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Spiro[2.4]hepta-4,6-dienes: synthesis and chemical reactions

L G Menchikov, O M Nefedov

Contents

I. Introduction	449
II. Methods of synthesis of spiro[2.4]hepta-4,6-dienes	449
III. Chemical reactions of spiro[2.4]hepta-4,6-dienes	458
IV. Conclusion	467

Abstract. Data on the chemistry of compounds of the spiro[2.4]hepta-4,6-diene series are surveyed and described systematically. The methods of their synthesis, the characteristic features of their reactivity, and their principal chemical reactions are examined. The applications of spiro[2.4]hepta-4,6-dienes in specific organic synthesis are noted. The bibliography includes 230 references.

I. Introduction

Compounds of the spiro[2.4]hepta-4,6-diene (SHD) series, the first representatives of which were synthesised only 40 years ago, have now become a class of chemical substances the interest in which is manifested from a wide variety of directions. Highly effective insecticides of the pyrethroid series[1–10] and new medicinal preparations[11,12] have been synthesised from these compounds. Methods have been proposed for the synthesis of a series of natural and biologically active compounds, in particular prostaglandins,[13] and polymeric materials of practical value have been obtained.[14–24] Furthermore, SHDs are interesting objects for the study of important problems in model organic chemistry such as that of spiroconjugation and complex formation.

SHD has a high degree of symmetry which, together with spiroconjugation, is responsible for a series of unusual chemical and physical properties. These have been investigated by means of a wide variety of instrumental[25–32] and quantum-chemical methods.[33–36]

Extensive data have now accumulated in the literature both on the synthesis of SHDs and on their chemical reactions and use in specific organic synthesis. However, there are no reviews in this field. The principal methods of synthesis of SHD and its derivatives and some of their chemical reactions of greatest synthetic interest are described systematically and examined below.

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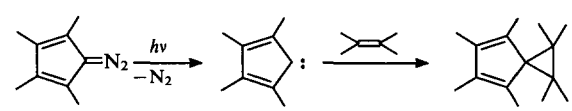
II. Methods of synthesis of spiro[2.4]hepta-4,6-dienes

Spiro[2.4]hepta-4,6-diene was synthesised by Levina et al.[37] as early as 1955 by the reaction of cyclopentadiene with 1,2-dibromoethane on treatment with sodium in liquid ammonia, but its first derivatives were obtained only later in 1965 by Moss,[38] who developed the first method of synthesis of compounds of the SHD series. Moss's method, which is based on the reaction of diazocyclopentadiene (DACPD) with unsaturated compounds, led to the possibility of synthesising a wide variety of SHD derivatives, and initiated the vigorous study of these compounds. Since then, numerous SHD derivatives have been obtained and new methods of their synthesis have been developed.

The methods of synthesis of compounds of the SHD series described in the literature hitherto can be divided arbitrarily into two groups. The first includes methods for the construction of the SHD skeleton by the cyclomethylenation of double bonds (reaction of DACPD and its derivatives with olefins) and also the cyclomethylenation of the exocyclic double bond in fulvenes. The second group includes methods based on nucleophilic substitution (in particular alkylation and cyclialkylation†) and nucleophilic addition (addition of carbanions to Michael acceptors) reactions of the cyclopentadienyl anion generated as an intermediate. In addition, the formation of compounds of the SHD series, usually in the form of minor products, has been observed in certain photochemical and carbene reactions.

1. Interaction of diazocyclopentadienes with unsaturated compounds

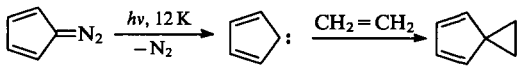
DACPD and its derivatives are highly reactive compounds, which decompose photochemically with formation of free cyclopentadienylidene (CPDI).[39–41]



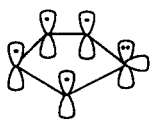
†Cyclialkylation is alkylation with formation of a new ring [see G L Mishchenko, K V Vatsuro *Sinteticheskie Metody Organicheskoi Khimii* (Synthetic Methods in Organic Chemistry) (Moscow: Khimiya, 1982) pp 400, 404].

An example of the catalytic decomposition of a substituted DACPD is also known.[42] The CPDI formed and its derivatives enter into reactions characteristic of carbenes, in particular they add to the C=C double bonds of unsaturated compounds, affording compounds of the SHD series in 10%–60% yields.

The reaction of free CPDI with ethylene, leading to SHD, has been detected in an $Ar-N_2O$ matrix at low temperatures (between 12 and 45 K).[43,44]



Since CPDI is an electrophilic carbene,[40,41,45–47] the rate of its addition, like that of other electrophilic carbenes,[40,41] to multiple bonds is retarded by electron-withdrawing substituents at the multiple bonds and is facilitated by electron-releasing substituents.[45,46] It is also noteworthy that, although CPDI has a triplet ground state,[40,41] nevertheless it reacts in an excited singlet state,[48] especially when it is generated photochemically, which also explains the stereoselectivity of its reactions involving addition to multiple bonds.[40,41,49]



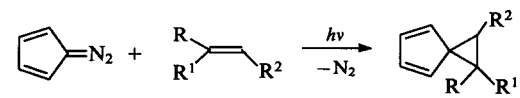
The availability of DACPD, which can be readily obtained[50] in 70%–80% yields from cyclopentadiene (CPD) and toluene-*p*-sulfonyl azide in the presence of diethylamine at 0 °C, as well as the simplicity of its carbene decomposition, promoted the synthesis of an appreciable proportion of the SHD derivatives known at the present time precisely by this method (Table 1).

Table 1. The yields of SHD derivatives **1** in the reactions of diazocyclopentadiene with olefins.

R	R^1	R^2	Yield of **1** (%)	Ref.
Me	Me	Me[a]	33	38, 51
Bu^t	H	H	46	38, 51
Bu	H	H	30	38, 51
Ph	H	H	18–20	45, 51
Me	H	Me	40	52, 53
Et	H	Et	50	52, 53
Me	H	Cl	[b]	54
4-$MeOC_6H_4$	H	H	17	45
4-MeC_6H_4	H	H	12	45
4-ClC_6H_4	H	H	12	45
3-BrC_6H_4	H	H	7	45
$MeSiCH_2$	H	H	[b]	46
$MeOCH_2$	H	H	[b]	46
$ClCH_2$	H	H	[b]	46
$NCCH_2$	H	H	[b]	46
Me	H	Pr^i	70	49
H	Me	Pr^i	70	49
$EtOCH_2$	H	H	35	55
Me	Me	H	15	56–59
$CH_2=CH$	H	H	59–68	60, 61
$CH_2=CH$	H	Me	[b]	61
H	$-(CH_2)_2-$		[b]	62
H	$-(CH_2)_4-$		23	38, 51
H	$-(CH=CH)_3-$		40–50	60, 63
H	$-(CH=CH)_2-$		25–35	60, 63
$CH_2=$	H		[b]	64

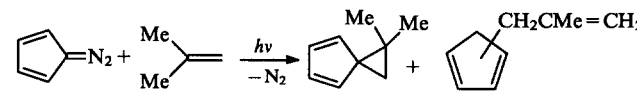
[a] In the reaction with tetramethylethylene, the yield of SHD is 35%.[38,51]
[b] The yield of SHD derivatives is not indicated.

The reaction is usually carried out in the presence of a (30–40)-fold molar excess of the initial unsaturated compound, its mixture with the DACPD being irradiated for several hours at 0–30 °C.



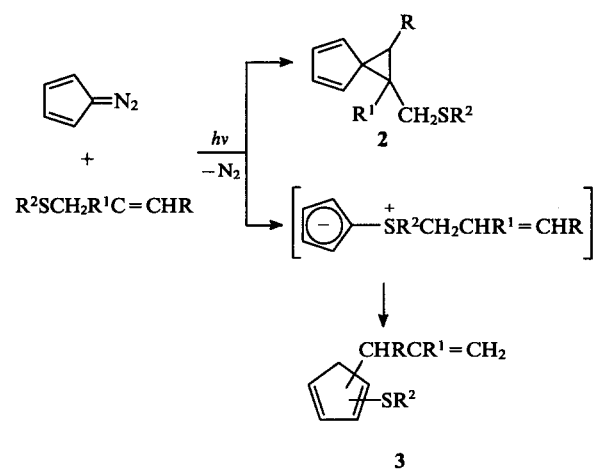
1

It is noteworthy that such reactions involve a side process in which the intermediate CPDI is inserted in different single bonds of the initial unsaturated acceptor.[55,59] For example, the insertion of CPDI in a C–H bond in the initial olefins leads to substituted cyclopentadienes.[59]



1 : 0.14–0.29

However, in the reaction of DACPD with allyl sulfides under similar conditions, the usual addition of CPDI to the double bonds is accompanied by the formation of unstable S ylides, which are subsequently converted into disubstituted cyclopentadienes (Table 2).[55]

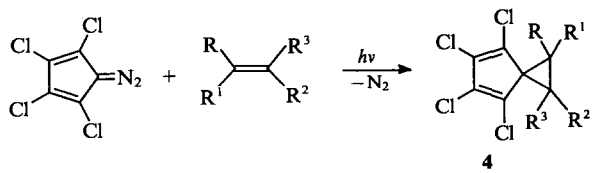


3

Table 2. The yields of SHD derivatives **2** and disubstituted cyclopentadienes **3** in the reaction of diazocyclopentadiene with allyl sulfides.

R	R^1	R^2	Yield (%)	
			2	**3**
H	H	Et	13	31
H	H	Bu^t	24	37
Me	H	Et	8	35
H	Me	Et	17	40
H	Me	Me	18	28

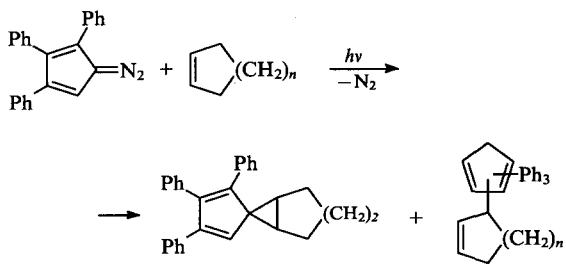
The reactions of substituted DACPD with unsaturated compounds, leading to SHD derivatives, have been studied only occasionally. Thus photolysis of tetrachlorodiazocyclopentadiene in the presence of a (30–40)-fold excess of the unsaturated compound afforded a series of 4,5,6,7-tetrachlorospiro[2.4]hepta-4,6-dienes (Table 3).[53,65,66]



4

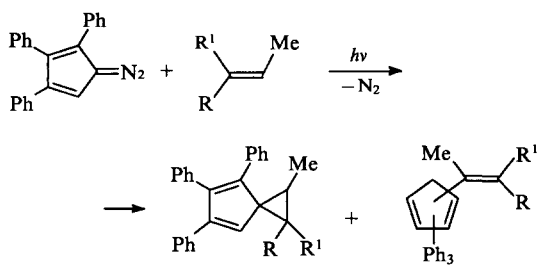
On the whole, the same behaviour has been observed for tetrachlorodiazocyclopentadiene as for the unsubstituted DACPD: first, the presence of electron-withdrawing groups (for example, COOMe) at the double bond of the unsaturated acceptor lowers significantly the yield of SHD derivatives and, second, the addition of the tetrachlorodiazocyclopentadiene takes place stereoselectively (Table 3).

