

Synthesis of the Butatriene C₄ Function: Methodology and Applications

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I. INTRODUCTION

C_{2n}H_{2n} hydrocarbons are the first representatives of the category of the so-called “carbon-rich” molecules (C/H ≥ 1).¹ The electronic strain of small C_{2n}H_{2n} species with filled valence shells ($n + 1$ unsaturations or cycles over n connected carbon atoms) makes the corresponding C_{2n} skeletons a priori reactive all-carbon functions, which are valuable for both their physicochemical properties and their use in organic synthesis. The first term ($n = 1$) defines the single acetylene function, for which it is not necessary to recall the tremendous extent of applications.² The third term ($n = 3$) defines 218 more or less reactive “carbon functions”,³ whose cyclic and most stable paradigm is the aromatic benzene. The intermediate term ($n = 2$) defines 11 highly reactive carbon functions only, whose cyclic paradigm is the antiaromatic singlet cyclobutadiene (Scheme 1). Theoretical studies have confirmed the intuition that the most stable C₄H₄ isomers are the two acyclic ones, containing two sp and two sp² carbon atoms, namely, butenyne (or vinylacetylene) and butatriene.⁴

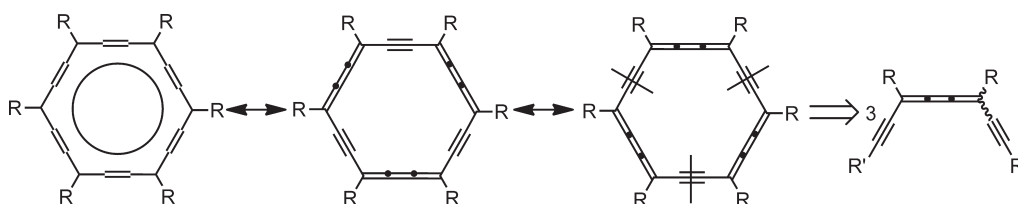
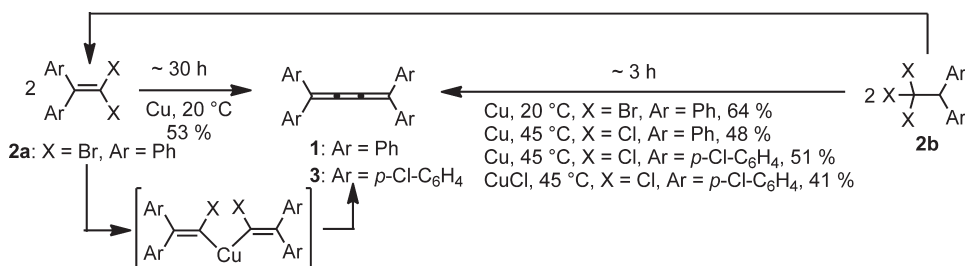
Butatriene is a priori slightly more reactive and more symmetric (D_{2h} in the singlet ground state, just as cyclobutadiene is) and belongs to the challenging family of the odd cumulenes. More than “carbon-rich”, $[2k + 1]$ cumulenes are indeed “carbon-enriched” molecules: the first term of the series, $[3]$ cumulene or butatriene, is also the first skeletal and functional *carbo*-mer of the “non-carbon-rich” ethene (C₂H₄, $k = 0$),^{5,6} and substituted derivatives exhibit the same *Z/E* (or *cis/trans*) stereoisomerism. For comparison, the even series of $[2k]$ cumulenes starts with the degenerate case of allene, whose substituted derivatives exhibit the *R/S* stereoisomerism of methane derivatives ($k = 0$). The first evidence of allenes and $[3]$ cumulenes was reported in 1921⁷ and 1888,⁸ respectively. Higher cumulenes are quite reactive,⁹ and beyond allenes, only a few examples of even cumulenes (with a

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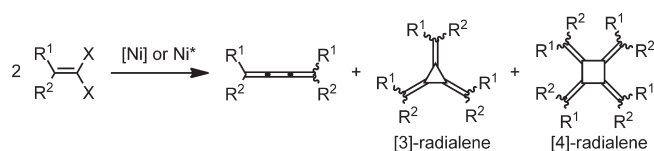
Scheme 1. Lewis Structures of the 11 Possible C₄H₄ Isomers with Filled Valence Shells^a

^a Carbenic and radical species are excluded. The nine first structures (from left to right) are ranked in increasing order of energy for the singlet ground state calculated at the DFT or MP2 level of theory.⁴ Both the cycloalkynes (at the extreme right) are not minimas on the C₄H₄ potential energy surface, but methylenecyclopropyne has been calculated to be a transition state of interconversion between carbenic isomers. Cyclobutene is a valence isomeric form of butatriene (through a putative four-electron electrocyclicization process).

Scheme 2. Butatrienes as Constitutive Motifs of *carbo*-Benzenes: Formal Cyclometathesis Products of Three Dialkynylbutatriene Precursors^{12,14}Scheme 3. Copper-Promoted Coupling of *gem*-Dihaloalkene or Trihaloethane Precursors¹⁹

total number of π electrons = $4k$) are known. Odd cumulenes (with a total number of π electrons = $4k + 2$) are more widely represented¹⁰ and have been characterized up to $k = 4$.¹¹ The first representatives ($k = 1$) are the butatrienes, which are thus generally relatively stable. Moreover, butatrienes can be further stabilized by resonance with but-2-yn-1,4-diylidene motifs, in particular in the Kekule structures of *carbo*-benzenes (Scheme 2),¹² whose C₁₈ ring exhibits aromatic character just as the parent C₆ benzene ring does.¹³ More precisely, 1,4-dialkynylbutatrienes are resonating motifs of the C₁₈ macrocycle, which can thus be formally considered as the metathesis product of three *cis*-dialkynylbutatriene precursors.¹⁴ The *cis*/*trans* isomerization barrier of acyclic di- and tetraalkynylbutatrienes was however found to be quite low.¹⁵

To our knowledge, only a few surveys on the synthesis of butatrienes are available in the literature: a review in 1961,¹⁶ three book chapters before 1980,^{11a,b,17} part of a book chapter in 2003,^{18a} and part of a review in 2007.^{18b} An extensive review of recent results in this field, including former benchmark reports, is thus presented hereafter. The methods employed for the preparation of butatrienes are first classified according to the basic processes governing the formation of the C=C=C=C unit in one-pot procedures: by either C₂ + C'₂ or C₃ + C₁ coupling of two smaller precursors (section II) or functional transformation of a pre-existing C₄ precursor (section III). Fragmentation of C_{*n*+4} precursors to C_{*n*} and butatrienic C₄ motifs is then shortly

Scheme 4. Nickel-Promoted Coupling of *gem*-Dihaloalkenes (See Table 1)²⁰

illustrated (section IV). A recently exemplified 2C₁ + 2C'₁ four-component scheme is highlighted (section V). A survey of the reactivity and physicochemical properties of butatrienes, which motivate the synthesis efforts, is finally presented (section VI).

II. SYNTHESIS OF BUTATRIENES BY C–C COUPLING OF C_{*n*} AND C_{4–*n*} PRECURSORS

This section is divided in two parts dealing with C₂ + C'₂ homo- or heterocoupling and C₁ + C₃ heterocoupling, respectively.

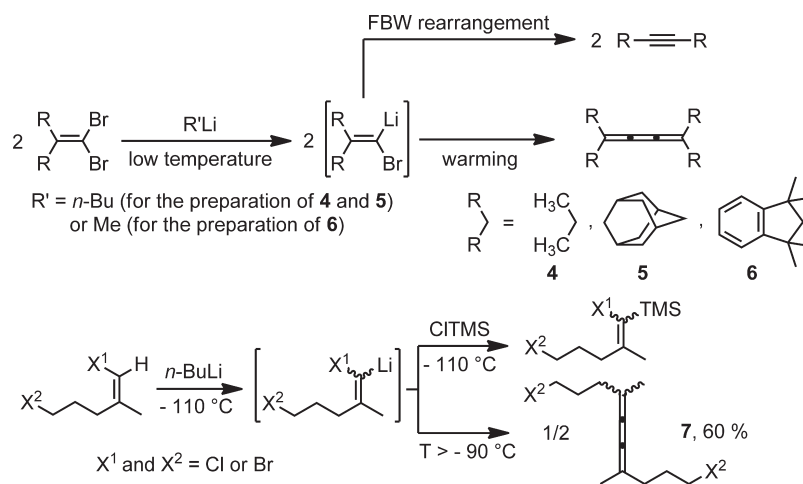
II.1. Coupling of C₂ Precursors

This coupling approach is the most widely illustrated. Two types of C₂ units can be distinguished, namely, alkenyl and alkynyl precursors.

Table 1. Coupling of Dihalalkenes in the Presence of Ni(0) Species (See Scheme 4)²⁰

precursor			Ni source	solvent	additive	butatriene (%)	other products (%)						
R ¹	R ²	X											
Ph	Ph	Br	Ni(PPh ₃) ₄	C ₆ H ₆		60							
			Ni(PPh ₃) ₄	THF		0							
			Ni [*] ^a	THF		23							
Me	Ph	Br	Ni(PPh ₃) ₄	C ₆ H ₆	Et ₄ Ni	29	[3]radialene (29)						
			Ni [*]	THF		5							
Me	C ₆ H ₄ CN	Br	Ni(PPh ₃) ₄	C ₆ H ₆	Et ₄ Ni	60	[3]radialene (58)						
			Ni [*]	THF		14							
Me	C ₆ H ₄ OMe	Br	Ni(PPh ₃) ₄	C ₆ H ₆	Et ₄ Ni	41							
Me	C ₆ H ₄ CO ₂ Me	Br	Ni(PPh ₃) ₄	C ₆ H ₆	Et ₄ Ni	44							
Me	C ₆ H ₄ Cl	Br	Ni [*]	THF		3	[3]radialene (57)						
Me	Me	Br	Ni [*]	THF		0	[4]radialene (14)						
							[5]radialene (7)						
							fluorene	Br	Ni(PPh ₃) ₄	C ₆ H ₆		67	
							Br	Ni [*]	THF		39	[3]radialene (1)	
xanthene		Cl	Ni [*]	THF		13	[3]radialene (1)						
		Cl	Ni [*]	THF		17	[3]radialene (2)						

^a Ni^{*} = activated metallic nickel.

Scheme 5. Competing Formation of Butatrienes and Disubstituted Acetylenes from Halolithium Carbenoid Intermediates, Generated by Metal–Halogen Exchange from *gem*-Dihaloalkenes or by Deprotonation of Terminal Monohaloalkenes^{21–23}

II.1.1. Homocoupling of Two Alkenylidene C₂ Precursors. The most commonly used method for the preparation of butatrienes is based on the reductive coupling of two *gem*-dihalovinylidene moieties. Over the last 40 years, many variations on this principle were described, with the alternative use of lithium, copper, or nickel carbenoid intermediates.

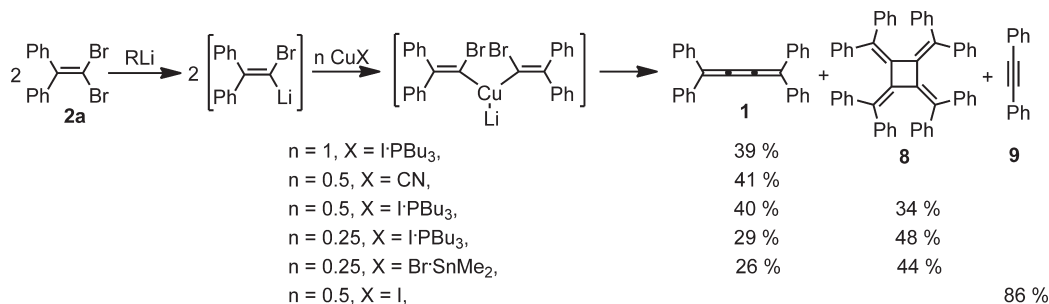
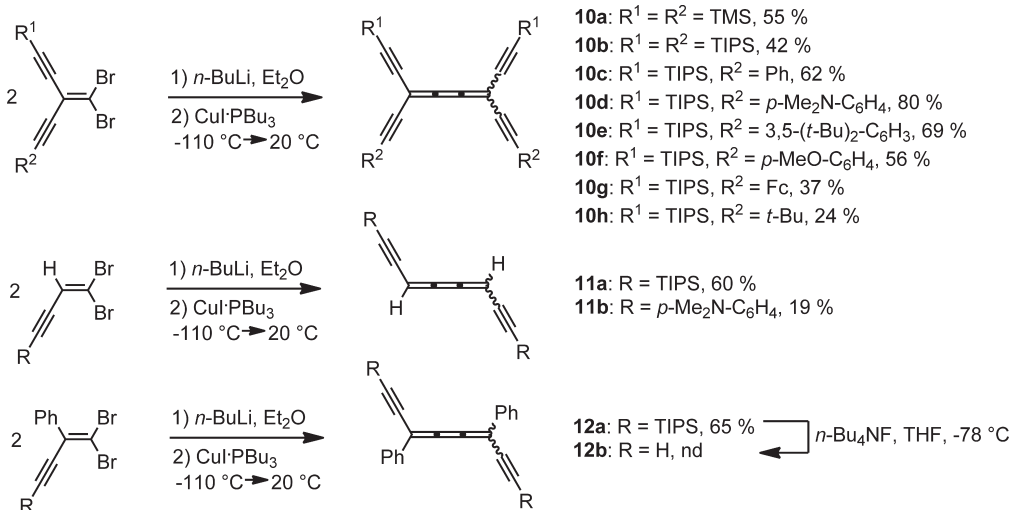
In 1977, Kunieda and Takizawa reported the preparation of tetraphenylbutatriene **1** by reaction of metallic copper with either the corresponding *gem*-dibromoalkene **2a** or with a trihalogenated precursor **2b** (Scheme 3).¹⁹ The chlorinated tetraarylbutatriene **3** could also be obtained by this method using metallic copper or copper chloride. Whatever the substrate is, the yields are however generally limited to ca. 50%.

The proposed mechanism involves first the oxidative addition of two *gem*-dihaloalkenes at the copper center, followed by a reductive elimination affording the expected butatriene. When

the reaction is performed from trihalogenated precursors, an analogous mechanism can be invoked, where the *gem*-dihaloalkenes appear as intermediates.

Iyoda and Oda reported that the use of metallic nickel or a nickel(0) complex could lead to butatrienes from dihaloalkene precursors (Scheme 4).²⁰

The Ni(0) complex Ni(PPh₃)₄, generated in situ by reduction of NiBr₂(PPh₃)₄ with zinc, led to better yields than activated metallic nickel Ni^{*} (Table 1). The reaction has to be performed in benzene and may require the use of [Et₄N]I as a iodide source serving to increase the coupling efficiency to butatrienes as major products. When activated metallic nickel was used, the yields in butatrienes were lower. They were always obtained in mixture with the corresponding [3]radialenes, and sometimes [4]- and [5]-radialenes. The steric effect appeared to be a determining factor in this reaction, butatrienes being

Scheme 6. Generation and Reactivity of a Bis-Carbenoid Cuprate Intermediate from Different Copper Salts²⁴Scheme 7. Synthesis of Di- and Tetraalkynylbutatrienes from *gem*-Dibromoalkynes^{14,15}

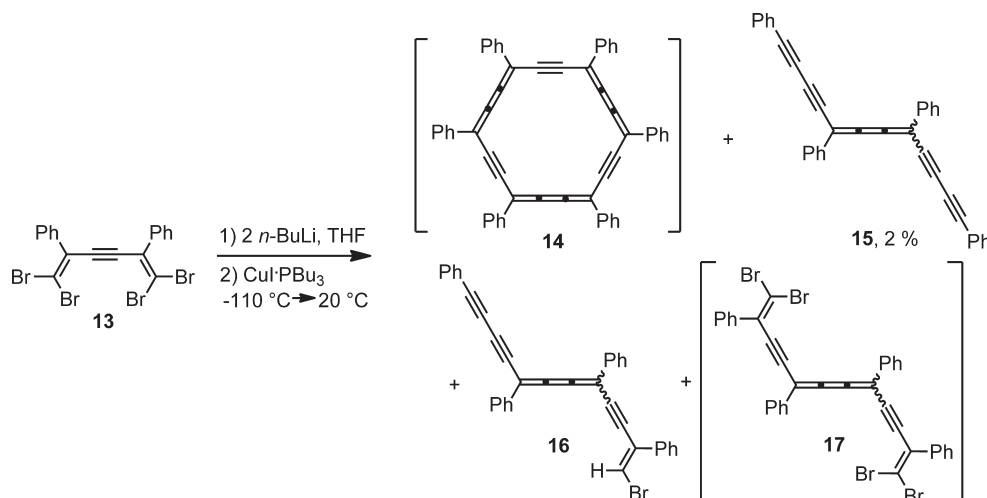
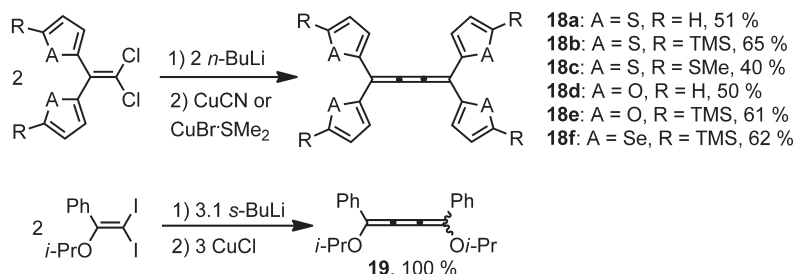
obtained more selectively from bulky dihaloalkene precursors, while radialenes were largely predominant from less hindered substrates.

Beside the above examples of transition metal-promoted coupling of *gem*-dihaloalkenes, most of the described reactions were performed via a halolithium carbenoid intermediate generated by a single metal–halogen exchange of the dihaloalkene with an organolithium reagent. Rare examples of direct dimerization of these carbenoids have been reported (Scheme 5),²¹ but addition of a copper salt to the carbenoid intermediate is generally required. In the absence of a copper salt, indeed, lithium carbenoids mainly give the corresponding disubstituted acetylene derivatives resulting from Fritsch–Buttenberg–Wiechell (FBW) rearrangements.²² In 1984, Wannagat et al. described an example of direct dimerization of halolithium carbenoids prepared from terminal monohaloalkenes,²³ instead of the classical corresponding dihaloalkenes. The intermediacy of the chlorolithium carbenoid was demonstrated by a treatment with chlorotrimethylsilane at very low temperature ($-110 \text{ }^\circ\text{C}$), which afforded the expected silylated chloroolefin. In contrast, the butatriene **7** could be isolated in 60% yield when the chlorolithium carbenoid was warmed up to $-90 \text{ }^\circ\text{C}$ (Scheme 5).

Addition of a copper salt to the $=\text{C}(\text{Li})\text{X}$ carbenoids induces the formation of a bis-carbenoid cuprate intermediate, which finally affords the butatriene after elimination of CuX and LiX

(Scheme 6). As shown by Iyoda et al. from the diphenyl precursor **2a**, the amount and nature of the copper salt used are crucial.²⁴ With 1 equiv of the $\text{CuI} \cdot \text{PBu}_3$ complex or with 0.5 equiv of CuCN , tetraphenylbutatriene **1** was obtained in 39 or 41% yield, respectively, while substoichiometric amounts of $\text{CuBr} \cdot \text{SnMe}_2$ or $\text{CuI} \cdot \text{PBu}_3$ afforded a mixture of **1** and [4]radialene **8**. Finally, the use of the poorly soluble CuI salt led mainly to diphenylacetylene **9** resulting from the FBW rearrangement. This last result is quite surprising, since the reactions were performed in THF, a polar solvent which generally prevents the FBW rearrangement.^{22d,e}

In 1993, Diederich et al. described the synthesis of the first examples of tetraalkynylbutatrienes **10a,b** using the same procedure from the corresponding *gem*-dibromoolefins.^{15a} In this case, the $\text{CuI} \cdot \text{PBu}_3$ complex appeared to be the most efficient salt, giving the butatriene products in moderate to good yields (Scheme 7). Later on, the same authors reported on the synthesis of 1,4-dialkynylbutatrienes **11a,b** and others tetraalkynylbutatrienes **10c–h**, with two kinds of substituents capping the ethynyl termini.^{15b,c} Using the same strategy, the preparation of 1,4-diphenyl-1,4-dialkynylbutatriene **12a** was recently reported.¹⁴ Treatment of **12a** with TBAF afforded the first example of uncapped diethynylbutatriene **12b**, all the previously described representatives being capped with either bulky silyl or aryl substituents (Scheme 7). In accordance with the

Scheme 8. Sequential Reductive Coupling from the Bis-*gem*-dibromodienyne Substrate **13**¹⁴Scheme 9. Synthesis of Butatrienes from Dichloro- and Diiodoalkene Precursors^{26,27}

experimental observation of slow *cis/trans* interconversion for the butatrienes **10–12**, Diederich et al. showed that the rotational barrier around the C_4 butatrienic axis is quite low, in particular in the case of tetraalkynyl representatives.^{15c,25} This was explained by a DFT-computed 1,4-biradical transition state, stabilized by resonance with the surrounding triple bonds.

