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Synthesis and reactions of mixed halogenobuta-1,3-dienes

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Abstract. The published data on the methods for the preparation of mixed halogenobuta-1,3-dienes are generalised and systematised with a special emphasis on compounds of high practical value. Chemical transformations of mixed halogenodienes are considered and broad possibilities of the use of these compounds for the synthesis of various valuable, but difficultly accessible polyfunctional products are demonstrated. The bibliography includes 115 references.

I. Introduction

The first representative of halogenobutadienes, *viz.,* hexachlorobuta-1,3-diene, was obtained as early as 1876.[1] However, in the subsequent 50 years studies on the synthesis of halogenobutadienes were episodic and only in the early 1930s did they become purposeful and systematic. The development of preparation methods and the search for possible uses of this class of compounds in organic synthesis were stimulated by the discovery that mono- and dichlorobuta-1,3-dienes easily polymerise.

The first data on the synthesis of halogen derivatives of butadiene were generalised by Petrov in 1944.[2] Later studies devoted mainly to the synthesis and transformations of chloro and fluoro derivatives of butadiene were systematised in a fundamental Houben – Weyl monograph.[3] Particularly intensive studies were carried out in the field of chloro derivatives of butadiene and their results were surveyed in reviews[4–6] and monographs.[7–9]

At present, there are numerous publications devoted to the synthesis of mixed halogenobutadienes (MHB) containing atoms of different halogens, *viz*., fluorine, chlorine, bromine and iodine. Mixed halogenobutadienes possess a broad spectrum of useful properties: they are good dielectrics, refrigerants and heat-transfer agents; they are used as aerosols, lubricants and floatation agents and possess algicidal, bactericidal and fungicidal activities.[10–15] A number of MHB manifest high antitumour activity.[16] Chlorine – fluorine-containing butadienes are employed as monomers for the preparation of valuable polymers and copolymers resistant to heat, light, chemical corrosion, *etc*.[13, 17, 18] And, finally, MHB are promising semi-products in organic synthesis. For example, the preparation of polyfluoromethine compounds is based on MHB, which opens a way to the synthesis of novel polymethine dyes.[19]

It should be noted that the introduction of atoms of different halogens into the butadiene molecule leads to a considerable increase in the number of theoretically possible isomers. Thus consideration of structural and geometric isomers shows that dichlorobuta-1,3-diene has nine isomers,[7] while for butadiene derivatives with two different halogen atoms the number of possible isomers increases tenfold. From a theoretical aspect, mixed halogenobutadienes, like other compounds with the butadiene system, are convenient subjects for studying the *s-cis* – *trans*-isomerism associated with the appearance of conformationally non-equivalent structures resulting from the hindered rotation of the vinyl fragments around the central C – C bond.[20–22] They are also promising as model substrates for studying regularities of the processes of nucleophilic vinylic substitution (S_NVin). This review surveys the literature data on the chemistry of mixed halogenobuta-1,3-dienes published up to 1999. We presume that such a review will fill the gap in the relevant literature and will contribute to the further development of research into the chemistry of halogen derivatives of alkenes and alkadienes.

II. Synthesis of mixed halogenobuta-1,3-dienes

The basic methods for the preparation of MHB are:

(1) Elimination reactions (dehydrohalogenation and dehalogenation) of polyhalogenobutadienes and -butenes;

(2) halogenation and hydrohalogenation of acetylenic hydrocarbons of the C_4 series;

(1) thermal decomposition of accessible polyhalogenated compounds.

Other methods of the synthesis of individual representatives of MHB are also known.

1. Elimination reactions

Numerous chlorofluoro- and bromochlorobutadienes were obtained by dehydrohalogenation and dehalogenation of polyhalogenobutanes and -butenes).

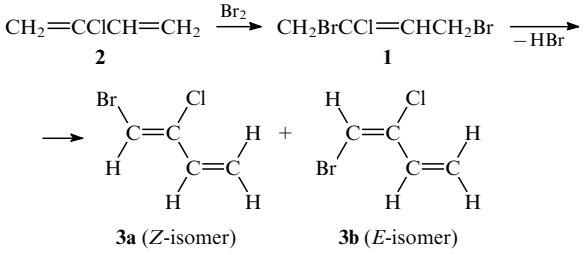
Dehydrohalogenation of polyhalogenobutenes under the action of various dehydrohalogenation agents proceeds as the 1,4- or 3,4-elimination of a molecule of hydrogen halide depending on the position of the C = C bond. Another conventional way for the synthesis of MHB is dehalogenation of polyhalogenobutanes and -butenes, which is carried out under the action of metals, zinc in most cases.

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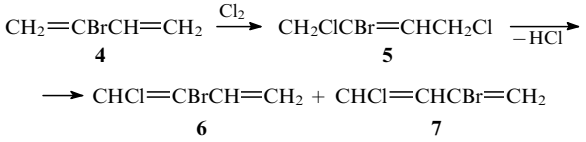
a. Dihalogenobutadienes

The simplest MHB containing two different halogen atoms can be obtained from trihalogenobut-1- and -2-enes. Thus the dehydrobromination of 1,4-dibromo-2-chlorobut-2-ene (**1**), which is the main product of chloroprene bromination (**2**), resulted in 1-bromo-2-chlorobuta-1,3-diene (**3**) in preparative yield.[23,24] The diene **3** formed in this reaction is a mixture of geometric isomers with the predominance of the *Z*-isomer **3a**.[25]

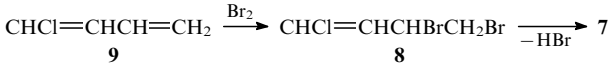


Papazyan *et al.* [26] have proposed performing the dehydrobromination of butene **1** in the presence of phase-transfer catalysts (PTC) that considerably simplified the process and made it more economical (the conditions for the synthesis of the diene **3**, its yield and the data related to all subsequent syntheses of MHB by the elimination reaction are presented in Table 1).

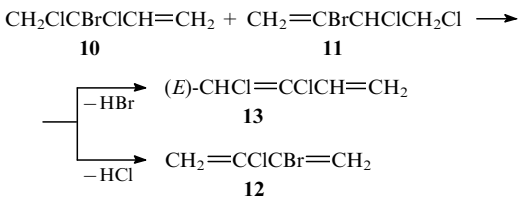
Chlorination of bromoprene (**4**) and subsequent dehydrochlorination of 2-bromo-1,4-dichlorobut-2-ene (**5**) leads to a mixture of *E*- and *Z*-isomers of 2- (**6**) and 3-bromo-1-chlorobuta-1,3-diene (**7**).[27,28]



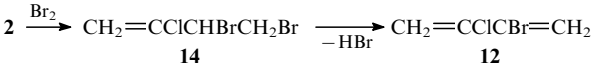
A more convenient synthesis of *E*- and *Z*-isomers of the diene **7** is based on the dehydrobromination of 3,4-dibromo-1-chlorobut-1-ene (**8**), which is the product of bromination of 1-chlorobuta-1,3-diene (**9**).[29]



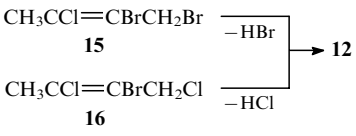
Dehydrohalogenation of the by-products of the chlorine addition to the diene **4**, *viz*., a mixture of 3- (**10**) and 2-bromo-3,4-dichlorobut-1-enes (**11**), yielded a mixture of 2-bromo-3-chlorobuta-1,3-diene (**12**) and (*E*)-1,2-dichlorobuta-1,3-diene (**13**) (GLC).[27]



The diene **12** was initially obtained by dehydrobromination of 3,4-dibromo-2-chlorobut-1-ene (**14**), which is a by-product of chloroprene **2** bromination.[24]



The preparative synthesis of the diene **12** is based on the 1,4-elimination of hydrogen halide from 1,2-dibromo-3-chlorobut-2-ene (**15**) or 2-bromo-1,3-dichlorobut-2-ene (**16**) or a mixture of these butenes with an alkali (KOH or NaOH) in the presence of PTC.[30]



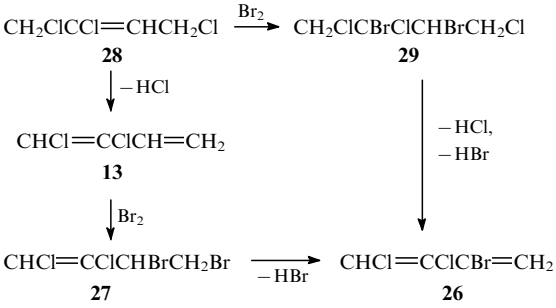
Of the disubstituted chlorofluorobutadienes, the following three compounds are known: 1-chloro-1-fluoro- (**17**), 1-chloro-2-fluoro- (**18**) and 3-chloro-2-fluoro-buta-1,3-dienes (**19**) (see Table 1).

The diene **17** was obtained as the result of dehydrochlorination of 4,4-dichloro-4-fluorobut-1-ene (**20**),[31,32] whereas the diene (**18**) resulted from the dechlorination of 3,4,4-trichloro-3-fluorobut-1-ene (**21**).[33] The diene **19** is formed upon dehydrohalogenation of a liquid mixture of mono-, di- and trifluoro compounds which are the products of the reaction of 1,2,3,4-tetrachlorobutane with HF.[34] Yet another route to the diene **19** consists in the dehydrohalogenation of 2,4-dichloro-1,3-difluorobutane (**22**), which is the main product of ClF addition to butadiene (see Table 1).[35,36]

b. Trihalogenobutadienes

The first representative of mixed trihalogenobutadienes, *viz*., 3-bromo-1,1-dichlorobuta-1,3-diene (**23**), was initially prepared by the thermal dehydrochlorination of 3-bromo-1,1,1,4-tetrachlorobutane (**24**)[37] and later, of 2-bromo-4,4,4-trichlorobut-1-ene (**25**), which is the product of bromotrichloromethane addition to allene [38] (see Table 1).

3-Bromo-1,2-dichlorobuta-1,3-diene (**26**) was obtained by a multistep synthesis the last stage of which was dehydrobromination of 3,4-dibromo-1,2-dichlorobut-1-ene (**27**), which is the main product of 1,2-dichlorobuta-1,3-diene (**13**) bromination. The latter is obtained by the dehydrochlorination of 1,2,4-trichlorobut-2-ene (**28**).[39] Papazyan *et al.*[26] simplified the synthesis of the diene **26** from the butene **28**. The target product **26** was obtained by direct bromination of the butene **28** and subsequent dehydrohalogenation of the adduct formed, *viz*., 2,3-dibromo-1,2,4-trichlorobutane (**29**). The by-product of this reaction is 2-bromo-1,3-dichlorobuta-1,3-diene (**30**).



Two methods for the synthesis of 1-bromo-2,3-dichlorobuta-1,3-diene (**31**) are known. It is obtained by dehydrobromination of either 1,4-dibromo-2,3-dichlorobut-2-ene (**32**)[39] [the product of 2,3-dichlorobuta-1,3-diene (**33**) bromination][39] or 1,2-dibromo-2,3,4-trichlorobutane (**34**) [the product of bromine addition to the accessible 2,3,4-trichlorobut-1-ene (**35**)].[26]

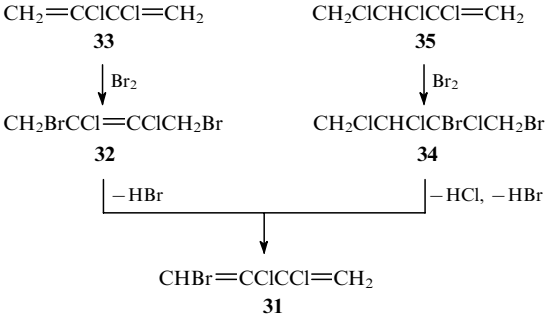


Table 1. Synthesis of mixed halogenobuta-1,3-dienes by the elimination from halogenobutanes and -butenes.