The reactions of 2,3,4-triphenyldiazocyclopentadiene with cyclic and acyclic olefins,[42] leading to the formation, together with compounds of the SHD series, of the products of the insertion of the corresponding carbene into a C–H bond in the initial olefin, have also been described.



5 6

n	Yield of 5+6 (%)	5:6 ratio
1	71	1.85
2	73	1.70
3	63	1.15
4	62	1.22



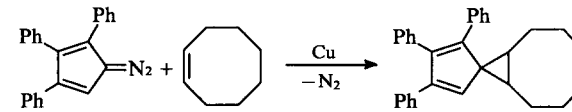
7 8

R	R^1	Yield of 7 + 8 (%)	7:8 ratio
Me	Me	49	4:1
H	Pr^i	85	19:1
Pr^i	H	58	2.8:1

Table 3. The yields of 4,5,6,7-tetrachlorospiro[2.4]hepta-4,6-dienes **4** in the reaction of tetrachlorodiazocyclopentadiene with olefins.

R	R^1	R^2	R^3	Yield of compound **4** (%) (*cis*/*trans* ratio)	Ref.
COOMe	H	COOMe	H	11	53, 65
COOMe	H	H	COOMe	8	53, 65
COOMe	H	H	H	42	65
H	—$(CH_2)_4$—		H	89	66
Bu	H	H	H	54	66
Me	Me	Me	H	87	66
Me	Me	Me	Me	80	66
Me	H	Me	H	63	66
Me	H	H	Pr	87 (77/23)	66
Me	H	H	Et	81 (78/22)	66
Me	H	H	Me	83.5 (79/21)	66

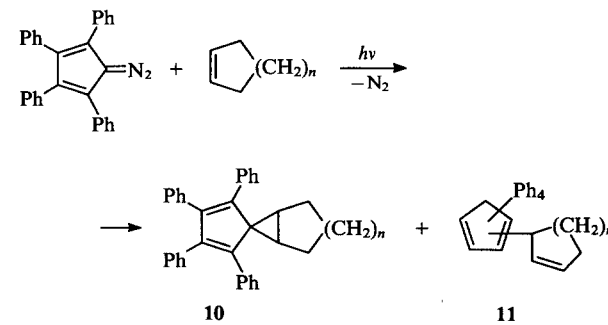
The catalytic decomposition of 2,3,4-triphenyldiazocyclopentadiene in the presence of cyclooctene also led to the formation of the corresponding substituted SHD **9**.[42]



9 (24%)

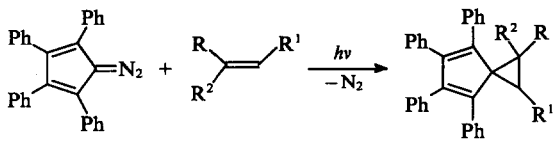
Although in the catalytic decomposition of triphenyldiazocyclopentadiene the yield of SHD derivatives is lower than on photolysis, nevertheless this example indicates the possibility of using the more convenient and simpler catalytic methods, in comparison with photolytic methods, for the generation of the corresponding carbenes from DACPD and its derivatives.

Tetraphenyldiazocyclopentadiene interacts with cyclic and acyclic olefins under the conditions of photolytic decomposition [(20–30)-fold excess of the initial unsaturated compound], which leads to the corresponding SHD derivatives **10** and **11**.[65, 67, 68]

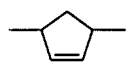


10 **11**

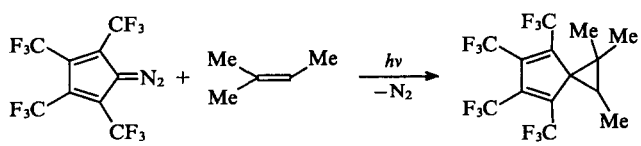
n	Yield of 10+11 (%)	10:11 ratio
1	47–55	9:1
2	60	2:1
3	74	1:1



12

R	R^1	R^2	Yield of 12 (%)	Ref.
Et	H	Me	48	67
Pr^i	Me	H	47–50	67
H	Pr^i	Me	60	67
Me	Me	Me	45–52	67
COOMe	H	H	–	65
COOMe	COOMe	H	–	65
		H	16	68

Finally there is an instance of the formation of the corresponding derivative **13** from tetrakis(trifluoromethyl)-diazocyclopentadiene under the conditions of photolytic decomposition.[69]

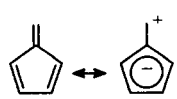


13

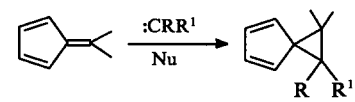
It follows from the data presented that the method of synthesis of compounds of the SHD series by the addition of cyclopentadienylidenes, generated photolytically from DACPD and its derivatives, to the double bonds of unsaturated compounds is fairly universal. At the same time, it suffers from a series of significant limitations. These are, in the first place, the low yields of the cycloaddition products and also the large number of side processes, in particular the insertion of the intermediate CPDI and its derivatives into the single bonds of the initial unsaturated compounds, especially when these contain heteroatoms (for example, sulfur and oxygen atoms). Furthermore, by virtue of the electrophilic nature of the cyclopentadienylidenes, electron-withdrawing functional groups in the initial unsaturated compounds lower significantly the rate of their addition to the double bonds, which increases the amount of side products, in particular the products of insertion in single bonds, and, since the majority of the known functional groups are electron accepting, the method may be relatively unsuitable for the synthesis of SHD with such functional-group substituents. Finally, the method is experimentally complex and has no preparative value because DACPD and its derivatives are extremely explosive, which necessitates the use of only small amounts of these substances (only 50–200 mg of DACPD are normally employed in the experiments). Nevertheless, the method is convenient for the synthesis of many complex SHD derivatives.

2. Cyclomethylenation of the exocyclic double bond in fulvenes

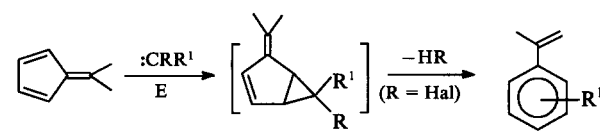
The high polarity of fulvene, which is responsible for the difference between the chemical properties of its double bonds, is generally known.[70–72]



The exocyclic double bond in fulvene is electrophilic, whereas the endocyclic double bond is nucleophilic. Therefore, as shown by Moss et al.,[73] electrophilic and nucleophilic carbenes react differently with fulvenes. Nucleophilic carbenes (Nu) add to the exocyclic double bond of the fulvene, affording SHD derivatives, but the range of such carbenes is extremely small, since it is restricted by the small number of electron-releasing substituents at the carbene centre (R = OAlk, OCOAlk).

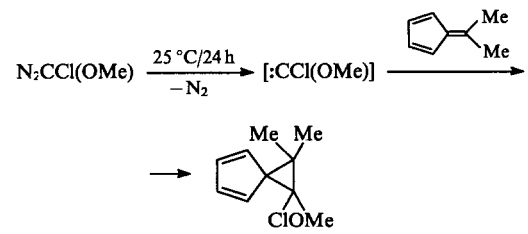


On the other hand, electrophilic carbenes, which constitute the vast majority of the known carbenes, add to the endocyclic nucleophilic double bonds, the product of such an addition usually being unstable and isomerising under the reaction conditions to aromatic derivatives.[73,74]

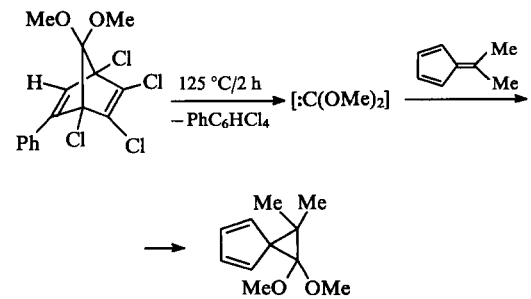


R, R^1 = Hal, COOMe, COMe, CN, etc.

Thus the addition of nucleophilic carbenes to the exocyclic double bond in fulvenes can be used to synthesise compounds of the SHD series containing electron-releasing groups in the cyclopropane ring. For example, nucleophilic carbenes such as chloromethoxycarbene and dimethoxycarbene, generated by the decomposition of chloromethoxyazirine and 1,2,3,4-tetrachloro-7,7-dimethoxy-5-phenylbicyclo[2.2.1]hepta-2,5-diene,[73] afford derivatives **14** and **15** respectively in their reaction with fulvene.

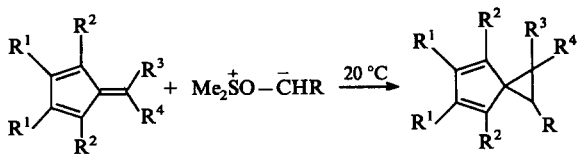


14 (35%)



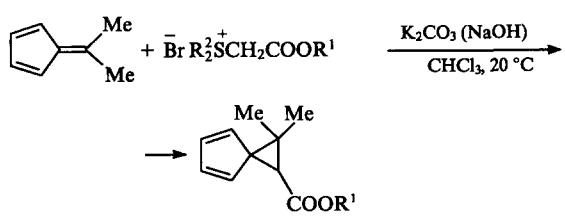
15 (8%)

Like nucleophilic carbenes, sulfur ylides, in which the reaction centre (the carbon atom linked to sulfur) has a negative charge, convert the exocyclic double bond in fulvenes into a cyclopropane group.[75,76] A series of derivatives **16** have been obtained in this way (Table 4).[77,78]



16

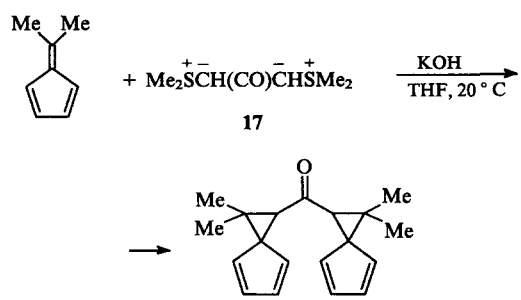
Special mention should be made of the use of the ylide method for the synthesis of a number of highly effective insecticides of the pyrethroid series (in 40%–80% yield); their toxicity to warm blooded animals is low.[1–8]



R^1 = CH_2—(OPh-m),[7] CH_2—(furan)—CH_2Ph,[6]

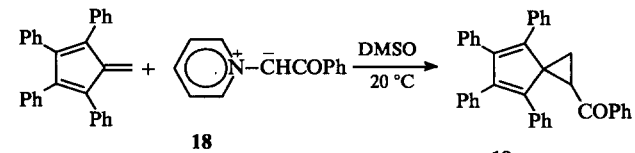
R^1 = —$CHRC_6H_4OPh$-*m*, where R = H, CN,[2–5]
R^2 = Me, R^2_2 = —$(CH_2)_4$—.[4]