Application of the same method to the bis-*gem*-dibromodienyne substrate **13** was also attempted in view of preparing the *carbo*-benzene **14** through a trimolecular sequential coupling processes (Scheme 8).¹⁴ These conditions produced only trace amounts of *carbo*-benzene, but they allowed for the characterization of three new dialkynylbutatrienes, **15–17**. The unprecedented dibutadiynylbutatriene **15**, resulting from one reductive coupling and two FBW rearrangement processes, was isolated in 2% yield as a mixture of two diastereoisomers and appeared to be surprisingly stable in the solid state at room temperature. The butatriene **16**, resulting from one coupling and one FBW rearrangement processes, can be considered as an intermediate in the formation of **15**, but it could not be completely purified. It was indeed obtained in mixture with ca. 10% of the tetrabromo derivative **17** (identified by mass spectrometry).

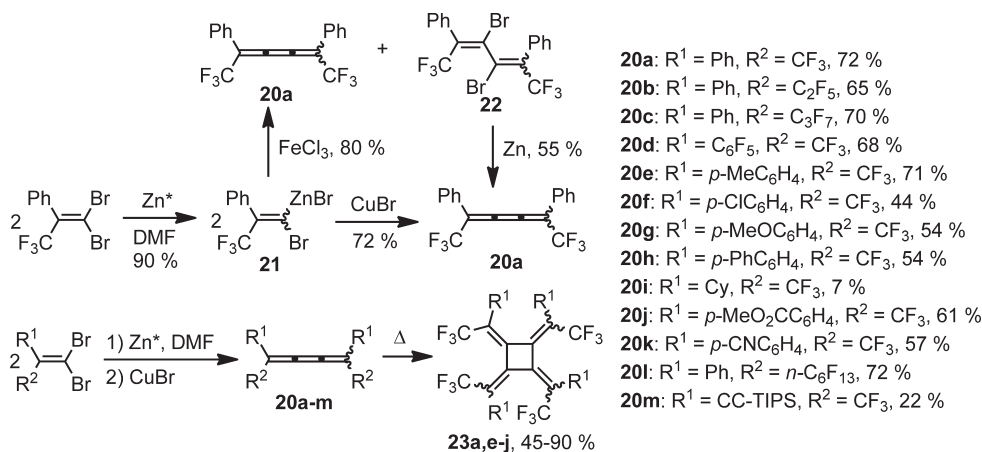
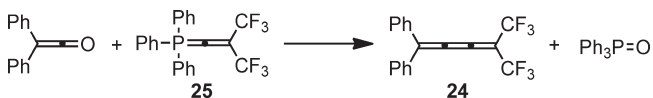
The reductive coupling strategy was also incidentally applied to *gem*-dichloro-²⁶ and *gem*-diiodoalkene²⁷ precursors for the preparation of the butatrienes **18a–f** and **19**, respectively, which were obtained in good to excellent yields (Scheme 9).

The trifluoromethylated butatrienes **20a–l** were targeted through zinc bromide carbenoid intermediates, which were

described to be more stable than the corresponding bromolithium analogues. Treatment of these Zn(II) species with a copper salt was first reported by Burton et al. to produce the corresponding butatrienic dimers **20a–d** in quite good yields.²⁸ This method was later used for the preparation of the butatrienes **20e–l**²⁹ and very recently for the synthesis of **20m** (Scheme 10).¹⁴ The bromoalkenylzinc intermediates were either isolated or directly treated in one-pot with stoichiometric or catalytic amounts of CuBr at low temperature. Alternatively, the coupling of the zinc bromide carbenoid **21** with FeCl₃ produced a mixture of the butatriene **20a** and diene **22**. The latter could be subsequently dehalogenated with zinc metal to give the butatriene **20a** in 55% yield.

The butatrienes **20a–m** were obtained as mixtures of *cis* and *trans* isomers, which could be separated by either crystallization or chromatography. Their thermal dimerization was reported by Uno et al. to produce the [4]radialenes **23a,e–j** in quite good yields.^{29b}

II.1.2. Heterocoupling of Alkenylidene C_2 and C'_2 Precursors. Few nonstereogenic butatrienes were synthesized from two different C_2 precursors. The first butatriene bearing trifluoromethyl substituents, **24**, was thus obtained by Birum et al. in 1967 via a Wittig reaction from the alkenylidene-phosphorane **25** and diphenylketene (Scheme 11).³⁰ Other butatrienes were synthesized by similar processes from C_1 and C_3 precursors (see section II.2).

Scheme 10. Synthesis of Trifluoromethylated Butatrienes through ZnBr₂ Carbenoid Intermediates^{14,28,29}Scheme 11. Synthesis of a *gem*-Bis(trifluoromethyl)-butatriene by a Wittig Reaction³⁰

The “push–pull” butatriene **26a** was prepared in 1993 by Viehe et al. through a base-promoted condensation of the dichloroalkene **27a** and 1,1-bis(dimethylamino)ethene **28** (Scheme 12).³¹ The synthesis of the dinitrile **26a** and its diester analogue **26b** had been previously described by Gompper et al. in 1978.³² Crystallographic studies of **26a** revealed a very short central C–C bond (1.201 Å), thus evidencing a highly dipolar character involving a triple bond spacer.

II.1.3. Homocoupling of Two Alkynyl C₂ Precursors. In 1975, Vermeer et al. reported on a *cis*-stereoselective synthesis of butatrienes from alkynylthioether substrates **29a,b**, through a divinylcopper complex that is an analogue of the intermediate proposed in the coupling of *gem*-dihaloalkenes (see Scheme 6).³³ Treatment of the heterosubstituted divinylcopper complex with an excess of iodomethane afforded the *cis*-butatrienes **30c–35c** stereospecifically (Scheme 13). Their configuration was first determined by analysis of their hydrogenation products and later confirmed by X-ray diffraction analysis.³⁴

Another example of butatriene synthesis from acetylenic precursors bearing heteroatomic substituents was reported by Schmidbaur et al. in 1993.³⁵ The substrate was here the diphosphinylacetylene **36** (Scheme 14), which first reacts with potassium diphenylphosphide to give the putative intermediate **37** and finally affords the tetraphosphinylbutatriene **38** in 33% yield after treatment with chlorodiphenylphosphine. The tetraphosphine **38** was finally converted to the tetrathio phosphine **39** in 90% yield by treatment with S₈.

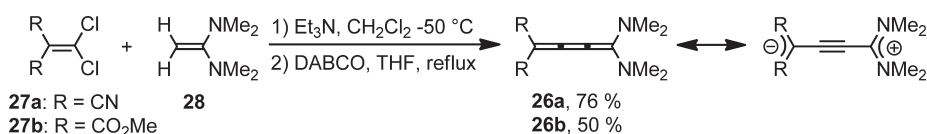
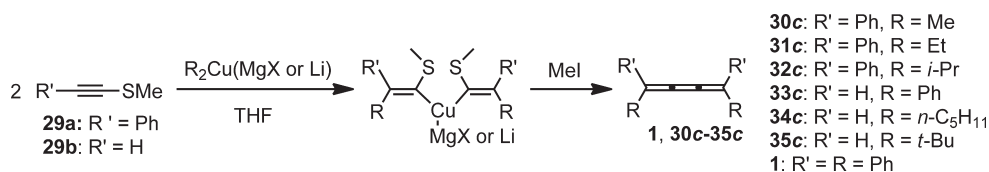
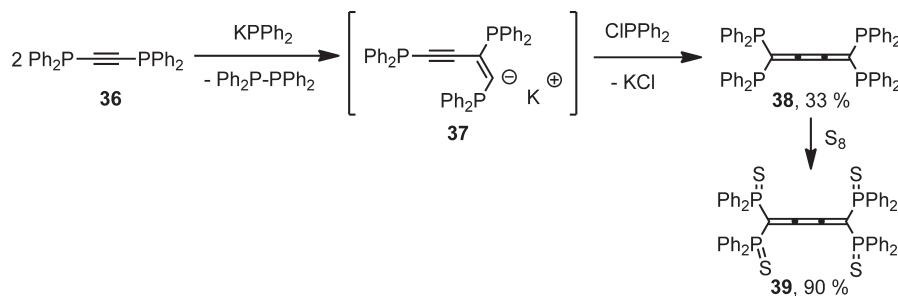
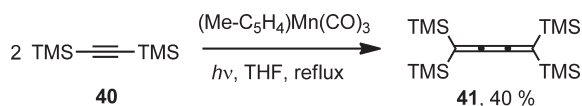
Beyond the above-mentioned examples, all the reported syntheses of butatrienes from heteroatom-substituted acetylenics involve an initial coordination of the substrates to a metallic center, in either catalytic or stoichiometric processes. Dimerization of bis(trimethylsilyl)acetylene **40** in the presence of an organometallic complex was first reported by Vollhardt et al. in

1979;³⁶ tetrakis(trimethylsilyl)butatriene **41** could thus be isolated from a mixture of products obtained by treatment of **40** with CpCo(CO)₂. In 2002, dimerization of the same alkyne **40** in the presence of (Me-C₅H₄)Mn(CO)₃ under irradiation in refluxing THF was reported to give the butatriene **41** in 40% yield (Scheme 15).³⁷

A copper-mediated additive homocoupling of terminal alkynes to butatrienes was observed by Higuchi et al. while trying to perform cyclizing Glaser couplings of diacetylenic precursors **42a–c** (Scheme 16).³⁸ Only the symmetric precursors (*m* = *n*) could, however, be cyclized in this way to give the corresponding endocyclic dichlorobutatrienes **43a–c**. The ¹H NMR spectra of the dichlorodihydroannulenediones **43a–c** in CDCl₃ showed that the outer protons, H_o, resonate at lower field than the inner protons, H_i (see Scheme 16), thus evidencing the existence of a diatropic ring current, which was found to increase with the ring size. The shielding (respectively deshielding) of the inner (respectively outer) protons was also observed to be enhanced upon recording the spectra in D₂SO₄. In acidic conditions, the contribution of the dicationic aromatic 14π-, 18π-, and 22π-electron forms **43'a–c** is indeed more important, thus inducing an increase of the diatropic ring current.

Dimerization of terminal alkynes in the presence of a stoichiometric amount of a rhodium complex was described by Werner in 1993.³⁹ The transformation proceeds via the intermediate alkynylvinylidene complexes **44** and **45**, which are treated first with CO and then with an acid to give the butatrienes **33** and **35** in very good yields (Scheme 17). By reversing the sequence of additions of CO and acid, the coupling of the two C₂ units of **44** proceeds in a different way, affording the enyne isomer **46** selectively.

Almost at the same time, Wakatsuki et al. reported on a catalytic version of this dimerization reaction using ruthenium complexes and phosphine ligands.⁴⁰ Dimerization of trimethylsilylacetylene was found to give either the butatriene **47** or the enyne **48** depending on the phosphine ligand used (Scheme 18). The use of tributylphosphine thus led selectively to the enyne **48**, while the use of triphenylphosphine gave the butatriene **47** with high *cis* stereoselectivity. Depending on the ruthenium catalyst used, different selectivities were also observed in the dimerization of *tert*-butylacetylene: while Ru(CO)(PPh₃)₃(H)₂ afforded the *cis* isomer of the butatriene **35** in high chemo- and stereoselectivity,

Scheme 12. Synthesis of Push–Pull Butatrienes^{31,32}Scheme 13. Stereoselective Synthesis of Butatrienes from Acetylenic Thioethers^{33,34}Scheme 14. Synthesis of a Tetraphosphinylbutatriene and Its Tetrathio phosphine Derivative³⁵Scheme 15. Dimerization of Bis(trimethylsilyl)acetylene in the Presence of a Manganese Complex³⁷

other catalytic systems led to mixtures of *cis* and *trans* isomers along with enyne side products.

Iridium-catalyzed dimerization of alkynes was described by Miyaura et al. to give different products depending on the substrates and the ligands used.⁴¹ While the triphenylphosphine ligand afforded mainly *trans*-enyne, tri-*n*-propylphosphine gave either *cis*-enyne from silylated or aromatic alkynes or butatrienes from *tert*-alkylacetylenes. This method is thus limited to the synthesis of butatrienes with tertiary alkyl substituents.

Esteruelas et al. reported that the use of an osmium complex allowed one to convert alkylacetylenes to the corresponding butatrienes **35** and **49** quantitatively (Scheme 19).⁴² However, application of the same catalytic system to trimethylsilylacetylene afforded mainly the corresponding *cis*-enyne **48**, in mixture with a small amount of butatriene **47**. When the reaction was performed at lower temperature, the butatriene product was however isolated in higher yield, thus suggesting that the enyne **48** arises from the isomerization of the butatriene **47**.

The above examples emphasize the difficulty to control the selectivity of these catalytic reactions for a wide range of alkyne substrates.

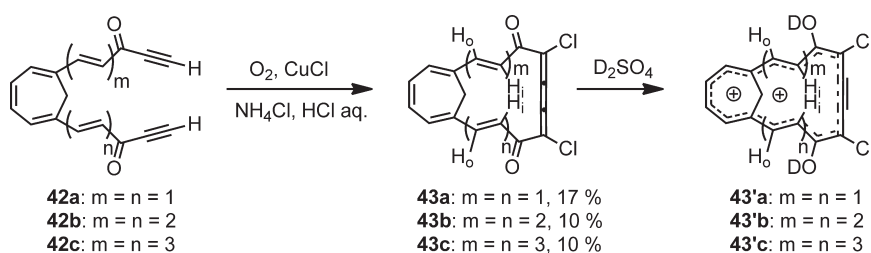
II.1.4. Homocoupling of Two Silyldiazoketone C₂ Precursors. In 1994, Maas et al. described a particular example of palladium-catalyzed synthesis of a butatriene from a (1-diazo-2-oxoalkyl)silane.⁴³ The reaction was found to occur only from the substrate **50** bearing a *tert*-butyl group and to produce the butatriene **51** as a mixture of diastereoisomers in 20–35% yield depending on the palladium catalyst used (Scheme 20).

The authors proposed a mechanism where the coordination of the substrate **50** at the palladium center is followed by the evolution of N₂ and by the addition of a second molecule of substrate. After [1,3] Brook-like rearrangement and reductive elimination, the butatriene **51** is finally formed. Although produced in mixture with several other products, it could be isolated by crystallization or distillation.

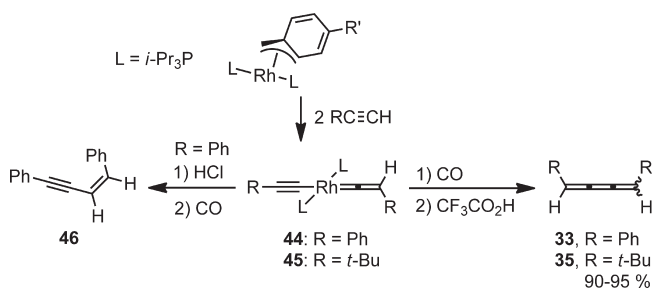
II.2. Coupling of C₁ and C₃ Precursors

The synthesis of butatrienes by heterocoupling of C₁ and C₃ precursors is much less exemplified than the coupling of two C₂ precursors (section II.1). The early method for the preparation of butatrienes by Wittig reaction from two C₂ precursors (section II.1.2, Scheme 11)³⁰ was however generalized to C₁ and C₃ precursors by Ziegler, Jr. et al. and by Browne et al.⁴⁴ More recently, Shi et al. reported the preparation of ester-functionalized butatrienes **52–54** by reaction of bromoallylphosphonium salts with α -keto esters in the presence of a base (Scheme 21).⁴⁵

Scheme 16. Synthesis of Endo-Macrocyclic Dichlorobutatrienes by Intramolecular Additive Coupling of Terminal Acetylene Moieties³⁸



Scheme 17. Rhodium-Promoted Coupling of Terminal Alkynes³⁹



After the first report on the preparation of the butatrienes **4** and **55–57** from allenic phosphonates by Horner–Emmons–Wittig reaction in 1985,⁴⁶ the method was later applied to the synthesis of other butatrienes, among which is the bicyclic representative **58** (Scheme 22).⁴⁷ In this case, after α -deprotonation of the allenylphosphonate **59**, intramolecular attack of the resulting anion to the carbonyl function leads to the butatriene **58** in 26% yield.

Beside the polar Wittig-type reactions, $C_3 + C_1$ formation of butatrienic C_4 units may involve neutral carbenic species as either C_3 or C_1 reactants. One example of allenylidene addition to a cyclopentanethione was reported in 1988.⁴⁸ The C_3 allenylidene reactants were formed from chloroallenes or chloroalkynes, and the butatrienes **60–63** were obtained as minor products in mixture with allenic and dienic main products (Scheme 23). All the other examples of apolar $C_3 + C_1$ processes involve the addition of carbenic C_1 precursors to various C_3 substrates.

The reverse $C_1 + C_3$ scheme, exemplified by additions of dichloro- or dibromocarbene to various C_3 substrates, is generally more selective. Whatever the allylic or allenic C_3 precursor used, the reaction proceeds through cyclopropane intermediates (Scheme 24). Addition of dichlorocarbene to allylic C_3 precursors was first described by Nagashima et al. in 1971 and later used by Islam et al.⁴⁹ Dehydrochlorination and ring-opening of the cyclopropane intermediates were performed by treatment with potassium *tert*-butoxide in *tert*-butyl alcohol, giving the butatriene products **1** and **64–69** in moderate to excellent yield. The alkenylidene cyclopropane intermediate of the overall $C_3 + C_1$ process could also be isolated before ring-opening (strictly speaking, the conversion of the latter to the butatriene is a skeletal rearrangement of a C_4 precursor; see section III.8). Thus, addition of dibromocarbene to allenic C_3 precursors

was reported to generate dibromocyclopropane intermediates which, upon treatment with alkyllithium reagents, afforded the butatrienes **4** and **70–74** in moderate overall yield (Scheme 24).⁵⁰

The stability of the endocyclic butatrienes **71** and **72** depends on the ring size.^{50d,e} In particular, the yield in the strained nine-membered cyclobutatriene **71** could not be calculated, but the authors determined that of its hydrogenation product (ca. 40% from the corresponding dibromocyclopropylidene intermediate). In 1992, using the same two-step method from C_3 allenic precursors, Santelli-Rouvier et al. reported the synthesis of the phosphonyl-substituted butatrienes **73** and **74** (Scheme 24).^{50f}

III. SYNTHESIS OF BUTATRIENES BY TRANSFORMATION OF PREFORMED C_4 PRECURSORS

Several kinds of C_4 precursors, either linear or cyclic, were envisioned for the direct preparation of butatrienes.

III.1. Synthesis of Butatrienes from “Butallenes”

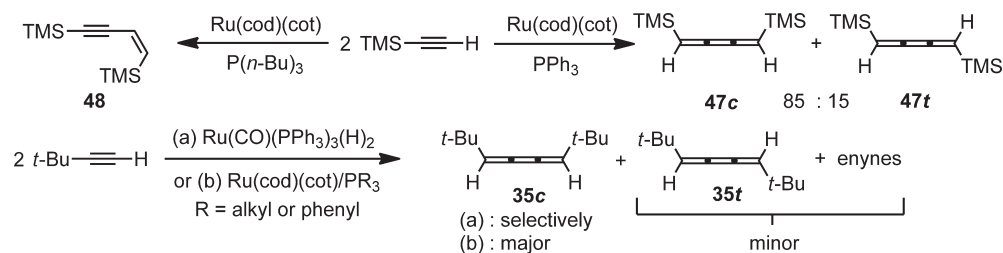
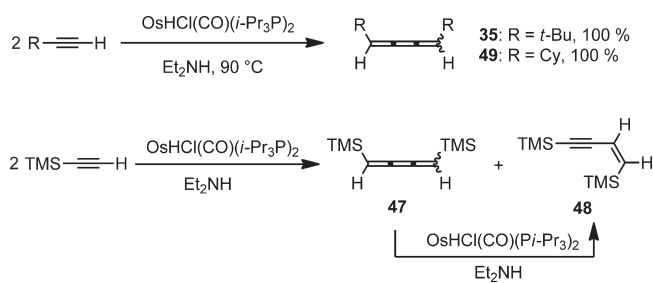
Only a few peculiar examples of butatriene synthesis from allenic C_4 precursors have been reported. In 1995, Saalfrank et al. described the base-promoted dehydrobromination of allenic precursors affording the ester-functionalized butatrienes **75–77** (Scheme 25).⁵¹ This cumulogation process could be performed in very good yields using the appropriate base, namely, sodium ethoxide for **75** or sodium bis(trimethylsilyl)amide, with or without silver acetate, for **76** and **77**.

