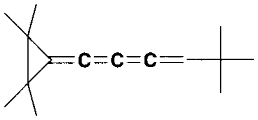
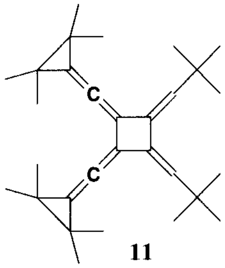
Scheme 2

Consequently, the question of the cycloaddition regiochemistry of these processes must first be addressed. Moreover, the stereochemistry of the resulting cyclodimers arising from unsymmetrical cumulenes must also be clarified.

Several examples of thermal dimerizations of cumulenes to (4)radialenes have been described (Table 1). However, the structure determinations in these series, when only the IR and NMR data were available, proved to be unreliable in some cases. As a consequence, several structures claimed to be radialenes were later corrected on the basis of single-crystal X-ray structure determinations (Table 2). Therefore, early reported cumulenes cyclodimers assumed to be radialenes[6,8,10,11] should be considered with caution in the absence of X-ray structure data.

The mechanism of this dimerization process, whether concerted or involving diradicals, and the factors controlling these cyclodimerizations has not been determined. However, in one very interesting study involving the solid-state cyclodimerizations of the carboxylic-acid butatriene diesters **6**[3] (Table 1), the precise stereochemistry of the resulting (4)radialene **7** has been determined, and the high stereospecificity of this solid state, crystal-lattice controlled dimerization, was attributed to a possible diradical mechanism.[12a] Such stereospecific cyclodimerizations have recently been attributed to the higher thermodynamic stability of the corresponding isomer.[12b]

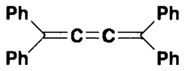
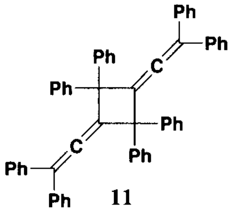
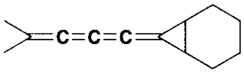
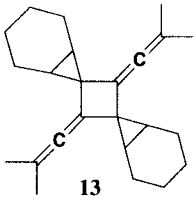
Table 1. Cumulene Cyclodimerization to [4]-radialenes

cumulenes	[4]-radialene	reaction conditions (% yield)	ref.[a]
 **4**	 **5**	cyclohexane reflux (25%)	(1)
 **6**	 **7**	100°C (solid) (75%)	(2)
 **8**	 **9**	270 - 275°C (solid) (51%)	(3)
 **10**	 **11**	RT (solid) (100%)	(4)

---

a) reference to a single crystal X-ray analysis

Table 2. Examples of Radialenes from Cumulenes Cyclodimers

Starting cumulene	Resulting cyclodimer[a]	Reaction condition (yield)	Ref
 **10**	 **11**	solid state photodimer	(6,7)
 **12**	 **13**	RT (65%)	(8,9)

a) reference to X-ray analysis

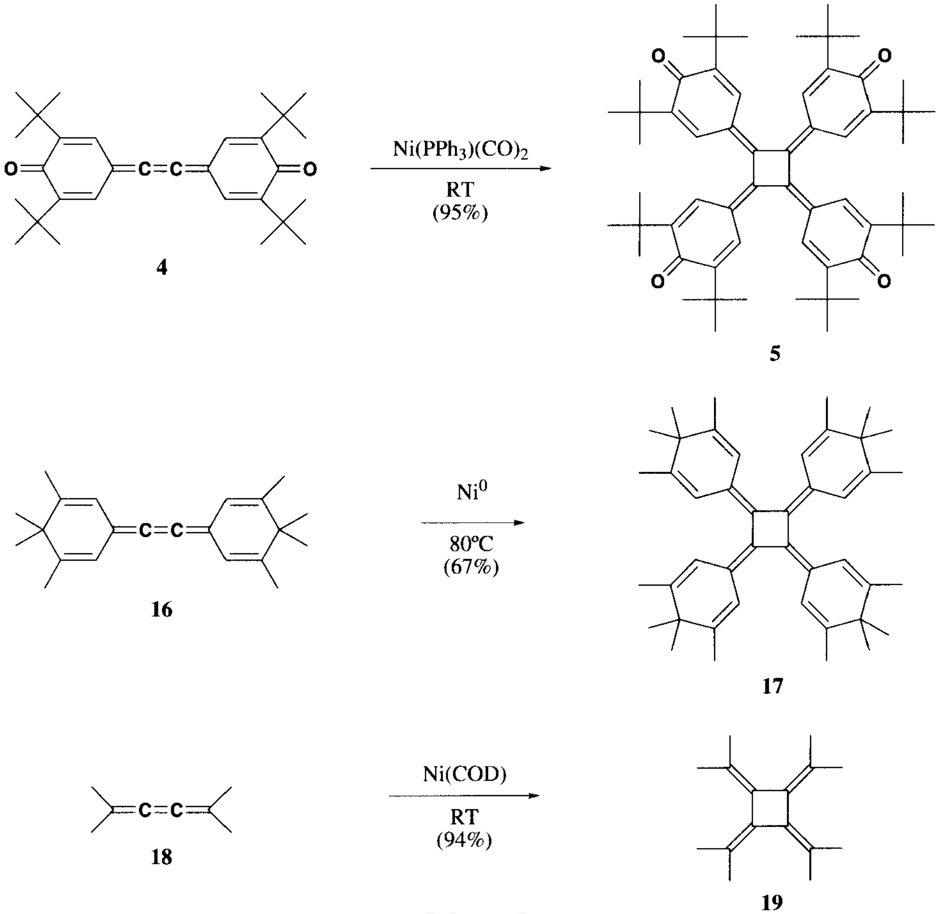
b. Metal Catalyzed Cyclooligomerizations

i. (3)Cumulenes

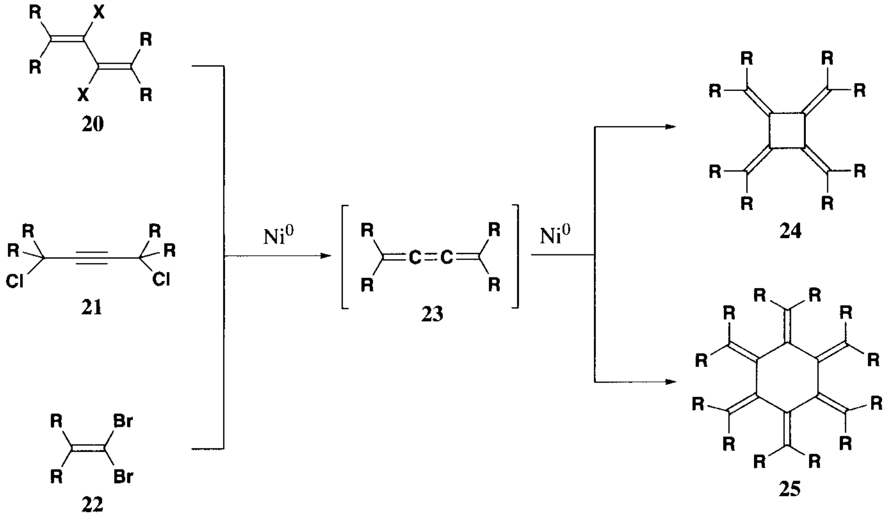
As an alternative to the above thermal (2+2) dimerizations, West and his co-workers initiated very interesting transition-metal catalyzed dimerizations of (3)cumulenes.[13] This approach, based on the use of catalysts known to promote the dimerization of alkenes and allenes,[14] greatly enlarged the access to (4)radialenes. Thus, the use of $Ni(PPh_3)_2(CO)_2$ in the dimerization of **4** gave the (4)radialene **5** in 95% yield (*Scheme* 3), while the thermal cyclodimer had previously been obtained in a much lower yield (25%) (Table 1). Other (4)radialenes **17**[15] and **19**[16] were subsequently prepared as well by this procedure in satisfactory yields.

Later, the scope of these catalyzed processes was broadly extended, by Iyoda and co-workers,[17] allowing the access to higher radialenes. Thus, based on the known reduction of *vic*-dihalides to olefins, these authors first generated (3)cumulenes from 2,3-dihalo-1,3-butatrienes **20** using Ni(0) complexes. The same result was also obtained from 1,4-dichloro-2-butynes **21** and from the vinylic *gem*-dibromo compounds **22** (*Scheme 4*). The resulting (3)cumulenes were subsequently cyclodimerized to (4)radialenes **24**, or cyclotrimerized to (6)radialenes **25**. The structures of these isolated radialenes were strongly dependent on the reaction conditions.

The main advantages of this strategy are the possibilities of: (i) a one-pot construction of the radialene framework from these precursors, (ii) a catalytic process by the use of the Ni(II) complexes combined with a reducing agent (zinc), (iii) the preparations of either (4) or (6)radialenes depending on the reaction conditions.



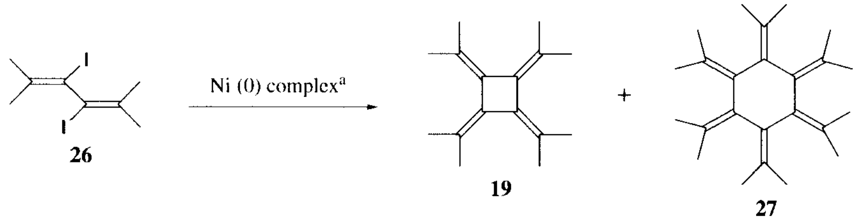
Scheme 3



Scheme 4

Thus, starting from the diodo compound **26**, either octamethyl(4)radialene **19** (48%) or dodecamethyl(6)radialene **27** (50%) have been obtained selectively, depending on the solvent (benzene or DMF) (Table 3).[17b]

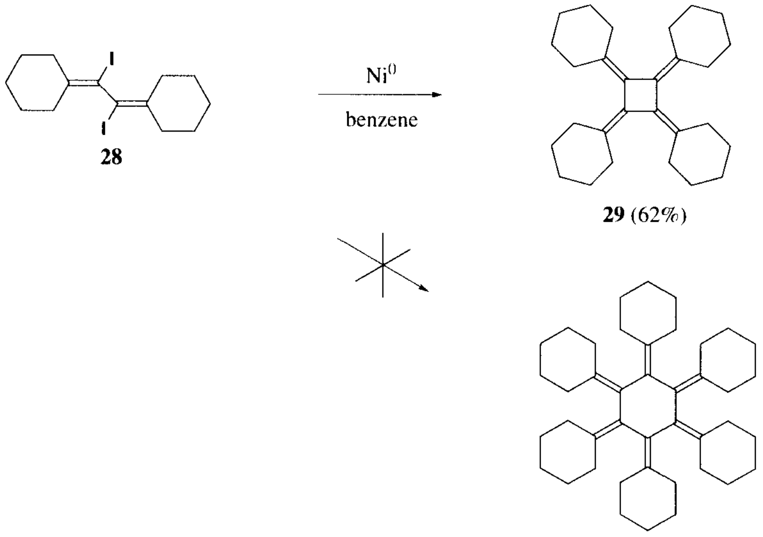
Table 3. Preparation of (4) and (6)Radialenes as a Function of the Reaction Conditions