Starting compound	Elimination agent	Reaction conditions	Halogenobutadiene	Yield (%)	Ref.
$CH_2BrCCl=CHCH_2Br$ (**1**)	KOH	EtOH	$CHBr=CClCH=CH_2$ (**3**)	38	23, 24
$CH_2BrCCl=CHCH_2Br$ (**1**)	KOH	96% EtOH, 0 °C, 14 h	(*Z*)-$CHBr=CClCH=CH_2$ (**3a**), (*E*)-$CHBr=CClCH=CH_2$ (**3b**)	31.5, 1.5	25
$CH_2BrCCl=CHCH_2Br$ (**1**)	10% NaOH	water, 1% katamin AB,	$CHBr=CClCH=CH_2$ (**3**)	72	26
$CH_2ClCBr=CHCH_2Cl$ (**5**)	NaOH	EtOH, 40 °C, nitrosodiphenylamine	(*E*)-$CHCl=CBrCH=CH_2$ (**6a**) + + (*Z*)-$CHCl=CBrCH=CH_2$ (**6b**) + + $CHCl=CHCBr=CH_2$ (**7**) (**6a** : **6b** : **7** = 72 : 2 : 26)	–	27, 28
$CHCl=CHCHBrCH_2Br$ (**8**) (*E* : *Z* = 3 : 1)	10% NaOH	water, katamin AB, 40 °C, 3 h	(*E*)- + (*Z*)-$CHCl=CHCBr=CH_2$ (**7**) (*E* : *Z* = 82 : 18)	66.8	29
$CH_3CCl=CBrCH_2Br$ (**15**)	NaOH	water, katamin AB	$CH_2=CClCBr=CH_2$ (**12**)	60.2	30
$CH_3CCl=CBrCH_2Cl$ (**16**)	NaOH	the same	$CH_2=CClCBr=CH_2$ (**12**)	51.6	30
$CH_2=CHCBrClCH_2Cl$ (**10**) + + $CH_2=CBrCHClCH_2Cl$ (**11**) (**10** : **11** = 1 : 4)	NaOH	EtOH, nitrosodiphenylamine, 46–48 °C	$CH_2=CClCBr=CH_2$ (**12**) + + (*E*)-$CHCl=CClCH=CH_2$ (**13**) (**12** : **13** = 9 : 1)	–	27
$CFCl_2CH_2CH=CH_2$ (**20**)	KOH	EtOH, boiling	$CFCl=CHCH=CH_2$ (**17**)	53.5	31
$CHCl_2CFClCH=CH_2$ (**21**)	Zn	the same	$CHCl=CFCH=CH_2$ (**18**)	–	33
$CH_2FCHClCHFCH_2Cl$ (**22**)	KOH	EtOH	$CH_2=CClCF=CH_2$ (**19**)	–	35, 36
$CCl_3CH_2CHBrCH_2Cl$ (**24**)	–	thermal dehydrochlorination, 450 °C	$CCl_2=CHCBr=CH_2$ (**23**)	45.0	37
$CCl_3CH_2CBr=CH_2$ (**25**)	Et_3N	boiling, 2 h	$CCl_2=CHCBr=CH_2$ (**23**)	~90	38
$CHCl=CClCHBrCH_2Br$ (**27**)	KOH	MeOH, 20 °C	$CHCl=CClCBr=CH_2$ (**26**)	65.0	39
$CH_2ClCBrClCHBrCH_2Cl$ (**29**)	NaOH	80% EtOH, 40–50 °C	$CHCl=CClCBr=CH_2$ (**26**) + + $CHCl=CBrCCl=CH_2$ (**30**) (**26** : **30** = 94.5 : 5.5)	80.0	26
$CH_2BrCCl=CClCH_2Br$ (**32**)	KOH	MeOH, 20 °C	$CHBr=CClCCl=CH_2$ (**31**)	54.0	39
$CH_2ClCHClCBrClCH_2Br$ (**34**)	NaOH	EtOH	$CHBr=CClCCl=CH_2$ (**31**)	47.0	26
$CH_2BrCBrClCHBrCH_2Br$ (**37**)	NaOH	80% EtOH	$CHBr=CClCBr=CH_2$ (**38**) + + $CHBr=CBrCCl=CH_2$ (**39**) (**38** : **39** = 93 : 7)	90.0	26
$CH_2ClCBr=CBrCH_2Cl$ (**41**)	KOH	EtOH, 25 °C	$CHCl=CBrCBr=CH_2$ (**40**)	58.0	42
$CCl_3CH_2CBrFCH_3$ (**46a**)	Bu_3N	140 °C, 100 Torr	$CCl_2=CHCF=CH_2$ (**42**)	–	43
$CBr_3CH_2CBrFCH_3$ (**46b**)	Bu_3N	the same	$CBr_2=CHCF=CH_2$ (**43**)	–	43
$CBrF_2CCl_2CH=CH_2$ (**48**)	Zn	EtOH	$CF_2=CClCH=CH_2$ (**44**)	–	16
$CFCl=CFCH_2CH_2Br$ (**50**) (*E* : *Z* = 44 : 56)	KOH	EtOH (KOH : EtOH = = 1 : 1)	(*E*)- + (*Z*)-$CFCl=CFCH=CH_2$ (**45**) (*E* : *Z* = 44 : 56)	80.0	47
$CCl_2=CClCHBrCH_2Br$ (**52**)	NaOH	70% EtOH, 20–25 °C	$CCl_2=CClCBr=CH_2$ (**54**) + + $CCl_2=CClCH=CHBr$ (**55**) (**54** : **55** = 10 : 1)	93.0	26
$CHBrClCHBrCHClCHCl_2$ (**57**)	KOH	water, TEBA [a]	(*Z*)- + (*E*)-$CHBrCl=CHCH=CCl_2$ (**56**) (*Z* : *E* = 4 : 1)	60	49
$CHBrClCHBrCH=CCl_2$ (**58**)	KOH	the same	$CBrCl=CHCH=CCl_2$ (**56**)	91.0	50
$CBrF_2CFClCCl=CH_2$ (**59**)	Zn	EtOH, boiling	$CF_2=CFCCl=CH_2$ (**61**)	43.5	51
$CBrF_2CFClCHClCHCl_2$ (**60**)	Zn	the same	$CF_2=CFCH=CHCl$ (**62**)	–	51
$CH_2=CBrCClFCBrF_2$ (**64**)	Zn	EtOH	$CF_2=CFCBr=CH_2$ (**63**)	17.0	3
$CCl_2=CHCBrClCHBrCl$ (**65**)	KOH	EtOH, 25 °C	(*Z*)- + (*E*)-$CCl_2=CHCCl=CBrCl$ (**66**) (*Z* : *E* = 1 : 1)	68.0	53
$CCl_2=CHCBrClCHBrCl$ (**65**)	20% NaOH	water, TEBA,[a] 40–45 °C, 4 h	(*Z*)- + (*E*)-$CCl_2=CHCCl=CBrCl$ (**66**) (*Z* : *E* = 1 : 3)	85	54
$CBr_2ClCHBrCH=CCl_2$ (**67**)	10% NaOH	water, TEBA,[a] 25 °C, 15 h	(*E*)- + (*Z*)-$CBrCl=CBrCH=CCl_2$ (**68**) (*E* : *Z* = 7 : 3)	55.0	55
$CBrCl_2CHBrCH=CBrCl$ (**69**)	10% NaOH	the same	(*E*)- + (*Z*)-$CBrCl=CHCBr=CCl_2$ (**70**) (*E* : *Z* = 3 : 2)	49	55
$CBrF_2CFClCCl=CHCl$ (**71**)	Zn	EtOH, boiling	$CF_2=CFCCl=CHCl$ (**73**)	19.0	51
$CFCl=CHCFClCF_2Cl$ (**72**)	Zn	Pr^nOH or Pr^iOH, boiling	$CFCl=CHCF=CF_2$ (**74**)	64	56
$CFCl_2CFClCFClCF_2Cl$ (**76**)	Zn	EtOH, boiling	$CF_2=CFCF=CFCl$ (**75**)	47.7	10, 12
$CFCl_2CFClCFClCF_2Cl$ (**76**) + + $CFCl_2CFClCFClCF_2I$ (**79**)	Zn	EtOH	(*E*)- + (*Z*)-$CF_2=CFCF=CFCl$ (**75**) (*E* : *Z* = 1 : 1)	73.0	57
$CF_2ClCFClCCl_2CF_2Cl$	Zn	EtOH	$CF_2=CFCCl=CF_2$ (**81**)	–	10
$CFCl_2CFClCFClCFCl_2$ (**77**)	Zn	BuOH, 85–95 °C	$CFCl=CFCF=CFCl$ (**82**)	48.0	60, 61
$CFCl_2CFClCFClCFCl_2$ (**77**)	Zn	dioxane, boiling	$CFCl=CFCF=CFCl$ (**82**) (*E*,*E* : *E*,*Z* : *Z*,*Z* = 1 : 2.5 : 1.5)	82.5	62

Table 1 (continued).

Starting compound	Elimination agent	Reaction conditions	Halogenobutadiene	Yield (%)	Ref.
$CFCl_2CFClCFClCF_2I$ (**79**) + + $CFCl_2CFClCF_2CFClI$ (**89**)	Zn	EtOH	$CFCl=CFCF=CFCl$ (**82**), $CF_2=CFCF=CFCl$ (**75**)	45 41	58
$CF_2ClCCl_2CCl_2CF_2Cl$ (**93**)	Zn	EtOH	$CF_2=CClCCl=CF_2$ (**92**)	–	10, 69
$CBrCl_2CHBrCCl_2CHCl_2$ (**98**)	Et_2NH	water, 25 °C	$CCl_2=CBrCCl=CCl_2$ (**99**), $CBrCl=CBrCCl=CCl_2$ (**100**)	88.0 10.0	70
(*E*)-$CBrCl=CClCHBrCBrCl_2$ (**101**)	KOH	20% KOH, TEBA [a]	(*E*)-$CBrCl=CClCBr=CCl_2$ (**102**) (*E*,*E*)- + (*E*,*Z*)-$CBrCl=CClCBr=CBrCl$ (**103**) (*E*,*E* : *E*,*Z* = 2 : 3)	60 16	71

[a] Triethylbenzylammonium chloride.

1,1-Dibromo-3-chlorobuta-1,3-diene (**36**) is obtained as an insignificant admixture in the synthesis of 1,1,3-tribromobuta-1,3-diene.[40]

Upon dehydrobromination of 1,2,3,4-tetrabromo-2-chlorobutane (**37**) [the product of exhaustive bromination of chloroprene (**2**)], 1,3-dibromo-2-chlorobuta-1,3-diene (**38**) is mainly formed. In addition, a small amount of 1,2-dibromo-3-chlorobuta-1,3-diene (**39**) was detected by GLC.[26]

$$CH_2=CClCH=CH_2 \xrightarrow{Br_2} \underset{\mathbf{37}}{CH_2BrCBrClCHBrCH_2Br} \xrightarrow[-HBr]{}$$
$$\rightarrow CH_2BrCBrClCBr=CH_2 + CH_2BrCCl=CBrCH_2Br \xrightarrow[-HBr]{}$$
$$\rightarrow \underset{\mathbf{38}}{CHBr=CClCBr=CH_2} + \underset{\mathbf{39}}{CH_2=CClCBr=CHBr}$$

2,3-Dibromo-1-chlorobuta-1,3-diene (**40**) was obtained by dehydrochlorination of 2,3-dibromo-1,4-dichlorobut-2-ene (**41**)[41] (see Table 1).

As regards the fluorine-containing trihalogeno derivatives of MHB, 1,1-dichloro-3-fluoro- (**42**), 1,1-dibromo-3-fluoro-(**43**), 2-chloro-1,1-difluoro- (**44**) and 1-chloro-1,2-difluorobuta-1,3-dienes (**45**) were obtained.

The synthesis of the dienes **42** and **43** is based on dehydrohalogenation of 3-bromo-3-fluoro-1,1,1,-trihalogenobutanes (**46a**,**b**).[42]

$$\underset{\mathbf{46a,b}}{CX_3CH_2CBrFCH_3} \xrightarrow[-HBr,\ -HX]{} \underset{\mathbf{42,\ 43}}{CX_2=CHCF=CH_2}$$

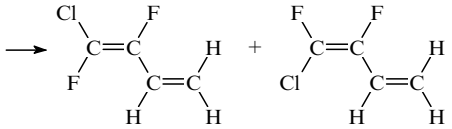
X = Cl (**42**, **46a**), Br (**43**, **46b**).