Photorearrangement of related allenylidene-cyclopropanes precursors was also reported by Mizuno et al. to produce butatrienes in good yields, through a skeletal rearrangement (so also relevant to section III.8).⁵² The proposed mechanism involves the homolysis of one of the endocyclic bonds via an excited singlet state generated under irradiation. The butatrienes **78–81** were then produced by migration of one of the methyl groups (Scheme 26).

III.2. Synthesis of Butatrienes from Buta-1,3-dienes

Two kinds of processes can be identified for the preparation of butatrienes from diene precursors. The first one, which is also the less exemplified, is actually a $C_{4+n} - C_n$ fragmentation process (see section IV), namely a thermolytic retro-Diels–Alder reaction. Butatriene **82** was thus prepared in poor yield by thermolysis of the oxygenated bicycle **83** in gaseous phase.⁵³ The same butatriene was also generated in good yield from the polycycles **84** and **85**, along with traces of butenyne (Scheme 27).⁵⁴

All the others methods of preparation of butatrienes from diene precursors involve elimination of dihalogens or

Scheme 18. Ruthenium-Catalyzed Coupling of Terminal Alkynes⁴⁰Scheme 19. Osmium-Catalyzed Dimerization of Terminal Alkynes to Butatrienes⁴²

halogenoboranes in milder conditions. Negishi et al. thus reported that treatment of the boranes **86** and **87**, generated in situ from 1-iodoalkynes and tetrylborane, with sodium methoxide afforded the dialkylbutatrienes **49t** and **88t** in 29 and 47% yield, respectively (Scheme 28).⁵⁵ Although these products turned out to be particularly unstable (the crude yields were only determined by GPC analysis), the reaction was found to be stereoselective in the trans isomers.

Iyoda et al. described the synthesis of various butatrienes by treatment of the corresponding 2,3-diiodobutadienes with Ni(0), Zn(0), or *n*-BuLi (Scheme 29).⁵⁶ The use of butyllithium is particularly efficient, producing the butatrienes **4**, **56**, and **89** quantitatively. Using *n*-BuLi, the butatriene **30** was isolated in lower yield (48%) but selectively in its *cis* configuration **30c**. Similarly, Pollack et al. reported that butyllithium-promoted reductive elimination of diiodide was totally stereoselective in the *trans*-diphenylbutatriene **33t**.⁵⁷ On the other hand, heating a solution of pure **30c** at 80 °C during 4 h restored a 1:1 mixture of *cis* and *trans* isomers, while the same mixture was directly obtained when the elimination was performed in the presence of Zn in refluxing acetonitrile. A rationale for the kinetic stereospecificity of the butyllithium-based method could be a mechanism of anti elimination from the *transoid* conformation of the diene. It should be mentioned that the zinc-based method was also used by Hartzler for the preparation of the symmetric butatriene **90** in 45% yield (Scheme 29).⁵⁸

Ibis et al. reported on an efficient synthesis of the tetrathio-butatrienes **91a,b** by treatment of hexachlorobutadiene with thiolates (Scheme 30).^{59,60a} In 2009, Schmidt et al. described the preparation of the representatives **91a,c–e** from hexachlorobutadiene via the formation of a tetrapyrindinium intermediate (Scheme 30).^{60b} More recently, treatment of tetrathiochlorobutadienes with potassium *tert*-butoxide was reported to provide a

high-yield synthesis of the corresponding tetrathio-butatriene **91f**. In the same way, trithio-butatrienes could be obtained in good yields from the corresponding butadiene precursors (Scheme 30).^{60c}

III.3. Synthesis of Butatrienes from But-2-enes

In 1959, a double dehydrohalogenation process was reported for the preparation of the first tetrahalogenated butatriene **92** (C₄F₄) in ca. 50% yield by treatment of the 1,4-dibromobutene **93** with potassium hydroxide (Scheme 31).⁶¹ The particularly unstable butatriene **92** was obtained as a colorless liquid, boiling around –5 °C and exploding violently at 0 °C. In 2002, Bach et al. used the same method for the preparation of crystals of **92** which were analyzed by X-ray diffraction.^{62a} The yield of this procedure was recently improved up to 80–100%.^{62b} In 1968, the same principle had also been applied for the synthesis of tetrachlorobutatriene **94**.⁶³

III.4. Synthesis of Butatrienes from Butenones

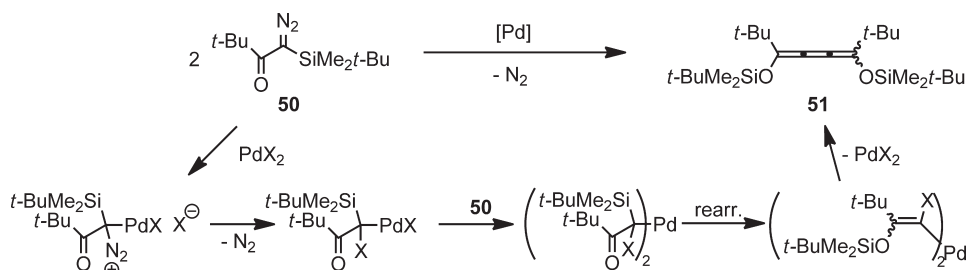
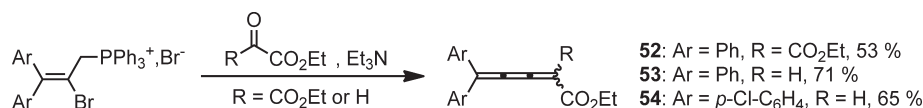
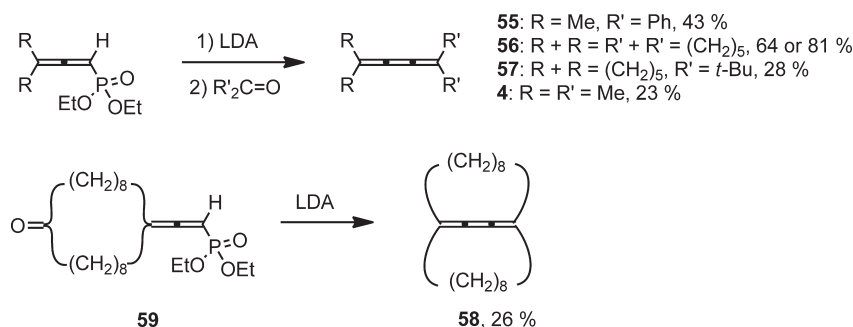
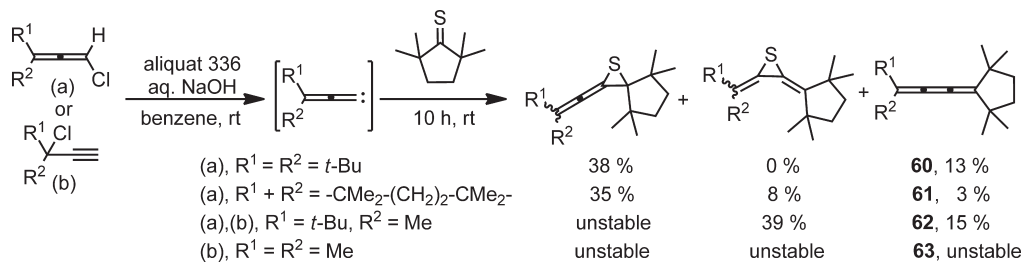
A more anecdotic method for the formation of butatrienes involves a skeletal rearrangement of cyclic butenones (also referring to section III.8). In 1987, sulfurization of the methylidenecyclopropanones **95–97** with P₂S₅ in pyridine was thus described by Ando et al. to produce the butatrienes **4**, **61**, and **98** in low yield, in mixture with allenic products.⁶⁴ The preparation of **61** (in 6% yield only) required ultrasonic activation of the rigidly hindered substrate (Scheme 32).

III.5. Synthesis of Butatrienes from Butenynes

Although 1,4-disubstituted butatrienes have been shown to be thermodynamically less stable than their butenyne isomers,^{4,40a} specific conditions allow for the preparation of butatrienes from 1,3-enynes by substitutive rearrangement, through either addition–elimination, concerted SN', or elimination–addition processes.

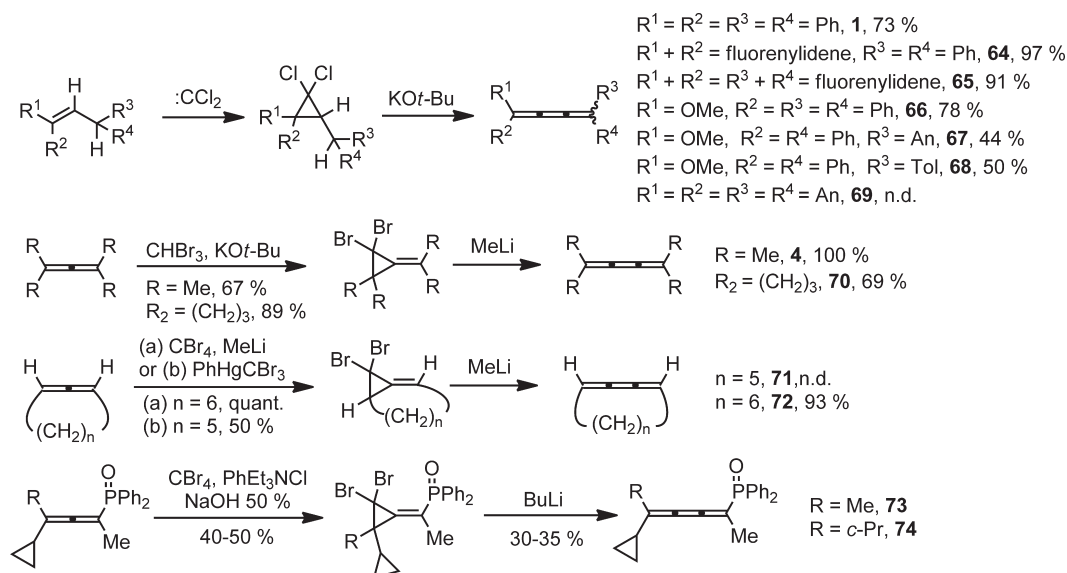
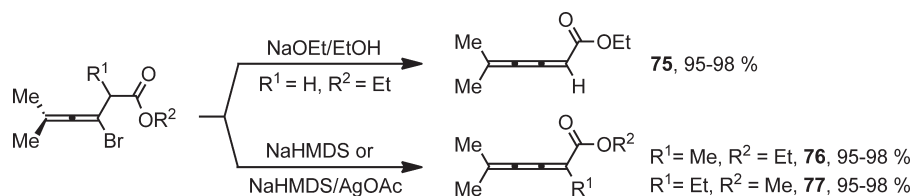
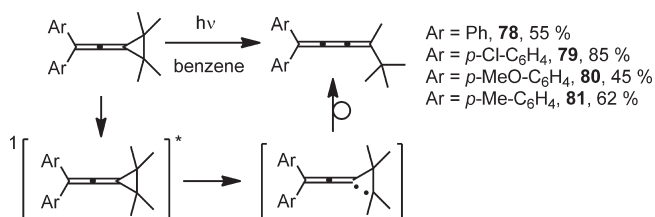
Sequential addition–elimination of thiolate anions at sp and sp² carbon atoms of tetrachlorobutenyne **99** was described by Roedig et al. in 1977.⁶⁵ This reaction, performed in two steps, allows for introducing two types of thioxy substituents at the butatriene moiety (Scheme 33). The first substitution occurs at the alkynyl terminus of **99**, thus giving the monothioether intermediate, which then reacts with 3 equiv of another sodium thiolate anion to produce the heterosubstituted tetrathio-butatriene. Homosubstituted butatrienes **91a,g** can thus be obtained in one step from either tetrachlorobutenyne **99** or tetrachlorobutatriene **94**. Such homosubstituted tetrathio-butatrienes **91** can also be obtained from butadiene precursors (Scheme 30, section III.2).^{59,60}

Anti-S_N2'-type nucleophilic substitutions of 3-bromobutenynes by organocopper reagents were described by Vermeer et al. to

Scheme 20. Proposed Mechanism for the Palladium-Catalyzed Coupling of the Silyldiazoketone **50** to the Dioxabutatriene **51**⁴³Scheme 21. Preparation of Butatrienes from Bromoallylphosphoniums and α -Keto Esters⁴⁵Scheme 22. Preparation of Butatrienes from Ketones and Allenylphosphonates^{46,47}Scheme 23. C₃ + C₁ Production of Butatrienes via Allenylidene C₃ Reactants⁴⁸

produce butatrienes in good yields.⁶⁶ In accordance with the proposed 1,3-anti substitution mechanism (Scheme 34), the reaction is totally *cis*-stereoselective. The chemoselectivity of the reaction was found to depend on the R¹ alkyl group of the copper reagent: while *iso*-propyl or *tert*-butyl nucleophiles afforded pure butatrienes, *n*-alkyl groups led to impurities, which were assumed to arise from subsequent attack of the formed butatrienes by the still nonreacted copper reagent. Finally, phenylcopper was found to be completely inert toward bromobutenynes.

Base-induced 1,3-elimination of triflic acid from triflic enol esters of ynones generates butatrienylidenes, which may then react by cyclopropanation of alkenes or by insertion into X–H bonds. Stang et al. showed that when using potassium *tert*-butoxide as a base, the resulting butatrienylidenes can be trapped with 2,3-dimethyl-but-2-ene to give the butatrienes **100** and **101** in moderate yields (Scheme 35).⁶⁷ With cyclohexene, only the [4]radialenic dimers **102** and **103** could be isolated. The same authors also reported that the transient butatrienylidenes

Scheme 24. $C_1 + C_3$ Production of Butatrienes from Dihalocarbene C_1 Reactants^{49,50}Scheme 25. Synthesis of Butatrienes from Butallenic Precursors⁵¹Scheme 26. Preparation of Butatrienes by Irradiation of Allenylidencyclopropanes⁵²

react with hydrides of group 14 elements to give silyl-, germyl-, or stannyl-substituted butatrienes in moderate to good yields.⁶⁸

Thermal isomerization of tetrakis(trimethylsilyl)butenyne to tetrakis(trimethylsilyl)butatriene **41** was also reported as a secondary process during the pyrolysis of tetrakis(trimethylsilyl)-tetrahedrane (see section III.8, Scheme 67).

III.6. Synthesis of Butatrienes from Butadiynes

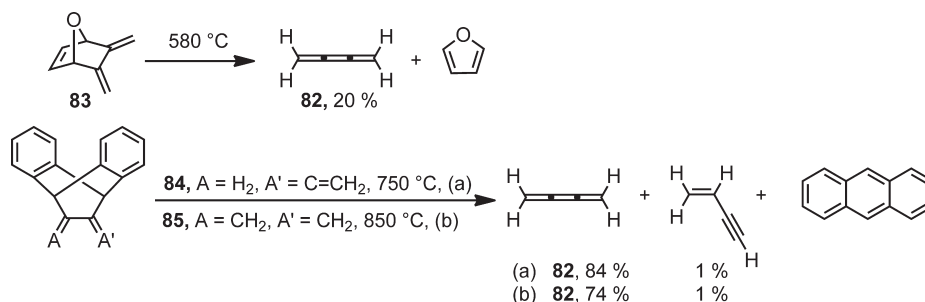
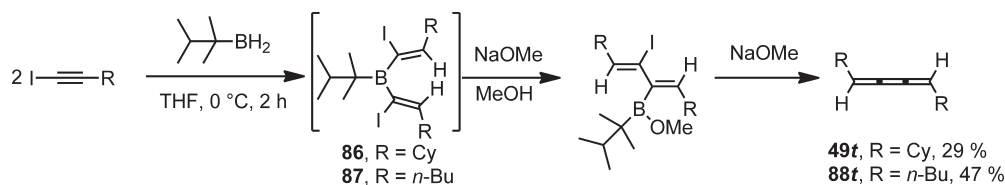
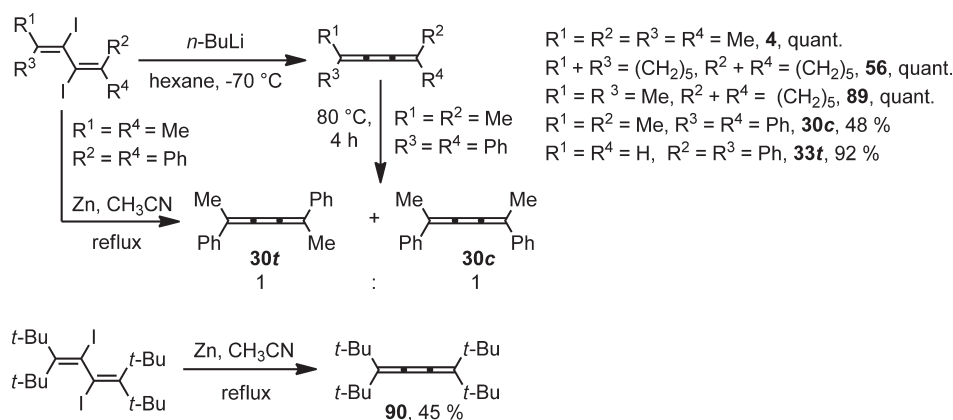
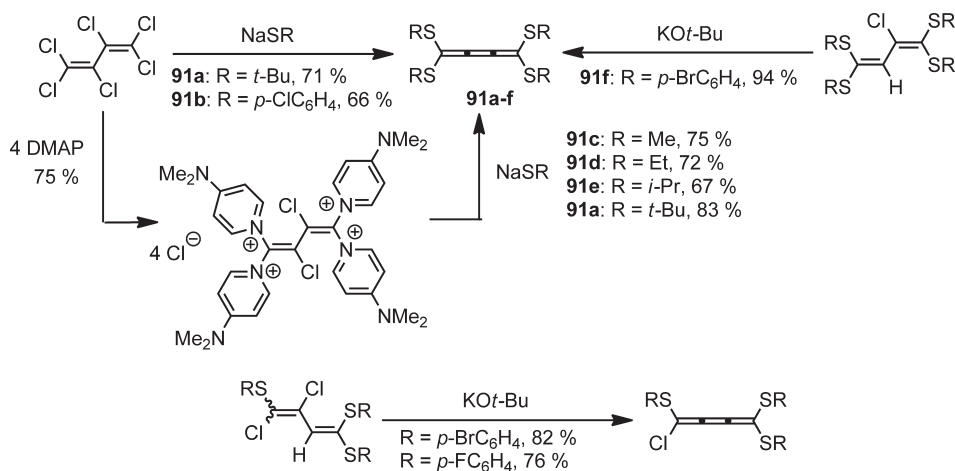
Except for two examples, most of the reported methods for the preparation of butatrienes from butadiynes involve the use of metallic complexes, in either catalytic or stoichiometric amounts.

The first exception is the synthesis of tetraiodo- and tetrabromobutatrienes **104** and **105**, described by Goroff et al. in 2002 and 2004, respectively.⁶⁹ They were prepared by halogenation

of the dihalobutadiyne precursors and obtained in mixture with the corresponding hexahalobutadienes arising from overhalogenation processes (Scheme 36). The second addition of bromine being faster than that of iodine (even at -25°C), overbromination appeared to be much more difficult to control, thus explaining the low yield in **105**. After the preparation of tetrafluoro- and tetrachlorobutatrienes **92** and **94** from hexahalobut-2-enes,⁶¹⁻⁶³ the two products **104** and **105** completed the tetrahalobutatrienes family (see section III.3). Their crystal structures could also be determined by X-ray diffraction analysis (see section VI, Table 4).

The second exception concerns the synthesis of tetrathiobutatrienes, the preparation of which from tetrachlorobutenyne or hexachlorobutadiene is reviewed in the previous section (see Schemes 30 and 33).^{59,60,65} In 2003, Block et al. envisaged the same targets and their tetraseleno analogues by reaction of the dilithium salt of butadiyne with dichalcogenides (Scheme 37).⁷⁰ The selectivity in butatriene vs butenyne or butadiene products was shown to strongly depend on the nature and stoichiometry of the reactant.