Substrate[b]	Solvent	Product (yield %)
26	Benzene	**19** (48)
26	DMF	**19** (1) **27** (50)

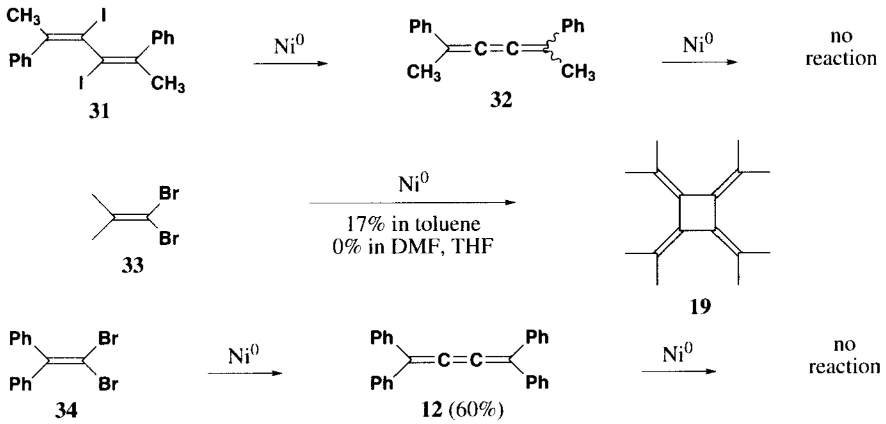
a) $NiBr_2(PPh_3)_2$, PPh_3, Zn (1:2:10), b) substrate over Ni ratio (1:2)

Similarly, the butadiene **28** afforded the corresponding (4)radialene **29** in benzene (62%). But trimerization to the (6)radialene **30** did not occur either in THF or in DMF (*Scheme 5*).



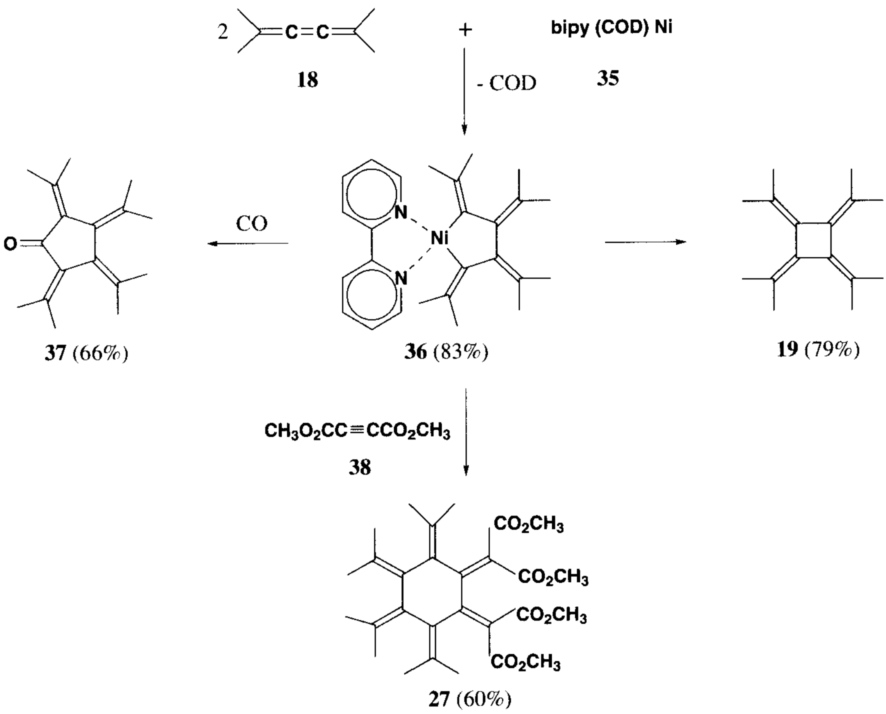
Scheme 5 **30**

However, there appear to be several limitations to this interesting process.[17b] For example, while the reaction of 3,4-diiodo-2,5-diphenyl-2,4-hexadiene **31** gave a poor yield of the (Z) and (E)-butatrienes **32**, 1,1-dibromo-2,2-diphenyl ethylene (**34**) produced the tetraphenylbutatriene **12** in a high yield (60%). In contrast, both **32** and **12** were recovered unchanged in the attempted cyclooligomerizations and did not react to give radialenes. It appeared that such highly crowded, phenyl substituted butatrienes are unreactive under these conditions (*Scheme 6*) in contrast to less hindered ones such as **33** which yields the (4)radialene **19**.



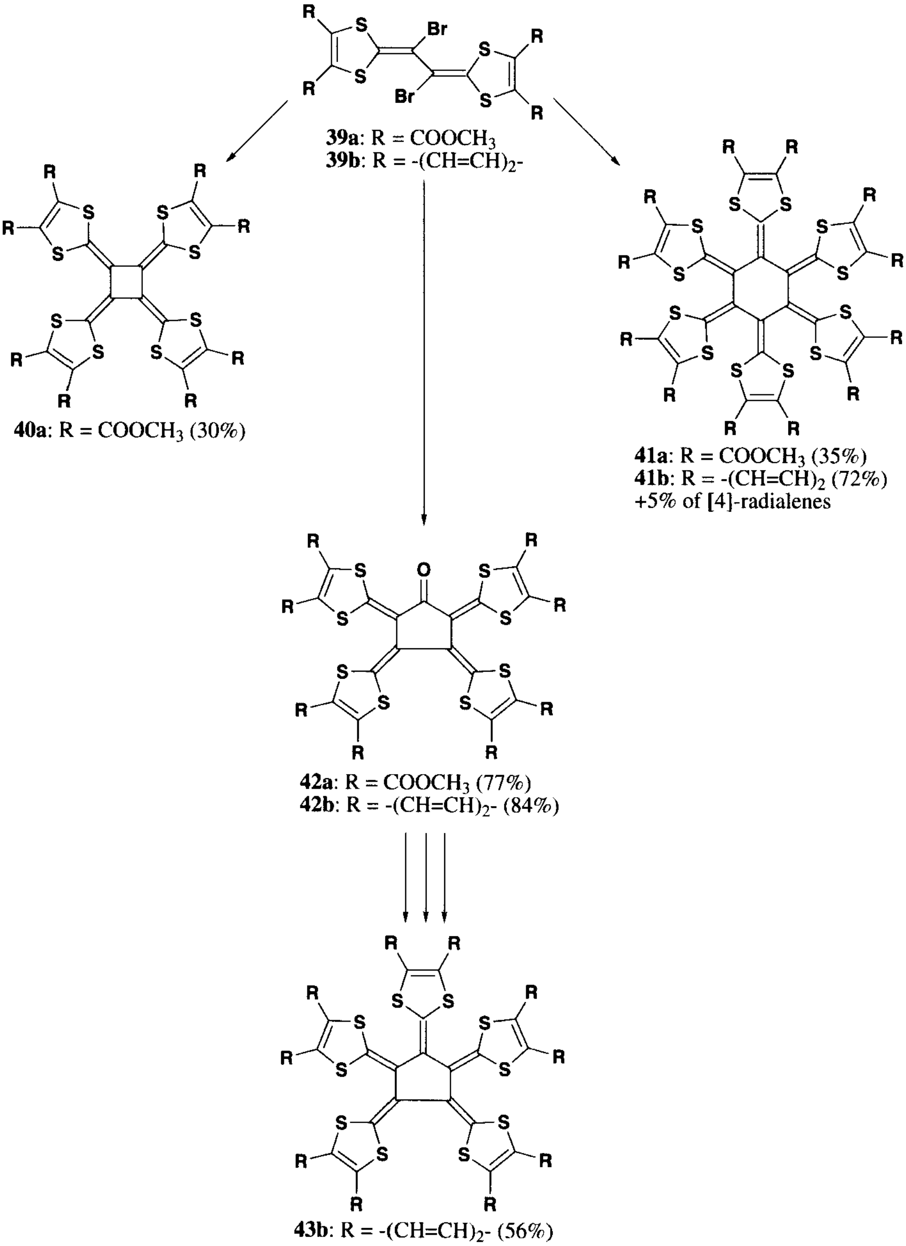
Scheme 6

The mechanism of these reactions involve the oxidative addition of two (3)cumulenes molecules to the Ni(0) catalyst resulting in carbon-carbon coupling. Thus, **18** reacts with **35** yielding the nickel cyclopentane derivative **36**, after the displacement of 1,5-cyclooctadiene (COD). Interestingly, compound **36** has been isolated as a single crystal and fully characterized by X-ray diffraction (*Scheme 7*).[16]



Scheme 7

In turn, this complex yielded the (4)radialene **19** by a reducive elimination. Alternatively, the reaction with methyl acetylenedicarboxylate **38** led also to the compound **27**. This process was also carried out under a CO atmosphere, and very interestingly, a CO insertion reaction led to the cyclopentanone derivative **37**, opening the way to the first synthesis of a (5)radialene.[16]



39a: R = $COOCH_3$
39b: R = $-(CH=CH)_2-$

40a: R = $COOCH_3$ (30%)

41a: R = $COOCH_3$ (35%)
41b: R = $-(CH=CH)_2$ (72%)
+5% of [4]-radialenes

42a: R = $COOCH_3$ (77%)
42b: R = $-(CH=CH)_2-$ (84%)

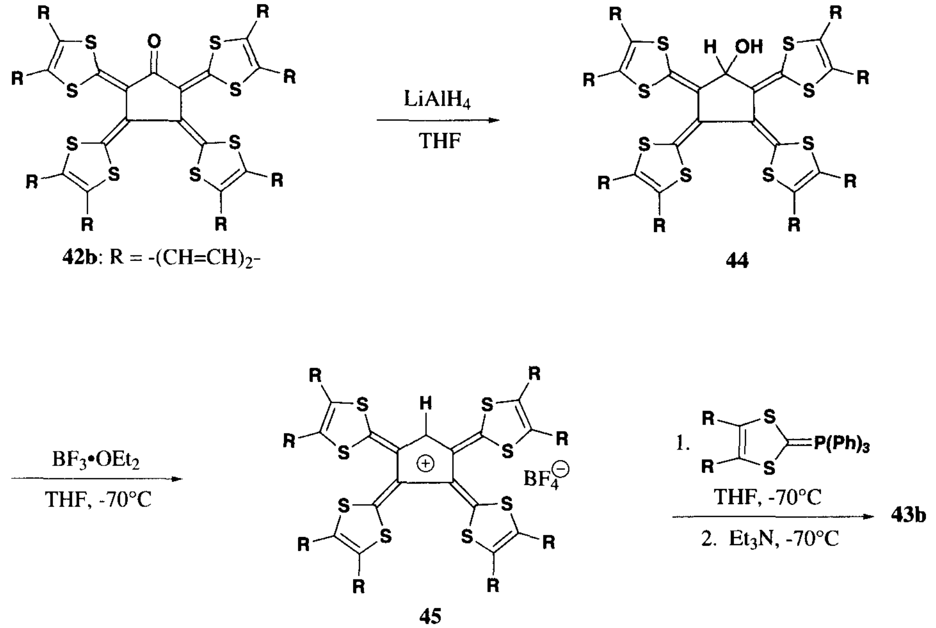
43b: R = $-(CH=CH)_2-$ (56%)

Scheme 8

The use of this methodology has allowed the preparation of an interesting series of 1,3-

dithiol substituted radialenes,[18-21] with modest (30% for the (4)radialene **40a**) to fair yields (72% for the (6)radialene **41b**) (*Scheme 8*).