The use of the diylide **17** in this reaction made it possible to obtain a compound with two SHD systems in 50% yield.[79]



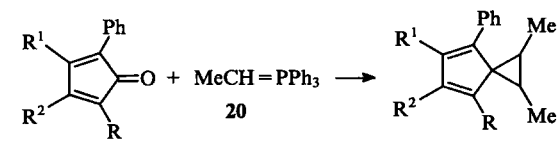
17

Nitrogen and phosphorus ylides (X^+-C^-, X = P, N) convert the exocyclic double bond of fulvenes into a cyclopropane group similarly to sulfur ylides. Thus the substituted SHD **19** has been obtained in 75% yield from the N ylide **18**.[77]

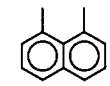


18 **19**

When the phosphorus ylide **20** was used, the corresponding substituted SHD **21** were obtained in 15%–30% yields from cyclopentadienones by the Wittig reaction with a subsequent secondary reaction involving the conversion of fulvenes into cyclopropane derivatives by reaction with the same phosphorane.[80]



20 **21a–c**

21a: R = R^1 = R^2 = Ph
21b: R = Ph, $R^1 + R^2$ = 
21c: R = Me, R^1 = R^2 = Ph

However, the attempt to synthesise SHD derivatives unsubstituted in the three-carbon ring from triphenylmethylenephosphorane was unsuccessful—the reaction stopped at the fulvene formation stage.[80]

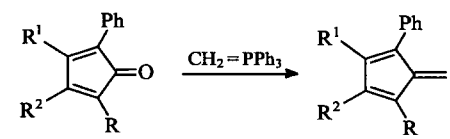
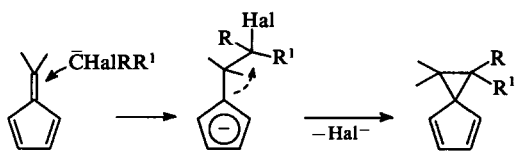


Table 4. The yields of SHD derivatives **16** in the reactions of fulvenes with sulfur ylides.

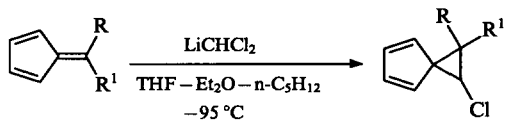
R^1	R^2	R^3	R^4	R	Solvent	Yield (%)
H	H	Me	Me	H	DMSO	80
H	H	H	4-$MeOC_6H_4$	H	DMSO	79
H	H	Me	4-$MeOC_6H_4$	H	DMSO	76
Ph	Ph	H	H	H	DMSO	70
4-MeC_6H_4	Ph	H	H	H	DMSO	64
4-$MeOC_6H_4$	Ph	H	H	H	DMSO	84
H	H	Me	Me	PhCO	$CHCl_3$	76
Ph	Ph	H	H	PhCO	$CHCl_3$	86
H	H	Me	Me	COOEt	THF	90
H	H	Et	Me	COOEt	THF	90
H	H	Me	*cyclo*-C_3H_5	COOEt	THF	60
H	H	Me	$(CH_2)_3OAc$	COOEt	THF	70
H	H	—$(CH_2)_4$—		COOEt	THF	40
H	H	H	α-C_4H_3O	COOEt	THF	35
H	H	Me	Ph	COOEt	THF	10
H	H	SMe	SMe	COOEt	THF	60
H	H	SEt	SEt	COOEt	THF	54
H	H	—$S(CH_2)_2S$—		COOEt	THF	30
Cl	Cl	H	α-C_4H_3O	COOEt	THF	30
Cl	Cl	H	Ph	COOEt	THF	90

A series of reactions are known in which the carbanions generated with the aid of highly basic agents and containing a halogen atom at the carbanionic centre ($-CHalRR^1$) add to the electrophilic exocyclic bond of fulvenes, forming the anion **22**, the intramolecular cyclisation (S_N) of which leads to compounds of the SHD series.

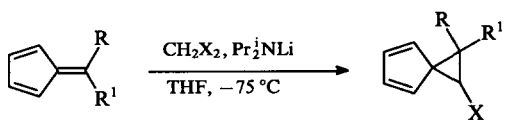


22

The interaction of fulvenes with equimolar amounts of an organolithium derivative $Li^+CHX_2^-$, generated in different ways, also leads to compounds of the SHD series.[54]

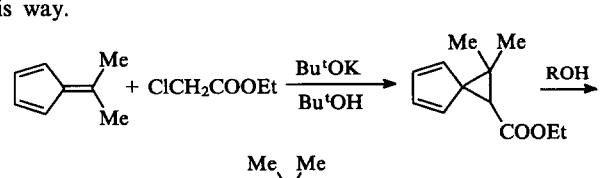


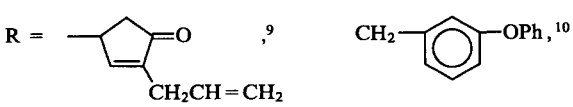
R	R^1	Yield (%)
H	H	56
Me	H	75
Ph	H	65
Pr^i	H	37
Bu^t	H	90
Me	Me	56
Ph	Ph	0



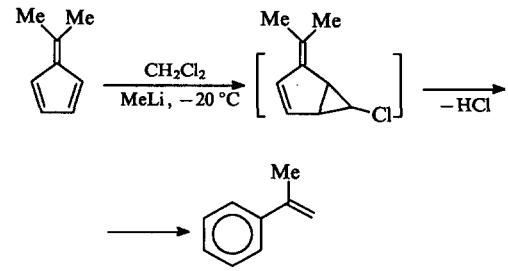
R	R^1	Yield (%)	
		X = Cl	X = Br
H	H	37	–
Me	H	63	72
Ph	H	63	–
Pr^i	H	33	30
Bu^t	H	90	72
Me	Me	80	92
Ph	Ph	0	0

The carbanion generated from ethyl chloroacetate reacts similarly with dimethylfulvene, affording the corresponding SHD in 13% yield.[9,10] A series of pyrethroids have been obtained in this way.

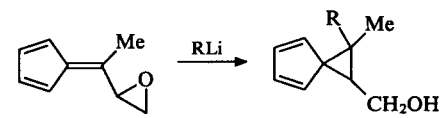


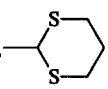


An alternative mechanism for the synthesis of compounds of the SHD series, involving the formation of monohalocarbenes or alkoxycarbonylcarbenes, is unlikely because in this case the nucleophilic endocyclic double bond of fulvene should be converted into a cyclopropane group by virtue of the electrophilic nature of these carbenes.[40,41,46] Thus it has been shown[54] that the monochlorocarbene, generated at −20 °C from CH_2Cl_2 by treatment with MeLi, does indeed add to the endocyclic double bond of fulvene, but the product of such addition is unstable and readily isomerises to methylstyrene under the reaction conditions.

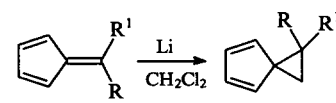


The rearrangements of the cyclopentadienyl anion, generated from alkyllithium and fulvene, constitute the basis of the synthesis of hydroxymethyl-substituted SHD (in 31%–55% yield).[81,82]



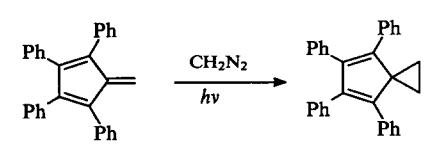
R = Me, Bu, CHMeEt, $CH=CH_2$, 

Finally, the anion of 6,6-diarylfulvenes enters into a nucleophilic substitution reaction with CH_2Cl_2, affording 1,1-diaryl-substituted SHD.[83]

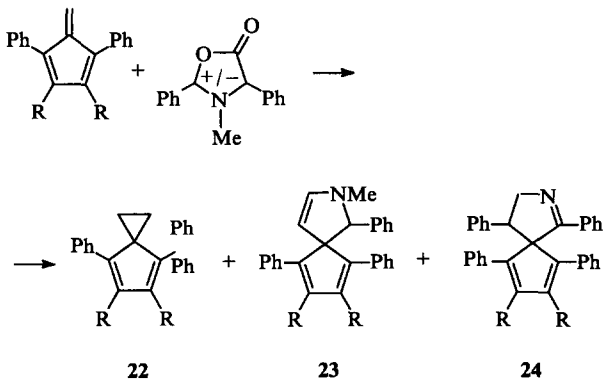


R = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4;
R^1 = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-C_5H_4N.

Among other reactions of fulvenes, mention should be made of the synthesis of the tetraphenyl derivative of SHD in a quantitative yield (99%) by the photolysis of the pyrazoline formed as a result of the 1,3-dipolar addition of a fourfold excess of diazomethane to tetraphenylfulvene.[77]



Finally, the synthesis of SHD derivatives (in 17%–27% yield) from fulvenes and 3-methyl-2,4-diphenyl-1,3-oxazolidinium-5-olate has been described.[84]



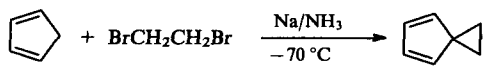
22 **23** **24**

R	Yield (%)		
	22	**23**	**24**
Ph	27	30	11
4-MeC_6H_4	24	22	19
4-$MeOC_6H_4$	17	30	17

Thus the methods of synthesis of compounds of the SHD series by the cyclomethylenation of the exocyclic double bonds in fulvenes, which have been examined above, have a number of characteristic features. In speaking of the carbene methods, one should emphasise that the formation of SHD derivatives is characteristic only of nucleophilic carbenes, which have an extremely limited range, while the methods of their generation are rather complex for wide-scale use in the synthesis of SHD derivatives. However, such methods do in fact make it possible to obtain most effectively derivatives of SHD with electron-releasing groups. Similar reactions are also characteristic of sulfur ylides, but the number of the latter is likewise small [75,76] and the syntheses of compounds of the SHD series from them involve multiple stages. In addition, it has to be mentioned that reactive ylides enter readily also into side reactions. For example, when the initial compounds or the products contain carbonyl groups, epoxidation side reactions take place to a significant extent. [75,76] Nevertheless, ylides have been used successfully in the synthesis of aryl- and carboxy-substituted SHD.

3. Cyclialkylation of cyclopentadiene by 1,2-dibromo derivatives and similar 1,2-difunctional compounds

As mentioned above, SHD was first obtained in 25% yield [37] by the cyclialkylation of cyclopentadiene (CPD) by 1,2-dibromoethane on treatment with sodium in liquid ammonia.



This method of synthesis of SHD still remains the most convenient preparative procedure, its improvement involving mainly the simplification of the method and an increase in the SHD yield (Table 5).

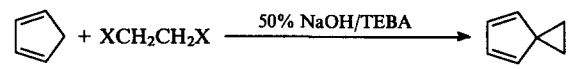
The appearance of a new method in organic synthesis—phase transfer catalysis (PTC) [100,101]—also made it possible to simplify significantly the cyclialkylation of cyclopentadiene, leading to the formation of SHD and its derivatives. [95–99,102,103] The advantages of the PTC method are not only its simplicity and the high yield of SHD but also the possibility of using ordinary NaOH instead of expensive bases and of carrying out the reaction in the absence of a solvent, which facilitates in its turn the isolation of SHD.