The butadiene **44** was first synthesised from 2-chloro-1,2-difluoro-4-iodobut-1-ene (**47**)[43] and later from 1-bromo-1,1-difluoro-2,2-dichloro-2-chlorobut-3-ene (**48**)[16] and 2,4-dichloro-1,1,1,-trifluorobut-2-ene (**49**).[44]

$$\underset{\mathbf{47}}{CF_2=CClCH_2CH_2I} \xrightarrow{-HI}$$
$$\underset{\mathbf{48}}{CBrF_2CCl_2CH=CH_2} \xrightarrow[-BrCl]{Zn} \underset{\mathbf{44}}{CF_2=CClCH=CH_2}$$
$$\underset{\mathbf{49}}{CF_3CCl=CHCH_2Cl} \xrightarrow[-ClF]{Zn}$$

The butadiene **45** is formed as a mixture of *E*- and *Z*-isomers upon dehydrobromination of the isomeric forms of 4-bromo-1-chloro-1,2-difluorobut-1-ene (**50**) obtained by dehalogenation of 1,4-dibromo-1,2-dichloro-1,2-difluorobutane (**51**), which is the product of telomerisation of CBrFClCBrFCl with ethylene under the action of benzoyl peroxide. It was shown that the starting butene **50** and the target diene **45** have the same ratio of isomers, *i.e.*, the elimination reaction occurs stereospecifically.[45]

$$CBrFClCBrFCl \xrightarrow{CH_2=CH_2} \underset{\mathbf{51}}{CBrFClCFClCH_2CH_2Br} \xrightarrow[-BrCl]{}$$
$$\rightarrow \underset{\mathbf{50}\ (E,Z)}{CFCl=CFCH_2CH_2Br} \xrightarrow[-HBr]{}$$



45a (*Z*-isomer) **45b** (*E*-isomer)

1,1,3-Trihalogenobutadienes are convenient subjects for the elucidation of characteristic features of conformational behaviour. The use of ^1H NMR and UV spectroscopy made it possible to establish that the bulky substituents (Cl, Br) in the 1,3 (or 2,4) positions of the diene chain destabilise the *s-trans*-form, which is characteristic of haloprenes and disubstituted butadienes, hence the 1,1,3-trihalogenobuta-1,3-dienes **23** and **36** exist in a skew conformation in the form of a single conformer.[40,46]

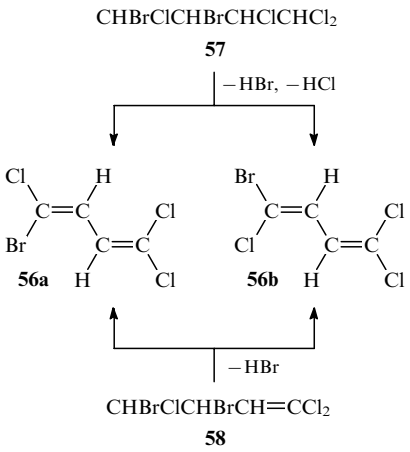
According to the ^1H NMR and IR spectroscopic data, the dienes **42** and **43** having a fluorine atom in the position 3 exist as a mixture of two conformers, *viz.*, the skew and *s-trans*-forms.[42,47]

c. Tetrahalogenobutadienes

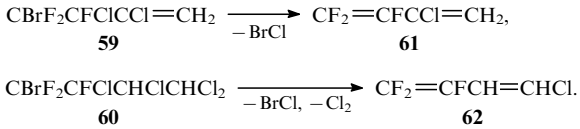
Several examples of the synthesis of tetrasubstituted MHB based on the elimination reaction are given below. Dehydrobromination of 3,4-dibromo-1,1,2-trichlorobut-1-ene (**52**), which is the product of bromine addition to the accessible 1,1,2-trichlorobuta-1,3-diene (**53**),[48] affords a mixture of 3- (**54**, the main product) and 4-bromo-1,1,2-trichlorobuta-1,3-dienes (**55**, the by-product).[26]

$$\underset{\mathbf{53}}{CCl_2=CClCH=CH_2} \xrightarrow{Br_2} \underset{\mathbf{52}}{CCl_2=CClCHBrCH_2Br} \xrightarrow[-HBr]{}$$
$$\rightarrow \underset{\mathbf{54}}{CCl_2=CClCBr=CH_2} + \underset{\mathbf{55}}{CCl_2=CClCH=CHBr}$$

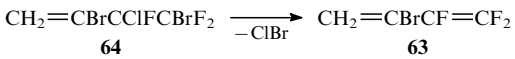
Two convenient methods have been developed for the synthesis of 1-bromo-1,4,4-trichlorobuta-1,3-diene (**56**). The first method consists in dehydrohalogenation of 1,2-dibromo-1,3,4,4-tetrachlorobutanes (**57**) in the presence of PTC. It was shown that the reaction product is a mixture of geometric isomers with the predominance of the *Z*-form.[49] The second method of the synthesis of the diene **56** is based on dehydrobromination of 3,4-dibromo-1,1,4-trichlorobut-1-ene (**58**) under the conditions of phase-transfer catalysis in the presence of triethylbenzylammonium chloride (TEBA).[50]



Information about tetra(chloro, fluoro) MHB can be found only in the patent literature. Thus dehalogenation of 4-bromo-2,3-dichloro-3,4,4-trifluorobut-1-ene (**59**) and 1-bromo-2,3,4,4,-tetrachloro-1,1,2,-trifluoro-butane (**60**) result in 3-chloro-1,1,2-trifluoro- (**61**) and 4-chloro-1,1,2-trifluorobuta-1,3-dienes (**62**), respectively.[51]

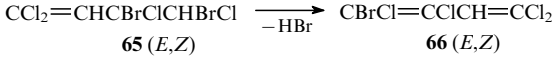


There is only one known representative of the bromine-containing tetrahalogenobutadienes, *viz.,* 3-bromo-1,1,2-trifluorobuta-1,3-diene (**63**), which was obtained in high yield by dehalogenation of 2,4-dibromo-3-chloro-3,4,4-trifluorobut-1-ene (**64**) (see Table 1).[3]

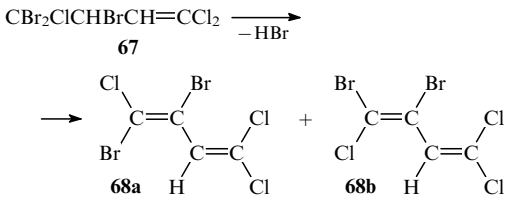


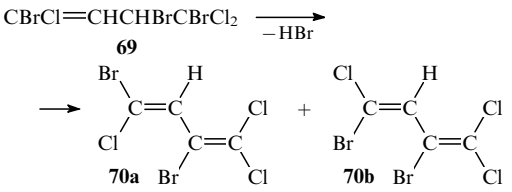
d. Pentahalogenobutadienes

Some pentasubstituted chlorobromo and chlorofluoro derivatives of butadiene can be obtained by an elimination reaction. Thus dehydrobromination of 3,4-dibromo-1,1,3,4-tetrachlorobut-1-ene (**65**) (the product of bromine addition to the *Z*- or *E*-isomers of 1,1,3,4-tetrachloro-1,3-butadiene) affords a mixture of geometric isomers of 1-bromo-1,2,4,4,-tetrachlorobuta-1,3-diene (**66**), the yield of which depends to a considerable extent on the reaction conditions (see Table 1).[52–54]



Dehydrobromination of 3,4,4-tribromo-1,1,4-trichlorobut-1-ene (**67**) in the presence of PTC leads to a mixture of *E*- and *Z*-isomers of 1,2-dibromo-1,4,4-trichlorobuta-1,3-diene (**68a**,**b**) Similarly, a mixture of *E*- and *Z*-isomers of 2,4-dibromo-1,1,4-trichlorobuta-1,3-diene (**70a,b**) [55] was obtained from 1,3,4-tribromo-1,4,4-trichlorobut-1-ene (**69**).

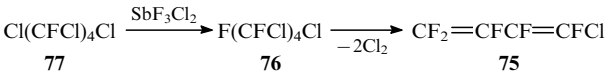




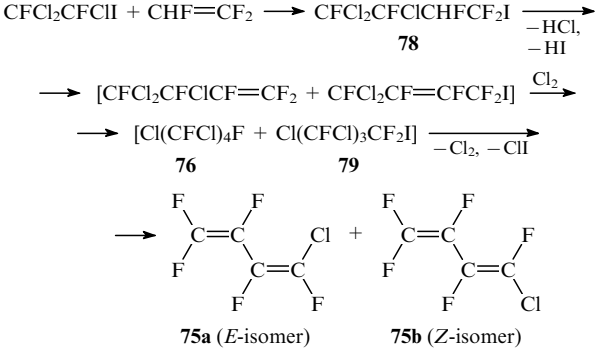
Dehalogenation of 4-bromo -1,2,3-trichloro-3,4,4-trifluoro- (**71**) and 1,3,4-trichloro-1,3,4,4-tetrafluorobut-1-ene (**72**) (see Table 1) yielded 3,4-dichloro-1,1,2-trifluorobuta-1,3-diene (**73**) and 4-chloro-1,1,2,4-tetrafluorobuta-1,3-diene (**74**),[56] respectively.

e. Hexahalogenobutadienes

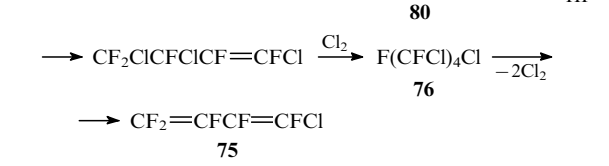
The synthesis of hexasubstituted MHB is documented; in particular, the methods for the preparation of some chlorine, fluorine-containing representatives are well developed. Thus 4-chloro-1,1,2,3,4-pentafluorobuta-1,3-diene (**75**) was first obtained by dehalogenation of 1,2,3,4,4,-pentachloro-1,1,2,3,4-pentafluorobutane (**76**), which is the reaction product of 1,1,2,3,4,4-hexachloro-1,2,3,4-tetrafluorobutane (**77**) with a slight excess of SbF_3Cl_2.[10, 12]



Later,[57, 58] two new methods for the synthesis of the diene **75** have been proposed. The first method is based on the transformation of a 1 : 1 mixture of *erythro*- and *threo*-forms of 3,4,4-trichloro-1,1,2,3,4-pentafluoro-1-iodobutane (**78**), which is the product of free-radical addition of 1,2,2-trichloro-1,2-difluoro-1-iodoethane to trifluoroethylene (GLC). Dehydrohalogenation of this product and subsequent chlorination of intermediate polyhalogenobutenes yield a mixture of polyhalogenobutanes (**76** and **79**). Dehalogenation of these compounds gives high yield of the diene **75** as a mixture of *E*- and *Z*-isomers.[57]



Another way to the synthesis of the diene **75** is based on the transformation of 1,3,4-trichloro-1,2,3,4,4-pentafluoro-1-iodobutane (**80**), which is the reaction product of 1,2-dichloro-1,2,2-trifluoro-1-iodoethane with 1-chloro-1,2-difluoroethylene.[58] Successive dehydroiodination, chlorination and dechlorination of polyhalogenobutane (**80**) yields the diene **75**.

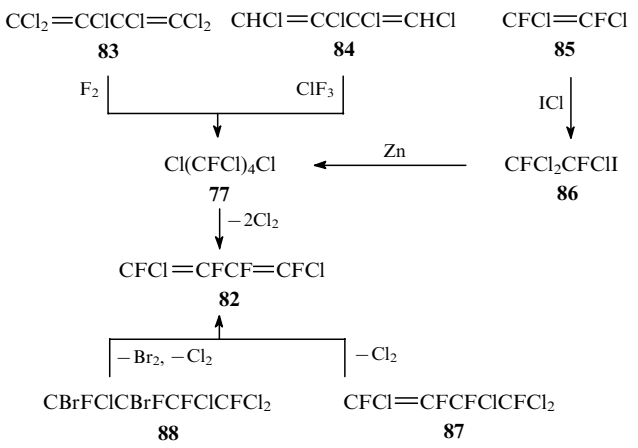


The synthesis of 3-chloro-1,1,2,4,4-pentafluorobuta-1,3-diene (**81**) is also based on elimination reactions.[10, 43]

$$CF_2{=}CClI + CF_2{=}CHF \longrightarrow CF_2{=}CClCHFCF_2I \xrightarrow{-HI}$$
$$\longrightarrow CF_2{=}CClCF{=}CF_2 \xleftarrow{-2Cl_2} CF_2ClCFClCCl_2CF_2Cl$$
81

The synthesis of 1,4-dichloro-1,2,3,4-tetrafluorobuta-1,3-diene (**82**) has attracted much attention. The diene **82** was obtained for the first time by dechlorination of perhalogenobutane **77**,[59] which in turn was synthesised by fluorination of hexachlorobuta-1,3-diene (**83**),[60] the reaction of 1,2,3,4-tetrachlorobuta-1,3-diene (**84**) with ClF_3 (see Ref. 61) or chloroiodination of 1,2-dichloro-1,2-difluoroethylene (**85**) with subsequent heating of the resulting 1,2,2-trichloro-1,2-difluoro-1-iodoethane (**86**) with acetic anhydride, dichloromethane and granulated zinc at 160 °C (Scheme 1).