In 1989, Yasuoka et al. described a method for the synthesis of tetrakis(trimethylsilyl)butatriene **41** from bis(trimethylsilyl)butadiyne **106**,⁷¹ using a procedure reported by Oshima from simple alkyne substrates.⁷² The butatriene **41** was previously prepared by dimerization of bis(trimethylsilyl)acetylene (see section II.1.3),^{36,37} but could be here generated in 33% yield by reaction of **106** with $(\text{TMS})_3\text{MnMgMe}$, formed in situ from a mixture of

Scheme 27. Generation of Butatriene (C_4H_4) by Thermolytic Retro-Diels–Alder Reaction^{53,54}Scheme 28. Two-Step Synthesis of *trans*-Dialkylbutatrienes via Iodoborylbutadienes⁵⁵Scheme 29. Synthesis of Butatrienes from 2,3-Diiodobutadienes^{56–58}Scheme 30. Synthesis of Thiobutatrienes from Chlorobutadiene Precursors^{59,60}

$\text{Me}_3\text{Si}-\text{SiMe}_3$, MeLi , MeMgI , and MnCl_2 . Hiyama et al. also reported a preparation of the same butatriene **41** by palladium-catalyzed double silylation of the same precursor **106** with $\text{Si}_2\text{Cl}_n\text{Me}_{6-n}$ followed by treatment with methylmagnesium bromide.⁷³ This procedure afforded the butatriene **41** in low to moderate yield, in mixture with other products, among which was the tetrasilylated enyne **107** (Scheme 38).

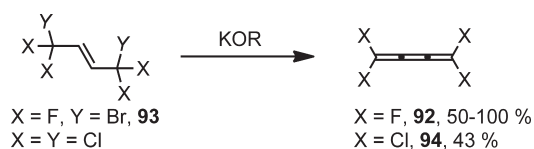
Later in 2000, Dyker et al. described a synthesis of tetraarylbutatrienes by a palladium-catalyzed reaction of butadiynes with aryl halides in the presence of a base (Scheme 39).⁷⁴ The tetraphenylbutatriene product **1**, selectively obtained at 60 or 80 °C, could be subsequently transformed into the benzofulvene **108** at higher temperature (>100 °C). With other aryl substituents ($\text{Ar}^2 \neq \text{Ph}$), only the butatrienes **109–112** were produced, even at high temperature. Mixtures of *cis* and *trans* isomers were

however systematically obtained, and the authors proposed that the *cis*–*trans* isomerization occurred at the level of the vinylpalladium intermediate.

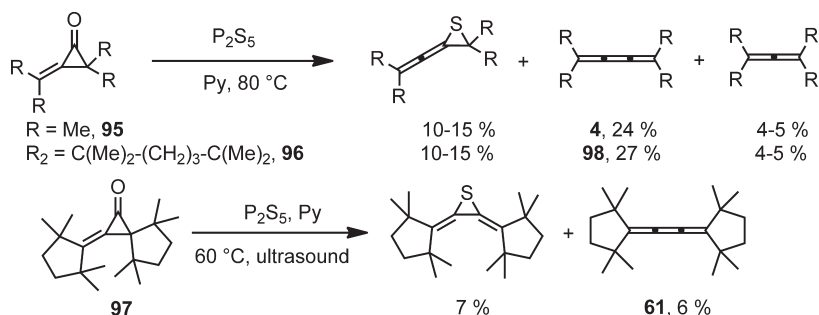
More recently, stoichiometric zirconium-mediated coupling of butadiynes with aldehydes or ketones was reported by Liu et al. to efficiently produce hydroxymethylbutatriene derivatives in a *cis*-stereoselective manner (Scheme 40).⁷⁵ Addition of aldehydes to the zirconacycle intermediates **113** was found to occur exclusively at the alkynyl carbon atom bearing the R^1 substituent, giving the *cis*-hydroxymethylbutatrienes **114c** in good yields after hydrolysis. Addition of ketones to the silylated zirconacycle **113a** generated from bis(trimethylsilyl)butadiyne **106** afforded the corresponding 2,3,4-hexatrien-1,6-diol derivatives **115c** in high *cis* stereoselectivity.

In their study of the preparation of pentenynols by selective monotitanation of butadiynes and subsequent reaction with benzaldehyde, Sato et al. also observed the formation of hydroxybenzylbutatrienes (Scheme 41).^{76a} Pentenynols were found as major products, but in two cases, the hydroxymethylbutatriene side products could be isolated as single (non-assigned) diastereoisomers. The use of a suitable Lewis acid (EtAlCl_2 , $\text{Et}_2\text{O} \cdot \text{BF}_3$) has been recently shown to make the process highly *cis*-stereoselective for a large range of aldehyde substrates.^{76b}

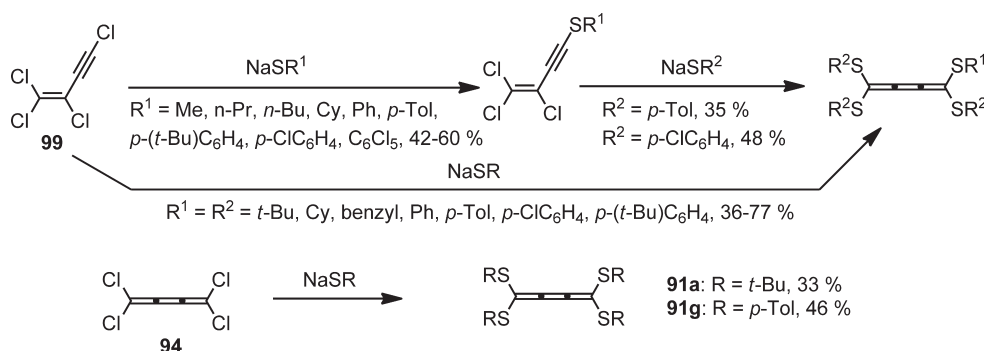
Scheme 31. Synthesis of Tetrahalogenated Butatrienes by Double Dehydrohalogenation of 1,4-Dihalobut-2-enes^{61–63}



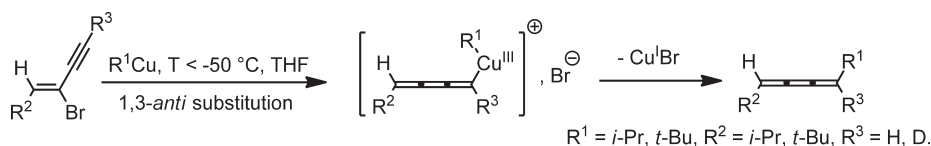
Scheme 32. Reduction of Alkylidenecyclopropanones to Butatrienes (and Other Products) by Sulfurization⁶⁴



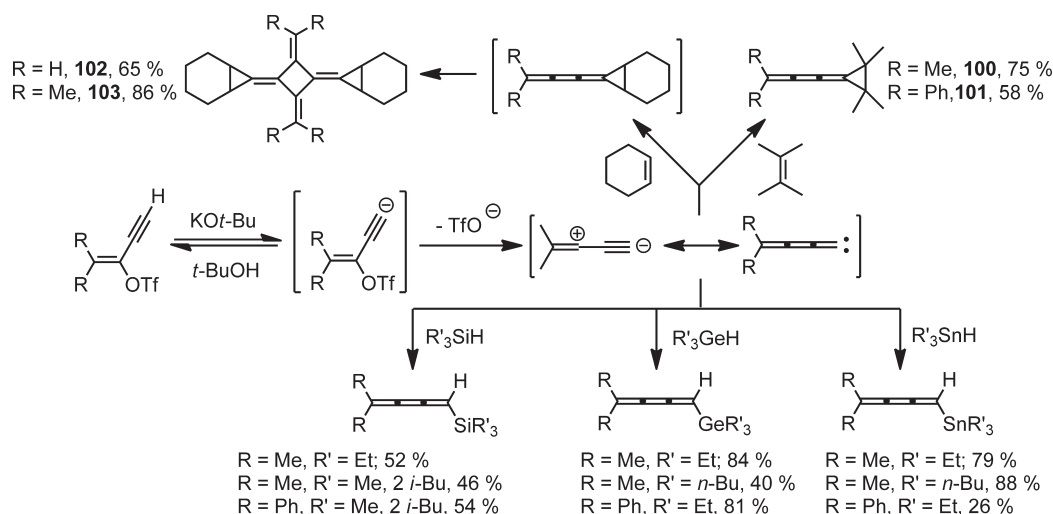
Scheme 33. Preparation of Tetrathiobutatrienes from Tetrachlorobutenyne or Tetrachlorobutatriene⁶⁵



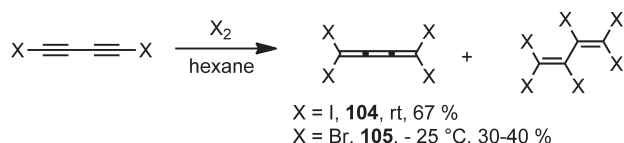
Scheme 34. Substitution of 3-Bromobutenynes by Alkylcopper(I) Nucleophiles⁶⁶



Scheme 35. Base-Induced 1,3-Elimination from Triflic Enol Esters of Ynones and Reactions of the Resulting Butatrienylidenes with Alkenes and Hydrides of Group 14 Elements^{67,68}



Scheme 36. Dihalogenation of Dihalobutadiynes to Tetrabromo- and Tetraiodobutatrienes⁶⁹



III.7. Synthesis of Butatrienes from But-2-yne Derivatives

Many examples of preparation of butatrienes from but-2-yne precursors have been reported. The large majority of them are based on the reduction of 1,4-dioxybut-2-yne substrates, but other functional but-2-ynes such as halogenated or unsaturated derivatives were also used in reductive, oxidative, or eliminative processes. The most particular cases are examined first.

III.7.1. Butatrienes from But-2-yne Precursors: Oxidative Methods. In 1967, Zecher and West described the synthesis of the butatriene **116** by oxidation of the butyne precursor **117**, itself produced by photolytic decarbonylation of the cyclopropanone **118** (Scheme 42).⁷⁷ Reduction of **116** back to **117** could be achieved using a Zn/HCl mixture. Direct oxidation of **118** with potassium ferricyanide afforded the bis-quinomethane intermediate **119**, which undergoes spontaneous decarbonylation to the butatriene **116** in a few hours (this $C_5 - C_1$ fragmentation process is thus also relevant in section IV). The reduction of **119** back to **118** was however possible by rapid treatment with hydroquinone.

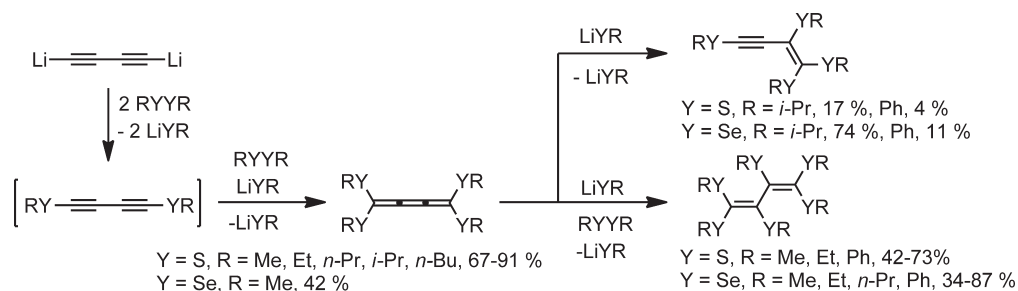
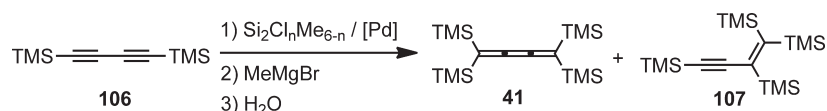
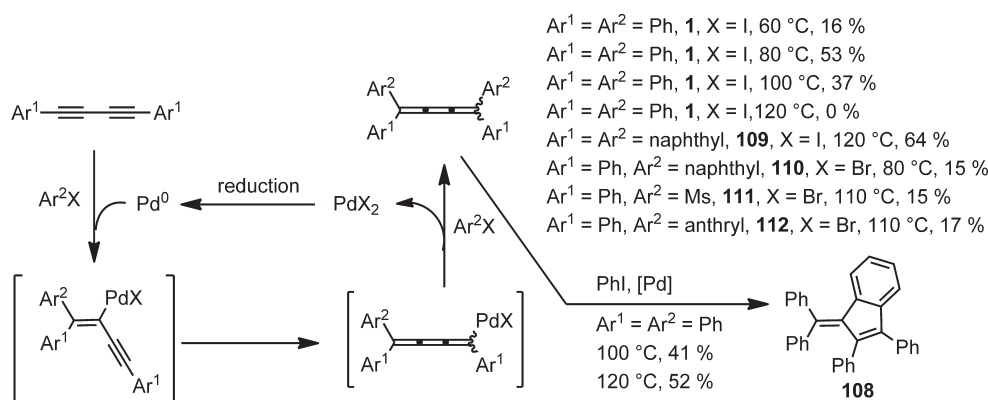
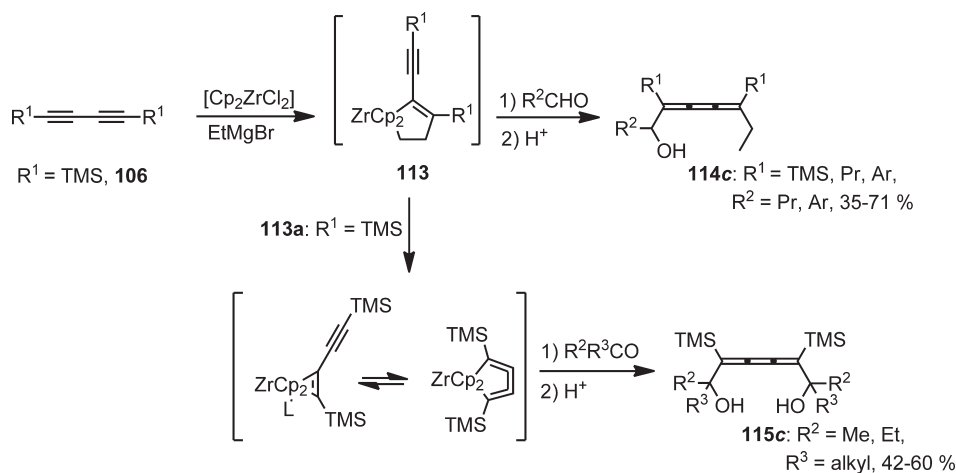
In 1982, Murata et al. reported a unique example of butatriene synthesis by dehydrogenation of the bis(phenalenyl)acetylene **120** (Scheme 43).⁷⁸ The reaction proceeds in two steps, starting with a hydride abstraction (using the trityl cation), to give the monocation **121**, which could be isolated. This cation was then deprotonated with a large excess of triethylamine to afford the butatriene **122** in 35% overall yield. In spite of its poor stability, this “functional carbo-mer” of

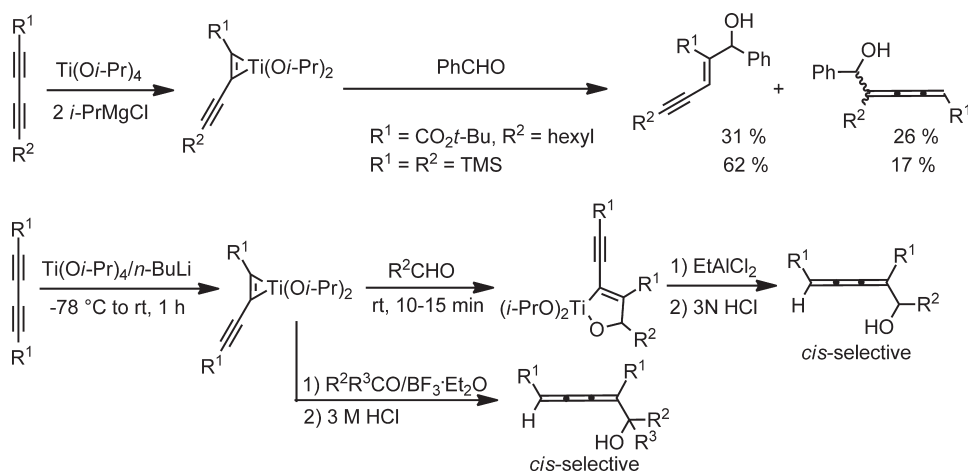
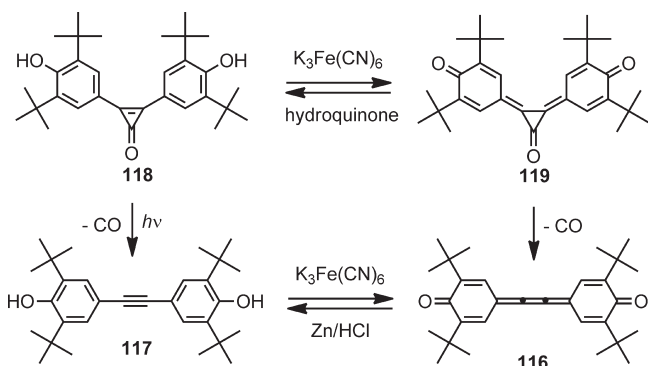
biphenalenylidene⁷⁹ could be purified by chromatography over Florisil and precipitation.

Tetrakis(trimethylsilyl)butatriene **41** could be generated by oxidative flash vacuum pyrolysis (FVP) of hexakis(trimethylsilyl)butyne **123** at 650 °C (Scheme 44).⁸⁰ The yield in **41** (ca. 40%) is similar to those of the above-described alternative methods starting from bis(trimethylsilyl)acetylene **40**^{36,37} (see Scheme 15) or bis(trimethylsilyl)butadiyne **106**^{71,73} (see Scheme 38). The FVP method afforded a mixture of products collected in a cold trap, from which the butatriene **41** could be separated by crystallization.

III.7.2. Butatrienes from But-2-yne Precursors: Isohypsic and Eliminative Methods. A few butatrienes were prepared by isohypsic elimination or SN' substitution from alkenylidene monooxybutyne precursors. Nucleophilic 1,5-substitutions of 1-oxypent-4-en-2-yne with alkylsilver reactants were thus reported to produce the corresponding butatrienes **124** in good yields (Scheme 45).⁸¹ The same vinylogous/cumulogous process is involved in the epoxy ring-opening of the butenyne-oxirane derivatives **125** to the butatrienes **126**, which were isolated in higher yields from *tert*-butylsilver than from less bulky silver reactants.⁸² Higher yields were however systematically restored when the reaction was carried out in the presence of 1 equiv of AgBr. In 1991, a further vinylogous version of the process was finally exemplified by Hiramata et al. by the 1,7-substitution of the diendiyne **127** to the enynylbutatriene **128** (Scheme 45).⁸³

The process of converse polarity, i.e., electrophilic 1,5-vinylogous/cumulogous substitution of 1-oxypent-4-en-2-yne substrates, can also be envisioned in acidic medium. The first example was reported by Kosower and Sorensen in 1963.⁸⁴ The formylbutatriene **129** was thus obtained by treatment of the methoxyenynyl carbinol **130** with traces of potassium hydrogen sulfate. The outcome of the reaction is however highly sensitive to the acidic conditions used: while the dihydropyrone **131** was obtained with catalytic amounts of acid, the formylallene **132** was produced in the presence of a large excess of potassium hydrogen sulfate (Scheme 46).