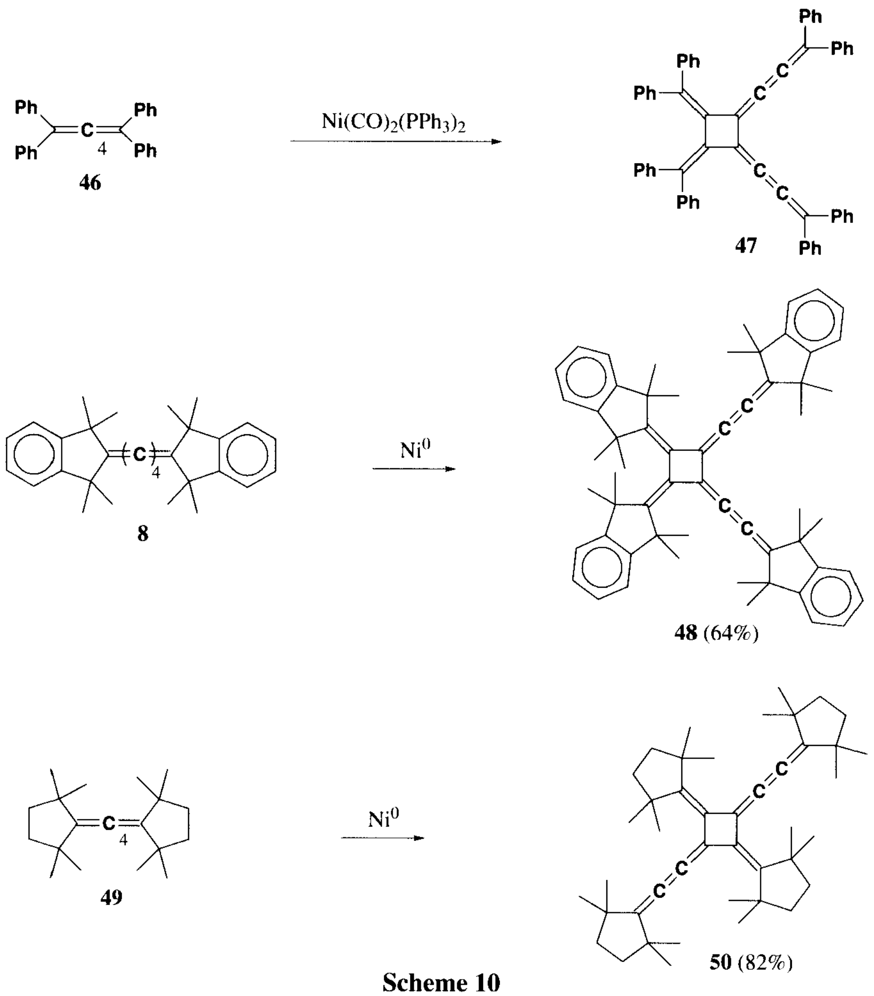
Moreover, the Ni(0)-catalyzed CO insertion reaction led to a very efficient synthesis of the cyclopentanone derivative **42b**. The corresponding (5)radialene **43b** was prepared therefrom by a sequence of reactions involving the isolation of the remarkably stable salt **45**[21](*Scheme 9*), with an acceptable overall yield (56%).



Scheme 9

ii. Higher Cumulenes

Several nickel-catalyzed dimerizations of (5)cumulenes have also been carried out (*Scheme 10*). However, in contrast to the unreactive (3)cumulenes **32** and **12** (*Scheme 6*) the tetraaryl substituted (5)cumulene **46** reacts smoothly with $Ni(CO)_2(PPh_3)_2$ to give the dimer **47**[22] (61%). Similarly, cumulenes **8** and **49** yield **48**[4] (64%) and **50**[23] (82%) respectively, although lower reactivities of the latter towards $Ni(CO)_2(PPh_3)_2$ involved much longer reflux periods (24h) than previously (30 min. for **47**). It is also worth noting that the structure of the dimer obtained previously by the purely thermal reaction of compound **8** (Table 1) corresponds to the more symmetrical (4)radialene **9**;[4] this is in contrast to the present Ni-catalyzed product **48**. On the other hand, treatment of the heavily-substituted (5)cumulene **51** with the $Ni(CO)_2(PPh_3)_2$ catalyst gave the (5)radialenone **52** as the main product (74%) together with a small amount of **53**[23] (6%) (*Scheme 11*). The uncertainty in the structural determinations of compounds **48**, **50** and **53** (based on only spectroscopic data), does not exist for **47** (synthesized by an alternate independent procedure[22]) and **52** (characterized by an X-ray diffraction analysis[23]).



46

47

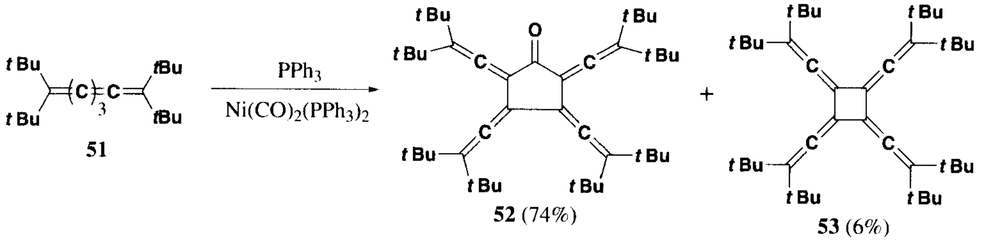
8

48 (64%)

49

50 (82%)

Scheme 10



51

52 (74%)

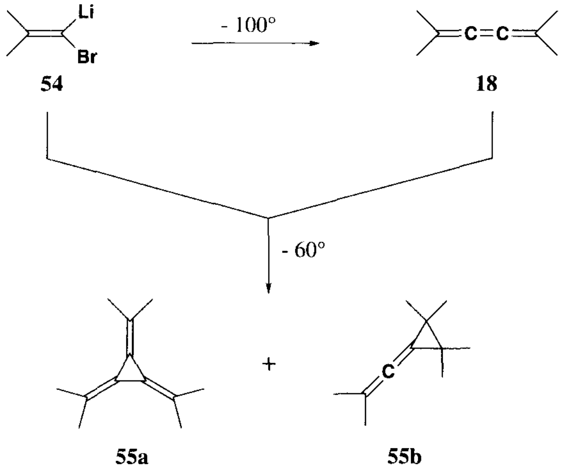
53 (6%)

Scheme 11

2. Carbenoid Cyclooligomerizations

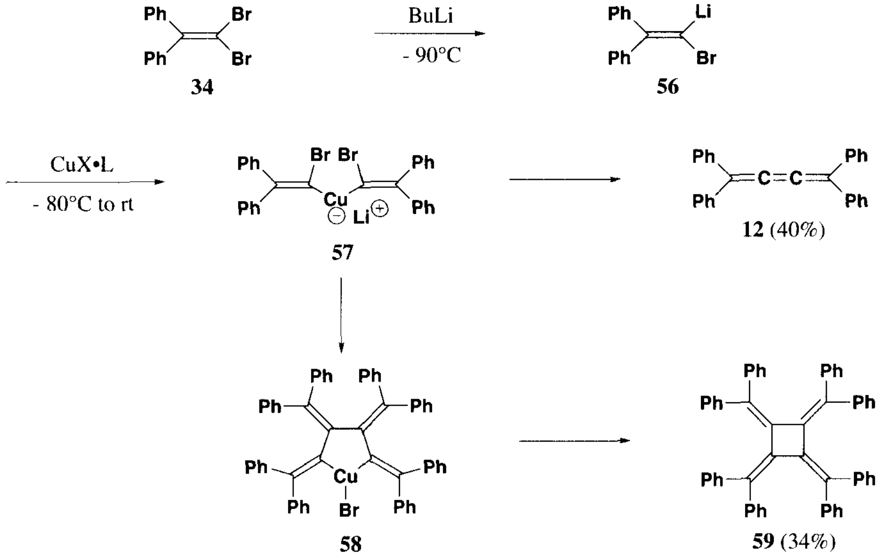
A very poor yield (2%) of compound **55** has been obtained, as early as 1965,[24a] by the reaction (at -60°) of a carbenoid species **54** (generated and subsequently dimerized at -100° in a one-pot procedure) with its dimer **18** (*Scheme 12*). Although the structure of this product was assigned to the

(3)radialene **55a**, this assignment is based only on spectroscopic data (proton NMR), and consequently the alternate possible isomer **55b** (unknown)[24c] may not be excluded.