Scheme 1



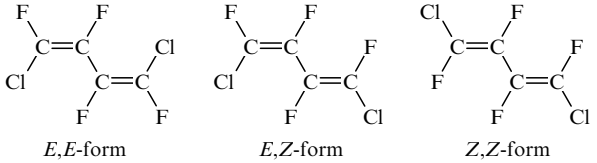
Yet another method for the synthesis of the diene **82** is based on dechlorination of 1,3,4,4-tetrachloro-1,2,3,4-tetrafluorobut-1-ene (**87**), which is the product of thermal dimerisation of the ethylene **85**.[63,64] The diene **82** is formed in preparative yield upon treatment of 1,2-dibromo-1,3,4,4-tetrachloro-1,2,3,4-tetrafluorobutane (**88**), which is the product of bromine addition to the butene **87**,[64] with zinc in dioxane (Scheme 1).

And, finally, there are data on the synthesis of diene **82** based on transformations of a mixture of perhalogenobutanes.[58] Thus dehalogenation of a mixture of telomers $Cl(CFCl)_3CF_2I$ (**79**) and $Cl(CFCl)_2CF_2CFClI$ (**89**) or $F(CFCl)_4F$ (**90**), $Cl(CFCl)_4F$ (**76**) and $Cl(CFCl)_4Cl$ (**77**) affords a 1 : 1 mixture of the dienes **75** and **82** (in the ratio 1 : 1) in the former case or a mixture of dienes **75**, **82** and hexafluorobuta-1,3-diene in the latter case.

$$CFCl_2CFClI + CF_2{=}CFCl \longrightarrow$$
$$\longrightarrow \underset{\mathbf{79}}{[Cl(CFCl)_3CF_2I} + \underset{\mathbf{89}}{Cl(CFCl)_2CF_2CFClI]} \longrightarrow$$
$$\longrightarrow \underset{\mathbf{75}}{CFCl{=}CFCF{=}CF_2} + \underset{\mathbf{82}}{CFCl{=}CFCF{=}CFCl}$$

$$\underset{\mathbf{90}}{F(CFCl)_4F} + \underset{\mathbf{76}}{Cl(CFCl)_4F} + \underset{\mathbf{77}}{Cl(CFCl)_4Cl} \xrightarrow{Zn}$$
$$\longrightarrow \mathbf{75} + \mathbf{82} + \underset{\mathbf{91}}{CF_2{=}CFCF{=}CF_2}$$

Theoretically, the diene **82** can exist in the form of three geometric isomers.



Indeed, as was shown by Kremlev *et al.*,[62] the diene **82** is an equilibrium mixture of *E*,*E*-, *E*,*Z*- and *Z*,*Z*-isomers in the ratio of 1 : 2.5 : 1.5. The ^{19}F NMR (Ref. 65) and UV (Ref. 21) spectral data and the values of dipole moments[66] make it possible to conclude that the isomers are in the non-planar *s*-*cis*-conformation similarly to hexachloro- (**83**)[67] and hexafluorobutadienes (**91**).[68]

Two methods for the synthesis of 2,3-dichloro-1,1,4,4-tetrafluorobuta-1,3-diene (**92**) are known, *viz.*, dehalogenation of 1,2,2,3,3,4-hexachloro-1,1,4,4-tetrafluorobutane (**93**)[10] and 1,4-dibromo-2,2,3,3-tetrachloro-1,1,4,4-tetrafluorobutane (**94**).[60,69]

$$\underset{\mathbf{93}}{CF_2ClCCl_2CCl_2CF_2Cl} \xrightarrow{-2Cl_2}$$
$$\underset{\mathbf{94}}{CF_2BrCCl_2CCl_2CF_2Br} \xrightarrow{-2BrCl} \underset{\mathbf{92}}{CF_2{=}CClCCl{=}CF_2}$$

Some other difficultly accessible MHB, *viz.*, 3,4-dichloro-1,1,2,4-tetrafluoro- (**95**), 1,2,3,4-tetrachloro-1,4-difluoro- (**96**) and 2,3,4-trichloro-1,1,4-trifluorobuta-1,3-dienes (**97**), were obtained similarly.[10,60]

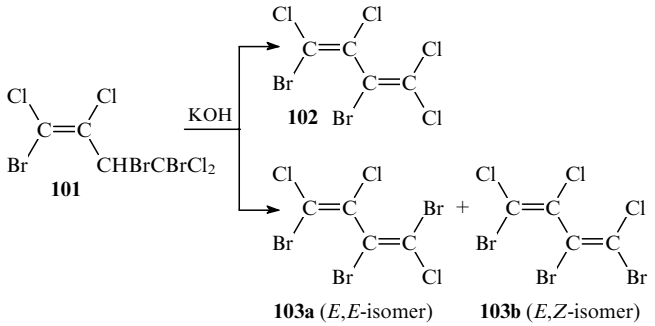
$$CF_2ClCFClCCl_2CFCl_2 \xrightarrow{-2Cl_2} \underset{\mathbf{95}}{CF_2{=}CFCCl{=}CFCl}$$
$$CFCl_2CCl_2CCl_2CFCl_2 \xrightarrow{-2Cl_2} \underset{\mathbf{96}}{CFCl{=}CClCCl{=}CFCl}$$
$$CF_2ClCCl_2CCl_2CFCl_2 \xrightarrow{-2Cl_2} \underset{\mathbf{97}}{CF_2{=}CClCCl{=}CFCl}$$

Bromine–chlorine-containing hexahalogenobutadienes were synthesised by an elimination reaction by the authors of this review. Thus dehydrohalogenation of 1,2-dibromo-1,1,3,3,4,4-hexachlorobutane (**98**) with aqueous-ethanolic solutions of alkalis yields two MHB, *viz.*, 2-bromo-1,1,3,4,4-pentachloro- (**99**) and 1,2-dibromo-1,3,4,4-tetrachlorobuta-1-3-diene (**100**), in the ratio of 2 : 1.

$$\underset{\mathbf{98}}{CBrCl_2CHBrCCl_2CHCl_2} \xrightarrow{-HCl,\ -HBr} \begin{cases} \underset{\mathbf{99}}{CCl_2{=}CBrCCl{=}CCl_2} \\ \underset{\mathbf{100}}{CBrCl{=}CBrCCl{=}CCl_2} \end{cases}$$

The use of an aqueous solution of diethylamine shifted the reaction towards the predominant formation of the diene **99**.[70]

Dehydrohalogenation of (*E*)-1,3,4-tribromo-1,2,4,4-tetrachlorobut-1-ene (**101**) under the conditions of phase-transfer catalysis yielded (*E*)-1,3-dibromo-1,2,4,4-tetrachloro- (**102**) and 1,3.4-tribromo-1,2,4-trichlorobuta-1,3-dienes (**103**) as a mixture of two geometric isomers. Since the β-bromo-α,β-dichlorovinyl group of the butene (**101**) having the *E*-configuration is not directly involved in the reaction, the formation of the two isomeric forms of the diene **103** occurs due to the *E*,*Z*-isomerisation of the α,β-dibromo-β-chlorovinyl group in the molecule. Consequently, the diene **103** is a mixture of *E*,*E*- (**103a**) and *E*,*Z*-isomers (**103b**).[71]



2. Halogenation and hydrohalogenation of the acetylenic hydrocarbons of the C_4 series

Acetylenic hydrocarbons, mainly conjugated halogenobutenynes and dihalogenobutadiynes, have served as the starting compounds for the synthesis of the first representatives of MHB.[2] The syntheses based on acetylene derivatives have not found wide uses because of their poor accessibility and explosiveness. Nonetheless, nowadays procedures for the preparative synthesis of a number of di-, tri- and hexasubstituted MHB have been developed.

It is also noteworthy that a new catalytic reaction of acetylene dimerisation has been recently discovered. This is carried out in methanolic solution of NaI in the presence of Pt(IV); it is accompanied by the addition of an iodine molecule and results in (*E*,*E*)-1,4-diodobuta-1,3-diene.[72]

$$HC{\equiv}CH \xrightarrow[I^-,\ I_2/MeOH]{Pt^{IV}} (ICH{=}CH)_2$$

E,*E*-isomer

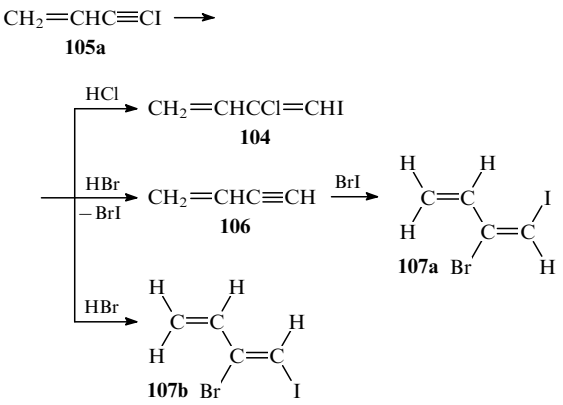
This reaction seems to be promising for the synthesis of certain MHB.

The currently used procedures for the synthesis of MHB by the addition of halogens and hydrogen halides to the carbon–carbon triple bond imply the use of the existing C_4 carbon chain.

a. Dihalogenobutadienes

The first representative of the dihalogenobutadienes, *viz.*, 2-chloro-1-iodobuta-1,3-diene (**104**), was prepared by hydrochlorination of 4-iodobut-1-en-3-yne (**105a**) in the presence of catalysts CuCl + NH_4Cl.[73]

In the reaction of this butenyne (**105a**) with HBr, the predominant direction is the reductive elimination of the iodine atom at the triple bond with the formation of vinylacetylene (**106**). Among the reaction products, a considerable amount of (*E*)-2-bromo-1-iodobuta-1,3-diene (**107a**) was also found as the addition product of BrI to the enyne (**106**). The yield of (*Z*)-2-bromo-1-iodobuta-1,3-diene (**107b**), which is the addition product of HBr to the initial butenyne **105a**, is insignificant.[74]



The addition of hydrogen halides to the conjugated enynes with a halogen atom at the triple bond in the presence of copper(I) halides is widely used for the synthesis of MHB.[74] It was established that 4-halogenobut-1-en-3-ynes (**105b**,**c**) add HBr and HI at the triple C≡C bond giving the corresponding dihalogenobutadienes. Thus hydrobromination of 4-chlorobut-1-ene-3-yne **105b** proceeds stereospecifically with the formation of the *Z*-form of 2-bromo-1-chlorobuta-1,3-diene (**6b**) in high yield. The reaction of hydroiodination of chloro- (**105b**) and bromo-substituted (**105c**) enynes proceeds similarly and results in the formation of (*Z*)-1-chloro- and 1-bromo-2-iodobuta-1,3-dienes (**108** and **109**), respectively (Table 2).

$$\underset{\textbf{105b,c}}{CH_2{=}CHC{\equiv}CX} \xrightarrow{HHal} \underset{\textbf{6, 108, 109}}{(Z)\text{-}H_2C{=}CHCHal{=}CHX}$$

6: X = Cl, Hal = Br; **108**: X = Cl, Hal = I; **109**: X = Br, Hal = I.

The addition of mixed halogens (ClI and BrI) to the conjugated butenyne **106** was studied.[74, 75] It turned out that the 1,4-addition of halogens occurred predominantly. Only with the use of a large excess of enyne and in the presence of CuCl were the 1,2-addition products, *viz*., the dienes **104** and **107** in the form of *E*-isomers, obtained.[74, 75]

Table 2. Synthesis of mixed halogenobutadienes based on acetylene derivatives.