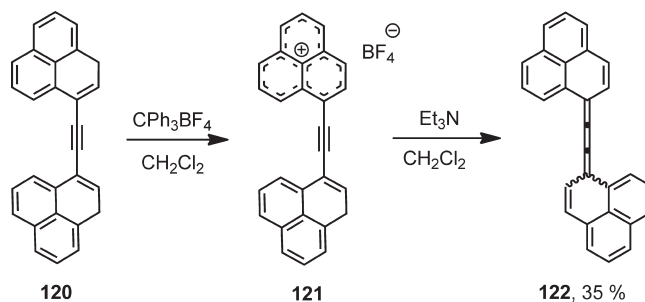
Scheme 37. Reactions of Dilithiobutadiyne with Dichalcogenides⁷⁰Scheme 38. Palladium-Catalyzed Synthesis of Tetrakis(trimethylsilyl)butatriene from Bis(trimethylsilyl)butadiyne⁷³Scheme 39. Palladium-Catalyzed Synthesis of Tetraarylbutatrienes from Diarylbutadiynes⁷⁴Scheme 40. Zirconium-Mediated Cis-Stereoselective Synthesis of Hydroxymethylbutatrienes from Butadiynes and Carbonyl Compounds⁷⁵

Scheme 41. Titanium-Promoted Synthesis of Hydroxymethylbutatriene Derivatives from Butadiynes and Aldehydes or Ketones⁷⁶Scheme 42. A Reversible Cumulogous Benzoquinone/Hydroquinone Redox System⁷⁷

By analogy with the Peterson-type 1,2-elimination from β -acetoxy silanes giving alkenes, 1,4-elimination from 1-silyl-4-acetoxybut-2-yne gives butatrienes. Chow et al. indeed reported that treatment of acetic esters of silylbutynols such as **133** with TBAF afforded the corresponding butatrienes, such as **134** in 71% yield (Scheme 47).⁸⁵ Simultaneously, Wang et al. described a one-pot procedure affording the same butatrienes in similar yields directly from the silylbutynol precursors via the mesylate intermediate.⁸⁶

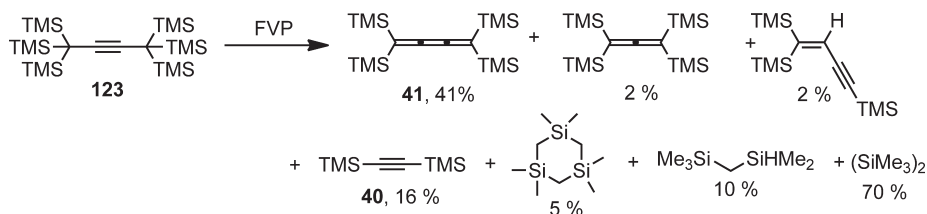
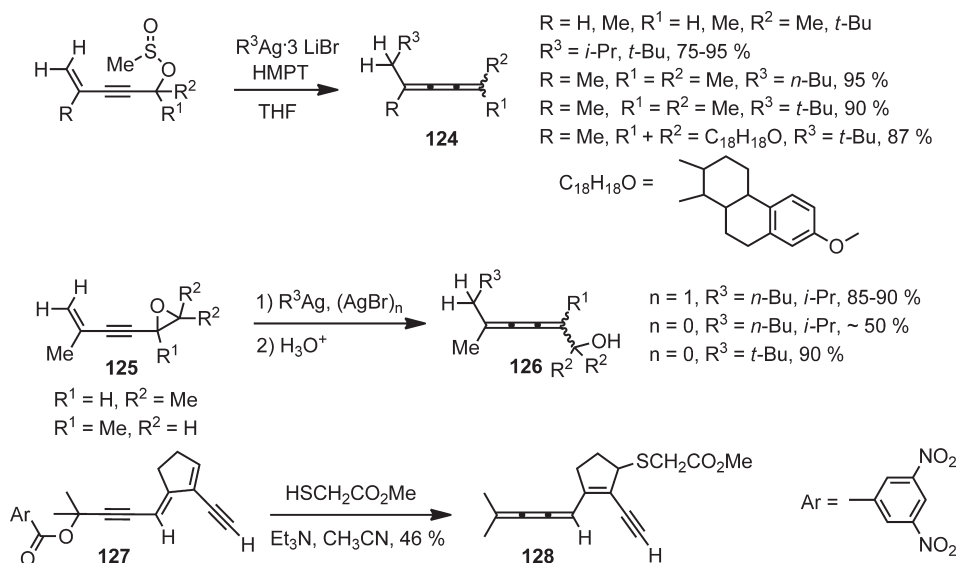
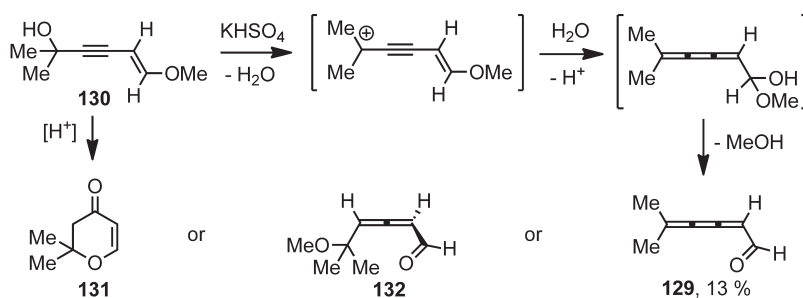
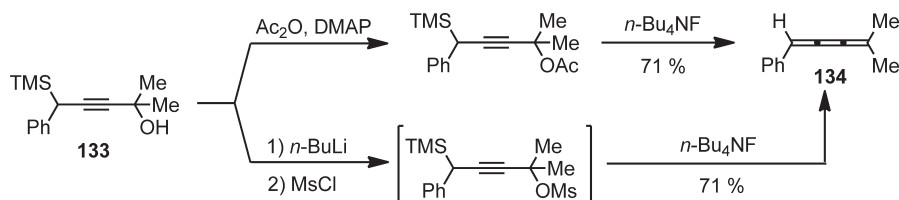
As shown by Konoike et al. in 1998, analogous stannylbutynol derivatives can be converted to butatrienes in a similar way.⁸⁷ Butynol precursors with a propargylic methylene group were thus sequentially treated first with butyllithium and Bu_3SnCl and then with methanesulfonyl chloride and triethylamine, to give the corresponding butatrienes **33** and **135** in moderate yields (Scheme 48). The intermediate stannylbutynols were actually generated as mixtures with the allenic stannylbutadienol isomers, both of them affording the same butatriene products. The procedure was also applied to the preparation of the conjugated enynylbutatriene **136**.

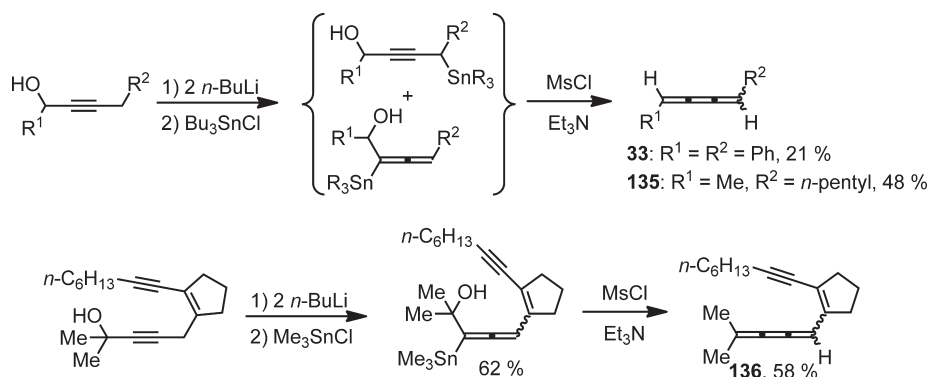
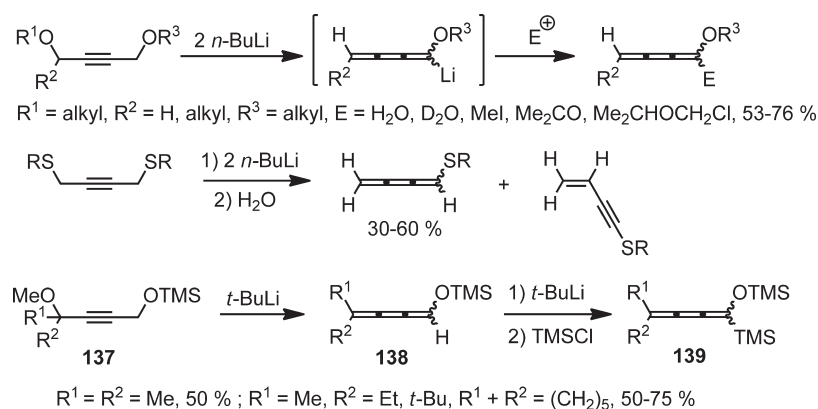
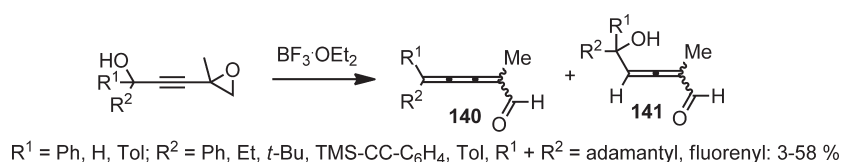
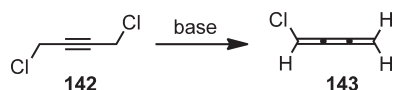
Brandsma et al. reported a quite general procedure for the preparation of butatrienyl ethers and thioethers by basic treatment of bispropargylic diethers or dithioethers containing a

Scheme 43. Two-Step Synthesis of a Butatriene from Bis(phenalenyl)acetylene, by Sequential Hydride Abstraction–Deprotonation⁷⁸

primary propargylic functional methylene groups (CH_2X , $\text{X} = \text{O}, \text{S}$), followed by a trapping of the butatrienyllithium intermediates with electrophiles (Scheme 49).⁸⁸ Butatrienyl ethers were thus obtained in quite good yields, while butatrienyl thioethers were generally obtained in mixture with their enynyl form of the lithiated intermediates. The same kind of base-promoted elimination was described by the same authors from methoxybutyne derivatives with primary propargylic silyl ether groups (Scheme 49).⁸⁹ Treatment of such precursors, **137**, with 1 equiv of *tert*-butyllithium afforded the sensitive silyloxybutatrienes **138**, which were then treated with 1 more equiv of *tert*-butyllithium and trapped with trimethylsilyl chloride to give the stable silyloxybutatrienes **139** in 50–75% yields (Scheme 49).

Dioxybutyne substrates in which one of the propargylic oxygen atoms is involved in an epoxide ring were studied by Rodriguez et al.⁹⁰ and later by Furuta et al.⁹¹ Treatment of such epoxybutynols with $\text{BF}_3 \cdot \text{OEt}_2$ was thus reported to give the formylbutatrienes **140**, possibly in mixture with hydroxymethylformylallenes **141**, which were assumed to result from the hydration of **140** (Scheme 50). Although the pentatrienals **140** occurred as major products in the crude material, they were isolated in low yields because of their poor stability.

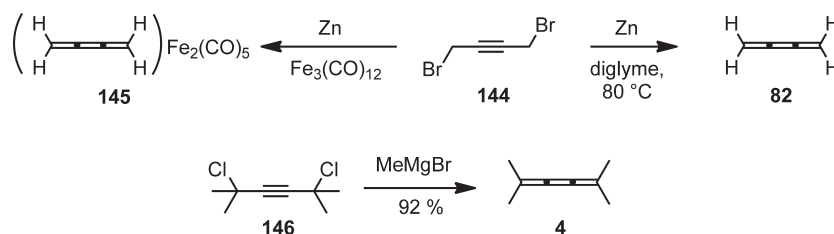
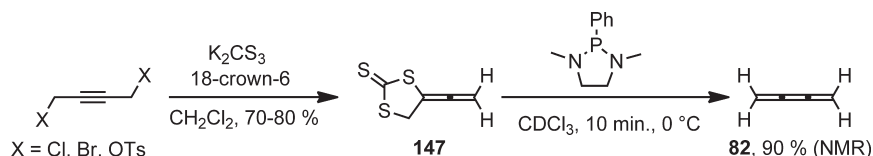
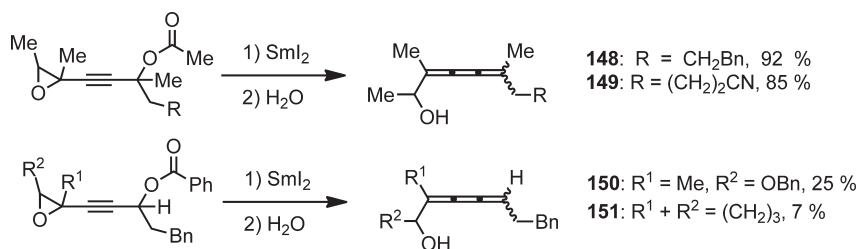
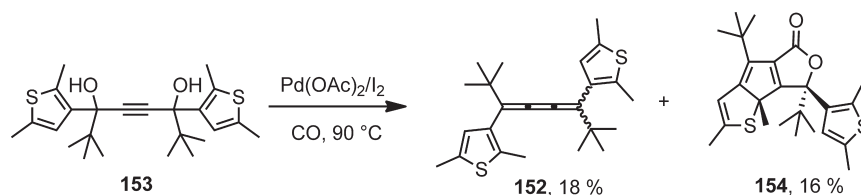
Scheme 44. Pyrolytic Preparation of Tetrakis(trimethylsilyl)butatriene from Hexakis(trimethylsilyl)but-2-yne⁸⁰Scheme 45. Synthesis of Butatrienes by Vinylogous/Cumulogous 1,5- or 1,7-Substitutions of Oxypentenyne Substrates^{81–83}Scheme 46. Reactivity of a Hydroxyenyne under Optimized Acidic Conditions⁸⁴Scheme 47. Synthesis of a Butatriene from a Silylbutynol Substrate^{85,86}

Scheme 48. Synthesis of Butatrienes via Stannybutynol Intermediates⁸⁷Scheme 49. Synthesis of Butatrienyl Ethers and Thioethers from the Corresponding But-2-yne Precursors^{88,89}Scheme 50. Synthesis of Formylbutatrienes from Epoxybutynols^{90,91}Scheme 51. Synthesis of Chlorobutatriene from 1,4-Dichlorobut-2-yne⁹²

Borg et al. also reported that treatment of 1,4-dichlorobut-2-yne **142** with a base, in the absence of a reducing agent, gave a mixture of products from which chlorobutatriene **143** could be isolated (Scheme 51).⁹²

III.7.3. Butatrienes from But-2-yne Precursors: Reductive Methods. The use of 1,4-dihalobut-2-yne derivatives as butatriene precursors was reported on several occasions. Except

the above-described isohypsic eliminative process (Scheme 51),⁹² all the other examples involved reductive elimination processes. In 1952 and 1954, the first preparation of the unsubstituted butatriene **82** was described by zinc-promoted Wurtz-type reductive elimination from 1,4-dibromobut-2-yne **144** (Scheme 52).⁹³ This method was later optimized by Traetteberg et al., who reported that treatment of **144** with metallic zinc in diglyme at 80 °C produced **82** as a gas, which could be trapped and isolated by distillation.⁹⁴ In 1965, the same transformation was performed in the presence of $\text{Fe}_3(\text{CO})_{12}$, affording the butatriene complex **145** (Scheme 52).⁹⁵ A similar Wurtz-type dehalogenation reaction was later applied to the dichlorobut-2-yne derivative **146** using methylmagnesium bromide as a reducing agent, giving tetramethylbutatriene **4** in 92% yield (Scheme 52).⁹⁶

Scheme 52. Synthesis of “Weakly Substituted” Butatrienes by 1,4-Dehalogenation of 1,4-Dihalobut-2-yne Substrates^{93–96}Scheme 53. Two-Step Synthesis of Unsubstituted Butatriene from 1,4-Dihalobut-2-yne Precursors, via a Thioallene Intermediate⁹⁷Scheme 54. Reductive Methods for the Preparation of Hydroxyalkylbutatrienes from Epoxybutynyl Esters⁹⁸Scheme 55. Carbon Monoxide as Reducing Agent in a Palladium-Catalyzed Conversion of a Hindered Butyndiol Derivative to the Corresponding Butatriene⁹⁹

In 1991, Herges et al. showed that butatriene can also be generated from 1,4-dihalobutynes in two steps.⁹⁷ A first treatment with potassium thiocarbonate in the presence of a crown-ether thus gives the allene intermediate **147** in 70–80% yield, which can then undergo desulfurization upon addition of a diazaphospholidine reagent. The yield in butatriene **82** was estimated as 90% by NMR spectroscopy (Scheme 53).

Reductive elimination from 1,4-dioxybut-2-yne derivatives is the most employed principle for the synthesis of butatrienes. Various reducing agents can be used.

SmI₂-mediated reduction of epoxybutynyl esters was thus reported by Aurrecoechea et al. to give the hydroxymethylbutatriene derivatives **148**–**151** (Scheme 54).⁹⁸ While the butatrienyl

carbinols **148** and **149** were obtained in good yields from acetate precursors, their congeners **150** and **151** were isolated in low yields from benzoate precursors.

A singular catalytic procedure described by Kiji et al. in 2003 involves carbon monoxide as reducing agent of hindered but-2-yn-1,4-diols.⁹⁹ The butatrienic product **152** was however obtained in low yield from the butyndiol **153**, along with the targeted carbonylation product, the lactone **154** (Scheme 55).

Since 1920, the most frequently used systems for the reduction of 1,4-butyndiols to butatrienes have been the KI/H₂SO₄, SnCl₂/AcOH, and SnCl₂/HCl systems. Numerous applications of these early methods have been reviewed before 1980,^{11a,b,17} and only the most recent results are mentioned below.

The reduction of tetraphenylbutyndiol to tetraphenylbutatriene **1** is selected for a comparative purpose (Table 2).¹⁰⁰ For this reference reaction, the most efficient reagent appears to be $\text{TiCl}_3/\text{LiAlH}_4$.^{100f} To the best of our knowledge, this is, however, the sole reported example of the use of this system. With the more classical systems, $\text{KI}/\text{H}_2\text{SO}_4$ ^{100b–e} and SnCl_2/HCl ,^{100a,e} the reported yields are quite variable, depending mainly on the purification method used. Nevertheless, these two systems afforded **1** in yields comparable with those obtained by $\text{C}_1 + \text{C}_3$ coupling (73%, Scheme 24)⁴⁹ or by C–C bond-forming reaction from butadiyne precursors (16–53%, Scheme 39).⁷⁴

The rigid biphenylene analogue of **1**, bis-fluorenylidene ethene **65**,^{100e} was obtained from the corresponding butyndiol precursor in 78% yield with the $\text{KI}/\text{H}_2\text{SO}_4$ system and in 34% yield only with the SnCl_2/HCl system.¹⁰¹ For comparison, the same butatriene **65** was prepared in 91% yield by $\text{C}_1 + \text{C}_3$ coupling (Scheme 24).⁴⁹

Beyond the tetraarylbutatrienes, other butatrienes bearing highly conjugated polyenyl substituents could also be efficiently prepared by the reductive elimination method. From 1979 to 1981, Nakagawa et al. thus reported on the synthesis of large dehydroannulenic bicycles with endocyclic or exocyclic butatriene functions, **155a** and **155b**, respectively, using the SnCl_2/HCl system (Scheme 56).^{102,103} Whereas the butatriene **155b** with two didihydro[13]annulenyliidene endings was obtained in 56% yield, the butatriene analogue with a single didihydro[13]annulenyliidene ending and two phenyl substituents was obtained in a much higher yield of 94%.¹⁰³ This and other examples (Scheme 56) illustrate the specificity of the SnCl_2/HCl system

Table 2. Comparison of Acidic Reductive Systems for the Conversion of Tetraphenylbut-2-yne-1,4-diol to Tetraphenylbutatriene **1**: $\text{Ph}_2\text{C}(\text{OH})-\text{C}\equiv\text{C}-\text{C}(\text{OH})\text{Ph}_2 \rightarrow \text{Ph}_2\text{C}=\text{C}=\text{C}=\text{Ph}_2$

reducing agent	acid	solvent/T	yield in 1 (%)	references
dry SnCl_2	HCl	CHCl_3/rt	57–71	100a,100e
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	HCl	CHCl_3/rt	32	100a
KI	H_2SO_4	EtOH/Δ	70–79	100b–100e
LiAlH_4	TiCl_3	$\text{THF}/0^\circ\text{C} \rightarrow \Delta$	83	100f

for butatriene targets bearing rigid or aromatic π -conjugated substituents.