Under the conditions of phase-transfer catalysis, SHD can be obtained by the reaction of cyclopentadiene with 1,2-dichloroethane or ethylene glycol di(benzenesulfonate). [102–104]

Table 5. Conditions in the cyclialkylation of cyclopentadiene by 1,2-dibromoethane and the yield of SHD.

Base	*T*/°C	*t*/h	Yield of SHD (%)	Ref.
Na/NH_3	−70–35	3–5	18–75	37, 85–88
Na/THF	0	–	[c]	89
$NaNH_2/NH_3$	–	–	69	90
$NaNH_2$/THF	20	3	54	91, 92
$NaH/MeO(CH_2CH_2O)_2H$	–	–	78	93
NaH/diglyme	0	4	38	94
NaOH (50%), TEBA[a]	30–50	4	76–85	95–97
NaOH, PEG[b]	20	–	–	98
KOH (solid), TEBA	0–20	3	80	97
K_2CO_3/DMSO	20	8	70	99

[a] TEBA = triethylbenzylammonium chloride. [b] PEG = poly(ethylene glycol). [c] The yield of SHD is not indicated.

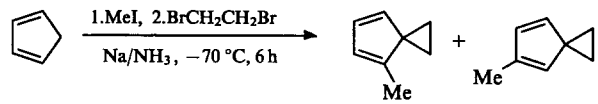


X = Cl, OSO_2Ph.

The reaction with dichloroethane can be carried out also on treatment with NaH as the base (THF, 20 °C, yield 83%). [105]

The use of the more readily available and cheaper 1,2-dichloroethane instead of 1,2-dibromoethane opens up new prospects for investigators. The possibility of using di(benzenesulfonate) in this reaction is of special interest in its turn, because di(benzenesulfonates) (together with ditosylates) are intermediates in the synthesis of the corresponding dihalo-derivatives.

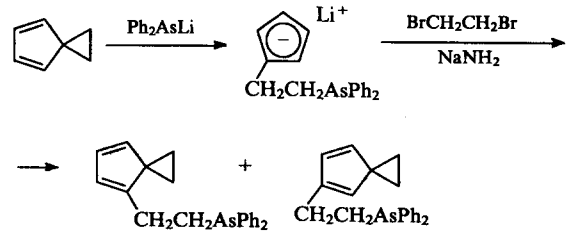
The use of substituted cyclopentadienes in the reaction with 1,2-dibromoethane makes it possible to obtain the corresponding SHD derivatives. Thus a mixture of 4- and 5-methyl-substituted SHD is formed in 30%–55% overall yield on successive alkylation of cyclopentadiene by methyl iodide and 1,2-dibromoethane. [87,106]



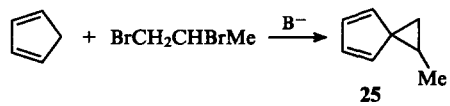
2.8 : 1

This evidently involves the initial formation of a mixture of isomeric methylcyclopentadienes in which the thermodynamically most stable 1- and 2-methyl derivatives predominate. [107] These are subsequently cyclialkylated by 1,2-dibromoethane.

Similar cyclialkylation by 1,2-dibromoethane of an arsenic derivative of cyclopentadiene has been described. [108] In this case, a mixture of the 4- and 5-substituted SHD is likewise formed.



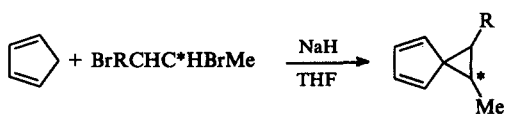
Apart from 1,2-dibromoethane, 1,2-dibromopropane, its closest homologue, is used in the cyclialkylation of cyclopentadiene.



25

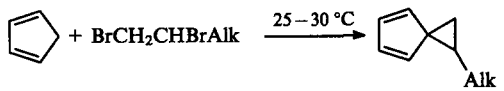
Base	Yield of **25** (%)	Ref.
Na/NH_3, −35 °C	54	57, 109
$NaNH_2/NH_3$	–	110
NaH/THF	–	111
NaOH (50%), TEBA	76–85	96, 97

The use of the optically active 1,2-dibromopropane in this reaction makes it possible to obtain the optically active 1-methyl-substituted SHD.[111]



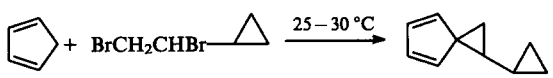
R = H, D.

Under the conditions of phase transfer catalysis, the cyclialkylation of cyclopentadiene by 1,2-dibromo-n-alkanes, in which one bromine atom is at a primary carbon atom and the other at a secondary carbon atom, proceeds just as smoothly as the reaction with 1,2-dibromoethane itself and leads to the corresponding 1-alkylspiro[2.4]hepta-4,6-dienes (in 65%–75% yield).[96, 97, 102, 103]

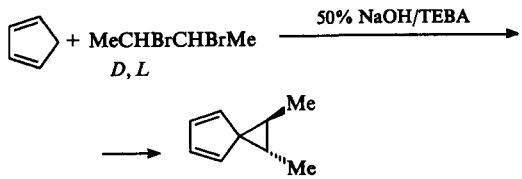


Alk = Me, Pr, Bu, Pe.

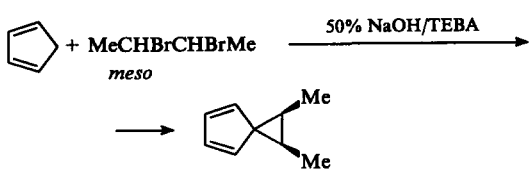
1-Cyclopropylspiro[2.4]hepta-4,6-diene has been obtained in 80% yield from 1,2-dibromo-1-cyclopropylethane under similar conditions.[96]



The possibility of using 1,2-dibromo-derivatives with the two bromine atoms at secondary carbon atoms in this reaction under PTC conditions has also been demonstrated. Thus the interaction of cyclopentadiene with *D,L*-2,3-dibromobutane readily affords *trans*-1,2-dimethylspiro-[2,4]hepta-4,6-diene in 70% yield.[96, 102, 103]

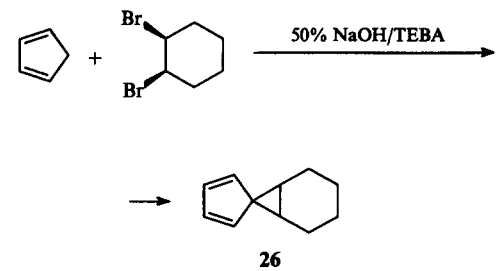


On the other hand, the reaction of cyclopentadiene with *meso*-2,3-dibromobutane leads to the corresponding *cis*-isomer in 60% yield.[96, 102, 103]



The formation of only one isomer of 1,2-dimethyl-SHD on reaction of cyclopentadiene with *meso*- or *D,L*-2,3-dibromobutane is evidence in support of the S_N2 mechanism of cyclialkylation of cyclopentadiene under PTC conditions and leads to the possibility of obtaining optically active derivatives of SHD in this way.[102, 103]

Under the same conditions, another dibromo-derivative — *cis*-1,2-dibromocyclohexane — reacts similarly with cyclopentadiene under the same conditions and leads to spiro(bicyclo-[4.1.0]heptane-7,5′-cyclopentadiene) **26**.[102, 103]

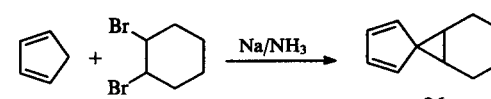


26

On the other hand, the reaction of cyclopentadiene with *trans*-1,2-dibromocyclohexane affords, instead of the corresponding SHD derivative, isomeric bromocyclohexylcyclopentadienes (the products of the monoalkylation of cyclopentadiene) as well as the products of the dehydrobromination of the latter and of the initial dibromocyclohexane.[97]

Thus the difference between the reactivities of *cis*- and *trans*-1,2-dibromocyclohexanes confirms the S_N2 mechanism of the cyclialkylation reaction.[102, 103]

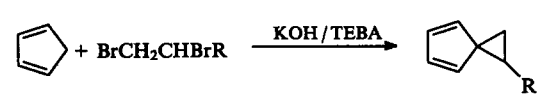
The cyclialkylation of cyclopentadiene by 1,2-dibromocyclohexane takes place also when the Na/NH_3 system is used as the base, which results in the formation of the corresponding tricyclic derivatives of SHD **26** in 10% yield.[86]



26

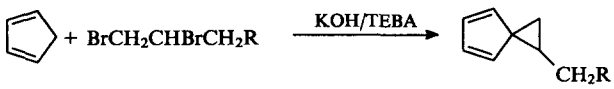
In contrast to primary and secondary dibromo- derivatives, dibromoalkanes containing at least one bromine atom at a tertiary carbon atom do not form SHD derivatives under the conditions of phase transfer catalysis because of the ease of their dehydrobromination.[96, 102, 103]

The cyclialkylation of cyclopentadiene under conditions of phase transfer catalysis by 1,2-dibromoethane with functional group substituents makes it possible to obtain various SHD derivatives.[102, 103, 112] The use of powdered KOH in CH_2Cl_2 in the presence of TEBA under these conditions fully rules out side reactions involving functional groups, for example hydrolysis. The yields of SHD derivatives depend significantly on the electronic properties of the functional group R in the initial 1,2-dibromoethane. Thus, when the group R linked directly to the reaction centre is an aryl substituent or possesses electron-withdrawing properties (COOMe, COMe, CN, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-BrC_6H_4, 4-$NO_2C_6H_4$, Cl), then the corresponding SHD derivatives are formed in a high yield (70%–95%).[112]

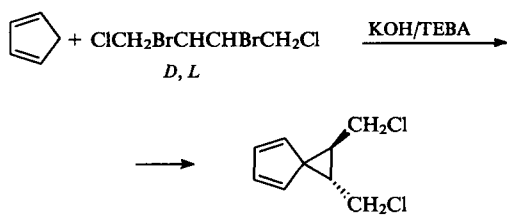


On the other hand, if the functional group in the initial 1,2-dibromoethane is markedly electron-releasing (R = OAc, OEt), then the yields of the SHD derivatives are significantly lower (25%–50%).[112]

However, if the functional group is separated from the reaction centre by a methylene unit, its electronic properties hardly affect the yields of the SHD derivatives, which in this case are 60%–80% for 1,2-dibromopropanes containing functional group substituents in the 3-position with both electron-withdrawing (R = CN, Cl) and electron-donating (R = OMe, OAc) properties.[112]