Scheme 12

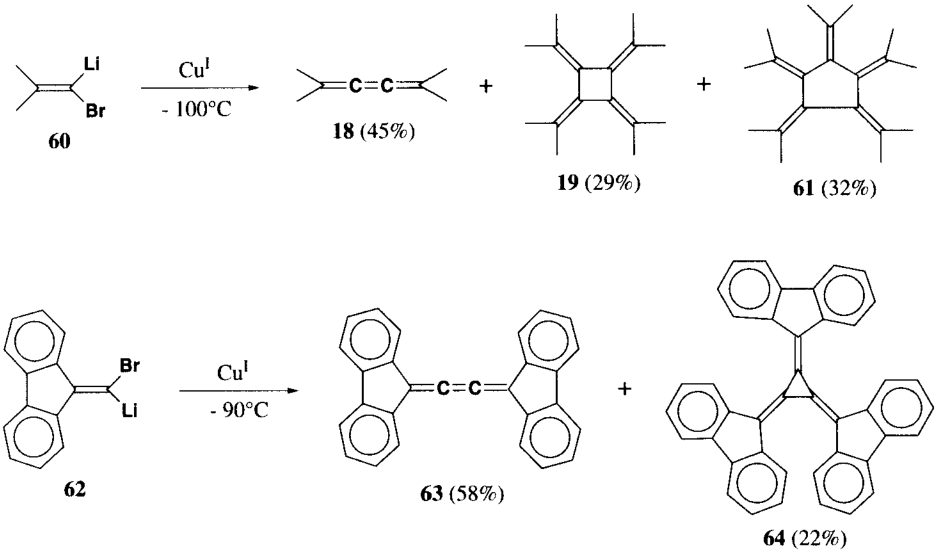
The reactivity of carbenoids towards the preparation of radialenes was later greatly improved by Iyoda and his co-workers who used the cuprate complexes derived from these species.[25-27] Thus, after the lithium carbenoid **56** was generated from 1,1-dibromo-2,2-diphenylethylene **34**, its subsequent treatment with 0.5 equiv. of CuI.PBu$_3$ gave octaphenyl(4)radialene **59** (34%), together with a considerable amount of the tetrabutadiene **12** (40%) (*Scheme 13*).[25]



Scheme 13

The formation of the radialene **59** involves the oligomerization of an *ate*-type complex **57** rather than a reaction with the butatriene as before (*Scheme 12*). Although the exact mechanism of the process was not established, the final step leading to **59** was assumed to involve reductive elimination of copper bromide from a metallacyclic intermediate **58**.[25]

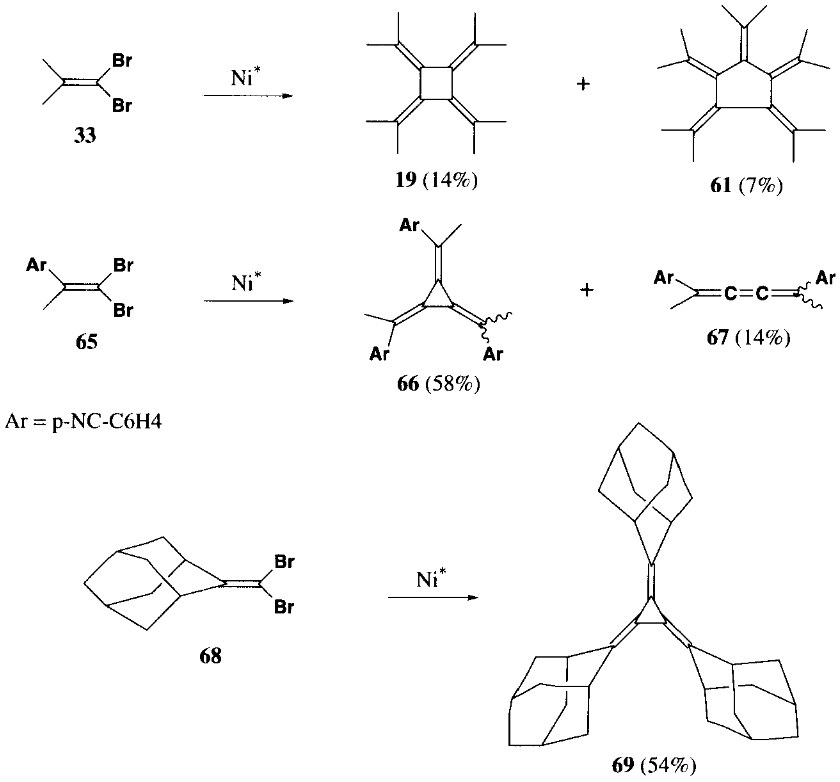
A similar procedure yields octamethyl(4)radialene **19** (23%), decamethyl(5)radialene **61** (32%),[26] as well as (3)radialene **64** (22%).[28] (*Scheme 14*). Steric factors were assumed to contribute to these oligomerization reactions, and to control the nature of the resulting radialenes [compare **56** (*Scheme 13*) to **62** (*Scheme 14*)]. However, unfortunately in all the cases investigated, the main reaction products are the corresponding undesired butatrienes [*i. e.* **18** and **63** (*Scheme 14*)].



Scheme 14

Another catalyst assumed to promote the formation of radialenes was also investigated by the same authors.[28] Thus, with activated metallic nickel[29] 2-methyl-1,1-dibromopropene **33** led to a mixture of the (4)radialene **19** and the (5)radialene **61** in respectively 14% and 7% yields[28] (*Scheme 15*). In contrast, the previous NiBr$_2$(PPh$_3$),PPh$_3$, Zn, Et$_4$NI system[17b] yields exclusively the (4)radialene **19** (17%) (*Scheme 3*).

The results of the metallic nickel catalyzed carbenoid reactions are reminiscent of the Cu(I)-catalyzed cyclooligomerization of the carbenoid **60** which also led to a mixture of (4) and (5)radialenes (*Scheme 14*). Therefore in some way, the reactivity of the nickel carbenoids, assumed to be derived from the *gem*-dibromoethylene **33**, may be analogous to that of cuprates involved in the carbenoid cyclooligomerization reactions. This fact probably also excludes the alternate possibility of an activated nickel catalyzed addition reaction of carbenes to (3)cumulenes, as previously supposed (See *Scheme 12*).



Scheme 15

On the other hand (*Scheme 15*), 2-aryl-1,1-dibromopropene **65** yields a mixture of isomeric (3)radialenes **66** (58%) along with the butatrienes **67** (14%) with activated nickel.[28] Recently, various catalysts were investigated for the preparation of radialene **69** and only this activated nickel catalyst was found to give a reasonable yield (54%) of **69**, starting from the dibromoolefin **68**.[30]

II. SYNTHESES OF THE EXOCYCLIC DOUBLE BONDS STARTING FROM AVAILABLE INNER RING SYSTEMS

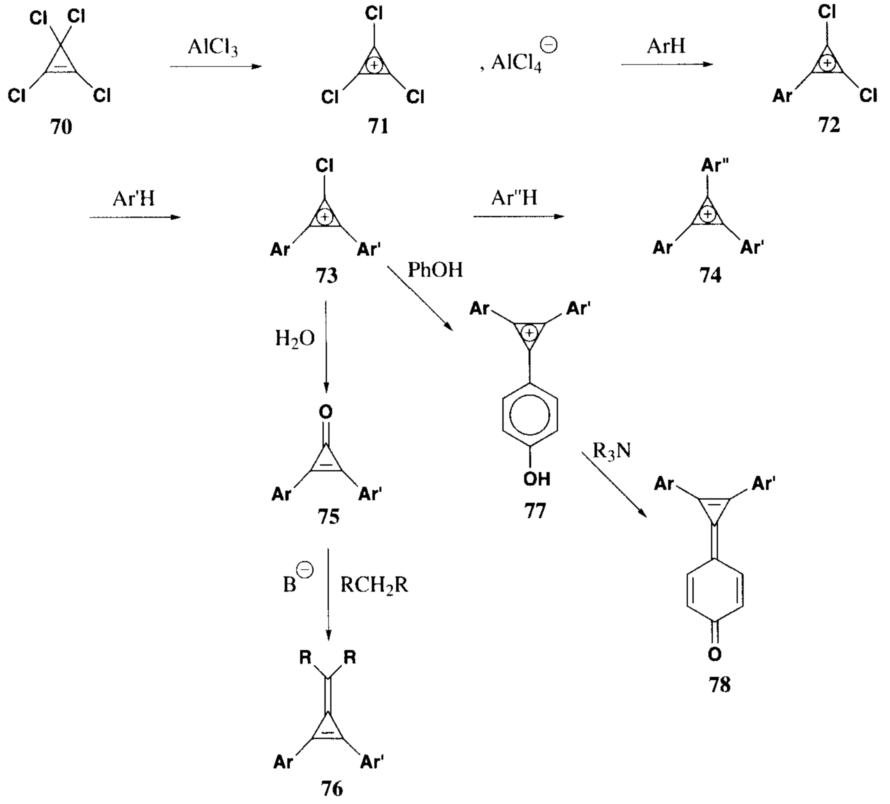
The literature results are divided, for convenience, into two sections involving: first the construction of substituted inner-ring carbon skeletons followed by introduction of the radial double bonds from these substituted intermediates.

1. Preparation of the Required Skeleton

a. By Reaction of the Inner-ring Carbons as Electrophiles

i. Halogen compounds

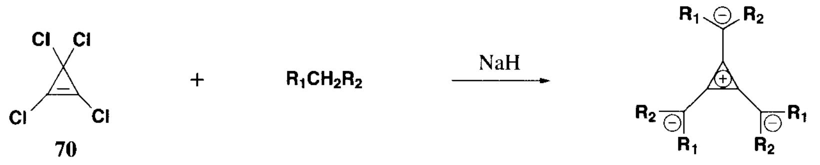
The stabilized cyclopropenium cation is an archetype of the non-benzenoid aromatic compounds. Although some cyclopropenium cations had been previously reported,[31] the stable and synthetically useful tetrachloroaluminate salt of tetrachlorocyclopropenium **70** was prepared for the first time in 1964 by West and his co-workers (*Scheme 16*).[32] This salt exhibits a highly



Scheme 16

interesting and versatile reactivity. Thus, depending mainly on the nucleophilicity of the reagents, Friedel-Crafts type alkylations lead to either mono, di, or triaryl substituted cyclopropenium compounds **72**, **73**, or **74**. It is possible to carry out these substitutions either stepwise, or at once to the more substituted stage. Consequently, multi-arylated compounds containing the same substituents, or alternatively derivatives bearing various aryl groups different from one another may be prepared as well. In addition, it is possible to hydrolyze the diaryl chlorocyclopropenium salts, *e. g.* **73**, to the diaryl cyclopropenone **75**, a precursor of **76**, an interesting intermediate (*vide infra*). The interesting product **77** is obtained by a reaction of the same salt **73** with phenols. The phenolic protons are then easily removed from the resulting *p*-hydroxyaryl substituted cyclopropenium salts **77**, converting them into the quinocyclopropene **78**.[32]

Fukunaga[33a] accomplished the direct nucleophilic substitution of **70**, thus bypassing the trichloropropenium salt **71** (*Scheme 17*), and synthesized the salts **79a,b** fully substituted by cyano or ester groups. Later Oda *et al.*[33d] showed that an important factor for the success of this reaction involve the pKa of the nucleophile: the higher the pKa the better the yield of the reaction. The higher homologue 3,3,4,4-tetrafluorocyclobutene **80** leads, by the same procedure, to the octacyano

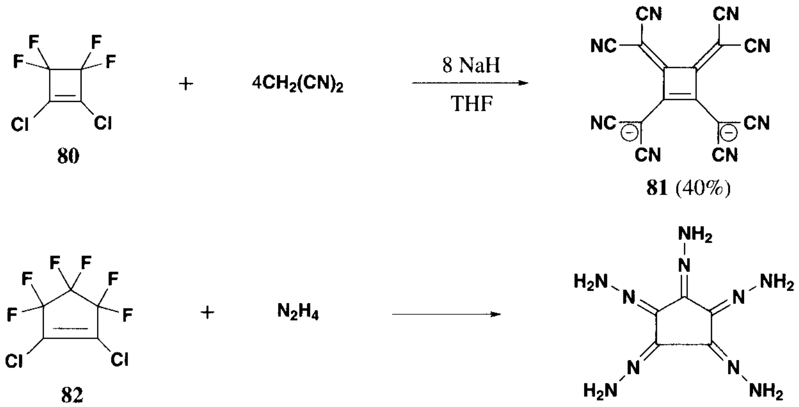


70

79a : $R_1 = R_2 = CN$
79b : $R_1 = R_2 = COOEt$

Scheme 17

tetramethylene cyclobutane dianion salt **81** (40%).[34] Remarkably, reactions of the available compound **82**, reported to yield the hydrazone **83**[35] (a derivative of the long known[36] pentaketone), have not been investigated (*Scheme 18*).