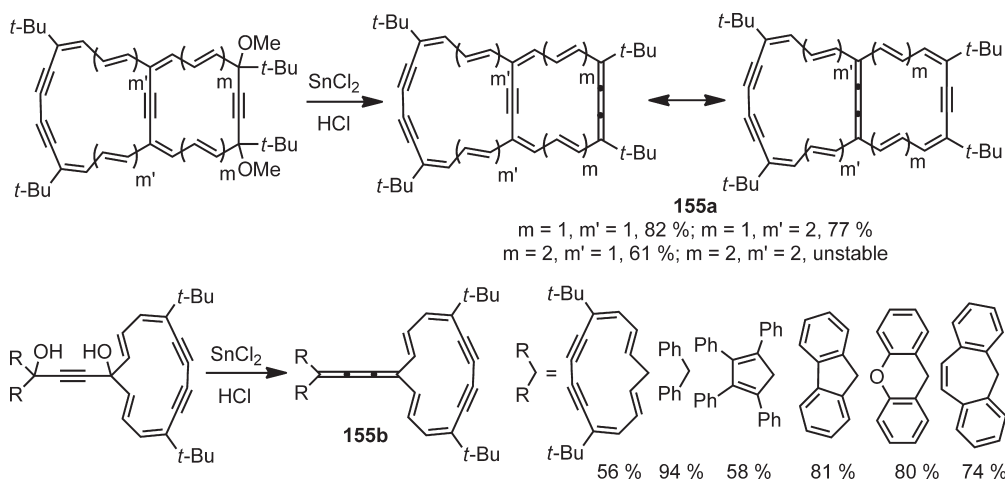
In 1981, the work of Murata et al. enlarged the range of butatrienes with geminal cyclic endings from fluorenylidene and didihydro[13]annulenyliidene representatives (**65** and **155b**) to thioxanthenylidene and dihydrothiopyranlyidene representatives **156** and **157**.¹⁰⁴ These products were obtained in good yields from the corresponding butyndiols using the SnCl_2/HCl system. The butatriene **157** could also be transformed into the thiopyranlyidene **158** in three steps (Scheme 57). In 2008, the same method was applied to the synthesis of butatrienes with tricyclic endings, **65** and **159**, albeit in lower yields.¹⁰¹ Oxidation of **159** in the presence of the superacid $\text{SbF}_6/\text{SO}_2\text{ClF}$ at low temperature afforded the annelated bis-tropylium dication **160**.

The SnCl_2/HCl system was also used for the preparation of other functional tetraarylbutatrienes from dioxybutynes precursors. In 1999 and 2000, Kijima et al. thus described an application of this reagent for the preparation of the bromoarylbutatrienes **161** and **162** in moderate yields (Scheme 58).¹⁰⁵ Whereas most reports indicate the use of commercially available SnCl_2 dihydrate, the authors here emphasize the use of monohydrated SnCl_2 . Further coupling of **161** with trimethylsilylacetylene under Sonogashira conditions, followed by protodesilylation, afforded the diethynyltetraphenylbutatriene **163** in 60% yield.

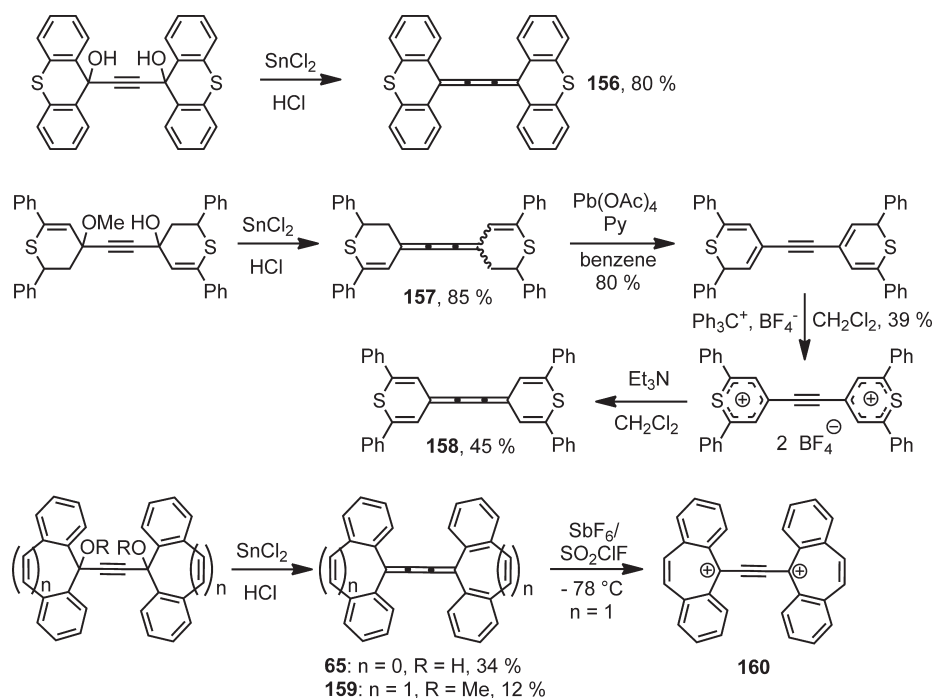
The ferrocenylbutatrienes **164** and **165** were prepared by Bildstein et al. from the corresponding methoxyhydroxybutyne precursors using a modified SnCl_2 -based reducing system: as the classical SnCl_2/HCl system was found to be inefficient, several alternatives were envisioned, and the system resulting from the replacement of hydrochloric acid by acetic acid ($\text{SnCl}_2/\text{AcOH}$) turned out to be optimal (Scheme 58).¹⁰⁶ While the $\text{Zn}/\text{Me}_3\text{SiCl}$ or SmI_2 reducing system afforded **164** in very low yield, and in mixture with many byproduct, the TiCl_3/Li system mainly gave the over-reduction product **166**, which could be isolated in 69% yield (Scheme 58).^{106a}

The SnCl_2/HCl reagent is therefore not universal. In 1975, Newkome also showed that it does not allow one to prepare the pyridylbutatrienes **167** from the corresponding butyndiols **168** but affords pyridylquinolinones such as **169** in 90% yield

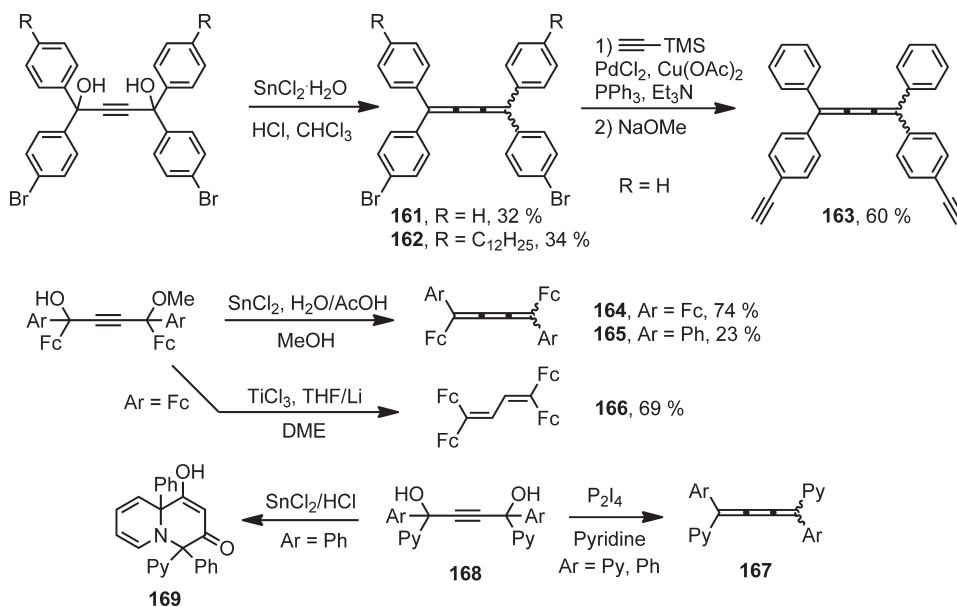
Scheme 56. Applications of the SnCl_2/HCl -Mediated Reductive Elimination Method to the Synthesis of Dehydroannulenic Bicycles with Endocyclic or Exocyclic Butatriene Functions^{102,103}



Scheme 57. Synthesis of Butatrienes with Geminal Tricyclic Endings by the Reductive Elimination Method Using the SnCl_2/HCl System^{101,104}



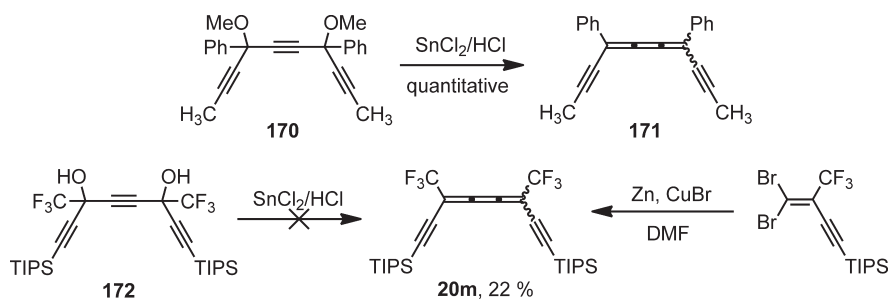
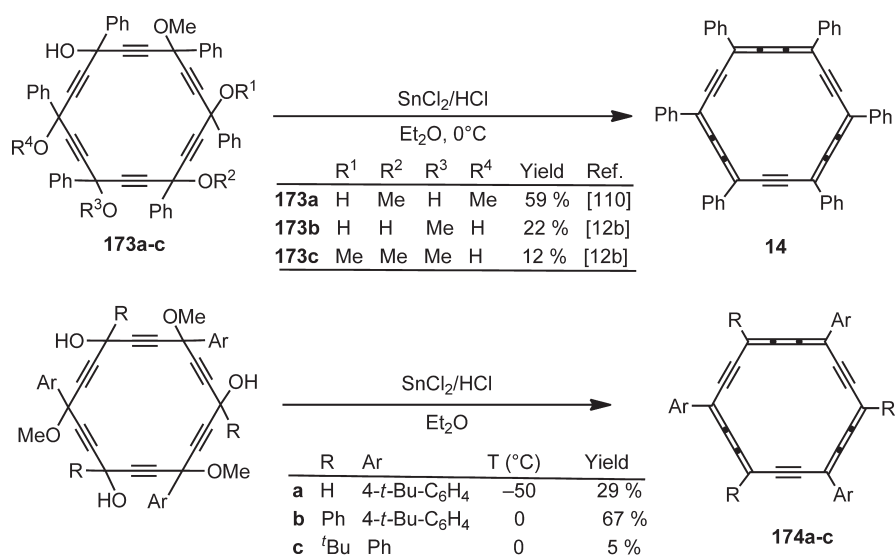
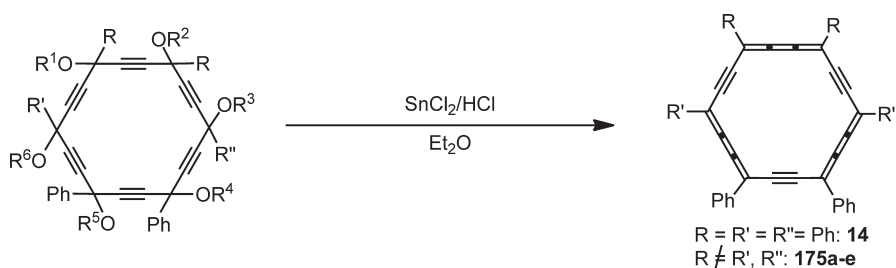
Scheme 58. Synthesis of Functional Tetraarylbutatrienes by the Reductive Elimination Method Using the Classical (SnCl_2/HCl) or Modified SnCl_2 -Based Reducing Systems^{105–108}



instead (Scheme 58).¹⁰⁷ By contrast, treatment of **168** with P_2I_4 , a reducing agent long ago used by Kuhn and Zahn for the preparation of octaheptaenes,¹⁰⁸ gave the pyridylbutatrienes **167** readily.

Even for the restricted class of the tetraaryl- or cycloalkenyl-substituted butatrienes, the above examples illustrate the absence of a general method to generate butatrienes from the “natural” 1,4-dioxybut-2-yne C_4 precursors: each case is unique.

Another class of conjugated butatrienes is constituted by the challenging alkynyl-substituted representatives, which can be prepared by $\text{C}_2 + \text{C}_2$ reductive coupling methods (see section II.1.1, Schemes 7 and 8). The ease of preparation of 1,4-dioxybut-2-yne C_4 precursors and the usability of the SnCl_2/HCl system make the reductive elimination route doubly attractive. Very recently, the “weakly capped” 1,4-dipropynylbutatriene **171** was thus prepared by

Scheme 59. Relative Efficiency of Reductive Elimination Methods for the Synthesis of Dialkynylbutatrienes from Dimethoxytriene Precursors¹⁴Scheme 60. Synthesis of Hexaphenyl-*carbo*-benzene **14** and Octupolar *carbo*-Benzenes **174a–c** from Corresponding Hexaalkoxy-[6]pericyclines by Sequential Reductive Eliminations with the SnCl₂/HCl System^{12b,109,110}Scheme 61. Synthesis of Dipolar and Quadrupolar *carbo*-Benzenes **14** and **175a–e** from Corresponding Hexaalkoxy-[6]Pericyclines by Sequential Reductive Eliminations with the SnCl₂/HCl System^{a12a,b,d}

^a See Table 3 for details.

this method from the dimethoxytriene precursor **170** (Scheme 59).¹⁴ As in the above examples where SnCl₂/HX systems proved to be efficient from aryl- or alkenyl-substituted precursors (Schemes 56, 57, 58), the presence of the phenyl substituents in **170** is crucial. For example, the bis(trifluoromethyl) homologue **172** turned out to be

completely inert in the presence of acidic reducing systems (SnCl₂/HCl, KI/H₂SO₄), even after complexation of the triple bond to a Co₂(CO)₆ moiety. The corresponding fluorinated butatriene **20m** could however be obtained through a C₂+C₂ coupling route (Scheme 10).¹⁴

Table 3. Reductive Aromatization of Hexaalkoxy[6]Pericyclines to *carbo*-Benzenes 14 and 175a–e by Sequential Reductive Eliminations with the SnCl₂/HCl System^a

<i>carbo</i> -benzene	R	R ^b	R ^{''b}	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	T (°C)	Y ₁ (%) ^c	Y ₂ (%) ^d	ref
14	Ph	Ph	Ph	H	Me	H	Me	H	Me	0	59	84	110
14	Ph	Ph	Ph	H	Me	H	H	Me	H	0	22	60	12b
14	Ph	Ph	Ph	H	Me	Me	Me	Me	H	0	12	49	12b
175a	H	Ph	Ph	H	H	Me	H	H	Me	−40	5	37	12b
175b	Ph	H	H	Me	Me	H	Me	Me	H	−20	nd	nd	12b
175c	Ph	4-An	4-An	Me	Me	H	Me	Me	H	−40	8	43	12d
175d	Ph	4-An	4-Py	H	H	H	H	Me	Me	0	16	54	12b
175e	Ph	TMS-C ₂	TMS-C ₂	H	H	Me	Me	Me	Me	−50	10	46	12b

^a See Schemes 60 and 61. ^b Acronyms: 4-An = 4-MeO-C₆H₄; 4-Py = 4-NC₅H₄; TMS-C₂ = Me₃Si-C≡C. ^c Y₁: yield in *carbo*-benzene C₁₈Ph₂R₂R'R''. ^d Y₂ = average yield per butatriene unit formed.

As mentioned in the Introduction, the dialkynylbutatriene motif is challenging for being the basic resonating constituent of the aromatic *carbo*-benzene ring. The SnCl₂/HCl system proved to be efficient for the aromatization of various hexaalkoxy-hexaphenyl[6]pericyclines 173a–c to hexaphenyl *carbo*-benzene 14 by three sequential reductive elimination processes (Schemes 60). All the substrates tested were used as quasis-tatistical mixtures of diastereoisomers and contained at least two CPh(OH) vertices with complementary CPh(OMe) vertices.¹⁰⁹ The hexaalkoxy-[6]pericycline 173a, with alternating CPh(OH) and CPh(OMe) vertices all around the C₁₈ ring, proved to be optimal, as it led to 14 in 59% yield.¹¹⁰ Indeed, the regioisomer 173b, with only two alternations of CPh(OH) and CPh(OMe) vertices, gave 14 in 22% yield, while the regioisomer 173c, without any alternation of the CPh(OH) and CPh(OMe) vertices, gave 14 in a still poorer yield of 12%.^{12b}

All other *carbo*-benzenes synthesized to date have also been obtained by reductive aromatization of hexaalkoxy[6]pericycline precursors (Scheme 60 and 61).^{12a,b,d,109,110}

Considering all the above-mentioned examples, SnCl₂/HCl-mediated reduction of pericyclic but-2-yn-1,4-diol moieties to butatrienes units of *carbo*-benzenes has been illustrated for aryl-substituted representatives only. This might be related to the stability of the corresponding benzylic carbenium ion, which, under the acidic conditions used, is likely the activated intermediate to be readily reduced by the Sn(II) reagent.¹¹¹ Beyond the inertness of the bis(trifluoromethyl)triyne 172 (Scheme 59), this requirement is also illustrated by the failure of the SnCl₂/HCl system to convert the hexaalkynylhexaalkoxy[6]pericycline 176 to the hexaalkynyl *carbo*-benzene 177 (Scheme 62).^{12c} Although trispropargylic in nature, the corresponding carbenium centers are indeed intrinsically much less stabilized than their benzylic counterparts. Nevertheless, coordination of triple bonds of 176 to Co₂(CO)₆ moieties allows one to generate Nicholas' cations, whose stability is compatible with the reduction process. After oxidative removal of the Co₂(CO)₆ moieties, the *carbo*-benzene 177 (the TES-protected version of the total *carbo*-mer of benzene C₃₀H₆)^{13d} could thus be isolated in 12% yield over the three-step–one-pot reaction sequence (Scheme 62).^{12c}

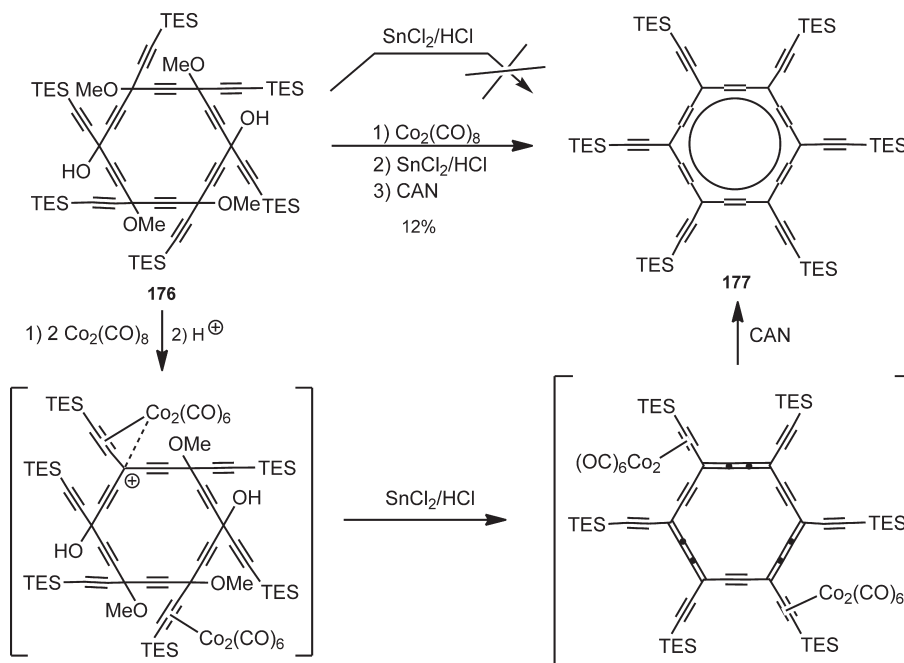
The relative stability of anisyl-substituted vs phenyl-substituted carbenium centers is likely also at the origin of the regioselectivity of the incomplete reduction, at low temperature, of the dianisyl[6]pericyclinediol precursor of the *carbo*-benzene

175c to the *carbo*-cyclohexadiene 175c' (Scheme 63).^{12d} The latter could however be quantitatively converted to 175c upon prolonged treatment with SnCl₂/HCl. In contrast, the dihydro-*carbo*-benzene side product 175c'' was shown to not result from an over-reduction of 175c.