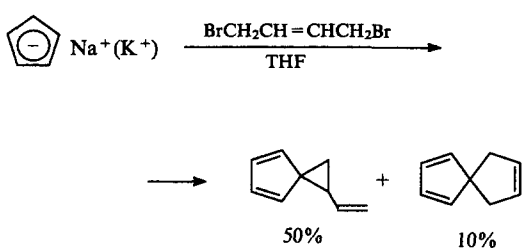


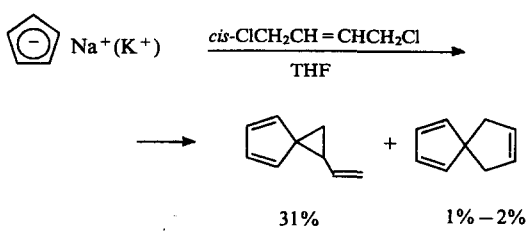
The possibility of synthesising SHD disubstituted in the 1,2-positions by functional groups has been demonstrated for the reaction of cyclopentadiene with *D,L*-2,3-di-bromo-1,4-dichlorobutane. The main product obtained in this case in 55% yield was *trans*-1,2-di(chloromethyl)spiro[2.4]hepta-4,6-diene.[112]

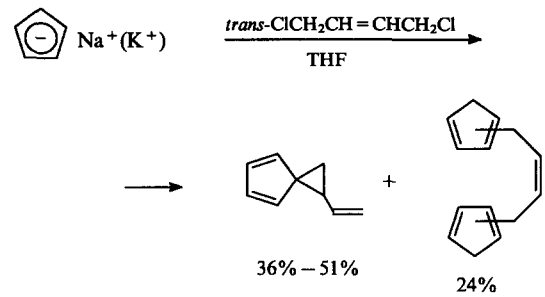


The exclusive formation of *trans*-1,2-bis(chloromethyl)-SHD is fully consistent with the S_N2 mechanism of cyclialkylation of cyclopentadiene under phase transfer catalysis conditions and at the same time indicates a higher reactivity of the bromo-derivatives compared with the chloro-derivatives, although bromine is attached to a secondary carbon atom whereas chlorine is attached to a primary carbon atom.[102,103,112]

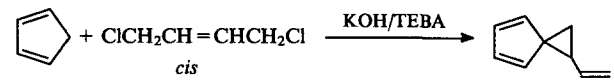
Among other alkylating agents used to obtain SHD derivatives by the cyclialkylation of cyclopentadiene, mention should be made of 1,4-dihalobut-2-enes and epichlorohydrin. Thus the interaction of cyclopentadiene with 1,4-dihalobut-2-enes is accompanied by the allyl rearrangement and leads mainly to 1-vinyl-substituted SHD.[60,113,114]



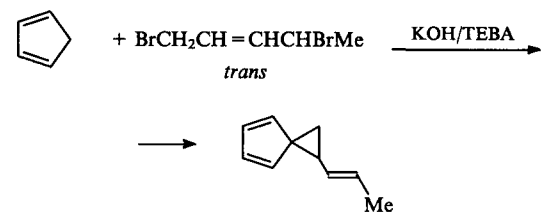




Under PTC conditions, the interaction of cyclopentadiene with *cis*-1,4-dichlorobut-2-ene on treatment with solid KOH in CH_2Cl_2 proceeds similarly, leading to 1-vinylspiro-[2.4]hepta-4,6-diene in 60% yield.[115]

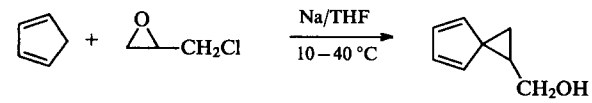


The cyclialkylation of cyclopentadiene by *trans*-1,4-dibromopent-2-ene also proceeds similarly, leading to the formation of propen-1-ylspiro[2.4]hepta-4,6-diene in 55% yield.[115]



The formation of vinyl-substituted SHD in these reactions indicates the possibility of using derivatives of 1,4-dihaloalk-2-enes for the synthesis of alken-1-ylspiro[2.4]hepta-4,6-dienes.[102,103]

Finally, the cyclialkylation of cyclopentadiene by epichlorohydrin leads to 1-hydroxymethylspiro[2.4]hepta-4,6-diene in 64%–77% yields.[116–118]

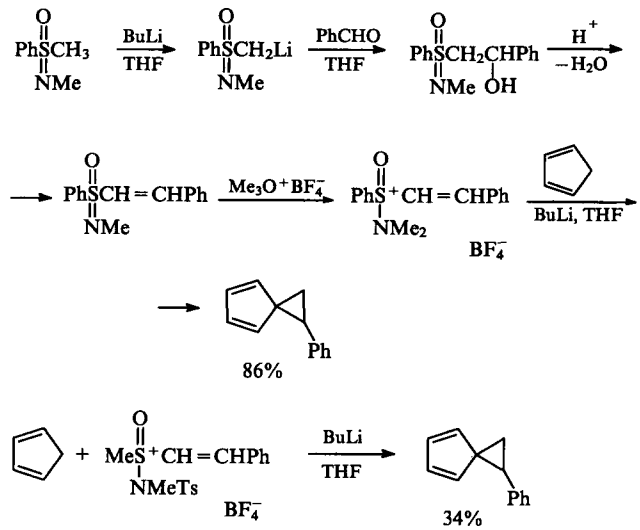


Thus the method involving the cyclialkylation of cyclopentadiene is universal and makes it possible to obtain easily and in high yield SHD derivatives with various functional groups, which renders these compounds readily available synthons for wide scale employment in specific organic synthesis. This method of preparation of SHD and its derivatives is the simplest and most effective compared with other procedures examined in previous sections of the review. The cyclialkylation of cyclopentadiene under the conditions of phase transfer catalysis with formation of compounds of the SHD series proceeds via an S_N2 mechanism,[102,103] which can be used in the synthesis of optically active SHD derivatives. The method is ineffective in the synthesis of SHD with electron-releasing substituents and of *gem*-disubstituted SHD.

4. Other methods of synthesis of spiro[2.4]hepta-4,6-dienes

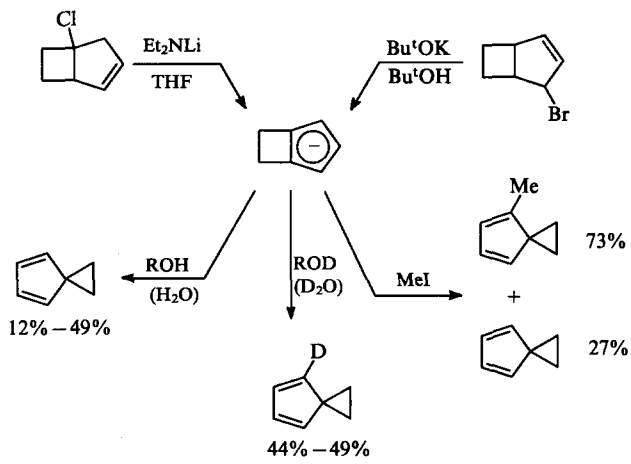
Certain further examples of the construction of the SHD system are considered below. They are frequently random in character and as a rule have no preparative value.

Thus the synthesis of the 1-phenyl derivative of SHD by the reaction of cyclopentadiene with derivatives of vinylsulfoxyimines on treatment with butyllithium has been described.[119]

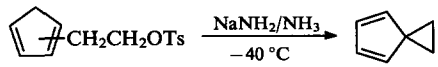


Apparently the mechanism of this reaction is similar to that of the addition of a nucleophile to a Michael acceptor,[119] the cyclopentadienyl anion, formed as an intermediate from cyclopentadiene on treatment with BuLi, acting as the nucleophile.

Several examples of the synthesis of SHD and its derivatives as a result of intramolecular reactions have been described. Thus halo-derivatives of bicyclo[3.2.0]hept-2-ene readily give up a hydrogen halide molecule on treatment with strong bases, affording the corresponding bicyclo[3.2.0]hepta-1,3-dienyl carbanion, which combines with a proton or a methyl group and rearranges to SHD and its derivatives.[120, 121]

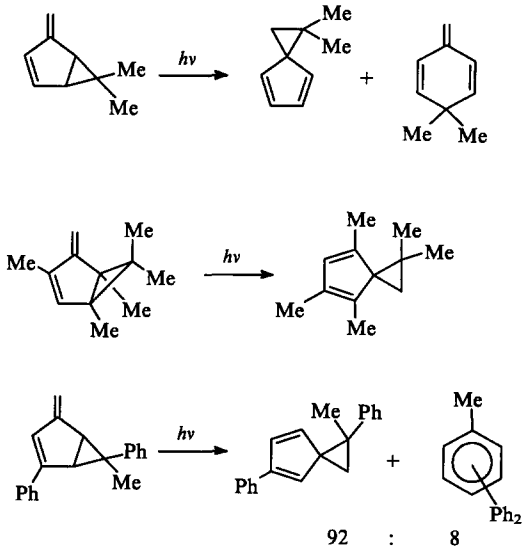


Furthermore, intramolecular alkylation of the β-tosylethyl derivative of cyclopentadiene also results in the formation of SHD.[122]

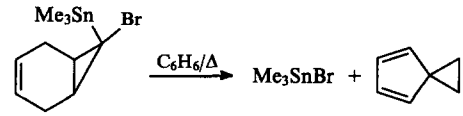


This reaction is very similar to those described in the previous Section.

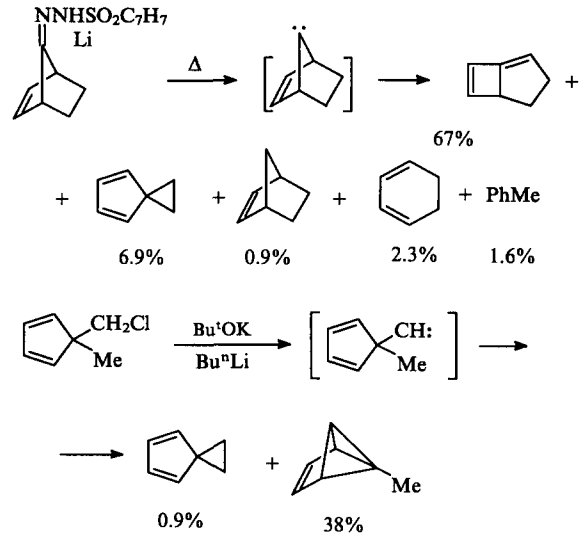
Examples also exist of the formation of compounds of the SHD series as a result of the photochemical isomerisation of derivatives of 4-methylenebicyclo[3.1.0]hex-2-ene.[56, 58, 123–126]



Spiro[2.4]hepta-2,6-diene has been synthesised in 76%–86% yield by the thermolysis (101–162 °C) of a derivative of norcarene[127] (degree of conversion 75%–85%). It has been suggested that the reaction proceeds via the intermediate formation of carbene.