Starting compound	Electrophilic agent (Hal_2 or HHal)	Reaction conditions	Halogenosubstituted butadiene	Yield (%)	Ref.
$CH_2{=}CHC{\equiv}CI$ (**105a**)	HCl	CuCl + NH_4Cl	$CH_2{=}CHCCl{=}CHI$ (**104**)	–	73
$CH_2{=}CHC{\equiv}CCl$ (**105b**)	HBr	CuBr	(*Z*)-$CHCl{=}CBrCH{=}CH_2$ (**6b**)	95	74, 75
$CH_2{=}CHC{\equiv}CCl$ (**105b**)	HI	CuI	(*Z*)-$CHCl{=}CICH{=}CH_2$ (**108**)	45.2	74, 75
$CH_2{=}CHC{\equiv}CBr$ (**105c**)	HI	CuI	(*Z*)-$CHBr{=}CICH{=}CH_2$ (**109**)	70.8	74, 75
$CH_2{=}CHC{\equiv}CI$ (**105a**)	HBr	CuBr	(*E*)- + (*Z*)-$CHI{=}CBrCH{=}CH_2$ (**107**)	41.5	74, 75
$CH_2{=}CHC{\equiv}CI$ (**105a**)	Cl_2	−40 °C, $CHCl_3$	$CH_2{=}CHCCl{=}CCll$ (**112**)	9.7	74
$CH_2{=}CHC{\equiv}CI$ (**105a**)	Br_2	the same	$CH_2{=}CHCBr{=}CBrI$ (**113**)	14.2	74
$CH_2{=}CHC{\equiv}CCl$ (**105b**)	Br_2	"	$CH_2{=}CHCBr{=}CBrCl$ (**114**)	7.3	74
$CH_2{=}CHC{\equiv}CBr$ (**105c**)	Cl_2	"	$CH_2{=}CHCCl{=}CBrCl$ (**115**)	8.5	74
$CH_2ClC{\equiv}CCH_2Cl$ (**117**)	Br_2, 1,8-diazabicyclo-[5.4.0]undec-7-ene	CCl_4	(*Z*)-$CHCl{=}CBrCBr{=}CH_2$ (**40**)	91	76
$CH_2ClC{\equiv}CCH_2Cl$ (**117**)	I_2, 1,8-diazabicyclo-[5.4.0]undec-7-ene	CH_2ClCH_2Cl	(*Z*)-$CHCl{=}CICI{=}CH_2$ (**118**)	71	76
$CH{\equiv}CC{\equiv}CH$	ClI	EtCl, −50 °C	$CHI{=}CClCCl{=}CHI$ (**119**) (*Z*,*Z* + *Z*,*E* + *E*,*E*)	84.0	78
$CHCl{=}CClC{\equiv}CH$	$CuBr_2$	MeOH, 1 h	$CHCl{=}CClCBr{=}CBr_2$ (**120**)	50.0	79
$CCl{\equiv}CC{\equiv}CCl$ (**121a**)	Br_2	CCl_4, 25–60 °C	$CBrCl{=}CBrCBr{=}CBrCl$ (**122**)	~98	11
$CCl{\equiv}CC{\equiv}CCl$ (**121a**)	I_2	$CHCl_3$	$CICl{=}CICI{=}CICl$ (**123**)	–	80, 81
$CBr{\equiv}CC{\equiv}CBr$ (**121b**)	I_2	$CHCl_3$	$CBrI{=}CICI{=}CBrI$ (**125**)	–	80, 81
$CI{\equiv}CC{\equiv}CI$ (**121c**)	Br_2	$CHCl_3$	$CBrI{=}CBrCBr{=}CBrI$ (**126**)	–	80, 81
$CCl_2{=}CClC{\equiv}CCl$ (**128**)	Br_2	CCl_4	$CCl_2{=}CClCBr{=}CBrCl$ (**100**)	84.0	42
$CCl_2{=}CClC{\equiv}CBr$	Br_2	CCl_4	$CCl_2{=}CClCBr{=}CBr_2$ (**130**)	–	42
$CCl_2{=}CClC{\equiv}CI$	I_2	dry ether	$CCl_2{=}CClCI{=}CI_2$ (**131**)	–	42

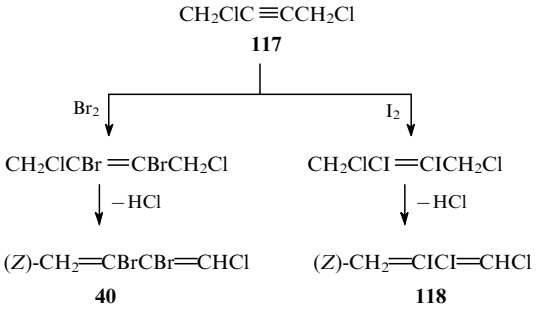
b. Trihalogenobutadienes

An attempt to obtain mixed trihalogenobutadienes by the addition of halogens to the triple bond of enynes **105a–c** did not give satisfactory results.[74,75] The reaction of chlorine and bromine with these enynes proceeded mainly as the addition of halogens to the double bond and the 1,4-addition of enynes with the formation of butynes **110** and allenes **111**, respectively. The addition of one mole of a halogen to the triple bond of enynes, which would lead to the corresponding trihalogenobuta-1,3-dienes, is less preferable, the yields of products **53**, **112–116** are low.[74,75]

$$\underset{\textbf{105a–c}}{CH_2{=}CHC{\equiv}CX} \xrightarrow{Y_2} \underset{\textbf{110}}{CH_2YCHYC{\equiv}CX} + \underset{\textbf{111}}{CH_2YCH{=}C{=}CXY} + \underset{\textbf{53, 112–116}}{CH_2{=}CHCY{=}CXY}$$

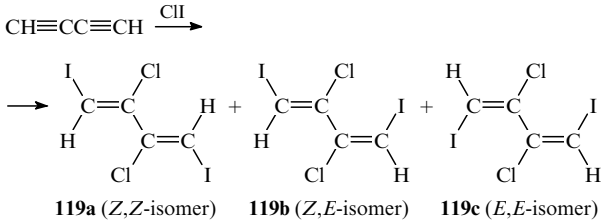
X = I: Y = Cl (**112**), Br (**113**);
X = Y = Cl (**53**); X = Cl, Y = Br (**114**);
X = Br, Y = Cl (**115**); X = Y = Br (**116**).

The addition of bromine or iodine to 1,4-dichlorobut-2-yne (**117**) yielded the corresponding halogeno-substituted butenes, which gave (*Z*)-2,3-dibromo-1-chloro- (**40**) and (*Z*)-1-chloro-2,3-diiodobuta-1,3-dienes (**118**) upon catalytic 1,4-dehydrochlorination.[76,77]



c. Tetra- and pentahalogenobutadienes

The synthesis of tetra- and pentasubstituted buta-1,3-dienes is demonstrated in separate examples. 2,3-Dichloro-1,4-diiodobuta-1,3-diene (**119**) was obtained as a mixture of *Z*,*Z*-, *Z*,*E*- and *E*,*E*-isomers by the reaction of diacetylene with chloroiodine.[78]



The reaction of copper(II) bromide with 1,2-dichlorobut-1-en-3-yne gives 1,1,2-tribromo-3,4-dichlorobuta-1,3-diene (**120**) (see Table 2).[79]

d. Mixed perhalogenobutadienes

In 1930, difficultly accessible perhalogenobutadienes (**122–127**), including first representatives of MHB, were obtained by halogenation of dihalogenobuta-1,3-dienes (**121**).[80,81]

$$\underset{\textbf{121a–c}}{CX{\equiv}CC{\equiv}CX} \xrightarrow{Y_2} \underset{\textbf{122–127}}{CXY{=}CYCY{=}CXY}$$

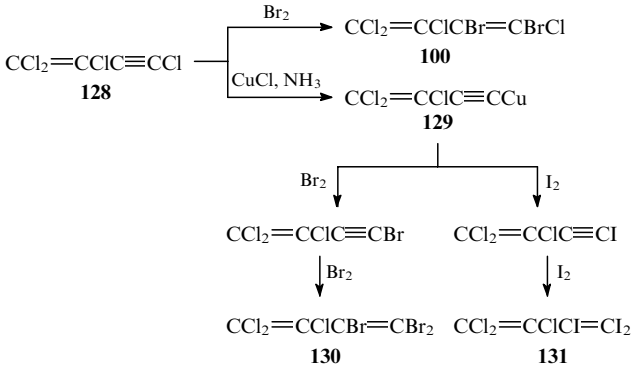
X = Cl (**a**), Br (**b**), I (**c**); Y = Br, I.

Compound	**122**	**123**	**124**	**125**	**126**	**127**
X	Cl	Cl	Br	Br	I	I
Y	Br	I	Br	I	Br	I

According to the patent data,[11] 1,4-dichloro-1,2,3,4-tetrabromobuta-1,3-diene (**122**) is formed in quantitative yield upon bromination of dichlorobuta-1,3-diene (**121a**).

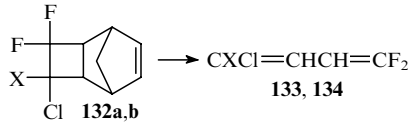
Synthesis of some mixed perhalogenobutadienes was carried out based on the accessible perchlorobutenyne (**128**).[42] Thus direct bromination of the enyne **128** gave 1,3,4,4-tetrachloro-1,2-dibromobuta-1,3-diene (**100**) in high yield, whereas the synthesis of 1,1,2-tribromo- (**130**) and 3,4,4-trichloro-1,1,2-triiodobuta-1,3-dienes (**131**) was carried out using copper trichlorovinyl acetylenide **129** (Scheme 2).[42]

Scheme 2



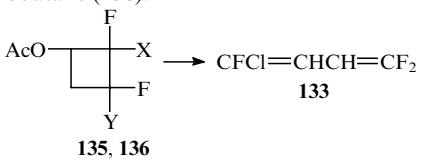
3. Synthesis of mixed halogenobutadienes by pyrolysis of polyhalogenated compounds

A number of preparative methods for obtaining MHB containing from four to six halogen atoms in the molecule are based on the pyrolysis of cyclic halogen-containing compounds. Thus the passage of 4-chloro-3,3,4-trifluoro- (**132a**) or 4,4-dichloro-3,3-difluoro-tricyclo[4.2.1,$0^{2,5}$]non-7-enes (**132b**) through a red-hot tube filled with rings of quartz glass yielded 4-chloro-1,1,4-trifluoro- (**133**) and 4,4-dichloro-1,1-difluorobuta-1,3-dienes (**134**), respectively.[82]



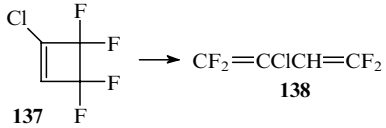
X = F (**132a**, **133**); X = Cl (**132b**, **134**).

A more convenient method for the preparation of the diene **133** is based on the pyrolysis of 1-acetoxy-2-chloro-2,3,3-trifluorocyclobutane (**135**) or 1-acetoxy-3-chloro-2,2,3-trifluorocyclobutane (**136**).[83]



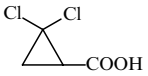
135: X = Cl, Y = F; **136**: X = F, Y = Cl.

Many MHB were obtained by the pyrolysis of the corresponding halogeno-substituted cyclobutenes. Thus the pyrolysis of 1-chloro-3,3,4,4-tetrafluorocyclobut-1-ene (**137**) gives 2-chloro-1,1,4,4-tetrafluorobuta-1,3-diene (**138**) in preparative yield (Table 3).[13,83]



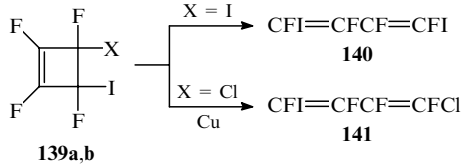
The main pyrolysis products of 1,2,3,4-tetrafluoro-3,4-diiodo- and 4-chloro-1,2,3,4-tetrafluoro-3-iodocyclobutenes (**139a**,**b**) are 1,2,3,4-tetrafluoro-1,4-diiodobuta-1,3-diene (**140**), formed as a

Table 3. Miscellaneous methods for the preparation of mixed halogenobutadienes.