Other conjugated bis-butatrienes were exemplified by Kuwata and Ueda in 1995 (Scheme 64).¹¹² The aromatic 14π-electron dehydro[14]annulenes 178a–d, where the occurrence of two butatrienic edges is enforced by benzannulation, were prepared by three different methods, either directly from the diketone 179 or via the intermediate formation of the corresponding diols 180a–c. The SnCl₂/HCl reagent, which was above-described on 1,4-dioxybut-2-yne substrates, was here applied to the conjugated tertiary enediynediols 180a,b to give the two conjugated butatriene motifs of 178a,b in moderate yields. The secondary diol 180c had to be treated with a mixture of triphenylphosphine, iodine, and imidazole to give the poorly stable unsubstituted bis-butatriene 178c. Direct reductive silylation of the diketone 179 using a mixture of dimethyl-*tert*-butylchlorosilane, zinc, and triethylamine afforded the bis-silyloxy-bis-butatriene 178d. The latter procedure was inspired by a method previously reported by Nakagawa et al. to produce acetoxy- or methoxy-substituted butatrienes from dehydroannulenediones.¹¹³

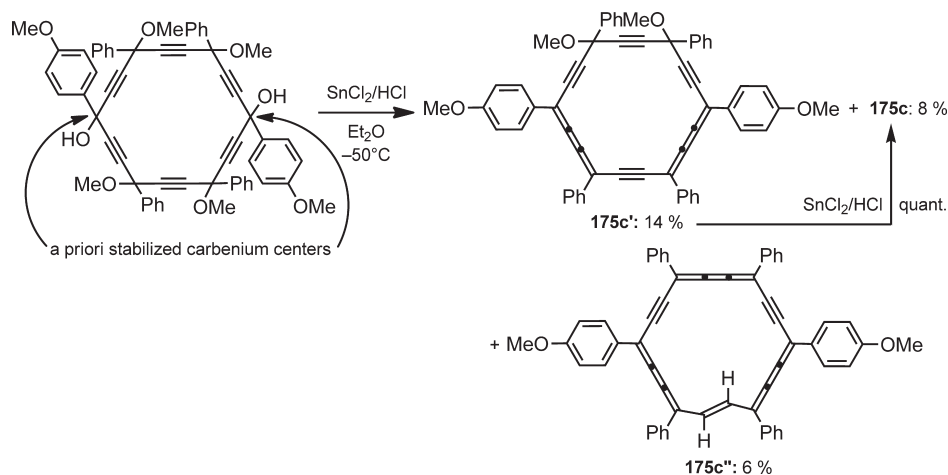
By analogy with the conversion of 180a–b to 178a–b (Scheme 64), the use of the SnCl₂/HCl system was recently reported by Iyoda et al. to generate the two exocyclic butatriene moieties of the extended [4]radialenes 181a–c from the corresponding enediynediols 182a–c (Scheme 65).^{114a} The authors evidenced a quite low rotational barrier around the butatriene motifs of 181a (ΔG[‡] = 13.7 kcal/mol), which was justified by the stabilization of the diradicaloid transition state 181'a through external delocalization within both the [4]radialene core and the thioxanthene end groups. In 2005, the bis-butatriene series 181 was enlarged with the synthesis of 181d–f.^{114b} The octaphenylated extended [4]radialene 181d was obtained in similar yields by either SnCl₂/HCl-mediated reduction of the enediynediol 182d or nickel-catalyzed cyclodimerization of the [5]cumulene 183d. The latter process is actually a cumulogous version of the nickel-catalyzed generation of [4]radialenes from butatrienes or butatriene precursors (see Schemes 4, 6, 10 and Table 1 in section II.1). It corresponds to a functional layout of the [5]-cumulenes preserving the pre-existing butatriene motif. The regioselectivity of the [2 + 2] cycloaddition was however found to depend on the bulkiness of the substituents of the

Scheme 62. Three-Step–One-Pot Synthesis of a Hexaalkynyl-*carbo*-benzene by in Situ Generation of a Nicholas' Cation, Followed by Sequential Reductive Elimination with the SnCl_2/HCl System and Oxidative Decoordination of the Cobalt Auxiliary^{12c a}



^a Acronym: TES = SiEt_3 .

Scheme 63. Regioselective Reactivity of the SnCl_2/HCl system with a Dianisyl[6]pericyclinediol: Reduction to the *carbo*-Benzene **175c** (Scheme 61), Subreduction to the *carbo*-Cyclohexadiene **175c'**, and Over-Reduction to the Dihydro-*carbo*-benzene **175c''**^{12d}



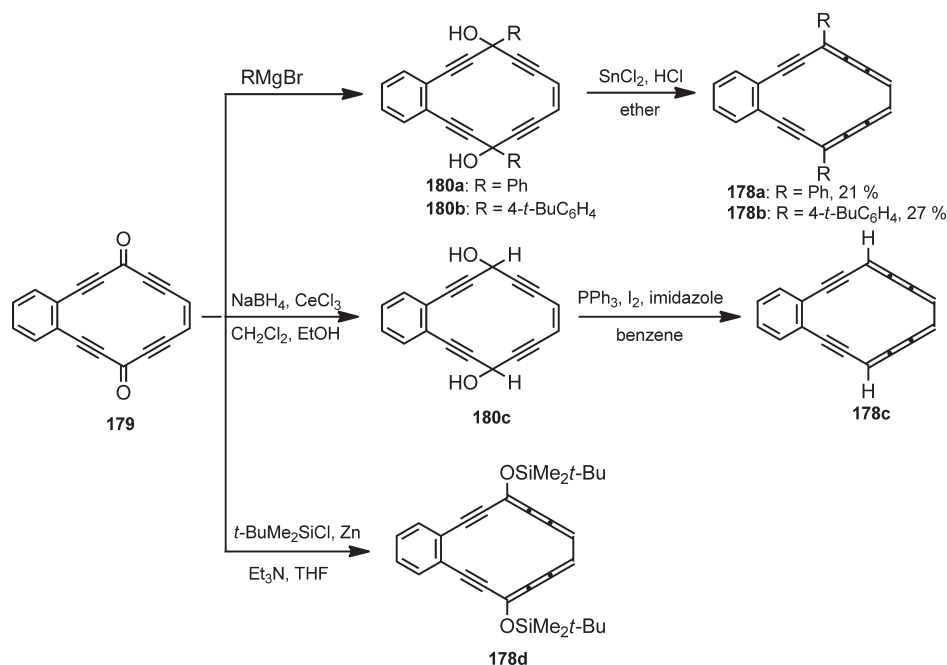
[5]cumulenes **183d–j** (Scheme 65). While the less hindered tetraaryl- and tetraalkyl-[5]cumulenes **183d–f** and **183g,h** respectively afforded the head-to-head dimers **181d–f** and the head-to-tail dimers **181g,h** in quite good yields, the more hindered [5]cumulenes **183i,j** gave mixtures of the “[4]radialallenes” **184i,j** and “radialallenones” **185i,j** (Scheme 65).

Beyond the conjugated bis-butatrienes **175c'**, **178a–d**, and **181a–h** (Schemes 63–65), non-conjugated representatives are less exemplified. Jasiobedzki's endocyclic bis-butatriene had thus been obtained by acidic treatment of

2,5-diphenylhex-3-yne-2,5-diol.¹¹⁵ In spite of its reducing character, the acid HI only induces dehydration of the substrate to an intermediate conjugated dienyne that undergoes spontaneous [6 + 6] cycloaddition to the 12-membered macrocycle (Scheme 66).

III.8. Synthesis of Butatrienes by Skeletal Rearrangement of C_4 Precursors

C_4 motifs may adopt four types of geometry: acyclic, unicyclic, bicyclic, or tetracyclic (Scheme 1). Beyond the skeletal

Scheme 64. Synthesis of Bis-butatrienes from 1,8-Dioxo- and 1,8-Dioxy-Endiynes Precursors¹¹²

rearrangement of alkylidene- or alkenylidene-cyclopropane intermediates (see section II.2, Scheme 24; section III.1, Scheme 26; section III.4, Scheme 32), skeletal rearrangements of larger cyclic precursors to linear butatriene motifs have been sporadically exemplified.

In 1965, Maier¹¹⁶ and Bond and Bradway¹¹⁷ thus described simultaneously the controlled pyrolysis of the C_4 -unicyclic dihydrazonide **186** to tetramethylbutatriene **4** (Scheme 67). The proposed mechanism proceeds through sequential extrusions of N_2 , affording sequential cyclic carbene intermediates, which respectively undergo a ring contraction and a ring-opening process.

In 2002, a thermal rearrangement of the C_4 -tetracyclic tetrakis(trimethylsilyl)tetrahydrene **187** was reported to afford tetrakis(trimethylsilyl)butatriene **41** in 19% yield, in mixture with bis(trimethylsilyl)acetylene **40** and tetrakis(trimethylsilyl)butenyne **107** (Scheme 67).¹¹⁸ Prolonged heating allowed for further isomerization of the enyne **107** to the butatriene **41** (see section III.5). The TMS substituents thus reverse the general stability order of the butatriene and enyne isomeric motifs.^{4,40a}

IV. SYNTHESIS OF BUTATRIENES BY $\text{C}_{4+n} - \text{C}_n$ FRAGMENTATION OF C_{4+n} PRECURSORS

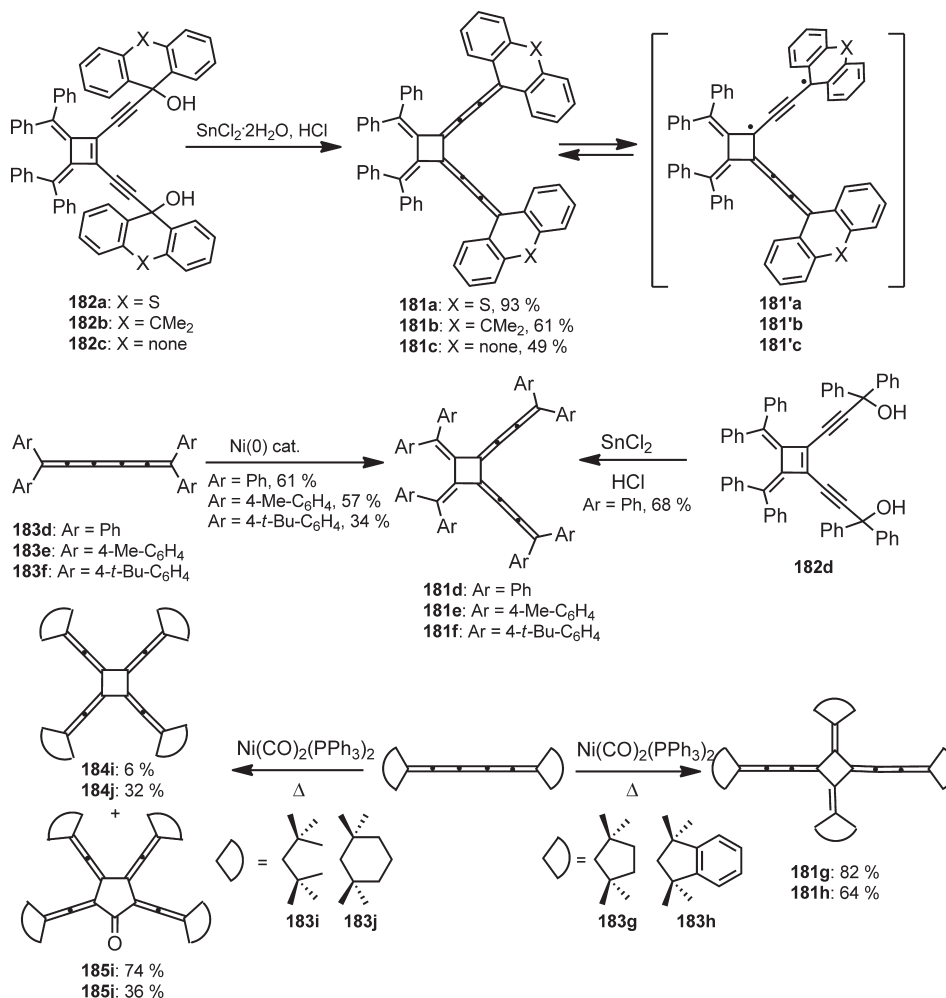
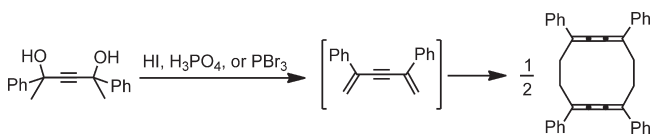
Butatriene C_4H_4 is nonselectively generated by pyrolysis of hydrocarbons, e.g., toluene (C_7H_8).¹¹⁹ More selective fragmentation processes have been detailed above in sections dealing with particular functional rearrangements (from butadienes, section III.2, Scheme 27; from cyclopropenones, section III.7.1, Scheme 42).

In the oxocarbon series, a selective fragmentation is also the key process of a rational synthesis of butatrienedione **188** (C_4O_2), which was the first isolated carbon dioxide with an even number of carbon atoms. In spite of its poor stability, it

could be generated through a formal $\text{C}_5 - \text{C}_1$ process and trapped in an argon matrix upon photolytic decarbonylation or decarboxylation of bisdiazido derivatives of $[\text{S}]$ oxocarbon **189-n** (Scheme 68).¹²⁰

V. SYNTHESIS OF BUTATRIENES BY A ONE-POT $2\text{C}_1 + 2\text{C}_1'$ FOUR-COMPONENT PROCESS

The most employed method for the synthesis of the C_4 butatriene function is based on butyllithium/ Cu(I) -mediated reductive coupling of alkenylidene C_2 precursors $\text{RR}'\text{C}=\text{CBr}_2$ (see section II.1.1). The latter are prepared by Wittig-like *gem*-dihaloolefination of ketones by CBr_4 (with aldehydes, the competing Corey–Fuchs reaction converting $\text{RCH}=\text{CBr}_2$ to $\text{R}-\text{C}\equiv\text{C}-\text{H}$ can be observed). CBr_4 thus plays the role of an atomic carbon source for the internal sp-carbon atoms of the butatriene. A one-pot procedure for the generation of the butatriene unit directly from 2 equiv of ketones and 2 equiv of an atomic carbon source has been recently disclosed by Baceiredo, Kato et al.¹²¹ The atomic carbon donor is here the bis-ylide of the phosphoniosulfoniomethane **190** (Scheme 69), readily prepared by reaction of a chlorophosphonium with 2 equiv of methylenediphenylsulfurane ($\text{Ph}_2\text{S}=\text{CH}_2$), followed by deprotonation with KHMDs . Reaction of the *P,S*-bis-ylide **190** with α, α, α -trifluoroacetophenone in THF gave the intermediate oxaphosphetane **191**, which could be completely characterized (including by X-ray diffraction analysis of single crystals). The latter was then treated with 5% $\text{Cu}(\text{OTf})$ to give a crude *cis/trans* mixture of the butatriene **20a**, which was isolated in 19% yield after chromatography on silica gel. The dissymmetric nature of the *P,S*-bis-ylide prevents the formation of the allenic product $(\text{CF}_3)_3\text{PhC}=\text{C}=\text{C}(\text{CF}_3)_3\text{Ph}$ that would result from subsequent olefination of the ylidooxaphosphetane **191**, as it was observed from symmetrical analogues

Scheme 65. Alternative Routes to Extended [4]Radialenes Featuring Conjugated Exocyclic Bis-butatrienes Motifs¹¹⁴Scheme 66. Generation of a Nonconjugated Endocyclic Bis-butatriene by Nonreductive Reaction of 2,5-Diphenylhex-3-yne-2,5-diol with Acids, Including HI¹¹⁵

of **190**, such as carbodiphosphanes R₂P=C=PR₂.¹²² This four-component 2C₁ + 2C₁' scheme for the one-pot preparation of butatrienes from ketones surely deserves further studies.¹²³

VI. SURVEY OF THE PHYSICOCHEMICAL PROPERTIES OF BUTATRIENES

This section illustrates the versatile “functional” character of the butatriene unit. It is thus devoted to emphasize the merit and specificity of the above reviewed efforts in the synthesis of butatrienes.

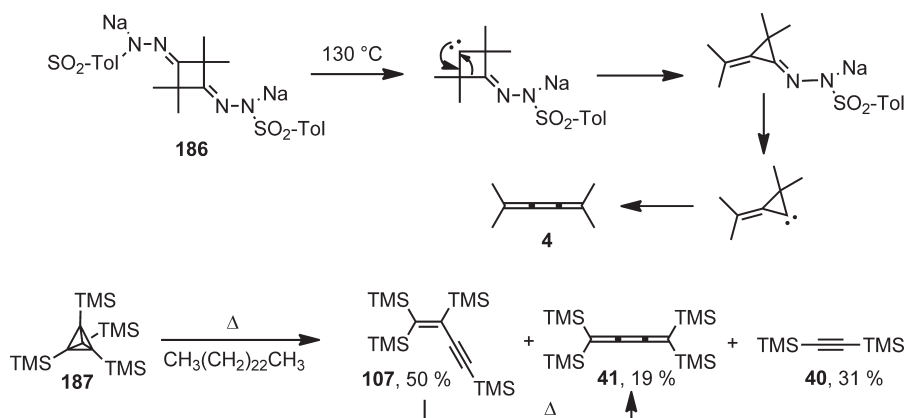
VI.1. Thermal Stability of Butatrienes

The unsubstituted butatriene **82** (C₄H₄) is an unstable colorless gas, prone to polymerize or cyclodimerize.⁹³ Mono-substituted butatrienes are also quite unstable, like chlorobutatriene **143** (C₄H₃Cl), which is also gaseous at room temperature and must be kept at −70 °C in mixture with hydroquinone as stabilizing agent to avoid polymerization (see section III.7.2, Scheme S1). Although the claim has been recently qualified,¹²⁴ tetrafluorobutatriene **92** (C₄F₄) has also been reported to explode violently at the boiling point (−5 °C) or in the gaseous phase in the presence of oxygen and to polymerize under an inert atmosphere (see section III.3, Scheme S1). The other tetrahalobutatrienes (chloro, **94**; bromo, **105**; and iodo, **104**) are however stable solids at room temperature. More generally, substitution of the C₄ unit provides enhanced stability to the butatriene function, in particular when several alkyl, aryl, alkenyl, or alkynyl substituents are attached.

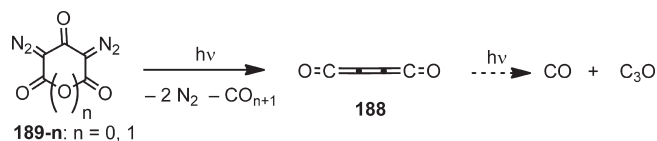
VI.2. Structural Features of Butatrienes

Reliable insights into the structures of butatrienes have been gained by DFT calculations,^{15c,25} and the results are validated by excellent agreement with experimental X-ray

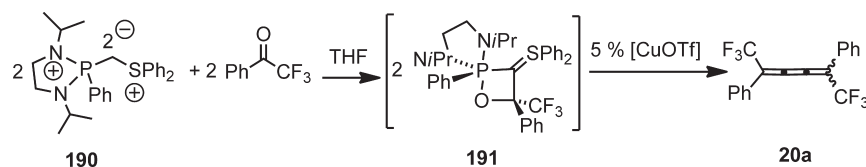
Scheme 67. Pyrolytic Preparation of Butatrienes by Skeletal Rearrangements of C₄-Unicyclic and C₄-Tetracyclic Precursors^{116–118}



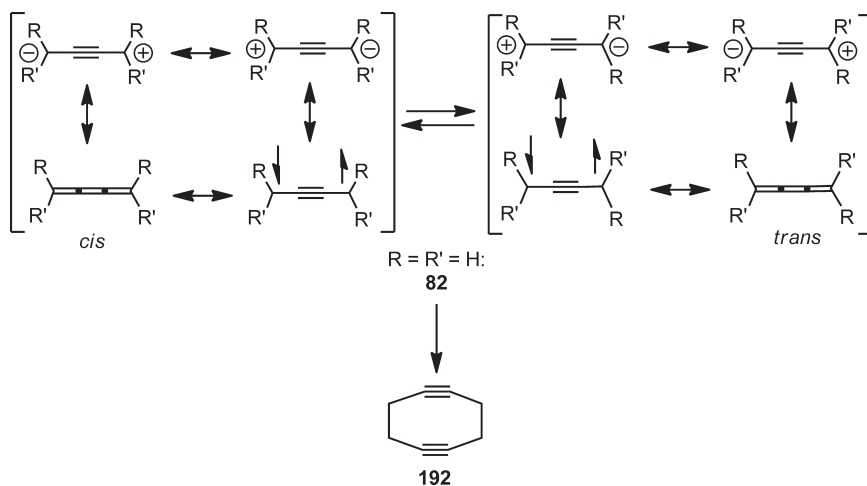
Scheme 68. Photolytic Generation and Trapping in Argon Matrix of Butatrienedione C₄O₂ through C₅ – C₁ Fragmentation from Bisdiazo Derivatives of [5]Oxocarbon¹²⁰



Scheme 69. Preparation of a Butatriene by a One-Pot–Two-Step Procedure from 2 equiv of a P,S-Bis-ylide Atomic Carbon Source and 2 equiv of α,α,α -Trifluoroacetophenone¹²¹

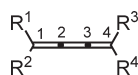


Scheme 70. Mesomeric (or V.B.) Description of the Butatriene Function, and Correlation of the Singlet Biradical and/or Charge-Shift Forms with Transition State Structures of the Cis/Trans Stereoconversion^{14,15c,2S,126 a}



^aThe contribution of these forms is evidenced by the cyclodimerization of butatriene 82 to cyclooctadiyne 192.