Finally, the formation of SHD has been observed, although only as a side product, in the following carbene reactions.[128–131]



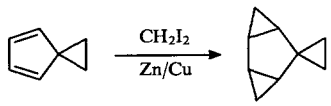
Whereas in the first case[128–131] the mechanism of the formation of SHD is not altogether clear, in the second reaction[131] SHD is apparently obtained as a result of the insertion of the intermediate carbene in a C–H bond of the methyl group.[128, 129, 131]

III. Chemical reactions of spiro[2.4]hepta-4,6-dienes

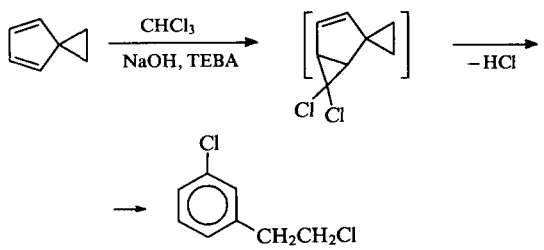
The [2 + 1]-, [2 + 2]-, [2 + 3]-, and [2 + 4]-cycloaddition reactions involving compounds of the SHD series as well as oxidation, reduction, and thermal isomerisation reactions will be considered in this Section. The review does not include the numerous thoroughly investigated complex formation[92, 132–151] (only

studies published during the last ten years are quoted), polymerisation,[14–24] and dehydrochlorination[152] reactions as well as the reactions of SHD and its derivatives with organolithium compounds of arsenic and other elements.[153]

In the [2 + 1]-cycloaddition reactions, i.e. in the reactions with carbenes, SHD yields the products of conversion into one or two cyclopropane groups. Thus the product resulting from the conversion of both double bonds of SHD into cyclopropane groups is formed from the latter in 50% yield under the conditions of the Simmons–Smith reaction.[154]

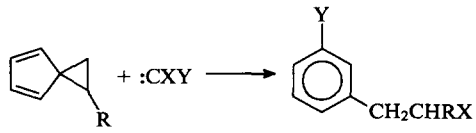


In the reaction of SHD with dichlorocarbene, generated under the conditions of phase transfer catalysis, the intermediate product of conversion of one of the double bonds of SHD into a dichlorocyclomethylene group is unstable, like the analogous monoadduct of dichlorocarbene and cyclopentadiene, and rearranges to the *meta*-derivative of benzene under the existing reaction conditions.[155,156]



50%

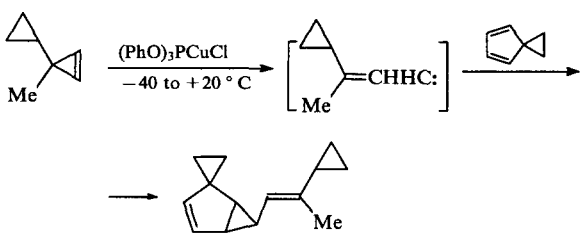
SHD and its substituted derivatives react similarly with other halocarbenes generated under of PTC conditions.[157,158]



X = Y = Cl, Br; X = Cl, Br, Y = F;
R = H, Ph, 3-ClC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4.

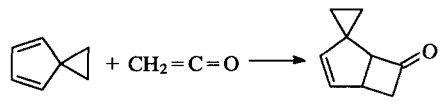
The exclusive formation of *meta*-substituted benzenes in these reactions is very important, since it opens up prospects for the creation of new convenient methods of synthesis of *meta*-substituted benzenes, which are of great practical value, from SHD derivatives (*meta*-substituted benzenes are usually obtained as a result of multistage synthesis). This demonstrates that compounds of the SHD series are likely to be useful as synthons in organic synthesis.

The reaction of SHD with vinylcarbene, generated from methylcyclopropylcyclopropene, leads to the formation of the stable product of the conversion of one of the double bonds of SHD into a cyclopropane group.[159]



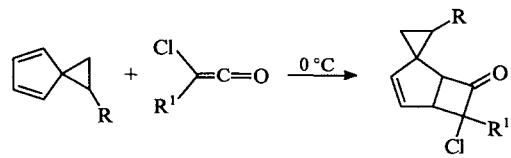
65%

The [2 + 2]-cycloaddition of SHD to ketene affords the corresponding cyclobutanone **27**, which may serve as a convenient intermediate for the synthesis of a series of analogues of natural icosanoids, for example thromboxane A_2 and prostaglandin D_2.[160]



27

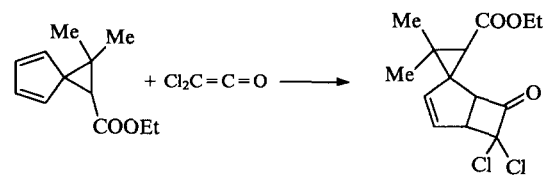
The reactions of SHD and 1-methyl-SHD with chloroketenes, obtained from dichloroacetic acid chloride on treatment with a (3–5)-fold excess of triethylamine, proceed similarly.[161–163]



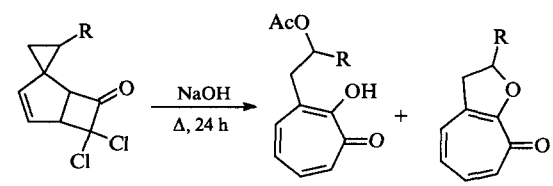
28

R	R^1	Yield of **28** (%)
H	Me	88
H	Pr^i	82
H	Ph	95
H	Cl	85
Me	Cl	92.5

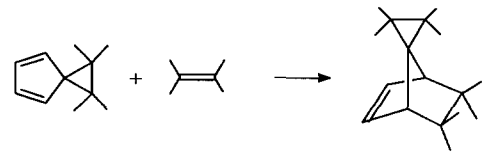
The addition of dichloroketene to trisubstituted SHD also proceeds in this way.[164]



The cyclobutanone derivatives obtained in the [2 + 2]-cycloaddition reaction isomerise with the opening of the four-membered carbon ring on treatment with alkali. The tropolones formed in 35%–40% yield are convenient intermediates for the synthesis of a series of important biologically active compounds and natural products.[162]



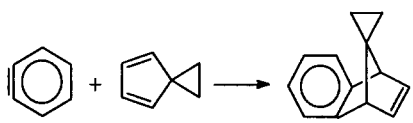
The majority of the reactions investigated, proceeding with participation of compounds of the SHD series, are [2 + 4]-cycloaddition reactions in which SHD and its derivatives usually react as the diene component, affording derivatives of spiro-(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane).



The vast majority of reactions of this type have been achieved for SHD itself and its 1-hydroxymethyl derivative. Reactions involving 1-vinyl-substituted SHD and certain other SHD derivatives are also known. The available literature data concerning the involvement of SHD itself in the [2 + 4]-cycloaddition reaction, summarised in Table 6, indicate its high reactivity. This opens up extensive prospects for the employment of SHD in the synthesis of skeletal structures.

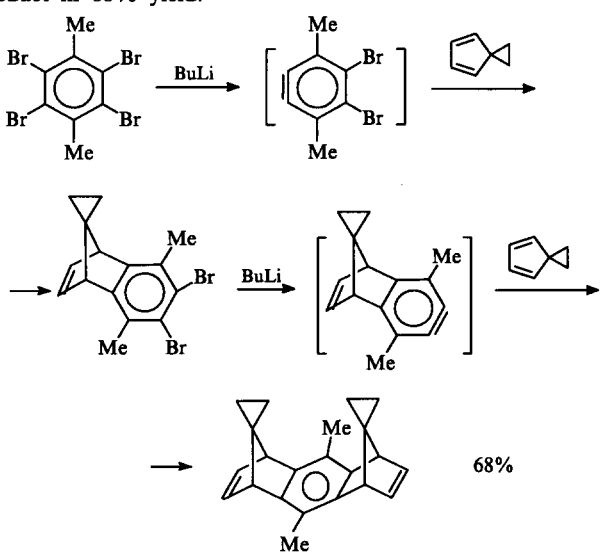
The Diels–Alder reaction involving SHD can proceed both via the usual thermal pathway and catalytically. For example, SHD and 1-methyl-SHD form exclusively cyclic *endo*-[2 + 4]-adducts (in 70%–75% yield) with 1,4-benzoquinone and 1,4-naphthoquinone under the conditions of micellar catalysis (an analogue of phase transfer catalysis) in an aqueous medium in the presence of cetyltrimethylammonium bromide as the micelle forming agent.[175–177] SHD may dimerise in the presence of Lewis acids[165] and on photoinduced electron transfer.[31,32]

SHD readily gives rise to cyclic [2 + 4]-adducts **28** on reaction with dehydrobenzene and its derivatives.[88,164,187]



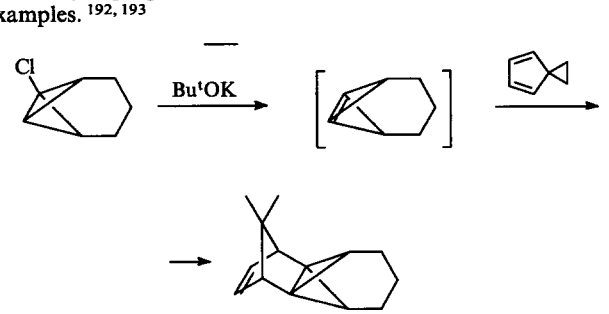
28 (50%–70%)

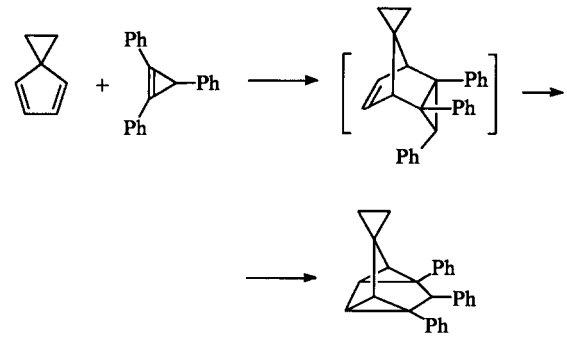
SHD reacts similarly with 1,2,4,5-tetrabromo-3,6-dimethylbenzene, affording the corresponding double cyclic [2 + 4]-adduct in 68% yield.[190]



The reactions of SHD with 1,2,4,5-tetrabromobenzene and 2,3,6,7-tetrabromonaphthalene proceed similarly, affording both mono- and di-adducts of dehydrobenzene derivatives.[191]

SHD is an effective 'trap' for highly reactive unstable unsaturated molecules, for example cyclopropenes. The intermediate unstable strained molecules, containing a double bond, readily afford in this case cyclic [2 + 4]-adducts with SHD. Similar products are also formed in the reactions with stable cyclopropenes. This is illustrated by the following examples.[192,193]

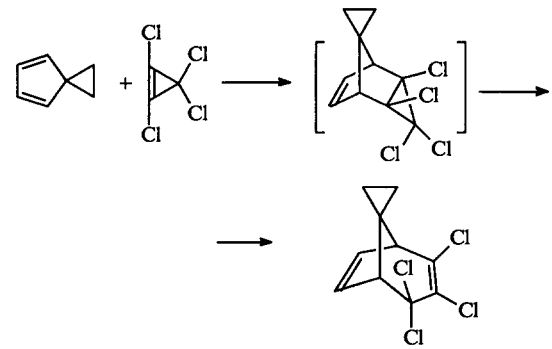




A series of highly strained polycyclic hydrocarbons have been obtained from SHD and its dimer (see, for example, Khusnutdinov et al.[165] and de Meijere et al.[194]).