80

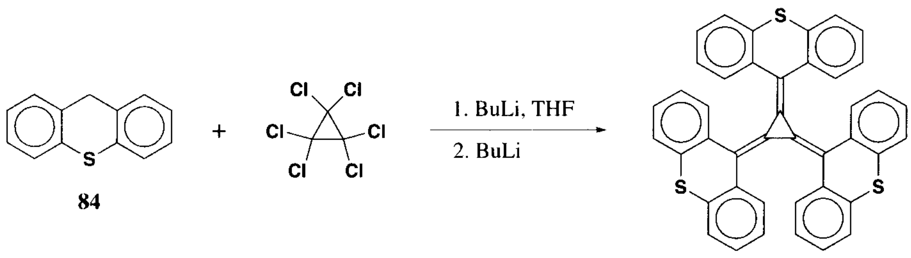
81 (40%)

82

83

Scheme 18

An interesting albeit isolated study involved an alternate nucleophilic substitution of the saturated hexachlorocyclopropane which gave a moderate yield of the (3)radialene **85** when reacted with the anion derived from thioxanthene **84**[37] (*Scheme 19*).

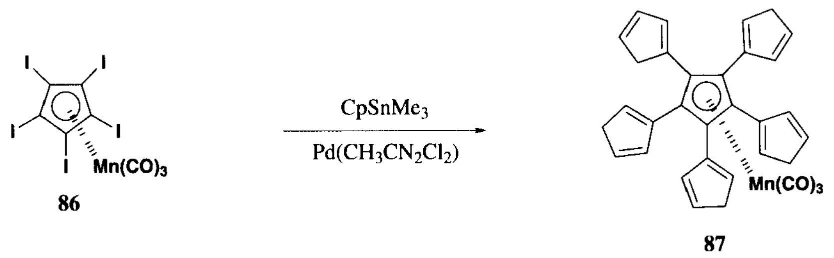


84

85 (25%)

Scheme 19

More recently, an elegant one-step procedure involving Pd-catalyzed cyclopentadienylations of tricarbonyl (μ5-pentaiodocyclopentadienyl)manganese **86** by trimethylcyclopentadienylstanane, and resulting in the penta substituted cyclopentadienyl complex **87** (as a mixture of the 1,3 and 1,4 tautomers) (*Scheme 20*) has been reported.[38]



Scheme 20

ii. Ketones

The widely studied oxocarbons **86-89** and pseudo-oxocarbon compounds (where oxygens are replaced by other elements) (Chart 2),[39] have been considered as possible precursors

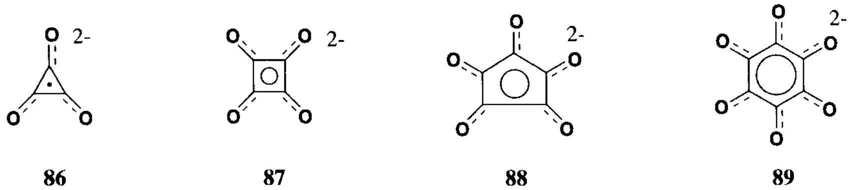
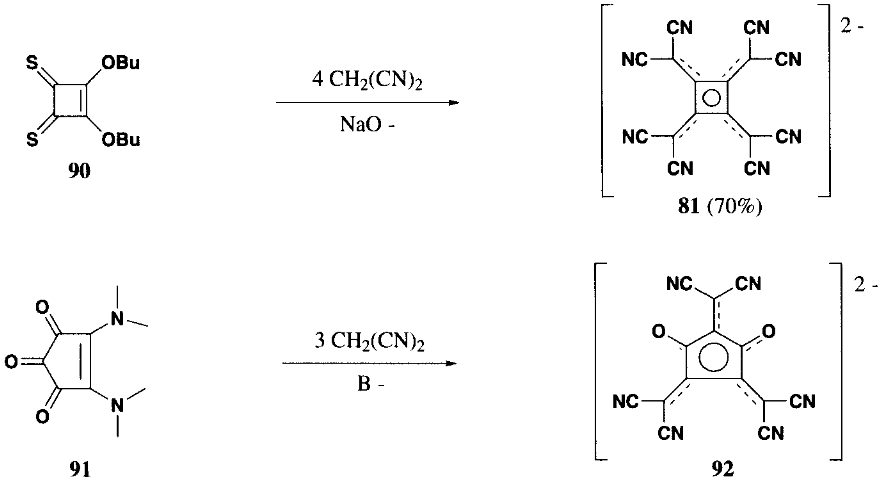


Chart 2

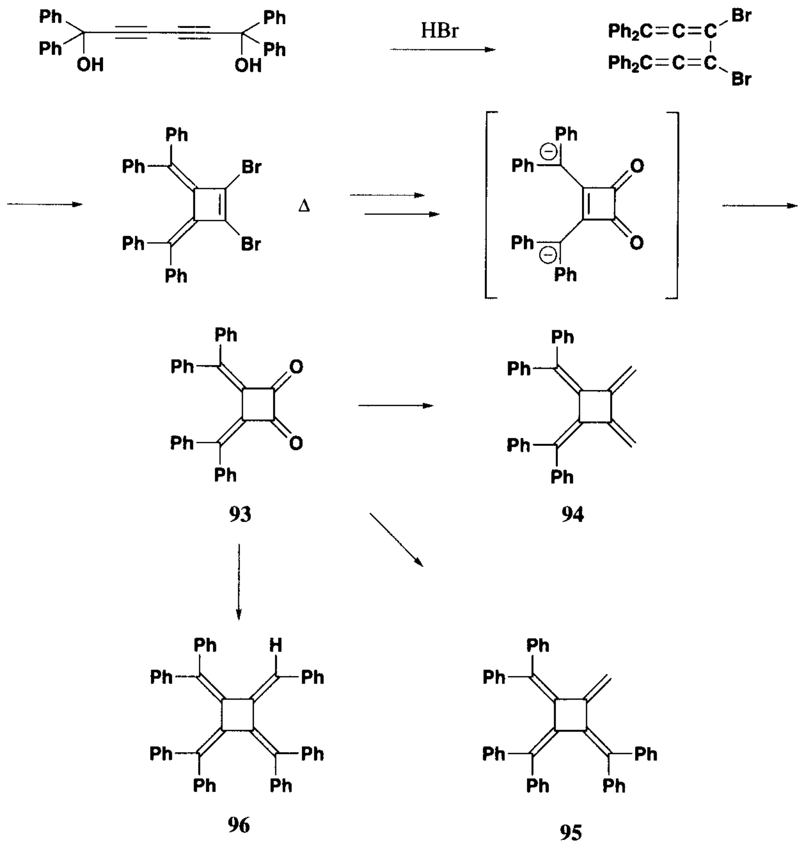
for the syntheses of radialenes.[40] These "aromatic" dianions might be considered as the equivalents of some of the previous halogen compounds (*i. e.* **70**, **80**, **82**). Thus, reaction of the pseudo oxocarbon **90** with the carbanion from malononitrile gives the dianion **81** (70%) (*Scheme 21*);[41]



Scheme 21

the latter salt had also been prepared from the halogen derivative **80** (*Scheme 17*). However, many studies in this field involved only the malononitrile nucleophile and the published attempts to prepare higher homologues of the compound **81** led at best to the trisubstituted condensation products, *i. e.* **92** from the pseudo oxocarbon **91**.[42]

On the other hand, the possibility of synthesizing (4)radialenes (*i. e.* **94**, **95**, and **96**) from *bis* (alkylidene)cyclobutadienone **93** has been demonstrated by a simple and versatile reaction sequence[43] (*Scheme 22*), based on the expected ketone reactivities. However, surprisingly the latter procedure was not investigated since the original publication; thus it is possible that the previous oxo(pseudo)carbon intermediates (*Scheme 21*) are worth some additional efforts.



Scheme 22

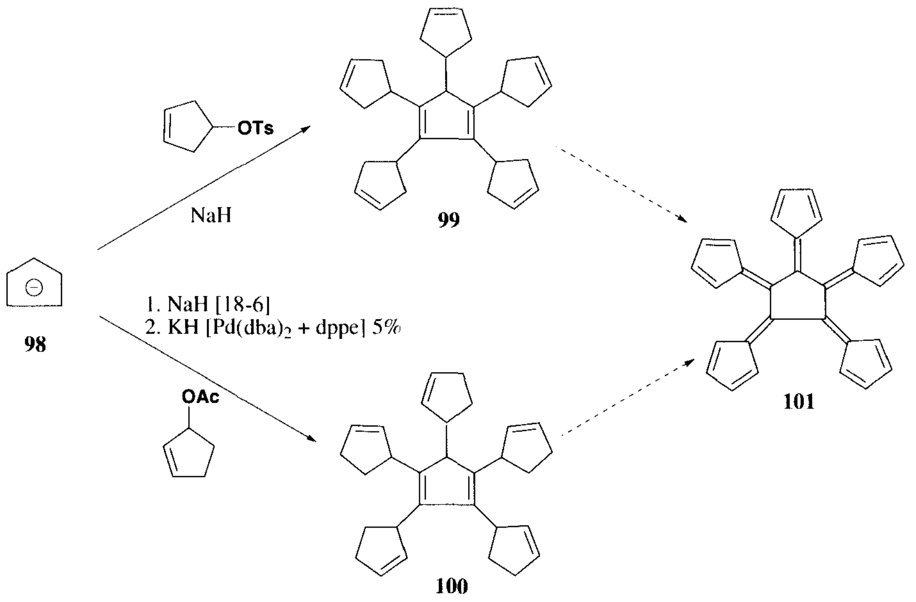
b. By Reaction of the Inner-ring Carbons as Nucleophiles

In contrast to the previous reactions involving the inner-ring carbons as electrophiles, the inner-ring carbons reactivity might also be considered nucleophilic, as this is the case for the cyclopentadienyl anion **98**. In fact, polyalkylations of the latter are well documented.[44] Thus, it is