Starting compound	Method of preparation [a]	Reaction conditions	Halogeno-substituted butadiene	Yield (%)	Ref.
132a (see [b])	A	700 °C (1 Torr)	$CFCl=CHCH=CF_2$ (**133**)	–	82
132b (see [b])	A	700 °C (1 Torr)	$CCl_2=CHCH=CF_2$ (**134**)	–	82
136 (see [b])	A	700 °C (10 Torr)	$CFCl=CHCH=CF_2$ (**133**)	56.0	83
137 (see [b])	A	700 °C (1 Torr)	$CF_2=CClCH=CF_2$ (**138**)	38.0	83
139a	A	580 °C (0.1 Torr)	$CFI=CFCF=CFI$ (**140**) ($E,E:E,Z:Z,Z$ = 21 : 16 : 8)	37.0	84
139b	A	Cu, 180 – 190 °C	$CFI=CFCF=CFCl$ (**141**)	–	84
$CFCl_2SO_nCH_2CH=CH_2$ (n = 1, 2)	A	heating	$CFCl=CHCH=CH_2$ (**17**)	–	85
$CHCl=CFCF_2CF_2COONa$ (**142**)	A	heating with a burner (1 Torr)	(Z)-$CF_2=CFCF=CHCl$ (**143**)	82.0	86
$CCl_2=CHCHO$ (**145**)	B	$Ph_3P=CBr_2$, CH_2Cl_2, 0 °C	$CCl_2=CHCH=CBr_2$ (**149**)	76.0	88, 89
$CCl_2=CClCHO$ (**146**)	B	the same	$CCl_2=CClCH=CBr_2$ (**150**)	62.0	88, 89
$CCl_2=CBrCHO$ (**147**)	B	"	$CCl_2=CBrCH=CBr_2$ (**151**)	57.0	88, 89
$CI_2=CClCHO$ (**148**)	B	"	$CI_2=CClCH=CBr_2$ (**152**)	44.0	88, 89
$CCl_2=CClCHO$ (**146**)	B	$Ph_3P=CHCOOEt$, Br_2	(Z)-$CHBr=CHCCl=CCl_2$ (**55**)	82.0	89
$CCl_2=CBrCHO$ (**147**)	B	$CCl_2=C=O$, dry ether	$CCl_2=CBrCH=CCl_2$ (**154**)	63.0	42
$CBr_2=CClCHO$ (**153**)	B	the same	$CBr_2=CClCH=CCl_2$ (**155**)	55.0	42
$CHCl=CClCCl=CClLi$	C	I_2, $FeCl_3$, ether, −110 °C	$CHCl=CClCCl=CClI$ (**157**)	60.0	90
 **158**	C	SF_4, 140 °C	$CF_2=CHCH=CCl_2$ (**134**)	–	91
$CFCl=CFI$	C	Cu, 145 °C	$CFCl=CFCF=CFCl$ (**82**) ($E,E:E,Z:Z,Z$ = 19 : 51 : 30)	49.0	92, 93

[a] A is pyrolysis; B is synthesis of MHB from polyhalogenoacroleins; C is other methods. [b] The starting compounds were obtained by the [2 + 2]-cycloaddition reaction.

mixture of *E,E*-, *E,Z*- and *Z,Z*-isomers, and 4-chloro-1,2,3,4-tetrafluoro-1-iodobuta-1,3-diene (**141**), respectively.[84]

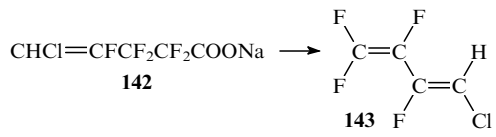


139a,**b** → $CFI=CFCF=CFI$ (**140**); $CFI=CFCF=CFCl$ (**141**)

X = I (**139a**), Cl (**139b**).

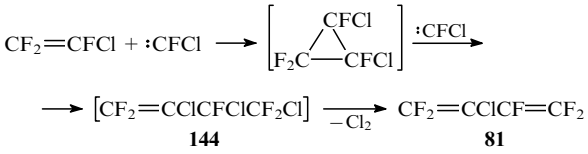
Mixed halogenobutadienes are also formed by the pyrolysis of some aliphatic compounds. Thus heating of sulfoxide $CFCl_2SOCH_2CH=CH_2$ or sulfone $CFCl_2SO_2CH_2CH=CH_2$ yielded 1-chloro-1-fluorobuta-1,3-diene as one of the reaction products (**17**).[85]

Decarboxylation of sodium 5-chloro-2,2,3,3,4-pentafluoropent-4-enoate (**142**) *in vacuo* gives high yield of (*Z*)-4-chloro-1,1,2,3-tetrafluorobuta-1,3-diene (**143**).[86]



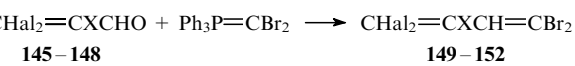
142 → **143**

The butadiene **81** is present among the pyrolysis products of chlorofluoroethylene. Presumably, this resluts from thrmal dechlorination of butene **144**, which appears in the reaction due to the addition of chlorofluorocarbene to the initial chlorotrifluoroethylene.



4. Synthesis of mixed halogenobutadienes based on polyhalogenoacroleins

An original way of the preparation of some bromine, chlorine-containing MHB is based on the reaction of polyhalogenoacroleins **145** – **148** with dibromomethylenetriphenylphosphorane.[88, 89]

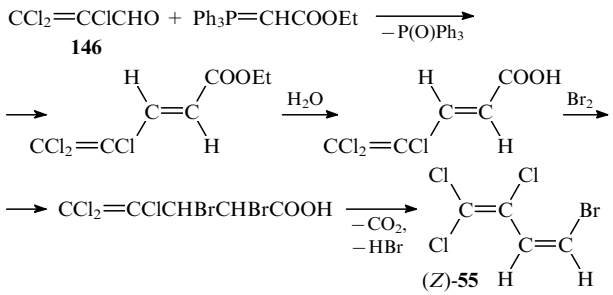


145 – **148** → **149** – **152**

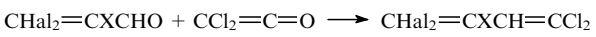
Hal = Cl: X = H (**145**, **149**), Cl (**146**, **150**), Br (**147**, **151**);
Hal = I: X = Cl (**148**, **152**).

The first representative of MHB containing three different halogen atoms, *viz*., 4,4-dibromo-2-chloro-1,1-diiodobuta-1,3-diene (**152**) was obtained in 1970 by the reaction of α-chloro-β,β-diiodoacrolein (**148**) with $Ph_3P=CBr_2$.[88, 89]

A method of preparation of (*Z*)-4-bromo-1,1,2-trichlorobuta-1,3-diene (**55**) from the acrolein **146** and phosphorylide $Ph_3P=CHCOOEt$ has been developed.[89]

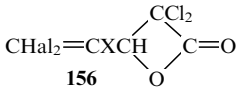


Yet another method of the synthesis of MHB is based on the reaction of halogenoacroleins with dichloro ketene. Starting from the acrolein **147** and β,β-dibromo-α-chloroacrolein (**153**), 2-bromo-1,1,4,4-tetrachloro- (**154**) and 1,1-dibromo-2,4,4-trichloro-buta-1,3-dienes (**155**) were obtained, respectively.[42]



147, **154**: Hal = Cl, X = Br; **153**, **155**: Hal = Br, X = Cl.

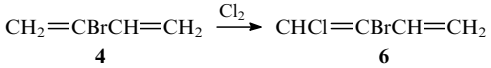
This reaction is supposed to proceed through the initial formation of a lactone **156**, which is easily decarboxylated with the formation of the target products **154** and **155**.



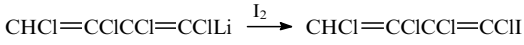
The yields of the dienes **55**, **149** – **152**, **154**, **155** and conditions of their synthesis are listed in Table 3.

5. Miscellaneous reactions for the preparation of mixed halogenobutadienes

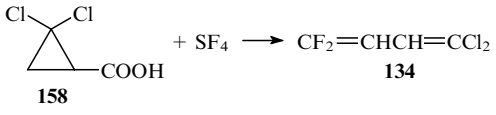
It was shown [28] that chlorination of bromoprene (**4**) yields, along with different addition products, also 2-bromo-1-chlorobuta-1,3-diene (**6**) as a mixture of *Z*- and *E*-isomers.



The reaction of lithium 1,2,3,4-tetrachlorobuta-1,3-dien-1-ide with iodine yielded 1,2,3,4-tetrachlorobuta-1-iodo-1,3-diene (**157**).[90]



The synthesis of 1,1-dichloro-4,4-difluorobuta-1,3-diene (**134**) in low yield by the reaction of sulfur tetrafluoride with 2,2-dichlorocyclopropanecarboxylic acid (**158**) has been reported.[91]



A convenient method for the preparation of 1,4-dichloro-1,2,3,4-tetrafluorobuta-1,3-diene (**82**) is the reducive dimerisation of a mixture of *Z*- and *E*-isomers of 2-chloro-1,2-difluoro-1-iodoethylene in the presence of a copper powder.[92,93] The diene **82** is formed as a mixture of *E*,*E*-, *E*,*Z*- and *Z*,*Z*-isomers in approximately the same ratio as reported elsewhere [62] (see Table 3).



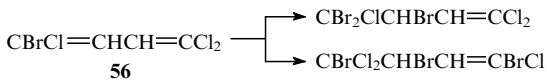
Unfortunately, the attempt to extend this reaction for the synthesis of other MHB has been unsuccessful because of inaccessibility of iodine-containing halogenoethylenes.

III. Chemical properties of mixed halogenobuta-1,3-dienes

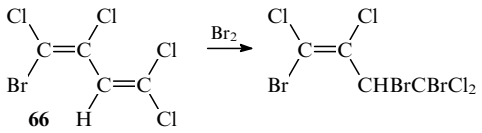
1. Addition reactions. Halogenation of mixed halogenobutadienes

Despite the fact that MHB possess electrophilic properties, they add, like other diene compounds with conjugated double bonds, halogens to both the terminal positions of the diene system (1,4-addition) and to one of the double bonds (1,2- or 3,4-addition). The direction of this reaction is determined to a considerable extent by the nature of MHB and the halogenation agent; experimental conditions are also highly important. The 1,4-addition is characteristic of the dienes having a small number of bulky substituents (Cl, Br or I) and low asymmetry. In the MHB with a high extent of substitution with bulky substituents, the π,π-conjugation is disturbed so that these dienes react as alkenes. Sometimes, an exhaustive halogenation takes place at both C=C bonds and results in the formation of polyhalogenobutanes.

It was shown that the bromination of a mixture of *E*- and *Z*-isomers of 1-bromo-1,4,4-trichlorobutadienes (**56**) (*E*:*Z* ratio = 1:4) occurs at the 1,2- and 3,4-positions and results in a mixture of two products, *viz*., 3,4,4-tribromo-1,1,4-trichloro- and 1,3,4-tribromo-1,4,4-trichlorobut-1-enes in the ratio 70:30 with a total yield of 76 %.[55,94]

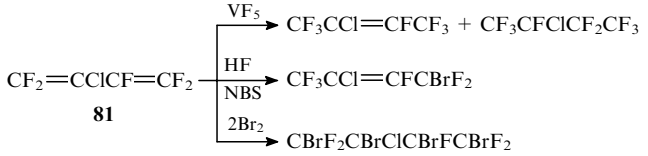


Bromination of the *E*-isomer of the diene **66** (45 – 50 °C, illumination with an incandescent 60 W lamp, 8 h) occurs exclusively at the β,β-dichlorovinyl group and results in (*E*)-1,3,4-tribromo-1,2,4,4-tetrachlorobut-1-ene in a yield of 93%.[71]

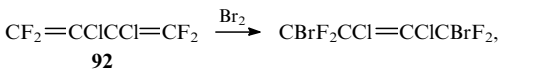


Monochloropentafluoro- and dichlorotetrafluorobuta-1,3-dienes (their structure has not been unequivocally established) add one molecule of bromine with the formation of the corresponding butenes of the general formulae $C_4ClBr_2F_5$ and $C_4Cl_2Br_2F_4$ at 20 – 150 °C.[61]

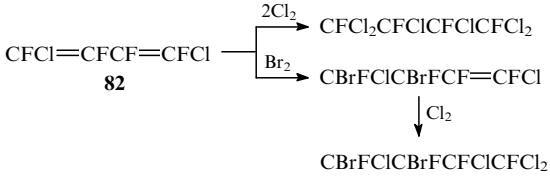
The diene **81** adds two molecules of bromine at 50 °C and gives 1,2,3,4-tetrabromo-3-chloro-1,1,2,4,4-pentafluorobutane, the structure of which was confirmed by the results of chromatomass spectrometry.[87] According to Petrov *et al*.,[95] the chlorination and bromination of the diene **81** occur exclusively as the 1,4-addition and lead to the corresponding but-2-enes. Thus treatment of the diene **81** with a mixture of *N*-bromosuccinimide (NBS) and HF in THF yielded a mixture of *E*- and *Z*-isomers of 3-chloro-1-bromo-1,1,2,4,4,4-hexafluorobut-2-ene (*E*:*Z* = 5:1) in a total yield of 82 %. Fluorination of the diene **81** with VF_5 from −20 to −30 °C occurs predominantly as the 1,4-addition and results in 2-chloroheptafluorobut-2-ene as a mixture of *Z*- and *E*-isomers (yields, 20% and 36%, respectively). A small amount (8%) of 2-chlorononafluorobutane is formed as the product of exhaustive fluorination.[96]



According to the patent literature,[97] the diene **92** reacts with bromine (illumination with a 100 W lamp) to give 1,4-dibromo-2,3-dichloro-1,1,4,4- tetrafluorobut-2-ene (1,4-addition),