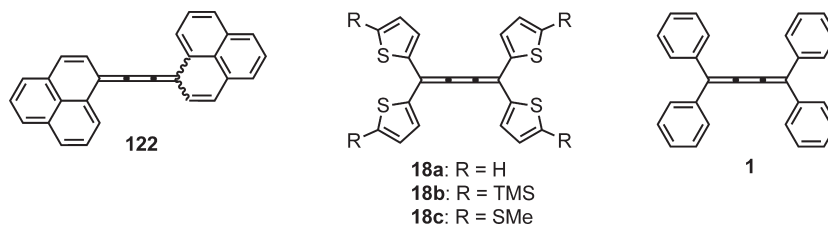
Table 4. X-ray Crystallographic Data on the C–C Bond Lengths (within esd errors, which are not precised here) of Non-Endocyclic Butatrienes with More or Less Symmetrical Substitution Patterns



butatriene				no.	bond lengths: 1–2; 2–3; 3–4	ref
R ¹	R ²	R ³	R ⁴			
Ph	Ph	Ph	Ph	1	1.348; 1.259; 1.348	19
TMS	TMS	TMS	TMS	41	1.319; 1.278; 1.319	70
F	F	F	F	92	1.316; 1.268; 1.316	62a
Br	Br	Br	Br	105	1.296; 1.265; 1.296	69b
I	I	I	I	104	1.315; 1.225; 1.315	69a
Fc	Fc	Fc	Fc	164	1.30; 1.11; 1.30 ^[a]	106
<i>St</i> -Bu	<i>St</i> -Bu	<i>St</i> -Bu	<i>St</i> -Bu	91a	1.317; 1.260; 1.317	59
SC ₆ H ₄ Cl	SC ₆ H ₄ Cl	SC ₆ H ₄ Cl	SC ₆ H ₄ Cl	91b	1.324; 1.260; 1.324	59
5-TMS-2-thienyl	5-TMS-2-thienyl	5-TMS-2-thienyl	5-TMS-2-thienyl	18b	1.353; 1.242; 1.353	26b
5-TMS-2-furyl	5-TMS-2-furyl	5-TMS-2-furyl	5-TMS-2-furyl	18e	1.360; 1.229; 1.360	26b
5-TMS-2-selenyl	5-TMS-2-selenyl	5-TMS-2-selenyl	5-TMS-2-selenyl	18f _{sym} ^b	1.353; 1.240; 1.353	26b
5-TMS-2-selenyl	5-TMS-2-selenyl	5-TMS-2-selenyl	5-TMS-2-selenyl	18f _{asym} ^b	1.354; 1.240; 1.356	26b
Me ₂ C(CH ₂) ₃ CMe ₂	Me ₂ C(CH ₂) ₃ CMe ₂	Me ₂ C(CH ₂) ₃ CMe ₂	Me ₂ C(CH ₂) ₃ CMe ₂	96	1.332; 1.261; 1.332	124
CC-TIPS	CC-TIPS	CC-TIPS	CC-TIPS	10b	1.353; 1.248; 1.353	15a
Ph	CC-TIPS	CC-TIPS	Ph	12a	1.351; 1.244; 1.351	14
Ph	CC-Me	CC-Me	Ph	171	1.342; 1.240; 1.342	14
Ph	Mes	Mes	Ph	111	1.340; 1.253; 1.340	74
Ph	C ₃ F ₇	C ₃ F ₇	Ph	20c	1.334; 1.245; 1.334	28
C ₆ F ₅	CF ₃	CF ₃	C ₆ F ₅	20d	1.329; 1.253; 1.329	28
Ph	C ₂ F ₅	C ₂ F ₅	Ph	20b	1.316; 1.252; 1.316	28
Ph	CF ₃	CF ₃	Ph	20a	1.338; 1.258; 1.338	120
Ph	CF ₃	Ph	CF ₃	20a	1.33; 1.25; 1.33	28
Ph	Fc	Ph	Fc	165	1.34; 1.25; 1.38	106
Ph	H	Ph	H	33c	1.343; 1.256; 1.322	34
TMS	Me ₂ C(OH)	TMS	Me ₂ C(OH)	115c	1.315; 1.271; 1.311	75
<i>t</i> -Bu	OTBDMS	<i>t</i> -Bu	OTBDMS	51	1.332; 1.260; 1.332	43
CN	CN	NMe ₂	NMe ₂	26a	1.377; 1.201; 1.397	31a
ClC ₆ H ₄	ClC ₆ H ₄	Me	<i>t</i> -Bu	79	1.34; 1.24; 1.34	52

^a Powder diffraction. ^b Symmetrical and nonsymmetrical isomers.

Scheme 71. Examples of Butatrienes with Amphoteric Redox Properties As Revealed by CV Measurements and Other Electrochemical Techniques^{26a,78,128}



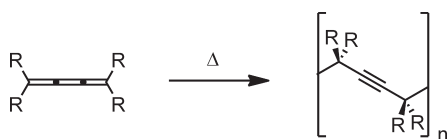
crystallographic data. The first structural studies of butatrienes were carried out by electron diffraction studies on the unsubstituted butatriene **82** and chlorobutatriene **143** in the gaseous phase, in 1961 and 1975, respectively.^{92b,94} In both cases, the central double bond (ca. 1.283 and 1.257 Å, respectively) was

found to be significantly shorter (beyond the esd uncertainty) than the external ones (1.318 and 1.327 Å, respectively) and shorter than the C=C bond length in ethene (1.33 Å). Later on, Irngartinger and Jäger reported on the X-ray diffraction analysis of the tetramethylcyclohexylideneethene symmetric

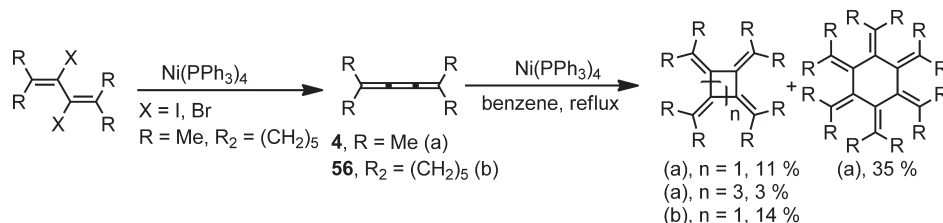
representative **96** (see section III.4, Scheme 32).¹²⁵ The results, and all the subsequent reports on X-ray crystallographic studies of butatrienes (Table 4), confirmed the trivial theoretical predictions that the central double bond is always shorter (ca 1.25 Å) than the two external ones (ca. 1.33 Å). This trivial feature, namely, the shorter length of sp–sp bonds as compared to the sp–sp² counterparts (or the smaller covalent radius of sp-hybridized atoms as compared to the sp² counterparts) is actually interpreted by the resonance of the all-octet apolar valence bond form (the main Lewis structure) with the singlet biradical form and/or the charge-shift forms (Scheme 70). The contribution of the latter forms has been invoked to be accounted for by the “aromatic character” of the C≡C triple bond, which could be regarded as a [2]annulene core.^{13f,14} The relevance of these forms is also chemically evidenced by the propensity of butatriene **82** to cyclodimerize to cyclooctadiyne **192** (Scheme 70).¹²⁶

The singlet biradical forms can actually be correlated with the structure of the transition state of the cis/trans interconversion of butatrienes. While the thermodynamic stereochemical preference is generally weak because of the remote positions of the facing substituents across the C₄ unit (with a length of ca 3.90 Å: see Table 4), the corresponding kinetic barrier was shown to be particularly low for alkynyl- and thioxanthenyldene-substituted butatrienes (see Schemes 7 and 65).^{14,15c,25,114} It is noteworthy that in *carbo*-benzene rings the open-shell singlet biradical or charge-shift forms of the three butatrienic edges merge into

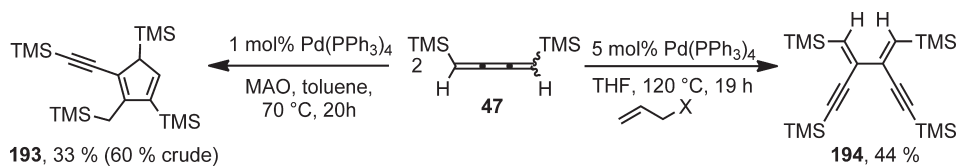
Scheme 72. Thermally Induced 1,4-Addition Polymerization of Butatrienes^{47b,57}



Scheme 73. Cyclo-Oligomerization of Butatrienes into Radialenes in the Presence of a Ni(0) Complex¹²⁹



Scheme 74. Dimerization Modes of a Butatriene in the Presence of the Same Palladium Catalyst Precursor and Different Additives¹³⁰

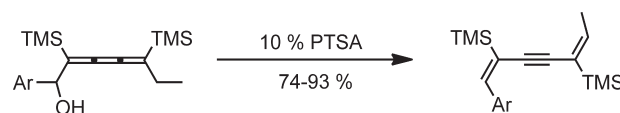


the closed-shell Kekule structure of the aromatic C₁₈ macrocycle (see Scheme 2).¹⁴

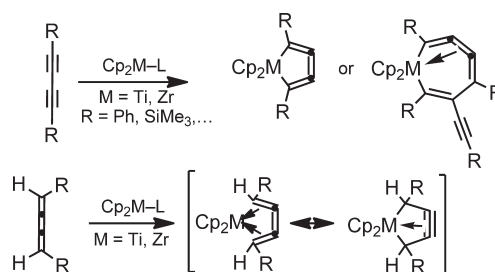
VI.3. Spectroscopic Properties of Butatrienes

The ¹H NMR chemical shifts of butatrienic CH ends are in the classical range of analogous alkenic or allenic CH ends ($\tau = 4.80$, $\delta = 5.2$ ppm for butatriene **82**).¹²⁷ In contrast, the ¹³C NMR chemical shifts of the butatriene moiety are characteristic, the external ¹³C nuclei resonating around 100 ppm, while the two central ones resonate around 150 ppm. The sp-¹³C chemical shift of the butatriene motif in resonance with the but-2-yne motif in the Kekule structures of hexaphenyl-*carbo*-benzene **14** ($\delta = 119$ ppm) (Schemes 2 and 60) was found to be almost exactly equal to the average of the corresponding chemical shifts in parent non-resonating motifs at 148 and 95 ppm, respectively.¹⁴

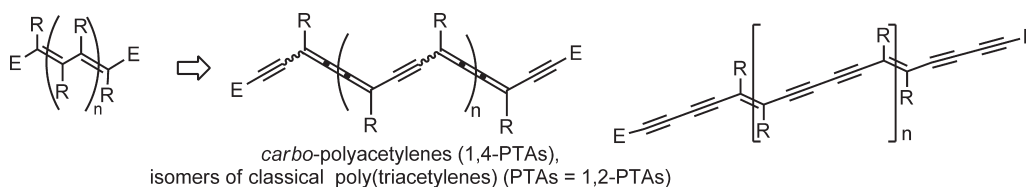
Scheme 75. Synthesis of Dienes from Hydroxymethylbutatrienes¹³³



Scheme 76. Principle of Group 4 Metallacyclocumulene Complexes Involving Strained Endocyclic Butatriene Motifs^{142,143}



Scheme 77. 1,4-Poly(triacetylenes) (1,4-PTAs), Skeletal *carbo*-Mers of Polyacetylenes, and Regioisomers of the Classical 1,2-Poly(triacetylenes) (PTAs = 1,2-PTAs)^{14,147,148}



The electronic absorption spectrum of butatrienes exhibits a strong band in the visible region. The corresponding wavelength however depends markedly on the nature of substituents, e.g., in the range 350–500 nm for 1,4-dialkynylbutatrienes, with strong bathochromic shifts for 1,4-diphenyl-substituted representatives.^{14,15}

VI.4. Electrochemical and Redox Properties of Butatrienes

As evidenced on several occasions, butatrienes may exhibit an amphoteric redox behavior depending on the nature of their substituents. Cyclic voltammetry (CV) of 1,2-bis(phenalene-1-ylidene)ethene **122** thus showed two reversible reduction waves (at -0.83 and -1.21 V) and two oxidation waves (at $+0.61$ and $+0.78$ V), the first one being reversible as well.⁷⁸ This behavior can be attributed to the electronic stability of the three oxidation states of the two phenalenyl ends. A similar behavior was however also observed by Oda et al. for the butatrienes **18a–c**, the cyclic voltammograms of which displayed two reduction waves and one two-electron oxidation wave, all of them being reversible.^{26a} A comparable behavior was also evidenced for tetraphenylbutatriene **1** (Scheme 71).¹²⁸

Detailed voltammetric studies of di- and tetraalkynylbutatrienes **10a–h**, **11a,b**, **12a,b**, **15**, **20m**, **171**, **175c**, **175c'**, **175c''** (Schemes 7, 8, 10, 59, 61, and 63) also revealed complex redox behaviors involving reversible reduction processes.^{12d,14,15}

VI.5. Organic Reactivity of Butatrienes

Butatrienes have been frequently reported to undergo spontaneous polymerization.^{93b} This process, which has to be avoided during the preparation of poorly stable butatrienes, has been studied for more stable representatives. For example, Pollack et al. described the 1,4-addition-polymerization of various butatrienic substrates initiated by simple thermal activation (Scheme 72).^{47b,57} These polymers can be regarded as the skeletal *carbo*-mers of the corresponding polyalkenes.

Dimerization or controlled oligomerization of butatrienes was also studied. In 1968, for example, the thermal dimerization of tetrachlorobutatriene induced by addition of traces amounts of hydroquinone was described to produce tetrachloro[4]radialene.⁶³ Later on, Iyoda and Oda showed that Ni(0)-mediated reductive elimination from 2,3-dihalobutadienes afforded the targeted butatrienes, which could be cyclo-oligomerized either in situ or sequentially, to give the corresponding radialenes (Scheme 73).¹²⁹

A catalytic version of dimerization was also reported by Suzuki et al. from bis(trimethylsilyl)butatriene **47** using a palladium complex. The cyclopentadienyne **193** was obtained in the presence of methylaluminoxane (MAO), while the dienediynes dehydro dimer **194** was obtained in the presence of allyl halides (Scheme 74).¹³⁰

Besides oligo- or poly-merization, butatrienes also undergo a wide range of more selective transformations (which are not detailed here), ranging from halogenation,^{69b} charge transfer,^{49b} photochemical rearrangement,¹³¹ to oxidations or reductions.¹³² Functional butatrienes may also serve as precursors for the selective preparation

of functional but-2-yne derivatives, from which they could be reversibly synthesized (see section III.7.2). Likewise, dienynes can also be generated in 80–90% yield by cumulogous dehydration of hydroxymethylbutatrienes in the presence of 10% of PTSA (Scheme 75).¹³³ Finally, butatrienic species were also invoked as intermediates in multistep transformations of alkyne substrates with propargylic functionalities.¹³⁴

VI.6. Organometallic Chemistry of Butatrienes

The early coordination chemistry of butatrienes first focused on carbonyliron complexes,^{95,135} before being extended to other transition metals, and in particular to rhodium(I)¹³⁶ and platinum(0) centers.¹³⁷ Today, beside the rich chemistry of metallabutatrienes, like the well-documented allenylidene complexes of ruthenium,¹³⁸ transition metal complexes of butatriene ligands continue to attract a great deal of interest due to the large diversity of coordination modes of the [3]cumulene moiety: η^1 -butatrienes,^{139a} (which must be distinguished from η^1 -butatrienyl metals, like the copper or zirconium intermediates shown in Schemes 34 and 40),^{66,75,139b,139c} η^2 -butatrienes (at the central or external double bond),^{135b,136,140} η^3 -butatrienes,¹⁴¹ five-membered C₄ metallacycles,¹⁴² seven-membered metallacycles containing a butatriene,¹⁴³ μ -butatrienes in polynuclear complexes,¹⁴⁴ or more complex bonding modes in higher metallic clusters.¹⁴⁵ Beyond transition metals, lanthanides also lend themselves to a rich coordination chemistry of butatriene ligands resulting from the coupling of terminal alkynes in the coordination sphere of the Ln centers (Ln = Y, Lu, ...).¹⁴⁶ By comparison to alkene and allyl complexes, the remarkable feature of these complexes is the high angular strain that the sp-carbon atoms can accommodate. For illustration, Buchwald et al. and Rosenthal et al. described highly strained titana- and zircona-cyclocumulenes containing η^3 - or η^4 -coordinated C₄ motifs (Scheme 76). Such complexes could be generated from butadiyne or 1,3-diene precursors or from preformed butatrienes and Cp₂Ti or Cp₂Zr sources.^{141a,142,143}

VII. CONCLUSION

The wide variety of synthetic methods that have been investigated for more than one century illustrates the chemists' fascination with the butatriene function. Each of them is however quite specific of certain types of targets, and even in this case, a general procedure for the selective synthesis of generic butatrienes, in particular those bearing different substituent pairs at the two sp² ends, remains a challenge.¹²³ Beyond the aesthetical viewpoint (butatriene is the skeletal and functional *carbo*-mer of ethene), the unique physicochemical properties of butatrienes will continue to instigate motivation for such efforts, especially with regard to the redox and chromophoric behavior of representatives embedded in extended π -conjugated systems. Polybutatrienic molecules are naturally challenging and essentially exemplified by *carbo*-benzenes, where the butatriene character is partly masked by

resonance between the two equivalent Kekule structures (Scheme 2). Recently, attention has been drawn to the challenge of the synthesis of non-aromatic, and particularly acyclic, oligobutatrienes like 1,4-poly(triacetylenes) (1,4-PTAs).¹⁴ The latter are skeletal *carbo*-mers of polyacetylenes (Scheme 77) and regioisomers of the well-known 1,2-poly(triacetylenes) (PTAs = 1,2-PTAs).¹⁴⁷ The first examples will be shortly reported.¹⁴⁸

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Léo Leroyer graduated in organic chemistry from the University Paul Sabatier (Toulouse, France) in 2006 working on the synthesis of natural polyacetylenic compounds in Remi Chauvin's group. He then received his Ph.D. in organic chemistry in 2010 from the University Paul Sabatier (Toulouse, France), where he studied, under the supervision of Remi Chauvin and Valérie Maraval, the synthesis of *carbo*-mers via classical and alternative routes and their physicochemical properties. During his Ph.D. studies, he also took an interest in the catalytic allylation of ynones in Xue Long Hou's group during three months (Shanghai Institute of Organic Chemistry, Shanghai, China). He is now working as a postdoctoral fellowship with Laurent Prat (Laboratoire de Genie Chimique, Toulouse, France) in collaboration with Sanofi-Avantis on transposition from batch to continuous phosgenation reaction, using microfluidic devices.



Valérie Maraval graduated from the University Paul Sabatier (Toulouse, France) in 1997. She then prepared a thesis in the field

of phosphorus dendrimer chemistry under the supervision of Jean-Pierre Majoral, and she received her Ph.D. in 2000. In 2001, she worked as a postdoctoral fellow with Bernard Meunier in collaboration with the Aventis Co. on oxidation of terpenes. She then came back to Jean-Pierre Majoral's team as a CNRS Engineer for two years. In 2005, she joined the group of Remi Chauvin at the Laboratoire de Chimie de Coordination (LCC) in Toulouse. Her research activity mainly focuses on two aspects of the chemistry of *carbo*-meric molecules: (i) the development of novel approaches to *carbo*-meric compounds based on organometallic catalysis (alkyne metathesis) and (ii) the synthesis and study of the chromophoric and optical properties of new *carbo*-meric molecules.



Remi Chauvin received his Ph.D. in 1988, in the field of asymmetric catalysis, under the supervision of Prof. H. Kagan in Orsay, France. He pursued as a postdoctoral fellow with K. B. Sharpless at MIT (Cambridge, MA) and then with A. Vasella in Zürich, Switzerland. Returning to France, he first worked at Roussel Uclaf in Romainville. In 1993, he came back to academic research at the CNRS in Toulouse, and in 1998 was appointed as a full Professor at the Paul Sabatier University. Today he is interested in four aspects of molecular chemistry in two different laboratories: the Laboratory of Coordination Chemistry, where his main research group is hosted, and the Laboratory of Molecules of Biological Interest. The corresponding domains are theoretical analysis (molecular modeling, aromaticity, etc.), acetylenic synthesis (*carbo*-mer chemistry), coordination chemistry and catalysis (chiral carbon-phosphorus ligands), and synthesis of biologically active products (natural polyynepolyols and analogues).

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