97


98

possible to prepare precursors to the penta-radialene **101** by one-pot procedure, *i. e.* **99** by simple nucleophilic reactions, or **100** by allylic polyalkylations catalyzed by Pd(O) (*Scheme 23*).[45]



Scheme 23

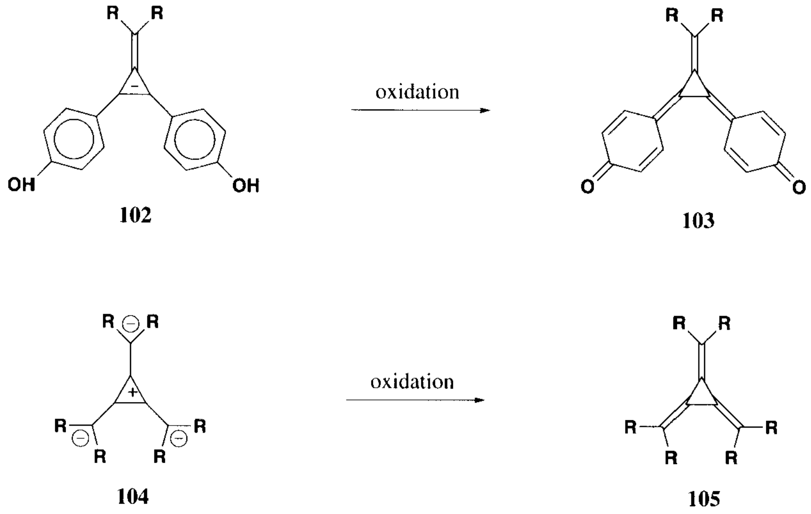
2. Introduction of the Radial Double Bonds

The exocyclic double bonds of the radialenes are formed in several examples along with the construction of the carbon skeleton [see **85** (*Scheme 19*) or **95** (*Scheme 22*)]. However, the formation of these double bonds might also involve specific difficulties that prevent the achievement of the projected synthesis (see **87**,[38] *Scheme 20*). For these last steps in the syntheses of radialenes, two main processes have been used to introduce the required unsaturations, namely oxidation elimination. These two processes are now considered.

a. Oxidation

A large series of (3)radialene[46,33] were successfully prepared by the chemical oxidation of phenolic-type compounds such as **102** or anionic salts such as **104** (*Scheme 24*). Some typical examples are summarized in the (Table 4). The oxidation of salts **104** prepared by the method of Fukunaga[33] is a very useful method to prepare (3)radialenes. Thus, the radialenes **108**[33c] and **109**[33d] not synthesized by the cyclooligomerisation procedure are now prepared according to the Fukunaga method.

The higher homologue octacyano tetramethylenecyclobutane dianion salt **81** (*Scheme 17*) exhibits only a single reversible oxidation wave at +1.25V by cyclic voltammetry, corresponding to the dianion/radical anion couple.[34a] The radical anion/neutral couple wave apparently occurs at much higher potentials (above +2.1V). By contrast, the dianion **79a** (*Scheme 17*) exhibits two such waves at lower potential values. and was consequently oxidized electrochemically to the corresponding radialene.[33b]



Scheme 24

Thus, electrochemical oxidations have also been sometimes required to prepare radialenes. In fact, in the case of **112**[47] (*Scheme 25*) chemical oxidation of the precursor **110** (by oxygen) stops at the stage of the intermediate **111**, and the desired radialene **112** has only been obtained electrochemically

Table 4. Examples of Radialenes Obtained by Oxidation

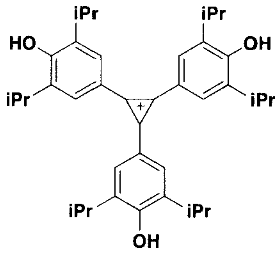
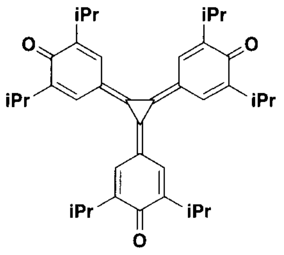
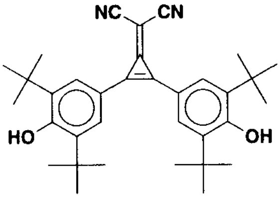
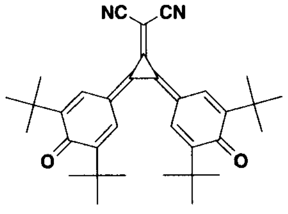
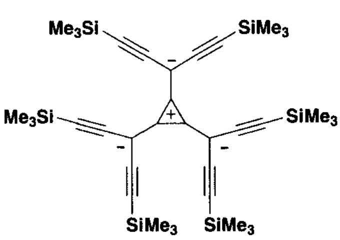
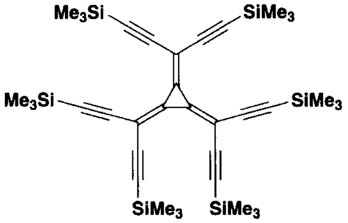
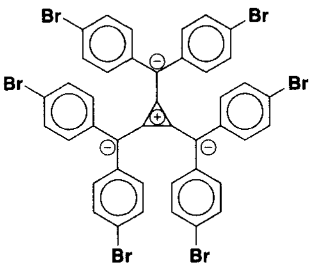
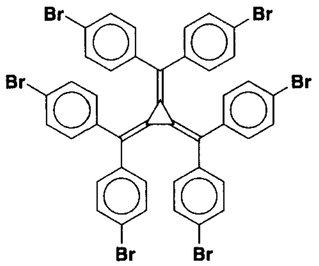
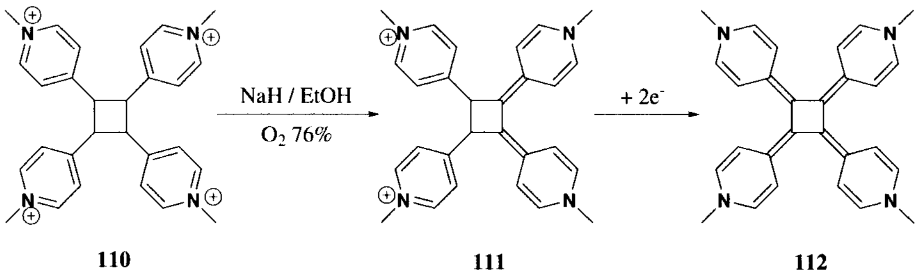
Precursor	Radialenes	Oxidant	Yield	Ref.
	 **106**	$K_3Fe(CN)_6$	88%	46c

Table 4. Continued...

Precursor	Radialenes	Oxidant	Yield	Ref.
	 **107**	K$_3$[Fe(CN)$_6$] H$_2$O / OH-		46m
	 **108**	DDQ	5%	33c
	 **109**	O_2	25-35%a	33d

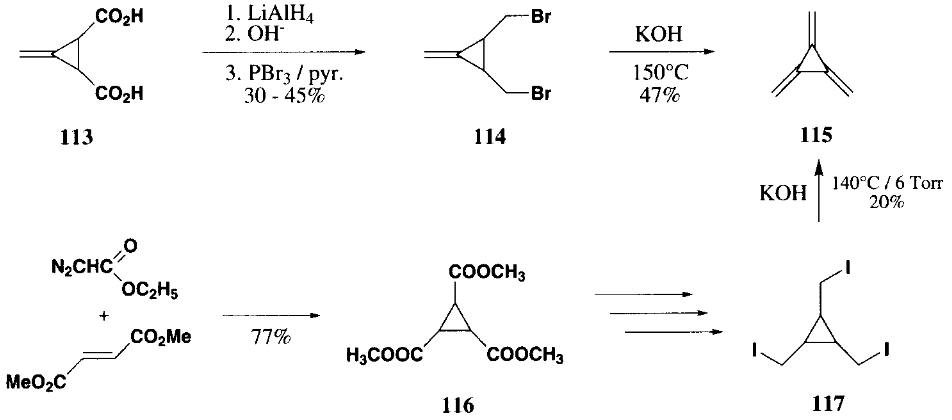
a) Overall yield for the synthesis of the radialene.



Scheme 25

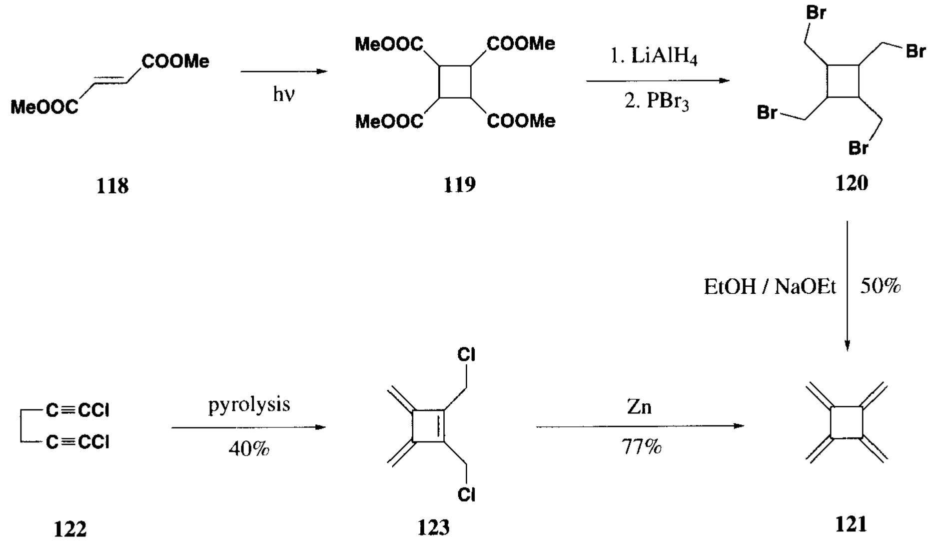
b. Elimination

As usual, several early syntheses of radialenes are based on the use of otherwise available substrates. Thus, the radialene **115**[48] was synthesized from the Feist acid[49] **113** according to the series of reactions (*Scheme 26*) involving dehydro-halogenations in basic medium of the dibromo compound **114**. A similar reaction[50] from the iodo derivative **117**, and the corresponding Hoffman type elimination reactions were also investigated,[50] the yields of the elimination steps for the latter reactions are lower.