In many cases, the primary adducts formed are labile and rearrange to thermodynamically stable products under the reaction conditions. Thus the product of reaction of SHD with tetra-chlorocyclopropene derives from the opening of the three-carbon ring of the intermediate chlorocyclopropane.[195]



Derivatives of SHD enter into the Diels–Alder reaction similarly to SHD itself (Table 7, see page 464)).

It is interesting to note that the adduct formed in the Diels–Alder reaction of tetracyanoethylene with dicyclopropyl-substituted SHD undergoes an unusual isomerisation under the conditions of its formation, in contrast to SHD itself and its other alkyl-substituted (methyl- and propyl-substituted) derivatives.[197,198]

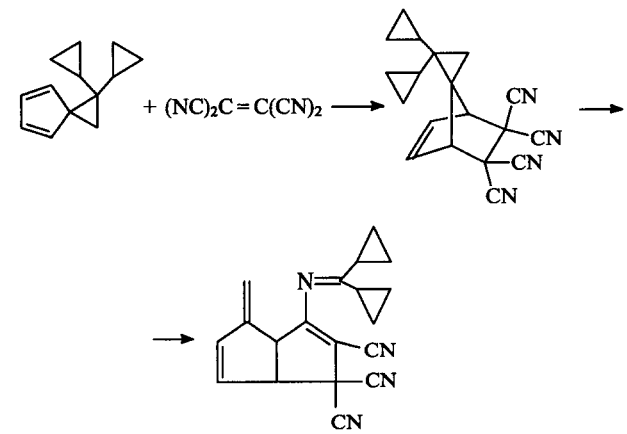


Table 6. The yields of the products of the [2 + 4]-cycloaddition reaction (the Diels–Alder reaction) of dienophiles with SHD.

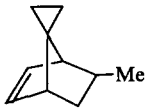
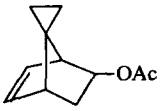
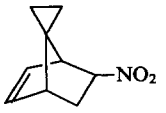
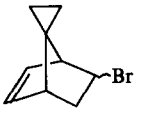
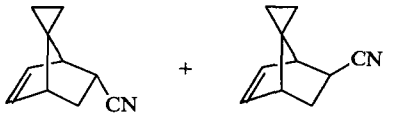
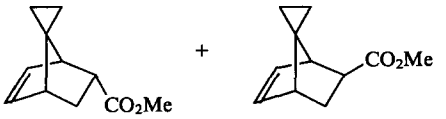
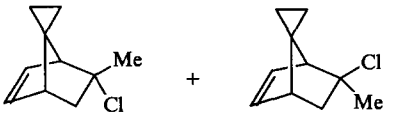
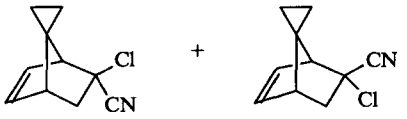
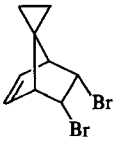
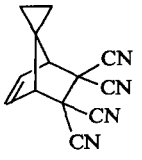
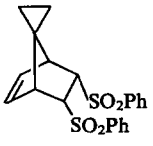
Dienophile	Final product	Yield (%)	Ref.
$CH_2=CHCH_3$		76	165
$CH_2=CHOAc$		60	87
$CH_2=CHNO_2$		89	166
$CH_2=CHBr$		62	167
$CH_2=CHCN$		71 (65:35)	168
$CH_2=CHCO_2Me$		77 (95.8:4.2)	168
$CH_2=CCIMe$		– (90:10)	168
$CH_2=CClCN$		– (94:6)	168
$BrCH=CHBr$		38	87, 105
$(CN)_2C=C(CN)_2$		90	130
$PhSO_2CH=CHSO_2Ph$		85	169
		29	170

Table 6 (continued).

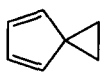
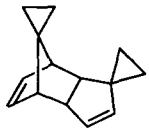
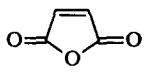
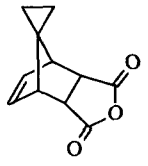
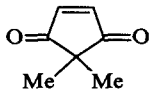
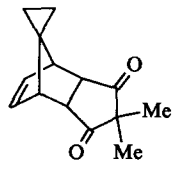
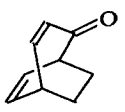
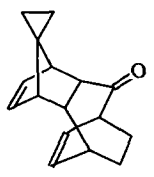
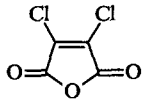
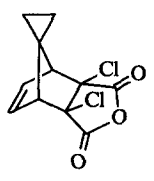
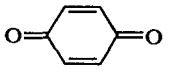
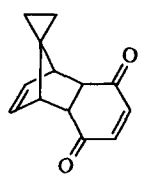
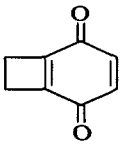
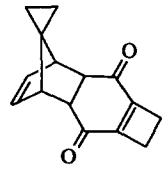
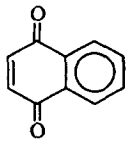
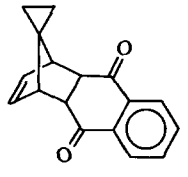
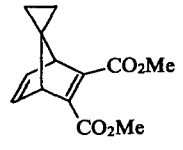
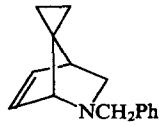
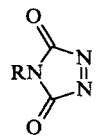
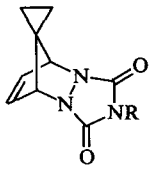
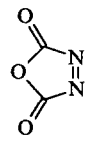
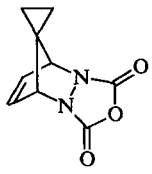
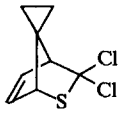
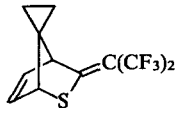
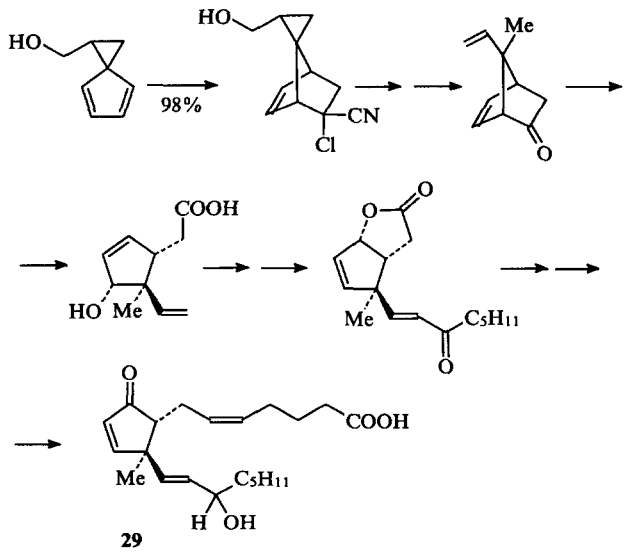
Dienophile	Final product	Yield[a] (%)	Ref.
		–	87, 165
		74–90	37, 87, 91
		73	171
		58	172
		–	109, 173, 174
		–	94, 175–177
		89	178
		100	179, 175–177
$MeO_2CC{\equiv}CCO_2Me$		64	180, 181
$PhCH_2N{=}CH_2$		62	182

Table 6 (*continued*).

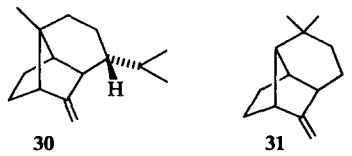
Dienophile	Final product	Yield[a] (%)	Ref.
		50–60	183, 184
		–	185
$S=CCl_2$		74	186
$S=C=C(CF_3)_2$		91	186

[a]A dash shows that the yield is not indicated; the *endo* : *exo* isomer ratio is indicated in brackets.

In speaking of useful practical properties of compounds of the SHD series, one should note that some of the Diels – Alder adducts of SHD possess physiological activity,[11,12] including insecticidal properties.[183] Interesting polymers have been obtained from the adducts of SHD with fluoroolefins.[16,17] The diene adducts of 1-hydroxymethyl-substituted SHD are of great interest as chemical intermediates. The simplest and most effective methods of synthesis of prostaglandins, for example prostaglandin A_2 (compound **29**) (overall yield 9%)[13] and their analogues,[199] as well as certain natural products such as cinularene **30**[118,200–202] and longifolene **31**,[118,202–204] have been proposed on the basis of the chemical reactions of such adducts.



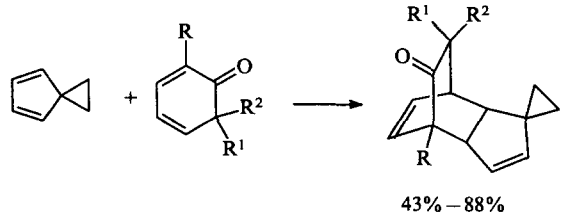
29



30 **31**

Such products are also convenient intermediates in the synthesis of norbornenes disubstituted by functional groups in the 7,7-positions.[205]

SHD and its derivatives can also enter into [2 + 4]-cycloaddition reactions as the dienophile, especially in reactions with highly reactive dienes such as 2,4-cyclohexadienones that are generated in situ.[206–210]

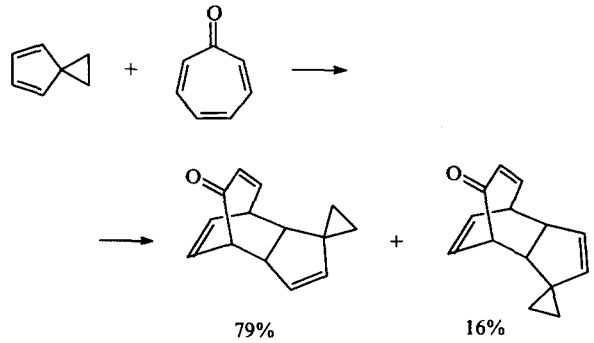


43%–88%

R = H, Me; R^1 = OH, OAc; R^2 = Me, CH_2Cl; $R^1+R^2 = CH_2O$.

The adducts of SHD with 6-hydroxymethylenecyclohexa-2,4-dienone are convenient intermediates in the stereoselective synthesis of natural polyquinane products[210] and compounds of the sesquiterpene series.[209]

SHD also reacts as the dienophile with tropone.[211]



79% 16%

Table 7. The yields of the products of the Diels–Alder reaction with substituted SHD.