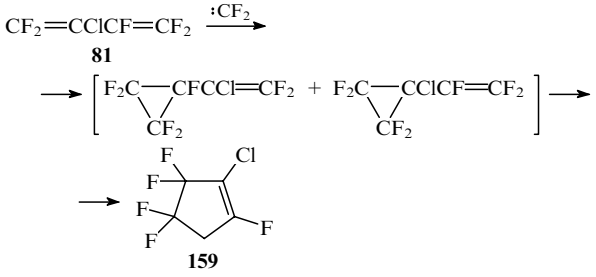
whereas with the diene **82** 1,2-addition occurs, which results in 3,4-dibromo-1,4-dichloro-1,2,3,4-tetrafluorobut-1-ene. Its chlorination gives 1,2-dibromo-1,3,4,4-tetrachloro-1,2,3,4-tetrafluorobutane.[64] Chlorination of the diene **82** affords 1,1,2,3,4,4-hexachloro-1,2,3,4-tetrafluorobutane.[64]



2. Cycloaddition reactions

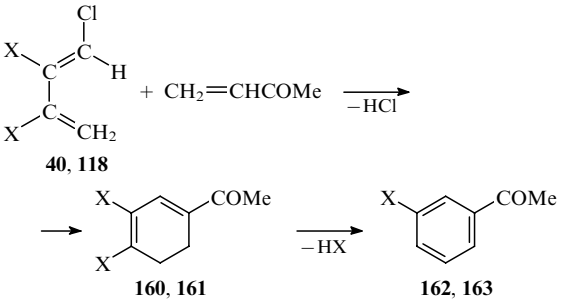
a. Reaction of mixed halogenobutadienes with difluorocarbene

The addition of carbenes to MHB was studied only for the reaction of difluorocarbene with the diene **81**. Petrov *et al.*[98] used hexafluoropropylene oxide as the source of difluorocarbene. Heating of an excess of the epoxide with the diene **81** in an autoclave gave the halogeno-substituted cyclopentene **159** in high yield. The cyclopentene **159** is one of the pyrolysis products of chlorotrifluoroethylene.[87] According to Petrov *et al.*,[98] the difluorocarbene formed in the course of pyrolysis adds to the diene **81** to give polyhalogenovinylcyclopropanes, whose intramolecular rearrangement yields the cyclopentene **159**.[87]



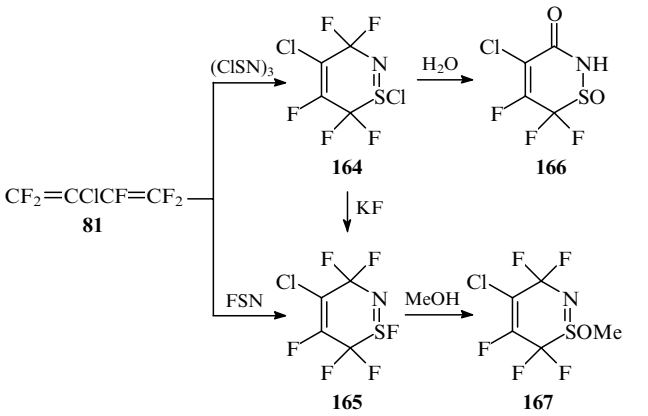
b. Diels – Alder syntheses involving mixed halogenobutadienes

Chloro-substituted buta-1,3-dienes (mostly, mono- and dichloro-derivatives) are convenient subjects for studying the Diels – Alder reaction and preparation of practically valuable compounds.[7] Some MHB were also studied in the [4 + 2]-cycloaddition. Thus upon prolonged boiling of an excess the dienes **40** and **118** with methyl vinyl ketone in the presence of Na_2CO_3, the corresponding 1-acetyl-3,4-dihalogenocyclohexa-1,3-dienes **160** (X = Br) and **161** (X = I) were obtained. Upon treatment of the cyclohexadienes **160** and **161** with 1,8-diazabicyclo[5.4.0]undec-7-ene, they are readily aromatised into the corresponding halogenoacetophenones **162** and **163**.[77,99]



The [4 + 2]-cycloaddition of $(ClSN)_3$ and FSN to the butadiene **81** yielded the difficultly accessible and highly reactive 6-membered heterocycles **164** and **165**, respectively, which are the derivatives of 1,2-thiazines (Scheme 3). Treatment of the 1,2-thiazine **164** with water yields the 1,2-thiazin-3-one-1-oxide **166**. The reaction of methanol with the 1,2-thiazine **165** results in the

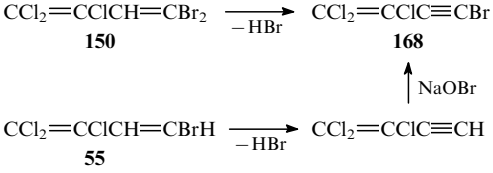
Scheme 3



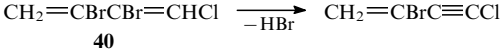
substitution of the methoxy group for the sulfur-bound fluorine atom by the methoxy group with the formation of the product **167**. Thiazine **164** is easily fluorinated with KF and gives a high yield of the thiazine **165**.[100]

3. Elimination reactions

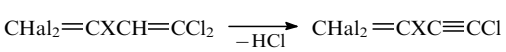
As has been shown above (see Section II.2), butenynes are widely used in the synthesis of MHB. In turn, the accessible MHB can be used in the synthesis of some highly reactive halogen-containing butenynes. Thus the preparation of 4-bromo-1,1,2-trichlorobut-1-en-3-yne (**168**) has been developed based on dehydrobromination of the dienes **55** and **150**. The synthesis of the butenyne **168** (yield 60 %) from the diene **55** (*Z*-isomer) includes two stages: the elimination of HBr under the action of the methanolic solution of potassium carbonate and the substitution of bromine for a hydrogen atom in the 1,1,2-trichlorobut-1-en-3-yne obtained under the action of sodium hypobromite. The second method of the synthesis of the butenyne **168** consists in the dehydrobromination of the diene **150**. It was established that the yield of the target product depends to a considerable extent on the nature of the dehydrohalogenation agent. When the methanolic solution of potassium carbonate is used, the yield of butenyne **168** is 57.5 %; this amounts to 70% with the use of benzyltrimethylammonium hydroxide (Triton B).[89,101,102]



It was shown that the dehydrobromination of the diene **40** under the action of finely ground KOH at 100 °C results in 2-bromo-4-chlorobut-1-en-3-yne in 51% yield.[42]



Dehydrochlorination of some pentahalogenosubstituted MHB yielded the previously inaccessible tetrahalogenobutenynes.



Hal = Cl, X = Br; Hal = Br, X = Cl.

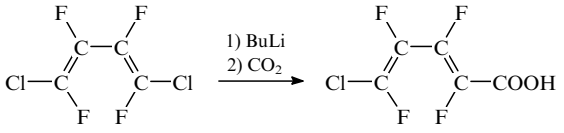
4. Substitution reactions

a. Interaction of mixed halogenobutadienes with organometallic compounds

Organolithium and -magnesium reagents found rather limited uses in the chemistry of MHB. The pronounced 'affinity' of these compounds to halogens, on the one hand, and the presence of a large number of halogen atoms in the MHB molecules, on the

other hand, largely prevent selective nucleophilic substitution in these substrates, though such reactions are known (see below). The metal–halogen exchange is more characteristic of MHB. Thus starting from 1,2,3,4-tetrachlorobuta-1,3-diene **84** and butyllithium, mono- and dilithium derivatives were obtained, based on which a number of fine syntheses were carried out.[103, 104]

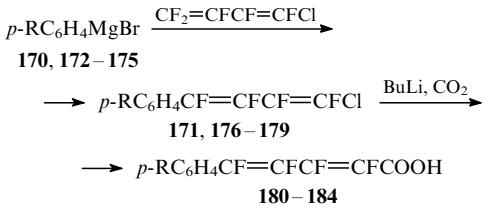
Syntheses involving MHB were studied in the example of 1,4-dichloro-1,2,3,4-tetrafluoro-1,3-butadiene (**82**).[62] Treatment of an isomeric mixture of the diene **82** (*E*,*E* : *E*,*Z* : *Z*,*Z* = 1 : 2.5 : 1.5) with butyllithium and then with CO_2 gave (*E*,*Z*)-5-chloro-2,3,4,5-tetrafluoropenta-2,4-dienoic acid (**169**) in 25% yield. Comparison of the ratio of isomeric forms of this diene and the yield of the acid shows that it is the *Z*,*Z*-isomer of the diene **82** that reacts. This reaction proceeds through the stage of exchange of an *exo*-chlorine atom for lithium (according to Kremlev *et al.*,[62] the starting diene exists in a non-planar *s*-*cis*-conformation).



(*Z*,*Z*)-**82** (*E*,*Z*)-**169**

The reaction of organomagnesium compounds with MHB occurs in a different way. The reaction of 1-chloroperfluorobuta-1,3-diene (**75**) (*E* : *Z* = 1 : 1) with phenylmagnesium bromide (**170**) includes the nucleophilic substitution of the phenyl radical for the terminal fluorine atom of the trifluorovinyl fragment, which results in the formation of 4-chloro-1,2,3,4-tetrafluoro-1-phenylbuta-1,3-diene (**171**) as a mixture of *E*,*E*-, *E*,*Z*- and *Z*,*Z*-isomers in the ratio 2 : 1 : 2 and in a total yield of 77%.[57]

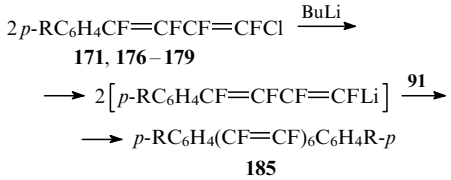
Various *para*-substituted arylmagnesium bromides (**172**–**175**) were used in this reaction, and this extended appreciably the synthetic possibilities of this method.[105] It was shown that the resulting 1-aryl-4-chloro-1,2,3,4-tetrafluorobuta-1,3-dienes (**176**–**179**) (yields of 40%–49 %) represent mixtures of *E*,*E*-, *E*,*Z*- and *Z*,*Z*-isomers in the ratio 1 : 1 : 1 (NMR data). The crystalline *E*,*E*-isomer of compound **176** was isolated in individual form. Metallation of products **171**, **176**–**179** with butyllithium and subsequent carbonisation yielded a series of (*E*,*E*)-5-aryl-2,3,4,5-tetrafluoropenta-2,4-dienoic acids (**180**–**184**).



R = H (**170**, **171**, **180**), Me_2N (**172**, **176**, **181**), MeO (**173**, **177**, **182**), Me (**174**, **178**, **183**), CF_3 (**175**, **179**, **184**).

^{19}F NMR studies of the electronic effect of substituents and determination of the acidity have shown that the 1,2,3,4-tetrafluorobuta-1,3-diene system is involved in the transfer of the electronic influence from a substituent in the aromatic ring to the corresponding reaction centre, *viz.*, the carboxyl group or a fluorine atom.[105]

Compounds **171**, **176**–**179** served as the basis for the synthesis of symmetrical α,ω-diarylperfluoropolyenes (**185**).[19]



Compounds of the type **185** with the $(CF=CF)_n$ groups are good conductors of the conjugation effect because the fluorine atoms do not create any steric hindrance to its transfer. This opens up a broad perspective for the synthesis of a novel type of polymethine dyes with a totally or partially fluorinated chain.[19, 105]

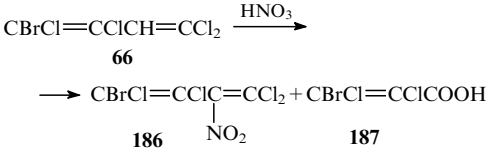
b. Nitration reactions

Of all the principal methods for the preparation of nitrobutadienes, the leading part belongs to the nitration of dienes with nitric acid or nitration mixtures.

Nitro- and especially polychloronitrobutadienes are widely employed in organic synthesis.[106] For example, pentachloro-2-nitrobuta-1,3-diene, which was obtained by the reaction of pentachloro-2*H*-buta-1,3-diene with nitric acid, proved to be a versatile starting material for numerous syntheses of compounds belonging to different classes.[107–109]

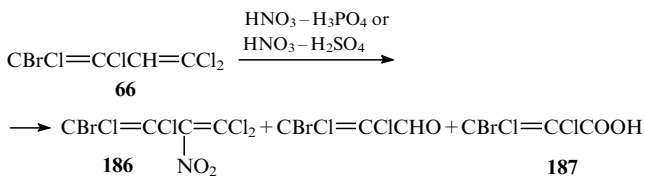
The first representative of nitroderivatives of MHB [4-bromo-1,1,3,4-tetrachloro-2-nitrobuta-1,3-diene (**186**)] was obtained by the reaction of 60% nitric acid with a 1 : 1 mixture of *Z*- and *E*-isomers of 1-bromo-1,2,4,4-tetrachlorobuta-1,3-diene **66** at 80–85 °C. The nitrodiene **186** is a mixture of two isomers (GLC).