Scheme 26

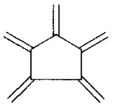
The (4)radialene **121** was first obtained by a similar process (Scheme 27) *by dehydro*halogenation of the tetrabromo derivative **120**.[51] The process was improved subsequently using the



Scheme 27

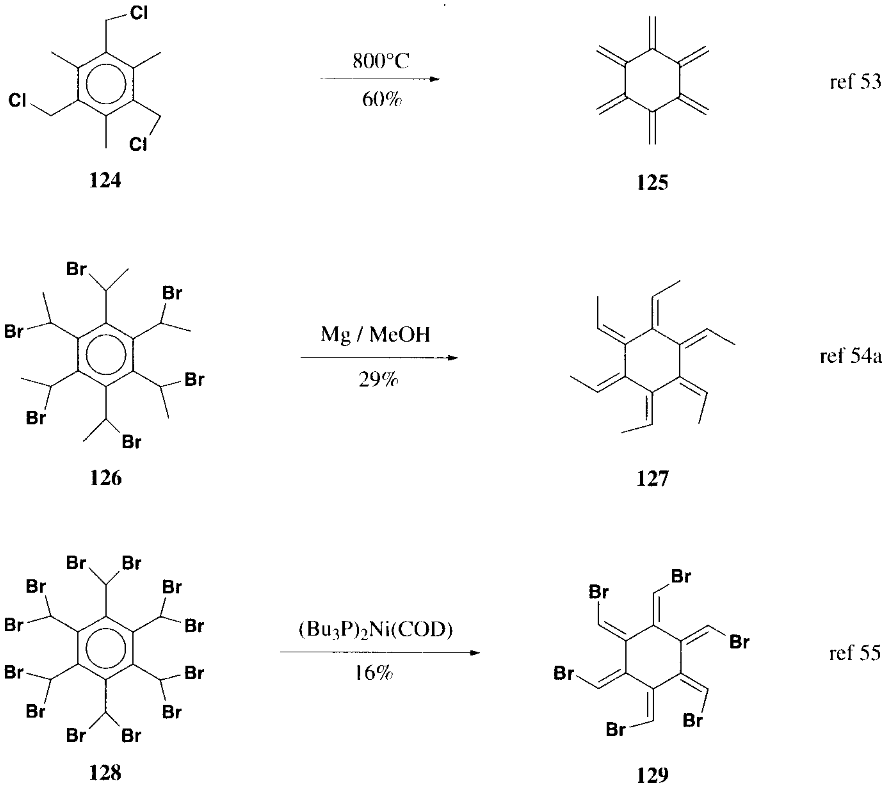
dichloro compound **123** according to the procedure of Hopf and coworkers.[52] Similarly to the (3)radialene series, the Hoffman type eliminations give the radialene **121** with much lower yields.[51a,b]

Several (6)radialenes[53,54,55] were also successfully prepared by dehydrohalogenation reactions, starting from halogenated hexamethyl, (or ethyl) benzene derivatives (*Scheme 28*).



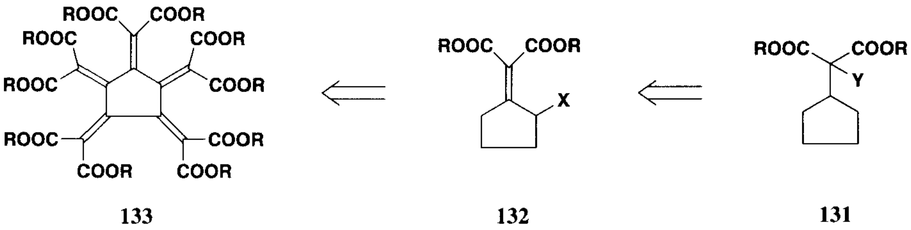
130

Chart 4



Scheme 28

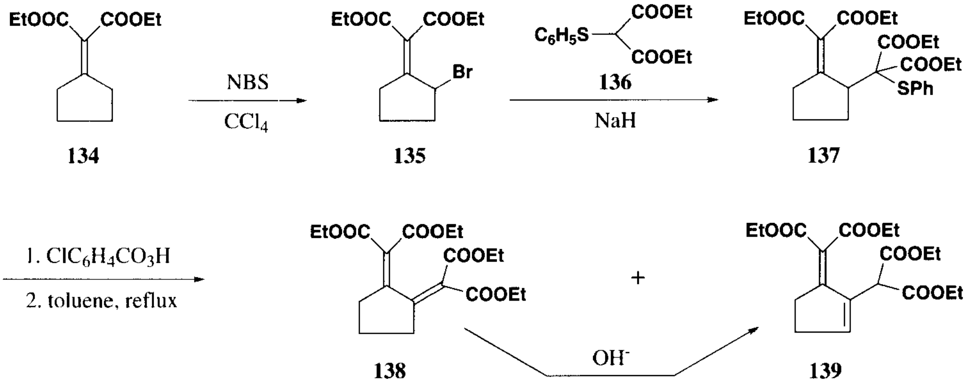
It is worth noting that (5)radialene **130** (Chart 4) has not yet been synthesized; apart from the problems related to its instability, one reason for this might be that the corresponding starting substrates are indeed not easily available, as was the case for the previous (3), (4), and (6)radialenes series. Therefore, we decided to investigate an alternate approach to this problem, by successive introductions around a cyclopentane ring of radial groups containing easily eliminated leaving groups (*i. e.* Y = Br in **131**) (*Scheme 29*).[56]



R = C_2H_5

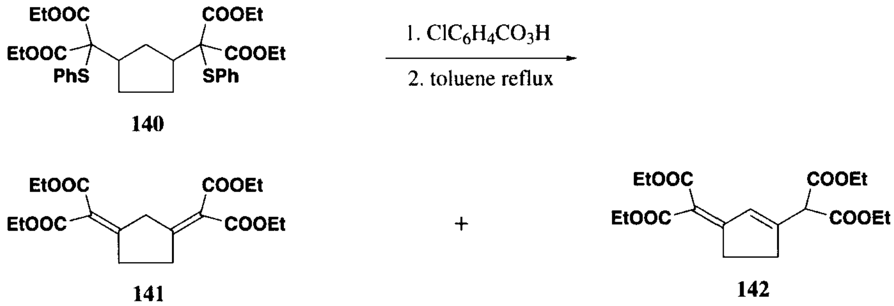
Scheme 29

The bromo allylic compound **135** prepared from the alkene **134** was reacted with the malonic phenylthioester **136** yielding the compound **137** (*Scheme 30*). Oxidation of **137** with *m*-chloroperbenzoic acid followed by mild heating led to a mixture containing the desired compound **138** and the endocyclic isomer **139** (40/60 composition). We were unable to avoid the formation of this undesired isomer **139** by any subsequent modifications of this procedure for the sulfoxide group elimination reaction. Moreover, we find that base-catalyzed processes efficiently isomerize the reaction mixtures containing **138** to the more stable regioisomer **139**.



Scheme 30

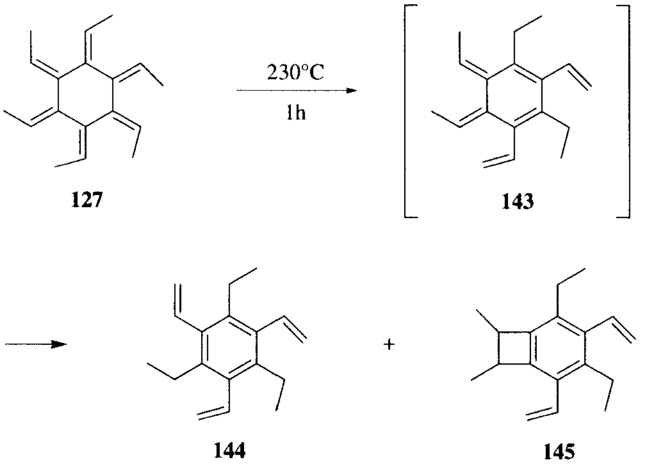
This unexpected result prompted us to investigate a similar double-bond formation process, but in a 1,3 regiochemistry on the cyclopentane ring. Therefore the compound **140** was also prepared. Similarly, this compound led to a mixture containing **141** and **142** in a 55/45 ratio (*Scheme 31*).



Scheme 31

In order to clarify these results and to anticipate the behavior of the higher tri- and tetrasubstituted homologues of this series, we have also computed the properties of these compounds using *ab initio* methods. The energy-minimized geometries of compounds **138**, **139** and **141**, **142** show that the driving forces for these double-bonds migrations are mediated by (i) the minimization of the steric constraints *within* and *between* the various substituents, and (ii) the conjugation enhancement within the carbon-carbon bond π-system.These calculations show also that the higher tri- and tetrasubstituted homologues will also exhibit the same endocyclic double-bond isomerisation.

These results raise the question of the possible general occurrence of such endocyclic double-bond isomerisation mechanisms to account for the limited number of present (5)radialenes syntheses. In fact, such an isomerisation process does not interfere with the formation of (3) and (4)radialenes, although a similar process is observed in the (6)radialene series. Heating the radialene **127** to 230°, results in the formation of the more stable regioisomer **144**, along with compound **145** from an electrocyclic ring-closure reaction (*Scheme 32*).[1b]



Scheme 32

CONCLUSION

The syntheses and the properties of the radialenes have been very actively investigated for nearly forty years. A number of (3), (4), (5) and (6)radialenes have been synthesized and isolated in good yields, by a variety of reactions, several of which were worked out specifically for this interesting series. Several of the available methods, such as the catalyzed cyclooligomerisations of Iyoda and coworkers,[17] the Friedel-Crafts reaction of the trichloropropenium salts,[32,47] or the Fukunaga[33] substitution reactions towards the synthesis of (3)radialene, allow a controlled preparation of the desired radialene. However, a general procedure for the synthesis of (5)radialene series is still lacking, and only two compounds have been synthesized so far in this interesting series. Efforts toward this particular objective and also towards any new and versatile procedures yielding radialenes will surely yield very interesting results in the future.

REFERENCES

1. (a) H. Hopf and G. Maas, *Angew. Chem. Int. Ed. Engl.*, **31**, 931 (1992); b) G. Maas and H. Hopf, *"The Synthesis of Dienes and Polyenes"*, Vol.1, p. 927, John Wiley & Sons Ltd, 1997.

2. (a) S. K. Kostler and R. West, *Chem. Commun.*, 1380, (1971); (b) S. K. Kostler and R. West, *J. Org. Chem.*, **40**, 2300 (1975).

3. F. W. Nader, C.-D. Wacker, H. Irngartinger, U. Huber-Patz, R. Jahn and H. Rodewald, *Angew. Chem. Int. Ed. Engl.*, **24**, 852 (1985).

4. M. Iyoda, M. Oda, Y. Kai, N. Kanehisa and N. Kasai, *Chemistry Lett.*, 2149 (1990).

5. (a) P. J. Stang and A. E. Learned, *Chem. Commun.*, 301, (**1988**); (b) A. E. Learned, A. M. Arif and P. J. Stang, *J. Org. Chem.*, **53**, 3122 (1988).