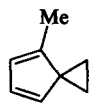
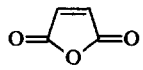
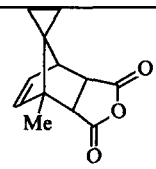
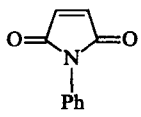
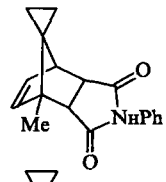
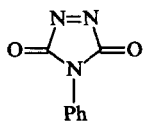
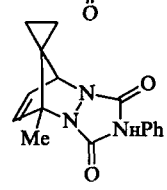
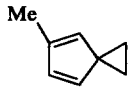
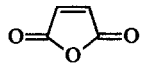
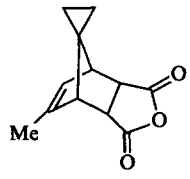
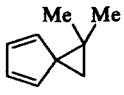
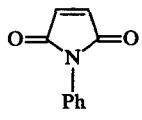
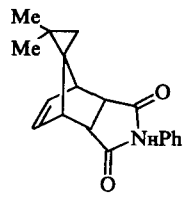
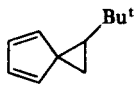
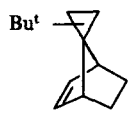
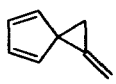
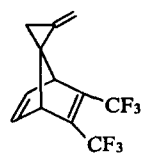
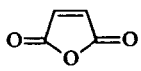
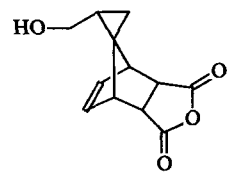
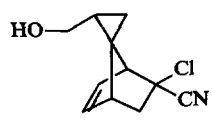
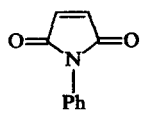
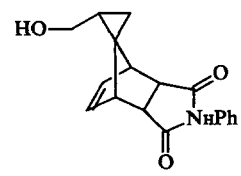
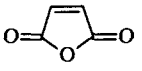
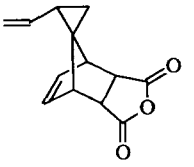
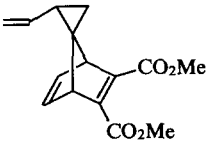
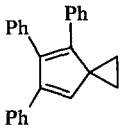
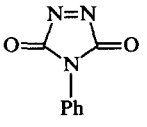
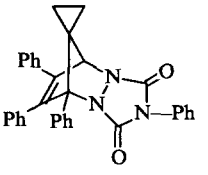
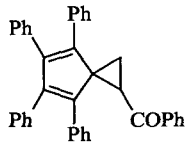
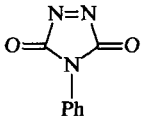
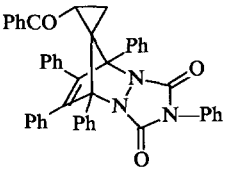
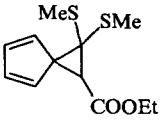
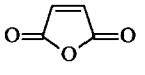
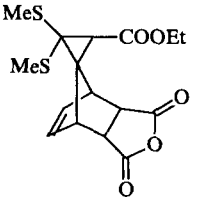
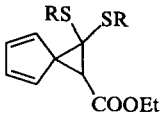
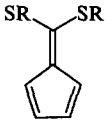
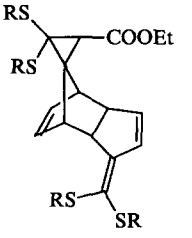
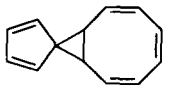
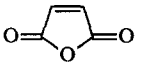
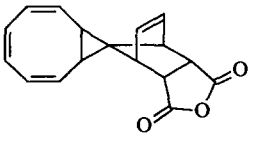
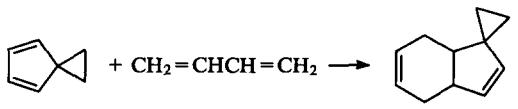
Diene	Dienophile	Product	Yield[a] (%)	Ref.
			80	106
			–	106
			50–60	121
			–	106
			–	124
	$CH_2=CH_2$		70	196
	$CF_3C\equiv CCF_3$		–	64
			–	22
	$CH_2=CClCN$		98	13
			–	116

Table 7 (continued).

Diene	Dienophile	Product	Yield[a] (%)	Ref.
			69	60
	$MeO_2CC{\equiv}CCO_2Me$		–	60
			94	77
			40 – 57	77
			94	78
			40	78
			76	60

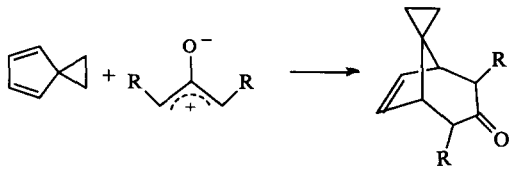
[a] A dash shows that the yield is not indicated.

SHD again assumes the role of the dienophile in a series of reactions with simple dienes. Thus its reaction with butadiene leads to the exclusive formation of spiro(bicyclo[4.3.0]nona-3,7-diene-9,1′-cyclopropane) (in 40% yield).[165]



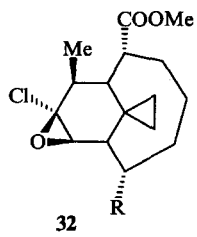
The reaction with cyclopentadiene proceeds similarly.[165]

The reactions involving the dipolar [3 + 4]-cycloaddition of propen-2-oxides, generated in situ, to SHD are also known; for example:[212–214]



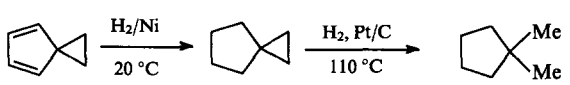
R = Cl, Me; R+R = CH_2CH_2.

The adducts obtained in this way are convenient intermediates in the synthesis of various natural products, for example taxane diterpenes **32**.[215]

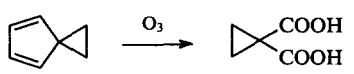


32

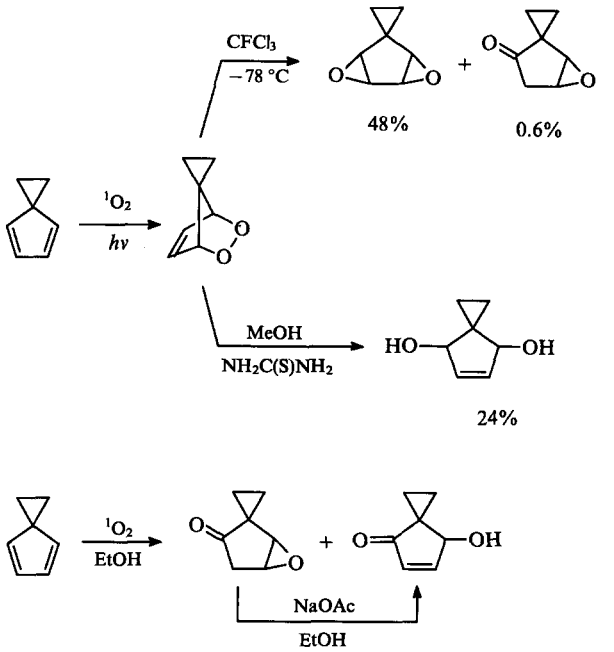
Among other reactions involving SHD, mention should be made of its catalytic hydrogenation, which, in the presence of Raney nickel at 20 °C, leads to the reaction of only the double bonds and yields the associated products, whereas at higher temperature the hydrogenolysis of the three-carbon ring also occurs.[86,216]



The ozonolysis of SHD involves both double bonds of the cyclopentadiene ring and leads to the formation of cyclopropane-1,1-dicarboxylic acid.[85]

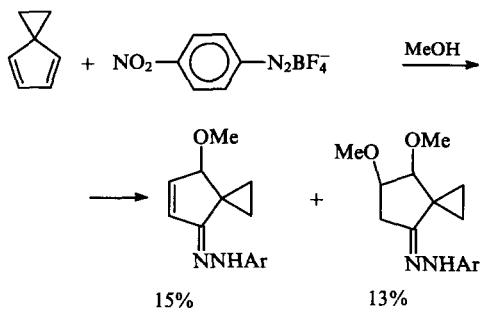


On the other hand, oxidation of SHD by singlet oxygen leads initially to the product of the 1,4-addition of oxygen to the diene system of SHD, which then undergoes further transformations under the reaction conditions.[217,218,219]

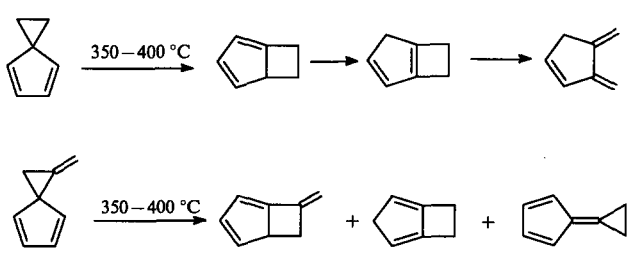


These reactions constitute the basis of the synthesis of natural pederol.[219]

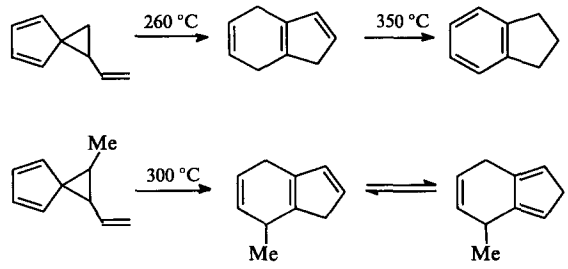
The reaction of SHD with 4-nitrobenzenediazonium fluoroborate in methanol likewise leads to 1,4-adducts.[220]



Finally, certain thermal reactions of compounds of the SHD series have been investigated. At 300–400 °C, SHD and its derivatives undergo irreversible isomerisation, similarly to 5,5-disubstituted cyclopentadienes, as a result of the 1,2-shift of the methylene unit of the three-carbon ring accompanied by 1,2-hydride transfer. Isomerisation leads to the thermodynamically more stable isomeric bicyclo[3.2.0]hepta-1,3-dienes, which may be subsequently trapped by reactive dienophiles in the Diels–Alder reaction.[64,151,220–225]



On the other hand, the thermal reactions of vinyl-substituted SHD are accompanied by the allyl rearrangement, which results in the formation of derivatives of bicyclo[4.3.0]nonatriene.[61]



These bicyclo[3.2.0]heptadienes formed in thermal reactions of SHD can participate subsequently in various [2 + 4]-cycloaddition reactions.[224,225]

The thermolysis of 1-substituted and 1,2-disubstituted SHD at temperatures above 200 °C can also entail their epimerisation.[111]

IV. Conclusion

As can be seen from the literature data examined in the present review, compounds of the SHD series constitute an extremely interesting class of chemical substances with considerable potential synthetic possibilities, both as such and as intermediates in the synthesis of physiologically active and other products of practical value. SHD derivatives have found applications in the synthesis of polyfunctional compounds[226,227] and skeletal structures. Furthermore, such compounds have been arousing an unflagging interest in connection with the problem of spiroconjugation[228–230] and complex formation.

The development of the chemistry of compounds of the SHD series depends to a large extent on the availability of effective methods for their synthesis. The methods of synthesis of SHD and its derivatives developed hitherto, principally the cyclialkylation of cyclopentadiene under the conditions of phase transfer catalysis, have made mono- and 1,2-disubstituted SHD derivatives readily available. It may be expected that further studies in this field will be directed to the development of new preparative methods of synthesis of such compounds by means of reactions involving the cyclomethylenation of the exocyclic double bond of fulvenes.

Finally, the above survey of literature data demonstrates that the chemical reactions of SHD and its derivatives have been studied mainly in relation to the most readily available compounds. Evidently the high availability of these interesting compounds will also stimulate a comprehensive study of their properties, including their chemical properties.

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