Along with the nitration of the initial diene **66** at the β,β-dichlorovinyl group, competitive oxidative destruction takes place, which leads to the formation of 3-bromo-2,3-dichloroacrylic acid (**187**) as a by-product.[110]

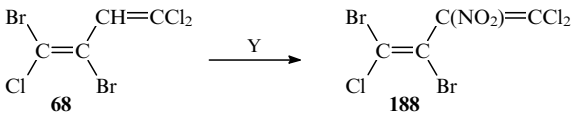


Recently,[54] the nitration of the diene **66** with nitrating mixtures $HNO_3-H_3PO_4$ and $HNO_3-H_2SO_4$ has been studied over a broad range of concentrations and temperatures. It was found that the optimum conditions for the nitration process are as follows: the temperature 95–100 °C, the ratio of the components of the nitration mixture $HNO_3 : H_3PO_4$ (or $HNO_3 : H_2SO_4$) equal to 10 : 1 and the ratio of diene : nitration mixture equal to 1 : 3 or 1 : 4. Under these conditions, the reaction is completed in 23 h; the yield of the nitrodiene **186** reaches 56% upon nitration with the $HNO_3-H_2SO_4$ mixture and 58% upon nitration with the $HNO_3-H_3PO_4$ mixture.

The nitration of the diene **66** (as a mixture of *Z*- and *E*-forms in the ratio 1 : 3) yields an isomeric mixture of the nitrodiene **186** in virtually the same ratio. Among by-products of this reaction, β-bromo-α,β-dichloroacrolein (yield 8%) and 3-bromo-2,3-dichloroacrylic acid (**187**) were detected.



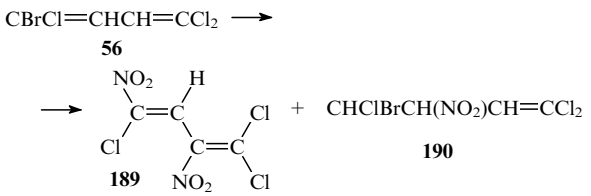
The nitration of other pentasubstituted MHB, *viz.*, 1,2-dibromo-1,4,4-trichloro- (**68**) and 1,3-dibromo-1,4,4-trichlorobuta-1,3-dienes (**70**) with nitric acid or nitration mixtures occurs similarly. Thus nitration of the *E*-isomer of the diene **68** with the 55%–60% nitric acid, fuming nitric acid or a nitration mixture $HNO_3-H_3PO_4$ yielded (*E*)-3,4-dibromo-1,1,4-trichloro-2-nitrobuta-1,3-diene (**188**).



Nitration agent Y	T /°C	Yield of **188** (%)
55% – 60% HNO_3	80 – 85	40
Fuming HNO_3	20	45
$HNO_3 - H_3PO_4$	90 – 95	50

The nitration of the diene **70** with the above-cited reagents under similar conditions gives 1,3-dibromo-1,4,4-trichloro-2-nitrobuta-1,3-diene in yields of 35%, 43% and 48%, respectively.

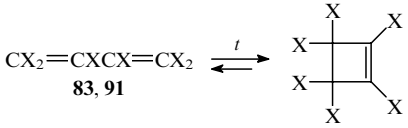
1-Bromo-1,4,4-trichlorobuta-1,3-diene (**56**) reacts differently with nitric acid and with nitration mixtures. In this case, the nitration proceeds in the two directions: (1) substitution of a hydrogen atom in the β,β-dichlorovinyl group and (2) substitution of a bromine atom in the β,β-bromochlorovinyl group resulting in the formation of 1,1,4-trichloro-1,3-dinitrobuta-1,3-diene (**189**). Another reaction product is 4-bromo-1,1,4-trichloro-3-nitrobut-1-ene (**190**). Under the optimum conditions [the nitration mixture $HNO_3 - H_3PO_4$ (10 : 1), 90 – 95 °C, 2 h], the yields of 1,4-dinitrobuta-1,3-diene **189** and nitrobutene **190** are 18% and 40%, respectively.[49]



According to the IR spectroscopy and the X-ray diffraction analysis, the diene **189** is the *Z*-isomer and has a virtually planar *s-trans*-configuration.[111, 112]

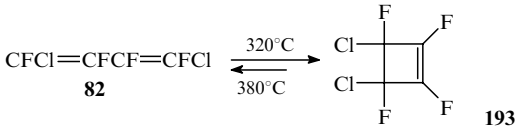
5. Isomerisation reactions

It was shown above (see Section II.3) that the accessible polyhalogenocyclobutenes are convenient starting compounds for the synthesis of some MHB. As early as 1949, the thermal cyclisation of hexafluorobuta-1,3-diene (**91**) at 150 – 180 °C was carried out and resulted in hexafluorocyclobutene (**191**) and a mixture of dimers C_8F_{12} and trimers $C_{12}F_{18}$.[113] Later, these transformations were also performed for hexachlorobuta-1,3-diene (**83**), and hexachlorocyclobutene (**192**) was isolated by distillation.[7] The isomerisation of halogenobutadienes into the corresponding cyclobutenes is a reversible reaction.



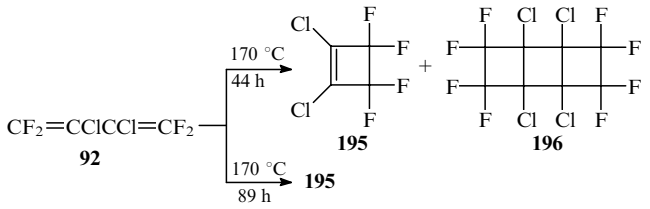
X = F (**91**, **191**), Cl (**83**, **192**).

The isomerisation of MHB was studied in the example of 1,4-dichloro-1,2,3,4-tetrafluorobuta-1,3-diene (**82**) and 2,3-dichloro-1,1,4,4,-tetrafluorobuta-1,3-diene (**92**). It was shown that heating of the diene **82** at 250 °C in a sealed glass tube results in 3,4-dichlorotetrafluorocyclobutene (**193**) in 56% yield. Upon heating of this diene in a platinum crucible over activated carbon to 320 °C, the yield of the butene **193** reaches 74%. The reverse process (transformation of cyclobutene into diene) occurs at 380 °C at a lower rate, therefore, the content of butadiene in the thermolysis products of the cyclobutene **193** is only 14%.[64]



Heating of a mixture of *E,E*-, *E,Z*- and *Z,Z*-isomers of the diene **82** in a nickel tube at 330 °C yielded three products, *viz,* 3,4-dichloro- (**193**), 1,4-dichloro- (**194**) and 1,2-dichlorotetrafluorocyclobutenes (**195**). Presumably, the cyclobutenes **194** and **195** are formed due to the double bond migration catalysed by the fluoride ion.[114]

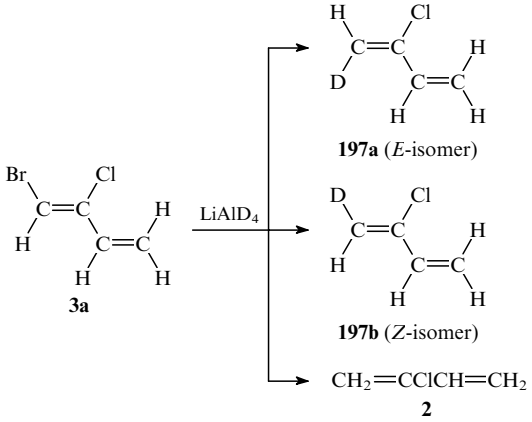
The diene **92** undergoes only partial transformation when heated in a sealed steel tube at 170 °C for 44 h. The unreacted diene **92** was recovered, 1,2-dichlorotetrafluorocyclobutene (**195**) and a small amount of unsaturated dimers and a dimer **196**[97] were isolated from the reaction mixture. The total conversion of the diene **92** into the cyclobutene **195** occurs after 89 h.[97]



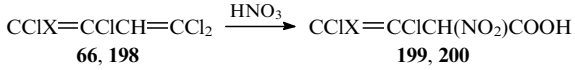
It was supposed[64] that the reaction diene ⇆ cyclobutene is a general characteristic of the polyhalogenobutadienes.

6. Miscellaneous reactions

The reduction of MHB was studied only in the example of (*Z*)-1-bromo-2-chlorobuta-1,3-diene (**3**). It was shown that the reduction of *Z*-diene (**3a**) with $LiAlD_4$ in diethyl ether occurs with high stereoselectivity and leads to the formation of a mixture of (*E*)- (**197a**), (*Z*)-2-chloro-1-deuteriobuta-1,3-diene (**197b**) and 2-chlorobutadiene (**2**) in the ratio 94.2 : 2.2 : 3.6, respectively.[25]



In example of the reaction of pentachloro-2*H*-buta-1,3-diene (**198**) with fuming nitric acid it was shown that the reaction product is 3,4,4-trichloro-2-nitrobut-3-enoic acid (**199**), *i.e.*, the β,β-dichlorovinyl group of the diene **198** is involved in the reaction and an earlier transformation into the $CH(NO_2)COOH$ group occurs.[115] An analogous reaction giving 4-bromo-3,4-dichloro-2-nitrobut-3-enoic acid (**200**) in high yield also occurs upon interaction of fuming nitric acid with 1-bromo-1,2,4,4-tetrachlorobuta-1,3-diene (**66**).[110]

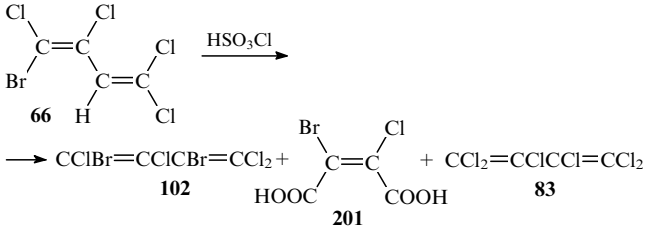


X = Cl (**198**, **199**), Br (**66**, **200**).

The reaction of the *E*-isomer of the diene **66** with chlorosulfonic acid proceeds in an unusual manner. Under the optimum conditions (70 – 80 °C, the diene : acid ratio equal to 1 : 2; 5 h), the reaction gives (*E*)-1,3-dibromo-1,2,4,4-tetrachlorobuta-1,3-diene **102** in 31% yield as the main product.

In addition, bromochloromaleic acid **201** (yield 6%) and hexachlorobuta-1,3-diene **83** (yield ~ 2%) were also found among the reaction products. Dienes **102** and **83** are apparently

formed upon halogenation of the starting compound **66** with chlorine and bromine, which appear in the reaction mixture upon destruction and resinification of the substances involved. Acid **201** is the hydrolysis product of the diene **102**.



When the diene **66** is used in the reaction in the form of *E*- and *Z*-isomers (1 : 1), the diene **102** is also formed as a mixture of two isomers in the ratio 1 : 1.[71]

IV. Conclusion

Analysis of the published data shows that constant attention is paid to the synthesis of mixed halogenobuta-1,3-dienes. Nowadays, there are rather well developed methods for the synthesis of hexasubstituted chloro-, fluoro- and chlorobromobutadienes, while the methods for the synthesis of MHB containing from 2 to 5 atoms of halogens are somewhat less developed.

Most of the methods for the preparation of MHB are based on the elimination reactions of accessible polyhalogenobutenes and -butanes, *i.e.* they rely on the use and transformations of the existing C_4 carbon chain. At present, novel methods have been proposed for the synthesis of MHB under the conditions of phase-transfer catalysis, which makes their preparation simpler and more efficient.

Virtually all of the synthesised MHB contain two kinds of the halogen atoms. At present, there is a convenient procedure for the synthesis of only one MHB representative containing three kinds of the halogen atoms. Unfortunately, until now no MHB have been prepared with four different halogen atoms (F, Cl, Br, I) which could be used as convenient models for studying regularities of competitive processes of nucleophilic vinylic substitution (S_NVin) of different halogen atoms.

Transformations of MHB are represented in the relevant literature to a lesser extent; nonetheless, the available data show that MHB possess broad possibilities for the development of new methods for the synthesis of polyfunctional compounds which are difficultly accessible or totally inaccessible by other ways.

We hope that a stimulus for the further development of studies in this field will be the fact that many MHB possess a broad spectrum of useful properties.

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