6. R. O. Uhler, H. Shechter and G. V. D. Thiers, *J. Am. Chem. Soc.*, **84**, 3397 (1962).

7. Z. Berkovitch-Yellin, M. Lahav and L. Leiserowitz, *ibid.*, **96**, 918 (1974).

8. P. J. Stang and T. E. Fisk, *ibid.*, **102**, 6813 (1980).

9. M. Kaftory, I. Agmon, M. Ladika and P. J. Stang, *ibid.*, **109**, 782 (1987) and references cited therein.

10. B. Heinrich and A. Roedig, *Angew. Chem. Inter. Ed. Engl.*, **7**, 375 (1968).

11. H.D. Harzler, *J. Am. Chem. Soc.* **88**, 3155 (1966).

12. (a) See also Fig 1, in ref. 7, as an interesting illustration of the required conformations of two reacting double bonds that would allow these dimerization processes to occur in the solid state; (b) H. Uno, N. Nibu, Y. Yamaoka and N. Mizobe, *Chemistry Lett.*, 105 (**1998**).

13. L. Hagelee, R. West, J. Calabrese and J. Norman, *J. Am. Chem. Soc.*, **101**, 4888 (1979).

14. G. Wilke, *Angew. Chem. Inter. Ed. Engl.*, **27**, 185 (1968).

15. B. Hagenbruch, K. Hesse, S. Hünig and G. Klug, *Ann.*, 256 (**1981**).

16. L. Stehling and G. Wilke, *Angew. Chem. Inter. Ed. Engl.*, **24**, 496 (1985).

17. (a) M. Iyoda, S. Tanaka, M. Nose and M. Oda, *Chem. Commun.*, 1058 (**1983**); (b) M. Iyoda, S. Tanaka, H. Otani, M. Nose, M. Oda, *J. Am. Chem. Soc.*,**110**, 8494 (1988).

18. T. Sugimoto, H. Awaji, Y. Misaki and Z.-I. Yoshida, *J. Am. Chem. Soc.*, **107**, 5792 (1985).

19. T. Sugimoto, Y. Misaki, T. Kajita and Z.-I. Yoshida, *ibid.*, **109**, 4106 (1987).

20. T. Sugimoto, Y. Misaki, Y. Arai, Y. Yamamoto and Z.-I. Yoshida, *ibid.*, **110**, 628 (1988).

21. K. Kano, T. Sugimoto, Y. Misaki, T. Enoki, H. Hatakeyama, H. Oka, Y. Hosotani and Z. Yoshida, *J. Phys. Chem.*, **98**, 252 (1994) and references cited.

22. M. Iyoda, Y. Kuwatani and M. Oda, *J. Am. Chem. Soc.*, **111**, 3761 (1989).

23. M. Iyoda, Y. Kuwatani, M. Oda, Y. Kai, N.Kaneshisa and N. Kasai, *Angew. Chem. Int. Ed. Engl.*, **29**, 1062 (1990).

24. (a) G. Köbrich and H. Heinemann, *Angew. Chem. Inter. Ed. Engl.* **4**, 594 (1965); (b) G. Köbrich, H. Heinemann and W. Zündorf, *Tetrahedron*, **23**, 565 (1967); (c) R. F. Bleiholder and H. Shechter, *J. Am. Chem. Soc.*, **86**, 5032 (1964).

25. M. Iyoda, H. Otani and M. Oda, *J. Am. Chem. Soc.*, **108**, 5372 (1986).

26. M. Iyoda, H. Otani, M. Oda, Y. Kai, Y. Baba and N. Kasai, *Chem. Commun.*, 1794 (**1986**).

27. M. Iyoda, H. Otani and M. Oda, *Angew. Chem. Inter. Ed. Engl.*, **27**, 1080 (1988)

28. M. Iyoda, A. Mizusuna, H. Kurata, M. Oda,, *Chem. Commun.*, 1690 (**1989**).

29. The activated nickel was prepared by reduction of NiI_2 with 0.7 - 0.8 equiv. of lithium powder and 0.1 equiv. of 4,4'-di-t-butylbiphenyl in THF, see: (a) R.D. Rieke, *Acc. Chem. Res.*, **10**, 301 (1977); (b) P. Boudjouk, D.P. Thompson, W.H. Ohrbom and B.-H. Han, *Organometallics*, **5**, 1257 (1986).

30. K. Komatsu, H. Kamo, R. Tsuji and K. Takeuchi, *J. Org. Chem.*, **58**, 3219 (1993).

31. A.W. Krebs, *Angew. Chem. Inter. Ed. Engl.*, **4**, 10 (1965).

32. R. West, *Acc. Chem. Res.*, **3**, 130 (1970), and references cited therein.

33. (a) T. J. Fukunaga, *J. Am. Chem. Soc.*, **98**, 610 (1976); (b) T. J. Fukunaga, M. D. Gordon, P. J. Krusic, *ibid.*, **98**, 611 (1976); (c) T. Lange, V. Gramlich, W. Amrein, F. Diederich, M. Gross, C. Bourdon, J.-P. Gisselbrecht, *Angew. Chem. Inter. Ed. Engl.*, **34**, 805 (1995); (d) T. Enomoto, T. Kawase, H. Kurata and M. Oda, *Tetrahedron Lett.*, **38**, 2693 (1997).

34. (a) T. A. Blinka and R. West, *Tetrahedron Letters*, **24**, 1567 (1983); (b) see also: L. A. Wendling, S. K. Koster, J. E. Murray and R. West, *J. Org. Chem.*, **42**, 1126 (1977).

35. (a) I. L. Knunyants, M. D. Bargamova and S. I. Pletnev, *J. Fluorine Chem.*, **29**, 161 (1985); (b) I. L. Knunyants, Y. T. Stuchkov, M. D. Bargamova, and A. A. Espenbetov, *Bull. Akad. Sci. USSR, Div. Chem. Sci.*, **34**, 1001 (1985).

36. (a) H. Will, *Ann. Chem. Pharm.*, **118**, 177 (1861); (b) A. W. Burgstahler and R. C. Barkhurst, *Trans. Kansas Acad. Sci.*, **71**, 150 (1968).

37. T. Sugimoto, Y. Misaki, T. Kajita, T. Nagatomi, Z.-I. Yoshida and J. Yamauchi, *Angew. Chem. Int. Ed. Engl.*, **27**, 1078 (1988).

38. R. Boese, G. Bräunlich, J. P. Gotteland, J.-T. Hwang, C. Troll and K. P. C. Vollhardt, *Angew. Chem. Int. Ed. Engl.*, **35**, 995 (1996).

39. G. Seitz and P. Imming, *Chem. Rev.*, **92**, 1227 (**1992**).

40. A. J. Fatiadi, *Synthesis*, 165 (**1978**).

41. G. Seitz, R. Sutrisno, B. Gerecht, G. Offermann, R. Schmidt, W. Massa, *Angew. Chem. Inter. Ed. Engl.*, **21**, 283 (1982).

42. (a) J. Auch, G. Baum, W. Massa and G. Seitz, *Chem. Ber.*, **120**, 1691 (1987); (b) A. J. Fatiadi, *J. Res. Nat. Bur. Sdt.*, **85**, 73 (1980).

43. (a) K. Tanaka and F. Toda, *Tetrahedron Lett.*, **21**, 2713 (1980); (b) see also: M. Iyoda, Y. Kuwatani and M. Oda, *J. Am. Chem. Soc.*, **111**, 3761 (1989).

44. See for example: C. Batz and P. Jutzi, *Synthesis*, 1296 (**1996**).

45. The classical polysubstitution reaction yields a mixture of **99** and the *gem*-substituted compounds; an improved procedure using a π-allyl palladium electrophile yields nearly pure **100** isolated with an estimated GC-Mass yield of 20%. Thus, these reactions might be efficient ways to build the required skeleton; F. Geneste, J. Porcheret and A. Moradpour, *Unpublished results.*

46. (a) R. West and D. C. Zecher, *J. Am. Chem. Soc.*, **89**, 152 (1967); (b) R. West, D. C. Zecher and W. Goyert, *ibid.*, **92**, 149 (1970); (c) R. West and D. C. Zecher, *ibid.*, **92**, 155 (1970); (d) J. L. Benham, R. West and J. A. T. Norman, *ibid.*, **102**, 5047 (1980); (e) D. E. Wellman, K. R. Lassila and R. West, *J. Org. Chem.*, **49**, 965 (1984); (f) K. Takahashi and M. Ogiyama, *Tetrahedron Lett.* **1991**, *32*, 3507; (g) K. Takahashi and S. Tarutani, *Chem. Commun.*, 519 (**1994**); (h) K. Takahashi and S. Tarutani, *Adv. Mater*, **7**, 639 (1995); (i) K. Takahashi and M. Ogiyama, *Chemistry Lett.*, 129 (**1991**); (j) L. A. Wendling and R. West, *J. Org. Chem.*, **43**, 1573 (1978); (k) L. A. Wendling

and R. West, *J. Org. Chem.*, **43**, 1577 (1978); (l) D. E. Wellman and R. West, *J. Am. Chem. Soc.*, **106**, 355 (1984); (m) K. Komatsu, R. West and D. Beyer, *ibid.*, **99**, 6290 (1977).

47. (a) M. Horner and S. Hünig, *Ann.* 1183 (**1982**); (b) M. Horner and S. Hünig, *ibid.*, 642 (**1983**); (c) M. Horner and S. Hünig, *Angew. Chem. Int. Ed. Engl.*, **16**, 410 (1977).

48. E. A. Dorko, *J. Am. Chem. Soc.*, **87**, 5518 (1965).

49. M. G. Ettlinger, *ibid.*, **74**, 5805 (1952).

50. (a) P. A. Waitkus, L. I. Peterson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 181 (1966); b) P. A. Waitkus, E. B. Sanders, L. I. Peterson and G. W. Griffin, *ibid.*, **89**, 6318 (1967).

51. (a) G. W. Griffin, *J. Am. Chem. Soc.*, **84**, 3398 (1962); (b) G. W. Griffin and L. I. Peterson, *ibid.*, **85**, 2268 (1963); (c) F. A. Miller, *Spectrochimica Acta*, *28A*, 1467 (1972).

52. L. Trabert and H. Hopf, *Ann.*, 1786 (**1980**).

53. (a) R. Gray, L. G. Harruff, J. Krymowski, J. Peterson and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2892 (1978); (b) P. Schiess and M. Heitzmann, *Helv. Chim. Acta*, **61**, 844 (1978).

54. (a) H. Hopff and A. K. Wick, *ibid.*, **44**, 19 (1961); (b) H. Hopff and A. K. Wick, *ibid.*, **44**, 380 (1961) (c) H. Hopff and A. Gati, *ibid.*, **48**, 1289 (1965).

55. A. Stanger, N. Ashkenazi, R. Boese, D. Bläser and P. Stellberg, *Chem. Eur. J.*, **3**, 208 (1997).

56. F. Geneste, A. Moradpour and G. Dive, *J. Org. Chem.*, **62**, 5339 (1997).

(Received July 30, 1999; in final form October 12, 1999)